



NATIONAL LIBRARY OF MEDICINE  
Bethesda, Maryland







2/2

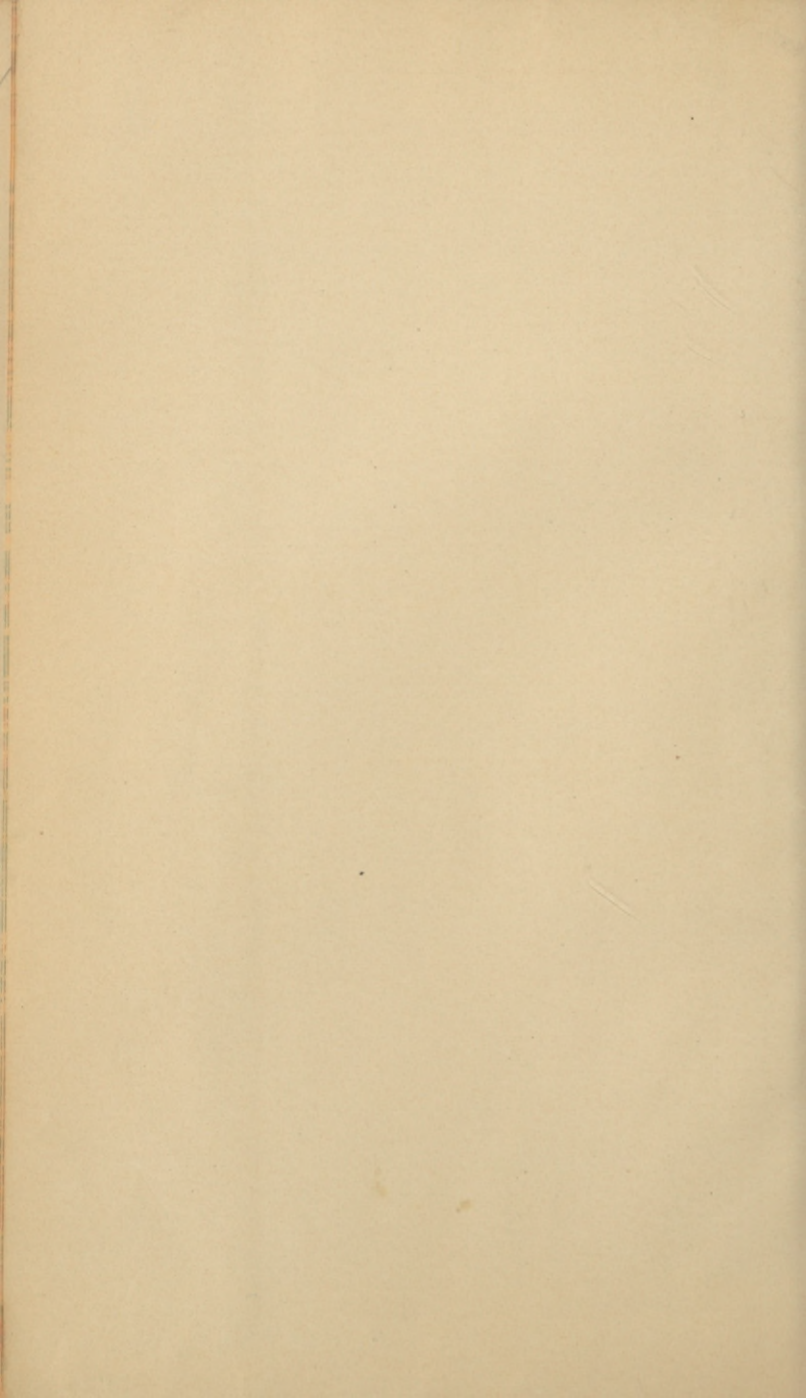














479  
          
ctm

INORGANIC CHEMISTRY.

          
RICHTER.

In Preparation.

A TEXT-BOOK.  
OF  
ORGANIC CHEMISTRY.

BY

PROFESSOR VICTOR VON RICHTER.

AUTHORIZED TRANSLATION FROM LAST GERMAN EDITION.

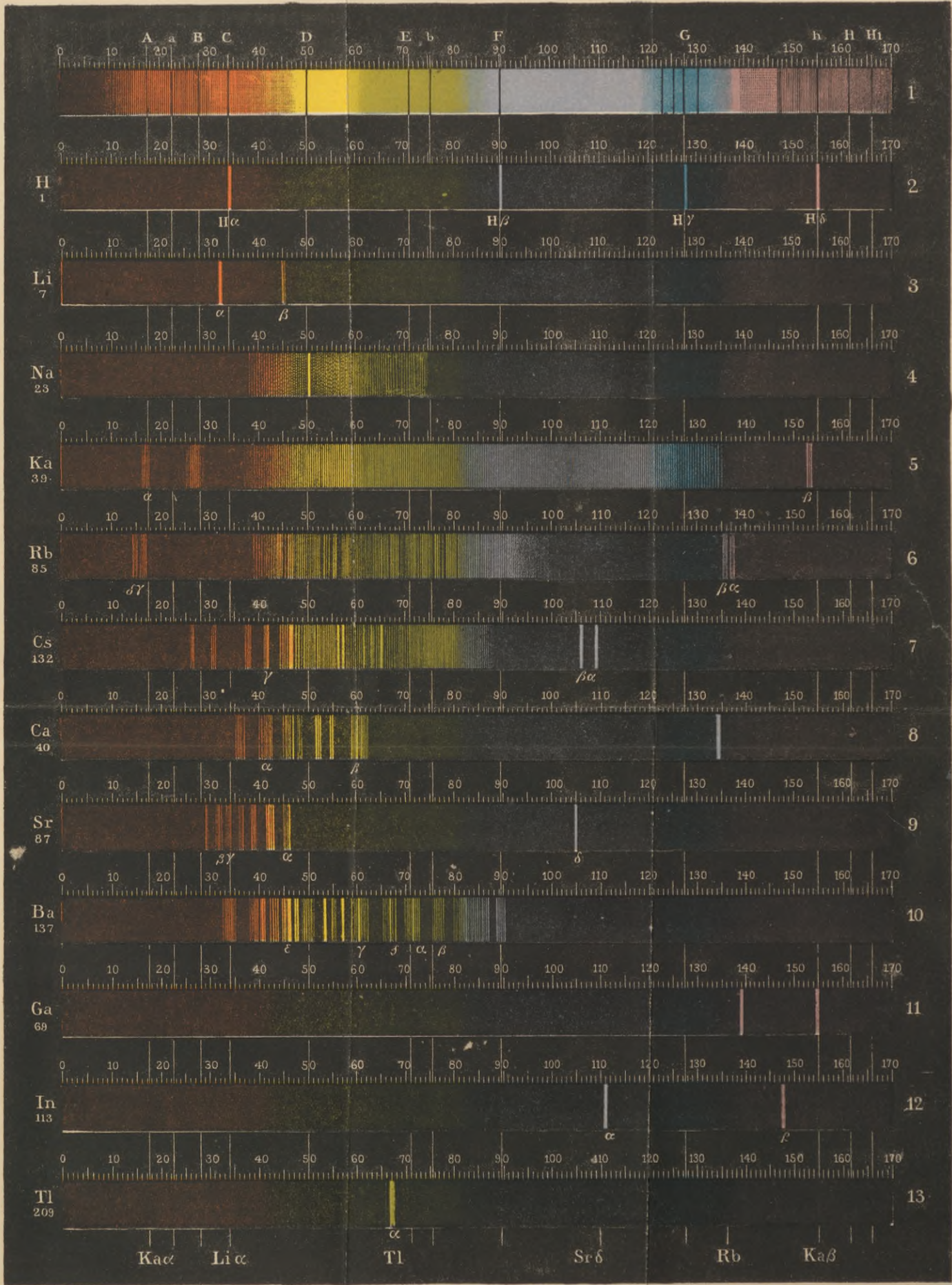
---

12mo. A Companion Volume to Inorganic Chemistry.











A

TEXT-BOOK

OF

INORGANIC CHEMISTRY.

BY

PROF. VICTOR VON RICHTER,  
UNIVERSITY OF BRESLAU.

AUTHORIZED TRANSLATION OF THIRD GERMAN EDITION,

BY

EDGAR F. SMITH, A.M., PH.D.,

PROF. OF CHEMISTRY IN WITTENBERG COLLEGE, SPRINGFIELD, OHIO; FORMERLY IN THE  
LABORATORIES OF THE UNIVERSITY OF PENNSYLVANIA AND MUHLENBERG COLLEGE;  
MEMBER OF THE CHEMICAL SOCIETIES OF BERLIN AND PARIS, OF THE ACADEMY  
OF NATURAL SCIENCES OF PHILADELPHIA, ETC.

EIGHTY-NINE ILLUSTRATIONS ON WOOD

AND

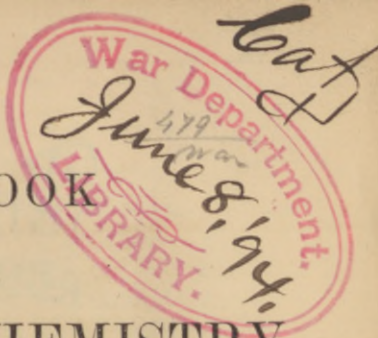
COLORED LITHOGRAPHIC PLATE OF SPECTRA.

PHILADELPHIA:

P. BLAKISTON, SON & CO.,

No. 1012 WALNUT STREET,

1883.



5/19/23  
occ copy 2  
J. Low

QD

151

R537LE

1883

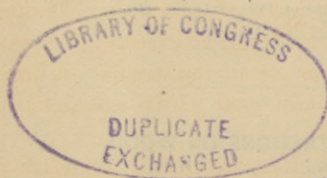
QD 253

. R53

---

Entered according to Act of Congress, in the year 1883, by  
P. BLAKISTON, SON & CO.,  
In the Office of the Librarian of Congress, at Washington, D. C.

---



By transfer  
JUL 20 1916







## PREFACE.

---

The success of PROF. VON RICHTER'S work abroad would indicate its possession of more than ordinary merit. This we believe true, inasmuch as, in presenting his subject to the student, the author has made it a point to bring out prominently the relations existing between fact and theory. These, as well known, are, in most text-books upon inorganic chemistry, considered apart, as if having little in common. The results attained by the latter method are generally unsatisfactory. The first course—that adopted by our author—to most minds would be the more rational. To have experiments accurately described and carefully performed, with a view of drawing conclusions from the same and proving the intimate connection between their results and the theories based upon them, is obviously preferable to their separate study, especially when they are treated in widely removed sections or chapters of the same book. Judging from the great demand for VON RICHTER'S work, occasioning the rapid appearance of three editions, the common verdict would seem to be unanimously in favor of its inductive methods.

In the third edition, of which the present is a translation, the Periodic System of the Elements, as announced by MENDELEJEFF and LOTHAR MEYER, is somewhat different, in the manner of development and presentation, from that appearing in the previous editions. This was done to give more prominence to and make more general the interesting relations disclosed by it. Persons examining this system carefully will be surprised to discover what a valuable aid it really has been, and is yet, in chemical studies. Through it we are continually

arriving at new relations and facts, so that we cannot well hesitate any longer in adopting it into works of this character. It is, indeed, made the basis of the present volume. In accordance with it, some change in the treatment of the metals, ordinarily arbitrarily considered, has been made.

A new feature of the work, and one essentially enlarging it, is the introduction of the thermo-chemical phenomena, briefly presented in the individual groups of the elements and in separate chapters, together with the chemical affinity relations and the law of periodicity. "Hereby more importance is attributed to the principle of the greatest heat development than at present appears to belong to it, because it was desired, from didactic considerations, by the explanation of the few anomalies, to afford the student the incentive and opportunity of deductively obtaining the majority of facts from the thermal numbers, on the basis of a simple principle. To facilitate matters, there is appended to the volume a table containing the heat of formation of the most important compounds of the metals."

Trusting that the teachings of this work will receive a hearty welcome in this country, and that they will meet a want felt and often expressed by students and teachers, we submit the following translation of the same.



## TABLE OF CONTENTS.

### INTRODUCTION.

Definition of Chemistry, 9. Chemical Elements, 12. Principle of Conservation of Substance, 12. Principle of Conservation of Force, 13. Chemical Energy, 15. Conditions of Chemical Action, 15. Chemical Symbols and Formulas, 17. Constitution of Matter, 19. Crystallography, 20.

### SPECIAL PART.

#### CLASSIFICATION OF THE ELEMENTS, 30.

Hydrogen, 31. Purifying and Drying of Gases, 33. Apparatus for Collection of Gases, 33. Condensation of Gases, 35. Chemical Properties of Hydrogen, 37.

#### GROUP OF HALOGENS, 39.

Chlorine, 39. Bromine, 43. Iodine, 44. Fluorine, 46. General Characteristics of the Halogens, 47. Compounds of the Halogens with Hydrogen, 47. Hydrogen Chloride, 47. Acids, Bases, Salts, 50. Hydrogen Bromide, 52. Hydrogen Iodide, 53. Hydrogen Fluoride, 55. Characteristics of the Hydrogen-Halogen Compounds, 56. Heat of Combination of the latter, 57. Compounds of the Halogens with each other, 58.

*Weight Proportions in the Union of the Elements, Law of Constant Proportions, Atomic Theory, 59. Gas Density of Compounds, Volume Proportions in the Union of Gases, Atomic Molecular Theory, 62. Law of Avogadro, 68. Status nascens, 69.*

#### OXYGEN GROUP, 71.

Oxygen, 71. Oxidation and Reduction, 75. Ozone, 76. Isomerism and Allotropy, 79. Compounds of Oxygen with Hydrogen, 80. Water, 80. Solutions, 82. Dissociation, 85. Quantitative Composition of Water, 86. Molecular Formula of Water, Atomic Weight of Oxygen, 87. Hydrogen Peroxide, 90. Chemical Molecules, 92. Sulphur, 94. Molecules of the Elements, 96. Compounds of Sulphur with Hydrogen, 97. Hydrogen Sulphide, 97. Hydrogen Persulphide, 100. Compounds of Sulphur with Halogens, 101. Selenium, 102. Tellurium, 103. Characteristics of the Elements of the Oxygen Group, 104. Heat of Combination of their Hydrogen Compounds, 105.



## NITROGEN GROUP, 106.

Nitrogen, 106. Atmosphere, 108. Eudiometry, 111. Measuring Gases, 112. Diffusion of Gases, 113. Compounds of Nitrogen with Hydrogen, 115. Ammonia, 115. Ammonium Salts, 118. Atomic Weight of Nitrogen, 120. Hydroxylamine, 121. Compounds of Nitrogen with the Halogens, 122. Phosphorus, 123. Compounds of Phosphorus with Hydrogen, 126. Compounds of Phosphorus with the Halogens, 129. Arsenic, 131. Arsine, 132. Compounds of Arsenic with the Halogens, 134. Antimony, 135. Stibine, 136. Compounds of Antimony with the Halogens, 136. Vanadium, Niobium, Tantalum, 137. Characteristics of the Elements of the Nitrogen Group, 139. Thermal Department, 139.

## CARBON GROUP, 140.

Carbon, 140. Compounds of Carbon with Hydrogen, 142. Methyl, 143. Atomic Weight of Carbon, 143. Ethyl, 144. Ethylene, 144. Acetylene, 145. Nature of Flame, 145. Compounds of Carbon with the Halogens, 151. Silicon, 152. Hydrogen Silicide, 152. Compounds of Silicon with the Halogens, 153.

*Atom and Molecule*, 157. *Determination of Molecular Size from Chemical Reactions*, 159. *Quantivalence of the Elements*, 160. *Chemical Structure*, 163.

## OXYGEN COMPOUNDS OF THE METALLOIDS, 168.

Oxygen Compounds of the Halogens, 169. Oxides of Chlorine, 170. Chloric Oxide, 172. Hypochlorous Oxide, 170. Chlorine Trioxide, 171. Chlorous Acid, 171. Chlorine Tetroxide, 171. Chloric Acid, 172. Perchloric Acid, 172. Oxides of Bromine and Iodine, 173. Hydrates of the Acids, 174. Heat of Combination of the Oxygen Compounds of the Halogens, 176.

## OXYGEN COMPOUNDS OF THE ELEMENTS OF THE SULPHUR GROUP, 177.

Oxides of Sulphur, 177. Sulphur Dioxide, 177. Sulphurous Acid, 179. Hydrosulphurous Acid, 180. Sulphur Trioxide, 181. Sulphuric Acid, 181. Disulphuric Acid, 186. Chloranhydride of Sulphuric Acid, 187. Polythionic Acids, 188. Thiosulphuric Acid, 189. Oxides of Selenium and Tellurium, 191. Heat of Combination of the Oxides and Acids of the Elements of the Sulphur Group, 192.

## OXYGEN COMPOUNDS OF THE ELEMENTS OF THE NITROGEN GROUP, 193.

Oxides of Nitrogen, 194. Nitric Acid, 194. Nitrogen Pentoxide, 196. Nitrogen Trioxide, 196. Nitrous Acid, 197. Nitrogen Tetroxide, 197. Nitrosylsulphuric Acid, 199. Nitrogen Oxide, 201. Hyponitrous Oxide, 203. Hyponitrous Acid, 204. Heat of Combination of Oxides and Acids of Nitrogen, 204. Oxides of Phosphorus, 205. Hypophosphorous Acid, 206. Phosphorous Acid, 207. Phosphoric Acids, 208. Phosphorus Pentoxide, 209. Chloranhydrides of Phosphoric Acid, 210. Phosphorus Sulphides, 210. Oxides of Arsenic, 211. Arsenic Trioxide,



211. Arsenic Acid, 212. Compounds of Arsenic with Sulphur, 213. Sulpho-Salts 214. Oxides of Antimony, 214. Antimonic Oxide, 215. Antimonic Acid, 216. Antimony Sulphides, 216. Heat of Combination of Acids of the Nitrogen Group, 217.

OXYGEN COMPOUNDS OF THE ELEMENTS OF THE CARBON GROUP, 218.  
Oxides of Carbon, 219. Carbon Dioxide, 219. Carbon Monoxide, 222. Sulphides of Carbon, 223. Cyanogen Compounds, 224. Heat of Formation of Carbon Compounds, 225. Oxides of Silicon, 226. Dialysis, 227. Crystalloids and Colloids, 227. Silicates, 227. Titanium, Zirconium, Thorium, 228. Boron, 230. Boron Chloride, 231. Boron Fluoride, 232. Boric Acid, 232.

THE PERIODIC SYSTEM OF THE ELEMENTS, 233.  
Periodicity of Chemical Valence, 240. Periodicity of Thermo-Chemical Phenomena, 242.

---

## METALS.

Physical Properties of the Metals, 244. Atomic Volumes, 245. Specific Heat, Atomic Heat, 247. Isomorphism, 251. Chemical Properties of Metals, 252. Alloys, 252. Halogen Compounds, 253. Oxides and Hydrates, 254. Peroxides, Salts, 256. Action of Metals upon Salts, 258. Electrolysis of Salts, 260. Double Transposition of Salts, 263.

### GROUP OF ALKALIES, 265.

Heat of Combination of the Alkali Metals, 266. Potassium, 267. Potassium Hydrate, 268. Potassium Chloride, 269. Potassium Chlorate, 270. Potassium Hypochlorite, 271. Potassium Sulphate, 272. Potassium Nitrate, 272. Gunpowder, 273. Potassium Carbonate, 273. Potassium Silicate, 274. Potassium Sulphides, 275. Recognition of Potassium Compounds, 276. Rubidium, 276. Cæsium, 276. Sodium, 277. Sodium Hydrate, 277. Sodium Chloride, 278. Sodium Sulphate, 279. Supersaturated Solutions, 280. Sodium Hyposulphite, 281. Sodium Carbonate, 282. Sodium Nitrate, 284. Sodium Phosphates, 284. Borax, 285. Recognition of Sodium Compounds, 286. Lithium, 286. Ammonium Compounds, 287. Ammonium Chloride, 288. Ammonium Carbonate, 289. Ammonium Sulphide, 290.

### METALS OF GROUP II, 290.

*Group of Metals of the Alkaline Earths*, 291. Calcium, 292. Calcium Oxide, 292. Cement, 293. Calcium Chloride, 294. Calcium Fluoride, 294. Chloride of Lime, 295. Calcium Sulphate, 296. Calcium Phosphates, 297. Calcium Carbonate, 298. Glass, 296. Calcium Sulphides, 299. Strontium, 300. Barium, 301. Barium Oxide, 301. Barium Peroxide, 302. Recognition of the Alkaline Earths, 303.

*Magnesium Group*, 303. Magnesium, 305. Magnesia, 306. Magnesium Chloride, 306. Magnesium Phosphates, 307. Magnesium Carbonates, 308. Recognition of Magnesium Compounds, 309. Beryllium, 309. Zinc, 310. Zinc Oxide, 311. Zinc Sulphate, 311. Zinc Sulphide, 312. Cadmium, 312. Heat of Formation of the Metals of Group II, 314.

*Mercury*, 316. Amalgams, 317. Mercurous Compounds, 318. Mercuric Compounds, 319.

*Copper, Silver, Gold*, 322. General Characteristics, 324. Forms of Combination, 325. Copper, 325; Metallurgy of Copper, 325. Cuprous Compounds, 327. Cupric Compounds, 328. Copper Sulphate, 329. Alloys of Copper, 330. Silver, 331. Metallurgy, 331. Silver Oxide, 333. Silver Chloride, 334. Photography, 335; Silver Nitrate, 335. Silvering, 336. Gold, 337. Aurous Compounds, 338. Auric Compounds, 339.

#### METALS OF GROUP III, 340.

*Group of Earth Metals*, 342. Aluminium, 342. Aluminium Chloride, 343. Aluminium Oxide, 344. Aluminates, 345. Alum, 347. Aluminium Silicates, 349. Porcelain, 349. Ultramarine, 349. Rare Earths, 350. Scandium, 350. Yttrium, 350. Lanthanum, 350. Cerium, 351. Didymium, 351. Erbium, 351.

*Gallium Group*, 351. Gallium, 352. Indium, 353. Thallium, 354. Thallous Compounds, 355. Thallic Compounds, 356.

#### TIN AND LEAD, 356.

Tin, 357. Stannous Compounds, 358. Stannic Compounds, 359. Lead, 361. Lead Peroxide, 362.

#### BISMUTH, 365.

#### CHROMIUM GROUP, 367.

Chromium, 367. Chromous Compounds, 369. Chromic Compounds, 369. Chromic Acid Compounds, 371. Chromium Oxychloride, 374. Molybdenum, 375. Tungsten, 377. Uranium, 378.

#### MANGANESE, 379.

Forms of Combination, 380. Manganous Compounds, 381. Manganic Compounds, 381. Manganic Acid, 383.

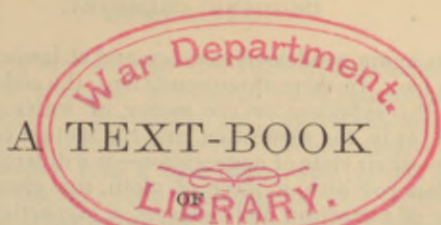
#### METALS OF GROUP VIII, 385.

*Iron Group*, 386. Iron, 387. Metallurgy of Iron, 388. Ferrous Compounds, 391. Ferric Compounds, 392. Ferric Acid Compounds, 394. Cyanogen Compounds, 394. Cobalt, 397. Cobalt-amine Compounds, 399. Cobalt-cyanogen Compounds, 399. Nickel, 400.

*Platinum Metals*, 401. Ruthenium and Osmium, 403. Rhodium and Iridium, 404. Palladium, 405. Platinum, 406.

#### SPECTRUM ANALYSIS, 409.

Periodicity of Spectra Lines, 415.



# INORGANIC CHEMISTRY.

## INTRODUCTION.

Upon contemplating Nature, surrounding us on all sides, we at once discover an endless multitude of objects or *bodies*. That which forms the basis of the latter, strongly characterized by extent and weight, we designate *substance* or *matter*. The investigation of the internal and external structure of bodies, their classification according to conformable or distinguishing characteristics, constitute the task of the descriptive sciences; of mineralogy, of geology, of descriptive botany and zoölogy, of anatomy, etc., etc.

A closer scrutiny of natural objects discloses the fact that they in time succumb to many more or less serious alterations or changes. We observe that minerals are formed, crystallize, then disintegrate and crumble to pieces; that plants and animals spring up, grow, and then fall into decay and decomposition. Such changes in the condition of bodies occurring with time are entitled *phenomena*. The investigation of these during their progression, the determination of the laws according to which they occur, the explanation of the causes underlying them, form the task of the *speculative sciences*, physics and chemistry—depending upon the nature of the phenomena.

Although nature does not present any abrupt boundaries, but throughout gradual transitions and intermediate steps, we yet can distinguish with tolerable distinctness two different classes of phenomena. Some changes in the condition of bodies are only superficial (external), and are not accompanied by material alteration in substance. Thus heat converts water into steam, which upon subsequent



cooling is again condensed to water, and at lower temperatures becomes ice. In these three conditions, the solid, liquid, and gaseous, the *substance* or the *matter* of water or ice is unchanged; only the separation and the motion of the smallest particles—their state of aggregation—is a different one. If we rub a glass rod with a piece of cloth, the glass acquires the property of attracting light objects; *e. g.*, particles of paper—it becomes electrified. An iron rod allowed to remain suspended vertically for some time slowly acquires the power of attracting small pieces of iron; through the earth's magnetism it has become magnetic. In both instances the glass and iron receive new properties; in all other respects, in their external and internal form or condition, they have suffered no perceptible alteration; the glass is glass, and the iron remains iron. All such changes in the condition of bodies, unaccompanied by any real alteration in substance, are known as *physical phenomena*.

Let us turn our attention now to the consideration of another class of phenomena. It is well known that ordinary iron undergoes a change, which we term *rusting*; *i. e.*, it is transformed into a brown substance which is entirely different from iron. On mixing finely divided copper filings with flowers of sulphur (pulverulent sulphur) there results an apparently uniform, grayish-green powder. If this be examined, however, under a magnifying glass, we can very plainly distinguish the red metallic copper particles in it from the yellow of sulphur; by treatment with water, the specifically lighter sulphur particles can easily be separated from those of the copper. From all this the powder above will represent nothing more than a *mechanical mixture*. If, however, this mixture be heated, *e. g.*, in a glass test tube, it will commence to glow, and on cooling, a black, fused mass remains, which in all respects differs from copper and sulphur, and even under the strongest microscope does not reveal the slightest trace of the latter, and elutriation with water fails to effect a separation of the ingredients. By the mutual action of sulphur and copper in presence of heat, a new body with entirely different properties has arisen, and is named copper sulphide. A mixture of sulphur and iron or other metals deports itself in a similar manner; the resulting bodies are termed sulphides.

Such mutual action of different bodies occurs not only under the influence of heat, but frequently at ordinary temperatures.



If, *e. g.*, mercury and sulphur are rubbed continuously in a mortar, there is produced a uniform, black compound called mercury sulphide. The action of gaseous chlorine upon various metals is quite energetic. When finely divided antimony is shaken into a flask filled with yellow chlorine gas, flame is produced; each antimony particle burns in the chlorine with a bright white light. The product of this action of solid metallic antimony and gaseous yellow chlorine is a colorless, oily liquid, known as antimony chloride. Such occurrences, therefore, in which complete, entire alteration of bodies entering the reaction follow, are termed *chemical phenomena*. *Chemistry, then, is that department of natural science which occupies itself with the study of those phenomena in which an alteration of substance has occurred.*

In the previously described experiments we observed the phenomena of *chemical combination*; from two different bodies arose new homogeneous ones. The opposite exist, consisting in the *decomposition* of compound bodies into two or more *dissimilar* ones. If red mercuric oxide be heated in a test tube it will disappear; a gas (oxygen) is liberated, which will inflame a mere spark on wood; in addition, we find deposited upon the upper, cooler portions of the tube, globules of mercury. From this we observe that on heating solid red mercuric oxide two different bodies arise: gaseous oxygen and liquid mercury. We conclude, then, that mercuric oxide holds in it, or consists of, two constituents—oxygen and mercury. This conclusion, arrived at by decomposition, by *analysis*, may readily be verified inversely by combination, by *synthesis*. It is only necessary to heat mercury at a somewhat lower temperature than in the preceding experiment, for some time, in an atmosphere of oxygen, to have it absorb the latter and yield the compound we first used, red mercuric oxide. The direct decomposition of a compound body into its constituents by mere heat does not often happen. Generally, the coöperation of another body is required, which will combine with one of the constituents and set the other free. In this manner we can, for example, effect the decomposition of the previously synthesized mercury sulphide, viz: by heating it with iron-filings; the iron unites with the sulphur of the mercury sulphide, to form iron sulphide, while the mercury is set free.

If, in a similar manner, natural objects be decomposed,

bodies or substances are finally reached which have withstood all attempts to bring about their division into further constituents, and which cannot be formed by the union of others. Such substances are the *chemical elements*, which also constitute the limit of chemical change. Their number, at present, is about 67; some have been only recently discovered. To them belong all the metals, like iron, copper, lead, silver and gold. Other elements do not possess a metallic appearance, and are known as *metalloids*; *i. e.*, they are substances resembling (as regards their further indivisibility) the metals. It would be more correct to term them *non-metals*. To these belong sulphur, carbon, phosphorus, oxygen, etc. The line between metals and non-metals is not very marked.

By the union of the elements with each other in smaller or larger number and quantity, result the compound bodies known to us. Water is a compound of two gaseous elements—hydrogen and oxygen; ordinary cooking salt consists of the metal sodium and the gaseous chlorine. These elements make up not only our own earth, but the heavenly bodies are composed of them, at least, so far as has been proven by spectrum analysis.

#### The Principle of the Indestructibility of Matter.

If the quantities by weight of substances entering into a chemical change be determined, we will discover that in all transpositions, in the decomposition of a compound into its constituents, and in the union of the elements to form compound bodies, loss in weight never occurs. *The weight of the resulting compounds is invariably equal to the sum of the weights of the bodies entering the reaction.* Well known, general phenomena apparently contradict this scientific conclusion. We observe plants springing from a small germ and constantly acquiring weight and volume. This spontaneous increase of substance, however, is only seeming. Closer inspection proves conclusively that the growth of plants occurs only in consequence of the absorption of substance from the earth and atmosphere. The opposite phenomenon is seen in the burning of combustible substances, where an apparent annihilation of matter takes place. But even in this, careful observation will discover that the combustion phenomena consist purely in a transformation of visible solid or liquid bodies into non-visible gases. Carbon and hydrogen, the usual constituents of

combustible substances, *e. g.*, a candle, combine in their combustion with the oxygen of the air and yield gaseous products—the so-called carbon dioxide and water, which diffuse themselves in the atmosphere. If these products be collected, their weight will be found not less, but indeed greater, than that of the consumed body, and this is explained by the fact that in addition to the original weight they have had the oxygen of the air added.

From what has been remarked we can conclude that in chemical transpositions loss in matter does not occur, nor is there a new creation of the same observed. Compounds are formed and disappear, because they are converted into new forms, but their substance (matter), their weight, does not disappear, and is not produced anew. This fundamental truth is called the *principle of the indestructibility of substance (matter)*. Lavoisier, in the eighteenth century, first determined it by convincing experiments, and in combination with the principle of the conservation of energy, it constitutes the firm foundation of all scientific knowledge.

#### **The Principle of the Conservation of Energy—Chemical Energy.**

Causes underlie and influence all material phenomena. The final cause of phenomena we term *force*, accepting for the various sorts of phenomena a variety of forces. Some of these are attraction and repulsion, light, heat, electricity, cohesion, chemical affinity, and others. These names, however, only represent kinds of phenomena, without explaining their true nature. The positive knowledge we possess of the nature of some forces is that they consist of modes of motion. Thus, the phenomena of light are explained by the vibrations of ethereal particles which penetrate all substances; and those of heat are dependent upon the motions of the smallest particles of matter. Accurate physical investigations have established that the different forces or causes of motion can *never* be destroyed, but merely changed from one kind to another. The movements or vibrations of one variety pass into those of another. For example, a discharged bullet is heated by coming in contact with any obstruction in its course; the visible motion of the entire mass in this instance is transformed into the invisible motions of the smallest particles, and appears as heat. The heat motions can, on the other hand, be again changed into



mechanical force (molecular motion), or into light, magnetism or electricity.

In all these transformations of the different forces into each other, we observe a perfect equivalence of their quantity; if a mechanical force can produce a certain degree of heat, so can, *vice versa*, the latter perform the same mechanical work (the mechanical equivalent of heat, light, electricity). Upon this *equivalence of force* rests the *principle of the conservation of energy*, according to which the various forces or motions of *matter* can neither be annihilated nor produced anew. This principle, forming one of the most important corner stones of natural science, was first sharply defined by the speculative observations of Dr. J. R. Mayer, of Heilbronn, in 1842, and since then has been repeatedly confirmed experimentally.

The most recent advance in physics has led to the negation of the objective existence of all abstract physical forces. Not considering the phenomena of electricity and those of chemical affinity—the reduction of which to forms of motion is clearly foreseen, and not to be doubted—the only remaining, as yet, enigmatical force is that of attraction or gravity. To affirm the existence of gravity is nothing more than to give expression to the fact that bodies in space tend to approach each other. The supposition that the active cause of gravity existed within the bodies themselves was long ago discarded by Newton as “*absurdum*”; it is merely a mathematical fiction. The action of a body in a place where it does not exist, without the aid of a medium, is inconceivable. The transference of the gravitation into material bodies, further, contradicts the principle of conservation of energy, as gravity is neither transferred nor exhausted—be it through the approach of bodies, whereby the force always increases; be it by planet movement, in which the centrifugal component is constantly overcome. Therefore, the active cause of gravity is not to be sought after in bodies themselves, but without them, and, indeed, in a substantial medium—ether—without the acceptance of which natural investigation cannot proceed.

If we desire to make a preliminary presentation upon these relations, the following would be the simplest and most probable: Space is filled by the smallest possible material particles, but as they are all alike, they do not possess gravity, and are found in constant transferable motion—*ether substance*. By the congress of the smallest ether particles to mass aggregates arise the chemical elementary atoms, which constitute material bodies—*substance or matter*. If, now, in addition to this *one* mass aggregate, a second appear in space, an effort to approach each other, produced by the action (collision) of the disturbed ether surrounding them, will appear; they possess gravity. By these suppositions the obscure ideas upon potential energy and



energy of place are removed. A clearer and more thoroughly distinct presentation and confirmation of these representations, and especially upon the nature of forces, are found in A. Secchi's "Die Einheit der Naturkräfte."

In the chemical union of bodies heat is almost invariably disengaged, and as it is a variety of motion, and as motion of *one* kind can only be derived from another, we must conclude that bodies acting chemically, especially the elements, do possess a peculiar sort of motion, which, in chemical union, is partially converted into heat motion (also into light and electricity). This special motion of *matter* is designated *chemical energy* or *chemical tension*. And in the chemical decomposition of a compound body into its constituents, heat is absorbed, disappears as such, and is transformed into chemical energy. Thus, for instance, in the union of 1 kilogram of hydrogen with 8 kilograms of oxygen a quantity of heat is liberated which can perform a mechanical work equal to  $34,462 \times 423.5 = 14,629,000$  kilos; in the decomposition, on the other hand, of 9 kilos of water into hydrogen and oxygen, the same force or quantity of heat is necessary; therefore, in the liberated hydrogen and oxygen, the same quantity of force or motion must be contained in the form of chemical energy.

Chemical energy is not only a quantitative phenomenon; it also presents qualitative differences. Although all bodies, and particularly the elements, possess it, they do not disclose it in the same way in their action upon each other. Some unite or react readily with each other; others, on the contrary, only with difficulty, or not at all. The reason of this deportment is to us entirely unknown. We designate it with the phrase *chemical affinity*, and add that bodies capable of union have affinity for each other (are related), and that by union they satisfy their *affinity*. This expression is incorrectly chosen, because, generally, the bodies least alike chemically unite with each other most readily.

#### Conditions of Chemical Action.

The main condition in the chemical action of bodies consists in their immediate contact. Whilst, in physical changes, the bodies act at smaller or greater distances upon each other (by aid of the ethereal fluid), in chemical alterations they act at immeasurably small distances. The indispensable intimate

contact of solid bodies is difficult to attain by mechanical mixture. Thus, no action results when we rub dry tartaric acid and soda together in a mortar, but as soon as some water is added to the mixture chemical action at once sets in, accompanied with effervescence. As shown in this case, the requisite intimate contact is generally obtained by bringing both or one of the constituents into liquid form, either by solution in a solvent or by fusion. The early chemists expressed these conditions by the sentence: *Corpora non agunt nisi fluido*. Liquid and gaseous bodies are, therefore, *eo ipso*, adapted to chemical action.

Besides intimate contact, a definite temperature and other conditions are necessary. Thus in the preparation of gunpowder, a mixture of carbon, sulphur and nitre, moistened with water, is strongly rubbed and worked through rollers without any chemical action occurring; but if a portion of the mixture be heated to 300° C., or an electric spark be conducted through it, chemical action with explosion immediately takes place. The explanation of these phenomena is based on the fact that the very powerful cohesion of *similar* particles in solid bodies opposes the chemical affinity of the *dissimilar* particles mixed in with each other. As heat works expansively and diminishes the cohesion of the bodies, it is easily comprehended that with the increase of temperature the chemical attraction of the various substances is in condition to overcome the cohesive force. Light and electricity behave like heat. Again, on the opposite hand, the chemical attraction between the different constituents of a compound body is sometimes so weak that the heat vibrations increasing with the temperature outweigh the chemical attraction, so that at a definite temperature decomposition or alteration of the compound body will result. At very high temperatures almost all compounds decompose into their constituents (compare Dissociation of Water). Heat is, therefore, an important agent in chemical changes, because it induces both the phenomena of combination and decomposition. Light and electricity do the same.

In addition to these circumstances we should remember that both the compound bodies and elements consist of several particles (atoms) combined with each other, and that this union must first be broken to render possible the action of the other particles.

Consequent upon the mutual action of all these influences follow the complicated phenomena observed in chemical changes. The qualitative phenomena of chemical energy are extremely different, and the determination of the laws controlling them remains for the future; in special instances reference will be made to individual generalizations. The quantitative relations, on the other hand, in the action of bodies on each other, in the combination of the elements, are thoroughly investigated, and lead to very important laws, speculations and theories, which constitute the main portion of the present scientific chemistry.

As briefly represented in the preceding, two different factors are to be considered in every chemical phenomenon. First is the material side, which finds expression in the solid weight proportions of the reacting and resulting bodies; secondly, a dynamical event presents itself. When hydrogen and oxygen chemically unite to produce water, there occurs, in addition, a considerable development of heat, by which the chemical energy and affinity become evident (p. 57). Although the physical cause of the latter, which formerly was identified with electrical differences, is as yet unexplained, the investigations of recent date have disclosed a close relation between chemical affinity and the thermal phenomena: the greater the liberation of heat in the union of two elements or bodies, the greater also is their affinity, so that the former may serve as an approximate measure of the latter. The general proposition follows, from this, that the qualitative alterations occurring in the reaction of bodies invariably pursue the direction in which the most heat is disengaged. This *fundamental proposition of the greatest development of heat* (Bertholet) is a special case of Clausius' proposition of the entropy of energy, according to which every form of energy tends to pass into heat motion. A closer deduction of this, for chemical changes, so important a proposition, will be given later in the most important special cases.

### Chemical Symbols and Formulas.

For simplicity and convenience, the elements are represented by the first letters of their names, derived either from the Latin or Greek. Hydrogen is represented by the letter H, from the word hydrogenium; nitrogen by N, from nitrogenium. When several elements happen to have the same letter there is added to the capital a second, small letter; thus Na represents natrium; Ni, nickel; Hg, mercury (hydrargyrum), etc., etc. The subjoined table comprises all the elements at present known (67), together with their chemical symbols and atomic weights:—



ELEMENTS.			ELEMENTS.		
	Symbol.	Atomic Weight.		Symbol.	Atomic Weight.
4	Aluminium.....	Al 27.4	Mercury..... <sup>2</sup>	Hg	200
3-5	Antimony (Stibium).....	Sb 122	Molybdenum..... <sup>2-4</sup>	Mo	96
3-5	Arsenic.....	As 75	Nitrogen..... <sup>3-5</sup>	N	14
2	Barium.....	Ba 137	Nickel..... <sup>2</sup>	Ni	59
2	Beryllium.....	Be 9.4	Niobium..... <sup>5</sup>	Nb	94
3-5	Bismuth.....	Bi 210	Osmium..... <sup>6</sup>	Os	199
3	Boron.....	B 11	Oxygen..... <sup>2</sup>	O	16
1	Bromine.....	Br 80	Palladium..... <sup>2-4</sup>	Pd	106.6
2	Cadmium.....	Cd 112	Phosphorus..... <sup>3-5</sup>	P	31
1	Cæsium.....	Cs 133	Platinum..... <sup>4</sup>	Pt	197
2	Calcium.....	Ca 40	Rhodium..... <sup>2-4</sup>	Rh	104.4
4	Carbon.....	C 12	Rubidium..... <sup>1</sup>	Rb	85.4
2-4	Cerium.....	Ce 92 (?)	Scandium..... <sup>3</sup>	Sc	44
4	Chromium.....	Cr 52.5	Sulphur..... <sup>2-4-6</sup>	S	32
2	Copper.....	Cu 63.5	Selenium..... <sup>2-4-6</sup>	Se	79.4
1	Chlorine.....	Cl 35.4	Silver (Argentum)..... <sup>1</sup>	Ag	108
2	Cobalt.....	Co 59	Silicon..... <sup>4</sup>	Si	28
3-5	Didymium.....	Di 95 (?)	Sodium (Natrium)..... <sup>1</sup>	Na	23
3	Erbium.....	Er 112.6 (?)	Strontium..... <sup>2</sup>	Sr	87
1	Fluorine.....	Fl 19	Tantalum..... <sup>3-5</sup>	Ta	182
3	Gallium.....	Ga 69.8	Tellurium..... <sup>2-4-6</sup>	Te	128
3	Gold (Aurum).....	Au 197	Thallium..... <sup>1-3</sup>	Thl	204
1	Hydrogen.....	H 1	Thorium..... <sup>2-4</sup>	Th	231
3	Indium.....	In 113.4	Tin (Stannum)..... <sup>2-4</sup>	Sn	118
1	Iodine.....	I 127	Titanium..... <sup>4</sup>	Ti	50
2-4	Iridium.....	Ir 198	Tungsten (Wolfram)..... <sup>4</sup>	W	184
2-4	Iron (Ferrum).....	Fe 56	Uranium..... <sup>2</sup>	Ur	240
1	Kalium (Potassium).....	K 39	Vanadium..... <sup>3-5</sup>	Vd	51.3
3	Lanthanum.....	La 92 (?)	Ytterbium.....	Yb	113
1	Lithium.....	Li 7	Yttrium..... <sup>3</sup>	Y	61.7 (?)
2	Lead (Plumbum).....	Pb 210	Zinc..... <sup>2</sup>	Zn	65.2
2	Magnesium.....	Mg 24	Zirconium..... <sup>4</sup>	Zr	89.6
2-4	Manganese.....	Mn 55			

The existence of some other elements, as Dianium, Jargonium, Terbium, Philippium, Wasium, Vesbium, Norwegium and Thulium, is yet doubtful.

Compounds produced by the union of the elements are represented by placing their corresponding symbols together and designating these *chemical formulas*. Cooking salt, a compound of sodium and chlorine, is represented by the formula NaCl; mercury oxide, a compound of mercury and oxygen, by HgO; iron sulphide by FeS; hypochlorous acid, a compound of chlorine, hydrogen and oxygen, by ClOH.

Chemical formulas not only express the nature of the elements, but also contain relative proportions of their weights, according to which they unite, and which are compared with hydrogen as unity. Thus H represents 1 pt. by weight of hydrogen; Cl, 35.4 pts. by weight of chlorine; Na, 23 pts. by weight of sodium. Then the formula NaCl would represent the union of 23 parts of sodium with 35.4 parts of chlorine, Na, 23 parts by weight of sodium.

These numbers indicate the relative weights of the *atoms* constituting the elements.

If we seek to obtain a representation of the constitution of the elements and substances in general, but two possibilities appear to be foremost. Either the substance continuously fills space, or it consists of very small, separated particles filling space, chemical individuals, which are termed *atoms*. The latter idea alone corresponds to the present view of physical and chemical investigation, so that the *atomic constitution of substance alone has at present any value*. The inductive derivation and establishment of the atomic theory will be given subsequently (see page 59); here only the following propositions are laid down. The elements consist of similar atoms, of like size and similar weight, while atoms of different elements possess a different weight. The absolute atomic weights are, at present, not determined with sufficient accuracy; the relative weights are referred to the hydrogen atom, which has the smallest weight, hence is made equal to 1 ( $H = 1$ ). By the chemical union of the atoms are formed the smallest particles of compound bodies, termed *molecules*, physical individuals; these are chemically divisible. By these premises chemical formulas acquire a very precise and intuitive importance. The formula NaCl designates the union of 1 atom of sodium (Na) with 1 atom of chlorine, and indicates that in it 23 parts, by weight, of sodium are combined with 35.4 parts of chlorine. If in a compound several atoms of an element are present, this is denoted by numbers attached to the symbol of the atom:—

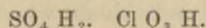
HCl	$H_2O$	$H_3N$	$CH_4$
Hydrochloric acid.	Water.	Ammonia.	Methane.

The formula of water ( $H_2O$ ) means that its molecule consists of two atoms of hydrogen (2 parts by weight) and 1 atom of oxygen ( $O = 16$  parts by weight.) The formula of sulphuric

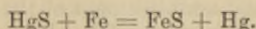
acid ( $\text{H}_2\text{SO}_4$ ) indicates it as a compound consisting of 1 atom of sulphur (32 parts), 4 atoms oxygen ( $4 \times 16 = 64$  parts), and 2 atoms of hydrogen ( $2 \times 1 = 2$  parts), from which the composition of the acid may be at once calculated into per cent., or in any desirable quantity by weight.

Atomic Composition.	In per cent.
Sulphur, S = 32.....	32.65
Oxygen, O <sub>4</sub> = 64.....	65.30
Hydrogen, H <sub>2</sub> = 2.....	2.05
H <sub>2</sub> SO <sub>4</sub> = 98	100.00

When the elements enter into combination in several proportions by weight, this is indicated by placing figures to the right and below the symbol, *e. g.* :—



The chemical union of bodies is shown by the sign +, and the resulting products are placed to the right, following the = sign :—



By this *equation of chemical transposition* is meant that by the union of mercury sulphide ( $\text{HgS}$ ) and iron ( $\text{Fe}$ ), iron sulphide ( $\text{FeS}$ ) and free mercury ( $\text{Hg}$ ) are formed. At the same time such equations show the proportions by weight of the substances entering into and resulting from the reaction; the weight of the acting substances is equal to that of those resulting. Therefore every chemical equation is at once an expression of the principle of the indestructibility of matter (substance). (See p. 13.)

### Crystallography.

Chemistry only occupies itself with the study of the chemical alterations of bodies. Its subject is not the latter for themselves, in their external properties, but only according to their material composition, and their genetic relations to other substances. The investigation of the physical properties of the non-organized bodies constitutes the province of Mineralogy, or, if the same is not limited to naturally occurring bodies, but also includes the numberless artificially prepared substances, it becomes the province of *Inorganography*. Pure chemistry considers the physical properties only in so far



as they serve for the external characterization and eventual recognition of the given substances and for the deduction of chemical regularities. The most important physical properties—state of aggregation, the temperature of fusion and boiling, the specific gravity, capacity for heat, etc.—are partly obtained from Physics, and, in part, will be considered later, in special cases.

Here, therefore, only the morphological characters of the solid bodies will receive a brief consideration.

The homogeneous solids exhibit either similar properties in all their parts, are *amorphous*, or show differences in certain definite directions, which permit them to appear as *crystalline*. The cause of this deportment lies in the arrangement of the smallest substance particles, of the molecules, which in the first instance is irregular, hence cannot cause differences in any direction, while in the crystalline structure the molecules are regularly grouped according to directions of varying density and coherence, which find expression in the cleavage and the optical and thermal behavior of bodies. A consequence of this regular arrangement is, in the case of undisturbed formation, the external limitation of bodies by planes, edges and angles, which represent the crystal form. The number and forms of these crystal elements are very much multiplied, since several thousand forms are known. It is, however, possible to reduce the numberless varieties to a few classes or *systems*, by comparing the same in their manner of formation, and by referring their principal elements—the planes—to definite axes, *i. e.*, to directions or lines, which are imagined so placed through the middle point of the crystals that their planes lie symmetrically with them. In this manner, by distinguishing the various axis intersection, *crystallography* arrives at the following six systems of crystallization:—

1. The Regular or Tesseral System.
2. Quadratic or Tetragonal System.
3. Rhombic System.
4. Hexagonal or Rhombohedral System.
5. Monoclinic System.
6. Triclinic System.

The position of any even plane in space is determined by three points of a system of coördinates, and also the position of a crystal plane by its points of intersection with the three axes, or by the distances from the centre of the axis

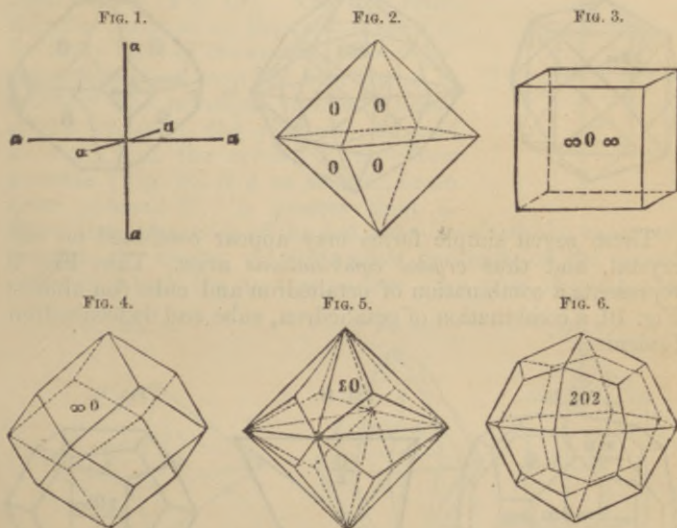
at which the plane (by suitable expansion) cuts or intersects the three axes. These distances are termed the *parameters* of the plane. In the regular system all three axes are of equal length and equal value, for which reason they are designated by the same letter *a* (Fig. 1). If a plane intersect all three axes at equal distances (as in the octahedron) the parameter ratio is  $a : a : a$ ; if at unequal distances the ratio is  $a : a : ma$ , or  $a : ma : na$ ; in which the parameter upon the first axis is also made  $= 1$ . If a plane lie parallel to an axis (intersecting it at infinity) its parameter with reference to this axis  $=$  infinity ( $a : a : \infty a$ ); if it be parallel to two axes, two parameters are  $=$  infinity ( $a : \infty a : \infty a$ ). Hence these parameter ratios designate the position of a plane; and as all the planes in simple crystal forms are similar, these marks represent also the entire simple form, *i. e.*, the whole of all planes, which are deduced from the same parameter ratio.

In the regular system, when all these axes are of equal length, the parameters *m*, *n* (the parameter of the first axis made  $= 1$ ) are, in accordance with experience in all crystals, simple rational numbers ( $1, \frac{2}{3}, 2, \frac{3}{2}, 3, 4$ , etc.) In other systems of crystallization the axes are unequal and do not stand in any rational ratio to their lengths ( $a : b : c$ ), and, therefore, also to the parameters of the planes ( $a : mb : nc$ ); but the ratio of the parameter coefficients  $1. m. n.$ , in them, as in the regular system, is, as learned from experience, a simple, rational one.

According to the number of axes, five of the crystallographic systems are triaxial or *trimetric*; for practical reasons we accept four axes in the hexagonal system—*tetrametric* system. The axes of the five trimetric systems are either all at right angles to each other, and are distinguished only by varying lengths—the *orthometric* systems, the regular, the quadratic and the rhombic; or they include also oblique angles—in the two *clinometric* systems, the monoclinic and triclinic. In the regular system the three directions of development are at right angles and perfectly similar, for which reason the bodies belonging to it, like amorphous substances, refract light simply—*isometric* system. The remaining five systems with unlike axes are, on the contrary, doubly refracting, and, indeed, they either only exhibit simple refraction in *one* direction (optically *uniaxial* systems—the quadratic and hexagonal), or truly in *two* directions (optically, *diaxial* systems—the rhombic, mono- and triclinic.) A necessary, geometrical derivation of the various systems of crystallization, based upon the molecular constitution of matter, has been recently proposed by Bravais and Sohncke, in that they proceed from the study of possible normal positions of points or molecules in space; *i. e.*, of such

positions in which about each point the grouping of the remaining points is the same. Thus, it is possible to embrace the point position possible in space into seven groups, which correspond to the six crystallographic systems; in this manner the rhombohedral forms, which crystallography views as the hemihedral of the hexagonal, appear as an independent system.

1. *Regular System.* The crystals of this system are similarly developed according to three directions, and therefore have three similar axes,  $a$ , of the same length, which intersect each other at right angles (Fig. 1). If we imagine the planes arranged in such manner that they intersect the three axes at



similar or dissimilar distances, then, for the various possible parameter ratios (page 22) we have the following seven simple forms:—

1. The *octahedron* (Fig. 2), with the parameter ratio  $a : a : a$ ; for which the abbreviated symbol  $0$  may be written. 2. The *cube* or *hexahedron* (Fig. 3), with the symbol  $a : \infty a :$



$\infty a$  or briefly  $\infty O \infty$ . 3. The rhombic dodecahedron, twelve sides,  $a : a : \infty a$  or  $\infty O$  (Fig. 4). 4. The trigonal tris-octahedron (Fig. 5),  $a : a : ma$  or  $mO$ ; there are several of these, when  $m = \frac{2}{3}, 2$  or  $3$ . 5. The trapezohedron (Fig. 6)  $a : ma : ma$  or  $mOm$ , in which  $m = 2$  (in garnet) or  $m = 3$  (in ammonium chloride). 6. The tetrahexahedron (Fig. 7)  $a : ma : \infty a$  or  $mO \infty$ , in which  $m = \frac{2}{3}, 2$  or  $3$ . 7. The hexooctahedron (Fig. 8)  $a : ma : na$  or  $mOn$ , when, *e. g.*, in fluorite,  $m = 2$  and  $n = 3$ .

FIG. 7.

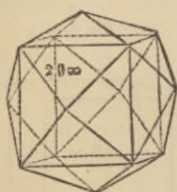
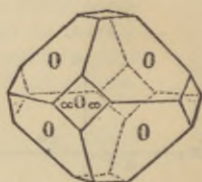


FIG. 8.



FIG. 9.



These seven simple forms may appear combined on one crystal, and thus *crystal combinations* arise. Thus Fig. 9 represents a combination of octahedron and cube (on alum); Fig. 10, a combination of octahedron, cube and dodecahedron (galenite).

FIG. 10.

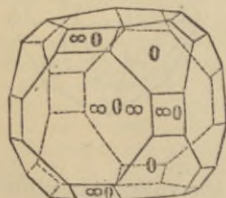


FIG. 11.

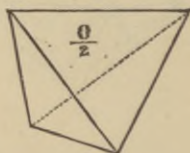


FIG. 12.



In addition to these simple forms, appearing with their full number of planes, hence termed *holohedral*, others appear having only the half or fourth of the possible forms, *hemihedral* or *tetartohedral* forms. We may suppose them produced by the enlargement of the symmetrically distributed

half number of faces of the holohehral form, and therefore we designate them with the corresponding holohedral symbol divided by 2. Such hemihedral forms are: The tetrahedron  $\frac{\pm 0}{2}$  (Fig. 11), resulting from the octahedron, and the pentagonal dodecahedron  $\frac{m 0 \infty}{2}$  (Fig. 12) derived from the tetrahexahedron.

2. *Quadratic System.* Crystals of this system are developed at right angles in three directions, of which two are alike, the third unlike the others. Therefore they possess two similar secondary axes,  $a$ , and an unlike, longer or shorter, principal axis,  $c$ , (Fig. 13). The axis ratio, therefore, is  $a : a : c$ ; the ratio of  $a : c$  is, for every body of the system, definite but not rational (see page 22), *e. g.* for tin 1 : 0.3857. The principal (ground) form\* of this system is the *quadratic pyramid*  $a : a : c$ , with the symbol  $P$ , an *obtuse pyramid* (Fig. 14) if  $c$  be smaller, or an *acute pyramid* if  $c$  is greater than  $a$ .

From these pyramids of the *first order*, in which the axes pass through the angles, we distinguish pyramids of the *second order*, in which the two secondary axes pass through the

FIG. 13.

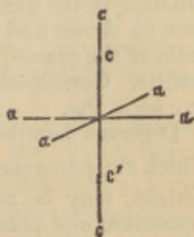


FIG. 14.



FIG. 15.

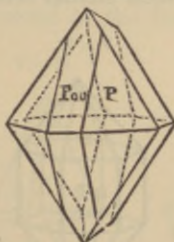
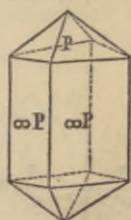


FIG. 16.



middle of the edges. The planes of the latter are parallel to one secondary axis, therefore its symbol is  $a : \infty a : c$  or  $P \infty$ . Fig. 15 represents a combination of a pyramid of the first and second orders.

\* The (ground) principal form is that to which the remaining forms of the same mineral may be most readily referred.

In addition to the above pyramids, others may occur in the same crystal, which intersect the principal axis at the distance  $mc$ . In this case  $m$  is also a simple rational number, *e. g.*, 3, 2,  $\frac{1}{2}$ ,  $\frac{1}{3}$ , etc. The symbol of such secondary pyramids of first order, is  $a : a : mc = mP$ ; that of the second order,  $a : \infty a : mc = mP\infty$ . The coefficient of the secondary axis is always written before  $P$ .

If the pyramid planes intersect the principal axis at infinity, the *quadratic prism* results, and, indeed, a prism of the first order, with the symbol  $a : a : \infty c = P\infty$ ; and a prism of second order,  $a : \infty a : \infty c = \infty P\infty$ . Fig. 16 represents a combination of the quadratic prism with the quadratic pyramid, as seen on zircon and potassium phosphate. With the parameter ratio of the planes,  $a : ma : nc$ , the ditetragonal pyramid  $nPm$  results. Corresponding to it is the ditetragonal prism,  $a : ma : \infty c = \infty Pm$ .

Different hemihedral forms are possible in this system, of which the *tetragonal sphenoid*,  $\frac{+P}{2}$ , corresponding to the tetrahedron, may be mentioned. Chalcopyrite, tin, prussiate of potassium and potassium phosphate crystallize in this system.

3. *Hexagonal System.* The forms of this system, like those of the preceding, exhibit *one* peculiarly striking direction of development, and hence this is chosen as the direction of the principal axis  $c$ . They are distinguished from the four-sided forms of the quadratic system by their sixfold symmetry, which finds expression in their similar secondary axes  $a$  (Fig. 17), in-

FIG. 17.

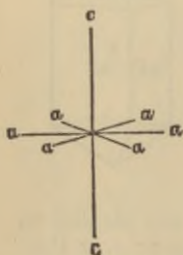
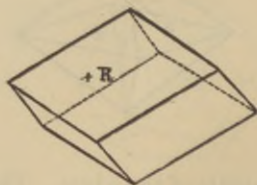


FIG. 18.



FIG. 19.



intersecting each other at  $60^\circ$ . The principal axis is at right angles to these. The ratio of the basal axis is  $a : a (: a) c$ , and the ratio of  $a : c$  for every substance is definite, but not rational; *e. g.*, in quartz, 1 : 1.100; calcite, 1 : 0.8543, etc.



The (ground) fundamental form of the system is the hexagonal pyramid  $a : a : (\infty a) : c = P$ , from which is derived the hexagonal prism  $a : a : (\infty a) : \infty c = \infty P$ ; and, indeed, as in the quadratic system, there are pyramids and prisms of first and second order—latter with the symbol  $a : 2a : (2a) : c = P_2$ , and  $a : 2a : (2a) : \infty c = \infty P_2$ . Further, other pyramids intersecting the principal axis, at the distance,  $mc$ , occur; their symbol is  $mP$  and  $mP_2$ . Fig. 18 represents the combination of pyramid and prism found on apatite. With the common parameter ratio  $a : na : (ra) : mc$  (in which the parameter of the third secondary axis,  $ra$ , as in all other hexagonal forms, is always given by the parameters of the two first secondary axes), results the dihexagonal pyramid,  $mP_n$ , and the dihexagonal prism,  $\infty P_n$ .

From the pyramids  $mP$  are derived, as hemihedral forms, by enlargement of the alternating planes, the rhombohedra  $\frac{\pm mP}{2} = \pm mR$  (Fig. 19). Another important hemihedral form is the *scalenohedron*  $\pm \frac{mP_n}{2}$  derived from the dihexagonal pyramid. Worthy of note is the fact that the hemihedral forms of the hexagonal system occur much more frequently in nature in numberless combinations (especially on calcite), whence sometimes they are treated as a separate system.

4. *Rhombic System.* Three axes of unequal length  $a$ .  $b$ .  $c$ . Any one, as  $c$ , is chosen as principal axis, and of the secondary axes the shorter  $a$  is designated as the brachydiagonal, the

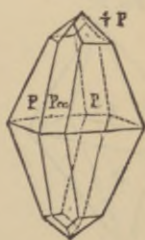
FIG. 20.



FIG. 21.



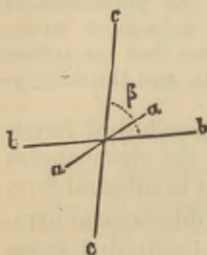
FIG. 22.



longer  $b$  as macrodiagonal (Fig. 20). The axis ratio  $a : b : c$  is definite for every substance, *e. g.*, for sulphur, 0.811 : 1.0899.

The principal forms of the system are the rhombic pyramid  $a : b : c = P$  (Fig 21), the rhombic prism  $a : b : \infty c = \infty P$ , and the domes—brachydiagonal  $\infty a : b : c = \bar{P} \infty$  and the macrodiagonal  $a : \infty b : c = \bar{P} \infty =$  consisting of two pairs of planes. Fig. 22 shows a combination of two pyramids with the brachydiagonal dome. Sulphur (native and that crystallized from carbon disulphide), potassium nitrate, aragonite and barite belong in this system.

FIG. 23.



5. *Monoclinic System.* Three unequal axes, two at right angles to each other, the third, however, at right angles with one and oblique to the other (Fig. 23);  $a$  to  $b$  and  $a$  to  $c$  at right angles,  $c$  to  $b$  oblique with the angle  $\beta$ . The crystals of this system are principally developed according to an axis oblique to another ( $c$  to  $b$ ), and hence one of these is chosen as principal axis  $c$ . Of the two secondaries, one,  $b$ , is called the clinodiagonal, and  $a$  the orthodiagonal. The axis ratio

is always definite for every substance; *e. g.*, for ferrous sulphate  $1.1704 : 1 : 1.5312$  with the angle  $\beta = 76^\circ 33'$ . The monoclinic pyramid is principal form  $a : b : c = P$ , consisting of two hemipyramids,  $+P$  and  $-P$ , (Fig. 24). It corresponds to the monoclinic prism  $\infty P$ . Sulphur (fused), soda, borax, disodium phosphate ( $\text{HNa}_2\text{PO}_4 + 12\text{H}_2\text{O}$ ), Glauber's salt, and orthoclase, crystallize in this system.

FIG. 24.

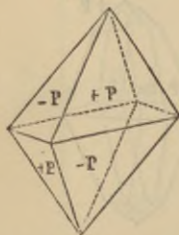


FIG. 25.

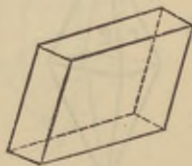
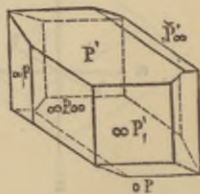


FIG. 26.



6. *Triclinic System.* Three unequal axes all oblique to each other. The axis ratio  $a : b : c$ , and the three angles are definite for each substance. The forms of this system are very complicated, as the triclinic pyramid  $P$  must be considered as

consisting of four quarter pyramids, and the triclinic prism  $\infty P$  (Fig. 25), of two hemiprisms. Potassium dichromate, albite, boracic acid, copper sulphate, crystallize in this system. Fig. 26 represents one of the common forms of the latter.

The crystals in nature, however, because they have grown, rarely occur so regularly developed as represented in the preceding drawings. Ordinarily they are developed more or less in the direction of single axes, whereby the faces of the same form are unlike and the entire crystal appears distorted. But the position of the planes with reference to the axes and the angles which they form with each other always remain unchanged. Therefore the measurement of the angle of the planes by means of the goniometer serves as the only accurate means of determining complicated crystalline forms; from the angles we calculate the axis ratio.

Substances crystallizing in two or three different systems are said to be *dimorphous*, or *trimorphous* (see sulphur). Various substances which crystallize in the same or very similar forms are termed *isomorphous* (compare Isomorphism).





## SPECIAL PART.

### CLASSIFICATION OF THE ELEMENTS.

Ordinarily we are accustomed to divide the elements into two groups: metals and metalloids (see p. 12). The former possess metallic appearance, are good conductors of heat and electricity; the latter or non-metals do not have these properties, or at least in less degree. In chemical respects the metalloids have the tendency to combine with hydrogen, forming volatile, generally gaseous, compounds: the oxygen derivatives form *acids* with water. The metals, on the contrary, rarely unite with hydrogen, and their oxygen derivatives yield the so-called *bases* with water. Further, the binary compounds of metals with the metalloids are so decomposed by the electric current that the metal separates at the electro-negative, and the metalloid at the electro-positive pole. From this we observe the metals are more electro-positive—more basic; the metalloids more electro-negative—of an acid-forming nature. A sharp line of difference between metals and metalloids does not exist. There are elements which in their external appearance appear as metals, while in a chemical respect they deport themselves throughout as metalloids, and *vice versa*. Thus hydrogen, a gaseous element, approaches the metals throughout in its chemical character, while metallic antimony arranges itself with the metalloids.

It is therefore advisable to divide the elements, according to their chemical analogies, in separate, natural groups. The best and only correct classification of all the elements depends on the law of *periodicity*, according to which the properties of the elements and of their compounds present themselves as a *periodic function* of the *atomic weights*. Later we will treat the periodic system more at length; it forms the basis of this text-book, and in accordance with this doctrine we consider the elements in single natural groups of similar chemical deportment. The first of these groups, comprising almost all the so-called non-metals and some metals, are the following:—

Fluorine.	Oxygen.	Nitrogen.	Carbon.
Chlorine.	Sulphur.	Phosphorus.	Silicon.
Bromine.	Selenium.	Arsenic.	.....
Iodine.	Tellurium.	Antimony.	.....
.....	.....	Bismuth.	Tin.

Hydrogen does not belong to either of the above; uniting the metal and non-metallic character in itself, it represents, as it were, the type of all elements, and therefore it will receive first attention. Boron, which has also been classed with the metalloids, although differing somewhat from them in chemical deportment, occupies an isolated position.

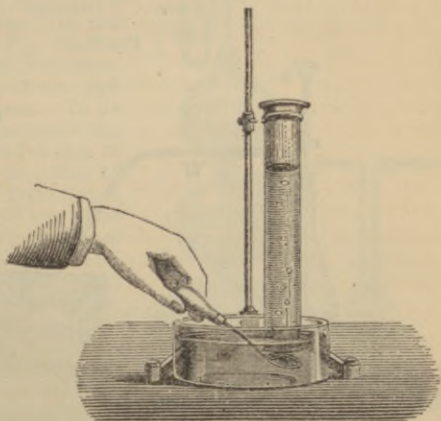
### HYDROGEN.

H - 1.     $H_2$  - 2.

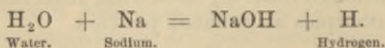
Hydrogen (Hydrogenium), a gaseous body, occurs only exceptionally in a free condition upon the earth's surface, as it combines readily with the oxygen of the air. Found in considerable quantity in the photosphere of the sun and fixed stars. In combination, we find it principally as water and in substances of vegetable and animal origin. Paracelsus first discovered this element in the sixteenth century, and called it inflammable air. In 1781 Watts and Cavendish showed that water resulted from the combustion of hydrogen in the air.

*Preparation.* It may be readily obtained from water, a compound of hydrogen and oxygen. The decomposition of the same by the removal of oxygen can be effected by some metals, like Na and K, at the

FIG. 27.



ordinary temperature. Both metals act very energetically upon it, liberating gaseous hydrogen. To perform the experiment, take a piece of sodium, roll it up in a piece of wire gauze, and shove it, with nippers, under the mouth of a glass cylinder filled with, and inverted over, water (Fig. 27). Bubbles of hydrogen are at once disengaged, which displace the water and collect in the cylinder. The reaction occurring between the sodium and water is expressed by the following chemical equation:—



The compound NaOH, known as sodium hydrate, remains dissolved in the excess of water.

Other metals decompose water in a similar manner, at an elevated temperature. To effect this with iron allow steam to pass through a tube filled with iron filings, which are exposed to a red heat in a combustion furnace. The iron withdraws oxygen from the water, combining with it, while the hydrogen set free is collected.

For laboratory purposes, hydrogen is prepared by the action of zinc upon hydrochloric or sulphuric acid. The reaction with the latter acid is as follows:—

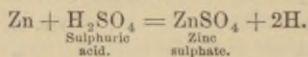
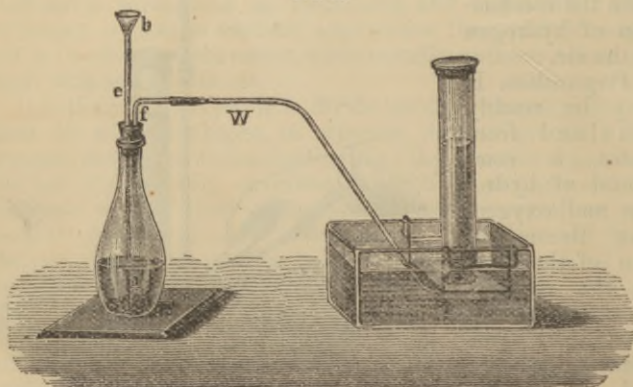


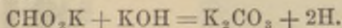
Fig. 28.





Place granulated zinc (obtained by dropping molten zinc into water) in a double-necked flask (Fig. 28), and introduce sulphuric acid through the funnel tube, *b* (diluted with about 3 vols.  $H_2O$ ). The liberation of gas begins immediately, and the hydrogen, escaping through the exit tube, *f*, is collected as previously described.

The hydrogen thus formed, in consequence of a slight admixture of foreign substances, has a faint odor. Pure hydrogen may be obtained by heating potassium formate with potassium hydrate:—

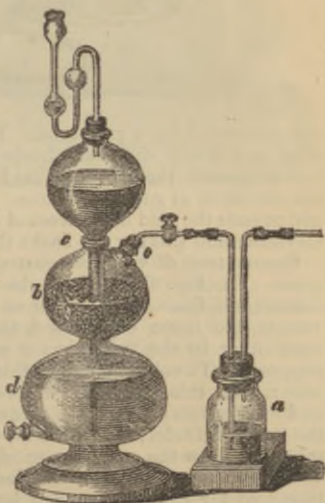


*Purifying and Drying of Gases.* To free gases of the substances which, during their disengagement, might have mechanically been carried along, it is best to conduct them through variously constructed wash bottles, filled with water or such liquids which will absorb the impurities. Ordinarily the so-called Woulff's three-necked bottles are employed (compare Figs. 36 and 42). The open tube, placed in the middle tubulure, is called the safety tube. It serves to equalize the inner pressure with that of the external atmosphere.

Gases liberated from an aqueous liquid are always moist, as they contain aqueous vapor. To remove this conduct them through vessels or tubes filled with hygroscopic substances (see Fig. 34). For this purpose calcium chloride, potassium hydrate, sulphuric acid and other reagents may be used.

*Apparatus for the Generation and Collection of Gases.* In the apparatus pictured in Fig. 28, the liberation of hydrogen continues uninterruptedly as long as zinc and sulphuric acid are present. To be able to control the generation of the gas at pleasure, different forms of apparatus are resorted to. One of the most practicable of these is that of Kipp. It consists of two glass spheres *d* and *b*, Fig. 29, in the upper opening of which, *c*, a third sphere, with an elongated tube, fits air-tight and serves as a funnel. In the middle sphere there is placed granulated zinc, through the tubulure *e*, and diluted sulphuric acid is poured in the spherical funnel, which first fills *d*, then ascends to *b*, where it comes in contact with the metal; at once the evolution of hydrogen

FIG. 29.



commences and the gas escapes through *e*. Upon closing the stop-cock of the tube fixed in *e*, the hydrogen that is being set free presses the sulphuric acid out of *b*, and consequently the liberation of gas ceases. On again opening the cock, the acid rises in *b* to the zinc, and the evolution of gas commences anew. The vessel *a* contains water to wash the escaping hydrogen.

The somewhat complicated Kipp apparatus may be advantageously replaced by the following simple contrivance (Fig. 30). Two bottles provided with openings near their bottom, in which are glass tubes,

FIG. 30.



are connected by a gum tube. The bottle *A* is filled with granulated zinc, and *B* with dilute sulphuric acid. The cock *R* closes *A*. When this is opened, the sulphuric acid flows from *B* to *A*, to the zinc, and the evolution of gas commences. On closing the stop-cock the hydrogen presses the acid back, from *A* to *B*; the evolution of gas ceases. By elevating and sinking the flasks the regulation can be hastened.

Gasometers of various construction serve to collect and preserve gases. In (Fig. 31) we have the ordinary gasometer of Pepys. It is constructed from sheet copper or zinc, and consists of two cylindrical vessels, the lower one closed, the upper open, communicating with each other by the two tubes *a* and *b*. The tubes *c* and *c'* are only supports. To collect gases in this apparatus it must first be filled with water. To this end, pour water into the upper cylinder, and open *a* and *e*; the water then flows through *a*, nearly reaching the bottom of the lower cylinder, while the air escapes through *e*. The side glass tubes, *b*, allow the operator to observe the height of the water level. When the lower cylinder is filled with water, close *e* and *a* (the last traces of air can be removed by opening *b*). To fill the gasometer with gas, remove the cover of the side tubulure *d*, and place in the

same the tube from which the gas is escaping. The latter rushes up into the cylinder, while the water flows out the tubulure. When the water is displaced by the gas, close *a*, after filling the upper cylinder, and then, if desired, open *a*, and the gas can be set free, either by *e* or *b*.

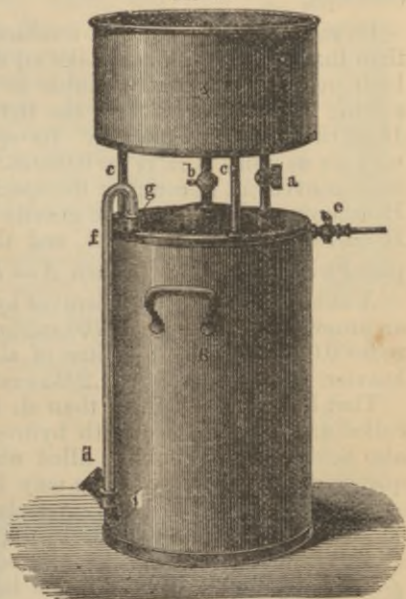
In addition to the gasometer described, various other forms are employed; gas bags are very well adapted for preserving gases.

#### *Physical Properties.*

Hydrogen is a colorless, odorless and tasteless gas. Its ability to refract light and conduct heat is, in accordance with the metallic nature of hydrogen, greater than that of all other gases. By cooling ( $-140^{\circ}$  C.) and powerful pressure (600 atmospheres), it is condensed to a steel-blue, non-transparent liquid, which upon evaporation even becomes solid; consequently liquid hydrogen resembles a molten metal, or, at ordinary temperatures, liquid mercury.

*Condensation of Gases.* Hydrogen and several other gases (oxygen, nitrogen, carbon oxide, nitrogen oxide, methyl), until recently, were considered non-coercible gases (permanent gases), because they could not even be condensed by the strongest pressure (over 2000 atmospheres). This supposed non-condensability was due to the fact that a general property of gases, called by Andrews their *critical temperature*, had been overlooked. All gases show, indeed, as first observed with carbon dioxide (see this), a definite temperature beyond which they cannot be condensed by any pressure. Conversely, all liquids, by the same corresponding temperatures, even under the greatest pressure, are transformed into gases (*absolute boiling temperature of Mendelejeff*). Consequently, in the condensation of gases, in addition to pressure, the corresponding lower temperature must be applied. In

FIG. 31.





fact, by this means, of late years, all the so called permanent gases have been condensed (Pictet and Cailletet). The lower temperatures are attained by the rapid evaporation of liquid carbon dioxide ( $-130^{\circ}$ ), or hyponitrous oxide ( $-140^{\circ}$ ) with aid of air pumps; or the strongly compressed gas is permitted to expand rapidly, whereby, through the evaporation, so much heat is absorbed that the remainder of the gas condenses.

Its refraction of light and conductivity of heat is greater than that of other gases. Like all difficultly coercible gases, hydrogen is but slightly soluble in water, 100 volumes dissolving 1.9 volumes H. It is the lightest of all gases, being 14.46 times lighter than air. Its specific gravity compared with air as unity is  $\frac{1}{14.46} = 0.06926$ . In many respects it is more convenient to compare the specific gravity of gases with H as unity. If the specific gravity of gases compared with H = 1 be represented by  $A$ , and the specific gravity compared with air = 1 by  $D$ , then  $A = D \times 14.46$  and  $D = \frac{A}{14.46}$ .

A cubic decimeter (= 1 litre) of hydrogen weighs at  $0^{\circ}$ , and an atmospheric pressure of 760 millimeters (in the  $49^{\circ}$  of latitude) 0.089578 grams; a litre of air, which is 14.46 times heavier, weighs, therefore, 1.2995 grams.

That hydrogen is lighter than air is shown by a balloon of collodium or gum filled with hydrogen rising in it; this can also be seen in soap bubbles filled with hydrogen. In consequence of its levity, hydrogen may be collected in inverted

FIG. 32.



vessels (opening turned down), by replacing the air, and can also be poured from one cylinder into another, as is represented in (Fig. 32). Owing to its levity, H flows from the inclined cylinder into the one held vertically and filled with air, which it expels. Such a separation of gases, based on

their varying specific gravity, is only temporary, as they soon mingle with each other by diffusion. Owing to its levity and mobility, hydrogen penetrates porous bodies with ease, and diffuses both through animal and vegetable membranes, as well as through gutta percha. Metals, such as iron, platinum, palladium, allow, when in glowing condition, a free passage to hydrogen, whilst for other gases they are impenetrable; this behavior

is probably dependent partly upon the chemical attraction of these metals for hydrogen.

*Chemical Properties.* Hydrogen is characterized by its ability to burn in the air, at the same time combining with the oxygen of the latter and forming water; hence its name hydrogenium (from ὕδωρ water, and γεννάω, I produce). Its flame is faint blue and almost non-luminous. When a mixture of hydrogen and air is ignited a violent explosion ensues; therefore, before bringing a light in the vicinity of hydrogen disengaged in a vessel filled with air, allow the latter to fully escape, otherwise the vessel will be shattered to pieces by the explosion.

As hydrogen itself is inflammable, it cannot sustain the combustion of other bodies which will burn in the air. If a burning candle be introduced into an atmosphere of the gas contained in an

FIG. 33.

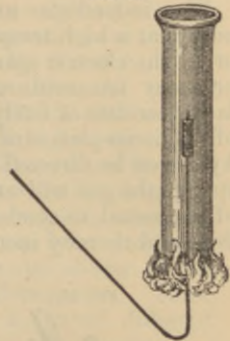
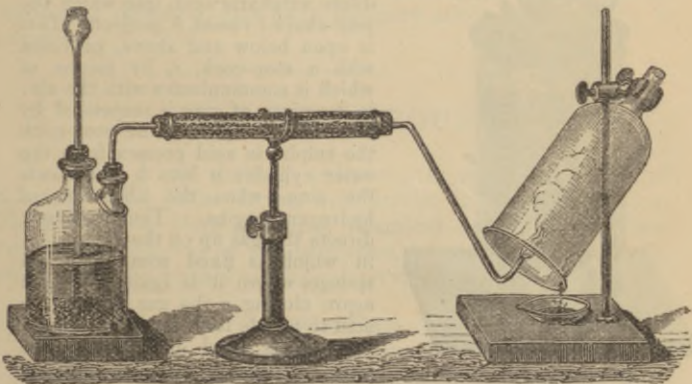


FIG. 34.



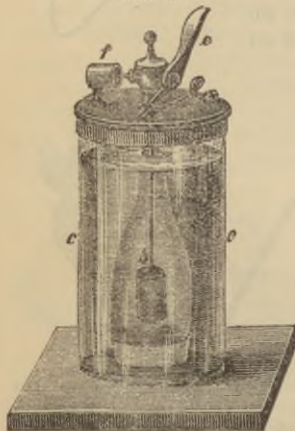
inverted cylinder (Fig. 33), the latter will ignite at the mouth of the vessel, but the candle is extinguished in the hydrogen gas.

Water is the product of the combustion of hydrogen in the air. It is a chemical compound containing hydrogen and

oxygen. To render the formation of it visible, by the combustion of hydrogen, the flame of the latter is made to burn under a cold glass jar (Fig. 34). The sides of the latter are soon covered with moisture, which collects in drops of water. To avoid any deception the hydrogen is first conducted through a tube filled with calcium chloride, to absorb all moisture.

The immediate union of hydrogen with oxygen only occurs at a high temperature, either in contact with a flame or by the electric spark. The combination can be effected at ordinary temperatures with the aid of platinum sponge; the latter consists of finely divided metal, obtained by the ignition of ammonio-platinum chloride (see Platinum). If a stream of hydrogen be directed upon a piece of freshly ignited platinum sponge the gas will at once ignite. This is due to the ability of the metal to condense hydrogen and oxygen upon its surface, and thereby increase the ability of the gases to unite.

FIG. 35.



Upon this behavior depends the action of the so-called *Doberiner Lamp* (Fig. 35). This consists of a continuous hydrogen generator. The outer glass cylinder, *c*, is filled with dilute sulphuric acid, into which the pear-shaped vessel, *b*, projects. This is open below and above, provided with a stop-cock, *e*, by means of which it communicates with the air; in it a piece of zinc is suspended by a wire. On opening the stop-cock the sulphuric acid presses from the outer cylinder *a* into *b* and meets the zinc—when the liberation of hydrogen begins. The stop-cock directs the gas up on the support, *f*, in which is fixed some platinum sponge, where it is ignited. Upon again closing *e* the gas causes the acid to recede from the inner vessel, the zinc is freed of acid and the hydrogen evolution ceases.

Very characteristic for hydrogen is its absorption by the metal palladium. As already known, water is so decomposed by the electric current that hydrogen separates at the electro-negative pole and oxygen at the electro-positive. If a piece of palladium, in sheet or wire form, be attached to the electro-negative pole, the disengagement of the gas ceases,



because it is absorbed by the palladium, and in the ratio of over nine hundred times its volume of gas. The palladium expands, becomes lighter in weight, but retains its metallic appearance. Its tenacity and power of conducting heat and electricity are but little impaired. The compound of palladium and hydrogen,  $\text{Pd}_2\text{H}$ , therefore, conducts itself like an alloy of two metals. From the specific gravity of the compound (according to Graham), the specific gravity of the condensed hydrogen is readily found to be 0.62 (water = 1), therefore, somewhat heavier than the metal lithium. Also the metals potassium and sodium when heated from 200 to 400° absorb hydrogen, forming the alloys ( $\text{Na}_2\text{H}$  and  $\text{K}_2\text{H}$ ), in which the density of hydrogen also equals 0.62. From these facts we could conclude that hydrogen possesses a metallic character, and that by condensation it will form a metallic, mercury-like liquid—a conclusion which at present has been confirmed by experiment. Its metallic character is also shown, as we will observe later, by its entire chemical deportment. Thus, under great pressure, hydrogen is able to expel different metals from their salt solutions, the same as other metals do. When palladium hydride is heated it suffers decomposition, hydrogen escaping, just as in mercury alloys the mercury is expelled.

---

## HALOGEN GROUP.

To this group belong chlorine, bromine, iodine and fluorine. The latter is not well known in a free condition. These elements show a similar chemical deportment. They are termed *halogens* or *salt-producers*, because by their direct union with the metals salt-like derivatives result.

### 1. CHLORINE.

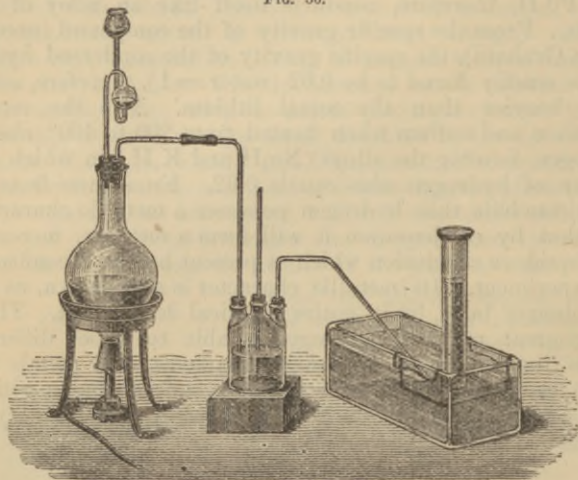
$\text{Cl} = 35.4$      $\text{Cl}_2 = 70.8$

It does not occur free in nature, as it is endowed with strong affinity for the majority of the elements. Its most important derivative is sodium chloride, or rock salt. The Swedish chemist, Scheele, discovered it in 1774. Gay-Lussac and Thénard, in France (1809), however, and Davy, in England (1810), first established its elementary character.

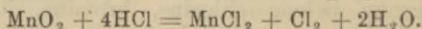
*Preparation.* To obtain free chlorine, heat a mixture of

black oxide of manganese ( $\text{MnO}_2$ ) and hydrochloric acid in a flask (Fig. 36), provided with a so-called Welter's safety tube, to equalize the gas pressure. The escaping gaseous chlorine is washed and freed from acid mechanically carried along by passing through the water in a three-necked Woulff's bottle,

FIG. 36.

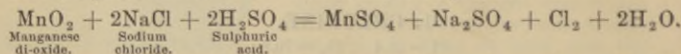


then collected over the same liquid. The reaction which occurs above is indicated in the following equation:—

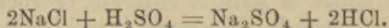


The manganous chloride formed dissolves in the water.

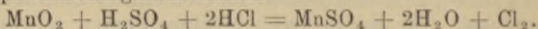
The evolution of the chlorine proceeds more regularly if a mixture of manganese oxide (5 parts), sodium chloride (4 parts) and sulphuric acid (12 parts diluted with six of water) is employed:—



This reaction comprises two phases: First, the sodium chloride ( $\text{NaCl}$ ) is decomposed by the sulphuric acid, yielding sodium sulphate and hydrochloric acid:—



The latter acid then acts, together with a new portion of sulphuric acid, upon the manganese dioxide:—



The second method is more advantageous for laboratory purposes; the first, however, is preferred in practice, as it is cheaper.

The resulting manganous chloride ( $MnCl_2$ ) is converted by the *Process of Weldon* into manganese superoxide (see this). Technically, chlorine is also obtained by the *Process of Deacon*, by conducting HCl mixed with air over glowing porous substances (bricks) saturated with metallic salts (copper sulphate).

As chlorine gas dissolves readily in cold water it is advisable to collect it over warm. Over mercury it cannot be collected, as it readily combines with the latter. When perfectly dry chlorine is sought, conduct the liberated gas through Woulff's bottles containing sulphuric acid, to absorb the moisture, then collect in an empty upright flask (compare Fig. 44, p. 54). As chlorine is so much heavier than air it will displace the latter.

*Physical Properties.* Chlorine is a yellowish-green gas (from  $\chi\lambda\omega\rho\delta\varsigma$ ), with a penetrating, suffocating odor. Its specific gravity compared with hydrogen (1) is 35.4; with air (= 1) it is  $\frac{35.4}{14.46} = 2.45$ . At  $15^\circ C.$ , and a pressure of 4 atmospheres (at  $-40^\circ C.$ , at ordinary temperatures) it condenses to a yellow liquid. To effect the condensation of chlorine take a bent glass tube (Fig. 37), introduce into the leg closed at one end some crystals of chlorine hydrate ( $Cl_2 + 10H_2O$ , see below), then seal the open end. The limb containing the compound is placed in a water bath; the other is cooled in snow. Upon heating the water to a little above  $30^\circ$  the chlorine hydrate is decomposed into water and chlorine gas, which condenses to a liquid in the covered limb. On reversing the position of the limbs and cooling the one previously warmed, the chlorine distills back and is reabsorbed by the water. Charcoal saturated with chlorine may be substituted for the chlorine hydrate. This substance takes up 200 volumes of chlorine, which are again disengaged on heating.



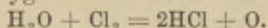
One volume of water, at  $20^\circ C.$ , absorbs 2 volumes of chlorine; at  $8^\circ C.$ , 3 volumes. The aqueous solution is known as chlorine water (*aqua chlori*), and possesses almost all the



properties of the free gas; therefore frequently employed for laboratory uses as a substitute for it. The yellow, scale-like crystals of chlorine hydrate ( $\text{Cl}_2 + 10\text{H}_2\text{O}$ ) separate when water saturated with the gas is cooled below  $0^\circ$ . This compound is regarded as one of chlorine with water. At ordinary temperatures it decomposes into its constituent atoms.

*Chemical Properties.* Chlorine has great affinity for almost all the elements. It combines, at ordinary temperatures, with the most of them, to form chlorides. When thin sheet copper (impure gold leaf), or, better, pulverized antimony or arsenic, are thrown into a vessel filled with dry chlorine, they burn with a bright light; a piece of phosphorus will also inflame in an atmosphere of the gas.

Chlorine unites with hydrogen just as energetically. A mixture of equal volumes of the gases combines in direct sunlight, with violent explosion. In dispersed sunlight the action is only gradual; in the dark it does not occur. The great affinity of chlorine for hydrogen is manifested in the hydrogen compounds; most of these are so decomposed by the chlorine that it removes the hydrogen from them, and forms hydrochloric acid. Thus water is decomposed by Cl into hydrochloric acid and oxygen:—



If a glass cylinder be filled with, and inverted over, chlorine water and exposed to the sunlight, the evolution of gas, which will collect in the upper portion of the vessel, will soon be observed; this is oxygen. In diffused light the decomposition will not be so rapid; it is hastened by heat.

Chlorine alters the hydrocarbons, in that it abstracts hydrogen. The reaction is sometimes so violent that carbon is separated in free condition. A piece of tissue paper saturated with newly distilled turpentine oil, introduced into a dry chlorine atmosphere, is immediately carbonized. An ignited wax candle immersed in chlorine burns with a smoky flame, with separation of carbon.

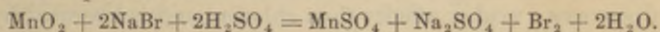
The organic (containing C and H) dye stuffs are decolorized by moist chlorine gas. The same occurs with the dark blue solutions of indigo and litmus; colored flowers are also rapidly bleached by it. On this principle depends the application of chlorine in bleaching goods, and in destroying decaying matter and miasmas (chlorine disinfection. See Bleaching Lime).

The bleaching action of chlorine is mostly influenced by the presence of water. It probably depends on the oxidizing action of the oxygen liberated by the chlorine (see above). This property free oxygen does not possess, it does, however, very probably belong to that which is in the act of forming—of becoming free. We will learn, later, that many other elements, at the moment of their birth (*in statu nascendi*), act more energetically than when free; the cause for this will be explained later.

## 2. BROMINE.

Br = 79.7. Br<sub>2</sub> = 159.4.

Bromine, the perfect analogue of chlorine, was discovered by Balard, in 1826. It occurs as sodium bromide, accompanied by sodium chloride in, however, much smaller quantity, in the sea (especially in the water of the Dead Sea), in many salt springs, as at Kreutznach and in Hall. When sea water, or other salt water, is evaporated, sodium chloride first separates; in the mother-liquor, among other soluble salts, are found sodium and magnesium bromides. The principal source for the bromine yield are the upper layers of the rock salt deposits of Stassfurth, near Magdeburg, which contain bromides together with other salts. At present, large quantities of bromine are obtained in America. The method of its preparation is similar to that employed under chlorine. A mixture of manganese dioxide and sodium bromide is warmed with sulphuric acid:—

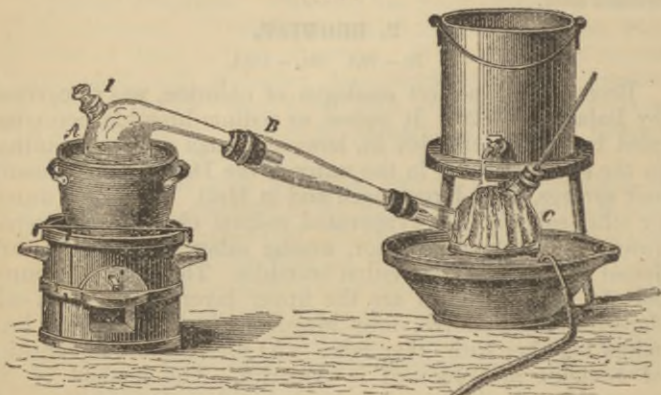


The operation can be executed in the apparatus pictured in Fig. 38. This can also be used for many other distillations. The retort *A*, containing the mixture, is heated in a water bath; the tube *B* serves to cool the vapors which are condensed by cold water or ice in the receiver *C*. When free chlorine is conducted into an aqueous solution of sodium bromide, bromine separates out.

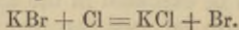
Bromine is a heavy, reddish-brown liquid, of an exceedingly penetrating, chlorine-like odor (hence the name Bromine, from *βρωμος*, *stench*). At 7.3° it crystallizes to a yellow-green, scaly mass, having metallic lustre and resembling iodine. Liquid bromine, at 0°, has the specific gravity, 3.18 (water = 1); it is very volatile, yielding dark brown vapors at medium temperatures, and boiling at 63° C., converting itself, at the same time, into a yellowish-brown vapor. Its density equals 79.7 (hydrogen = 1), or 5.53 (air = 1).

Bromine is more soluble in water than chlorine. Cooled below  $4^{\circ}$  C., the hydrate ( $\text{Br}_2 + 10\text{H}_2\text{O}$ ), analogous to that of chlorine, crystallizes out. This is decomposed at medium temperatures. Bromine dissolves with ease in alcohol, and especially in ether, chloroform and carbon disulphide.

FIG. 38.



In a chemical point of view, bromine is extremely like chlorine, combining with most metals to form bromides; but it possesses a weaker affinity than chlorine, and is liberated by the latter from its compounds:—



With hydrogen it only combines on warming, not in sunlight. Upon hydrocarbons it acts like chlorine, withdrawing hydrogen from them. Bromine water gives starch an orange color.

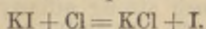
### 3. IODINE.

$\text{I} = 126.5$   $\text{I}_2 = 253.$

Iodine occurs, as well as bromine, in combination with sodium, in sea water and some mineral springs, especially at Hall, in Austria, and the Adelheit Spring, in Bavaria. In most springs the iodine can easily be directly detected; in sea water it is, however, only present in such minute quantity that its separation, practically, is disadvantageous. Sea-algae absorb it from the water, and these are then thrown by the tide on



various coasts, where it is burned, yielding an ash (known as *kelp* in Scotland, as *varec* in Normandy) which represents the principal source for the manufacture of iodine. It was in this ash that the element was accidentally discovered, in 1811; in 1815, it was investigated by Gay-Lussac, and its elementary character established. To obtain the iodine, the ash is treated with water, the solution concentrated and the sodium and magnesium iodides are further worked up. Lately, iodine has been obtained from the mother-liquors of the crude Chili salt-petre. It is set free from its compounds in the same manner as chlorine and bromine—by distillation with manganese dioxide and sulphuric acid. It is more convenient to pass chlorine (or, better, nitrous acid) through a solution of the salt, when all the iodine will separate:—



The grayish-black powder thus liberated is collected on a filter, dried, and then sublimed.

Iodine is a gray-black solid, subliming in large rhombic crystals, possessing strong metallic lustre. It has a peculiar odor, reminding one somewhat of that of chlorine; it stains the skin brown, and is corrosive, although not as strong as bromine. Its specific gravity is 4.95. Fuses at  $113^{\circ}$  to a dark brown liquid, and boils near  $200^{\circ}$ , passing at the same time into a dark violet vapor (hence the name iodine, from *ιώδης*, *violet-blue*).

The vapor density of iodine equals 8.7 up to  $600^{\circ}$  C., (air = 1) or 126.5 (H = 1), corresponding to the molecular value  $\text{I}_2 = 253$ . Above  $600^{\circ}$  the vapor density gradually diminishes and about  $1500^{\circ}$  it is only half the original. This is explained by the gradual decomposition (see Dissociation of water) of the normal diatomic molecule  $\text{I}_2$  into the free atoms  $\text{I} + \text{I}$ . In like manner, the bromine molecules  $\text{Br}_2$  also, at high temperatures, suffer a separation into the free atoms, while the vapor density of chlorine remains unchanged.

Iodine is very slightly soluble in water, more readily in alcohol (*Tinctura Iodi*), very easily in ether, chloroform and carbon disulphide, the two last assuming a deep red violet color in consequence. It crystallizes particularly beautiful, in forms of the rhombic system, from a solution of glacial acetic acid.

In chemical department iodine closely resembles bromine and chlorine; it possesses, however, weaker affinities, and for this reason is set free, by those elements, from its compounds.

With the metals it usually only combines when warmed; with hydrogen it does not combine directly, and it does not remove hydrogen from its carbon compounds.

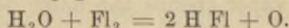
Characteristic for iodine is the deep blue color it imparts to starch. On adding starch-paste to the solution of an iodide, and following this with a few drops of chlorine water, the paste will immediately be colored a dark blue by the separated iodine. This reaction serves to detect the smallest quantity of it.

Iodine is largely employed in medicine, photography, and in the preparation of aniline colors.

#### 4. FLUORINE.

Fl = 19 (Fl<sub>2</sub> = 38).

Fluorine possesses such strong affinity for almost all substances that it cannot be obtained free; it attacks glass and even platinum vessels. Its most important compound is fluorite (calcium fluoride CaFl<sub>2</sub>), which is used for the preparation of the others, which are very similar to the chlorine derivatives. When silver fluoride is heated in a stream of chlorine, or calcium fluoride in a current of oxygen, there escapes a colorless, very violent smelling gas, which attacks glass and all the metals. Upon conducting the same into water, oxygen is disengaged from the latter:—



This gas is probably fluorine. Its affinity for the metals and hydrogen is much greater than that of chlorine.

Upon the basis of theoretical observations developed later the specific gravity of free fluorine is 19 (hydrogen = 1).

The four observed and similar elements, fluorine, chlorine, bromine and iodine, exhibit gradual differences in their properties, and what is remarkable, this gradation stands in direct relation to the specific gravity of the elements in the state of gas or vapor.

	Fl	Cl	Br	I
Specific Gravity	19	35.4	79.7	126.5.

With the increase of specific gravity occurs a simultaneous condensation of matter, which expresses itself in the diminished volatility. Fluorine is a gas; chlorine can readily be condensed to a liquid; bromine is a liquid at medium tempera-

tures, and iodine finally is a solid. Other physical properties, as seen in the following table, are also in accord with the preceding.

	Fluorine.	Chlorine.	Bromine.	Iodine.
Fusing point.....	.....	.....	- 7°	+ 107°
Boiling point.....	.....	- 33°	+ 63	+ 200°
Specific gravity in liquid or solid condition.....	.....	1.33	3.18	4.97
Color.....	Colorless	Yellow	Brown	Black

Just such a gradation, as we have seen, is observed in the chemical affinities of these four elements for the metals and hydrogen; fluorine is the most energetic, iodine the least. Therefore, each higher element is separated from its soluble metal and hydrogen compounds by the lower. We will discover, later, that in the affinity of the halogens for oxygen and some other metalloids, the reverse is true.

## COMPOUNDS OF THE HALOGENS WITH HYDROGEN.

With hydrogen the halogens form compounds of an acid nature, readily soluble in water.

### 1. HYDROGEN CHLORIDE.

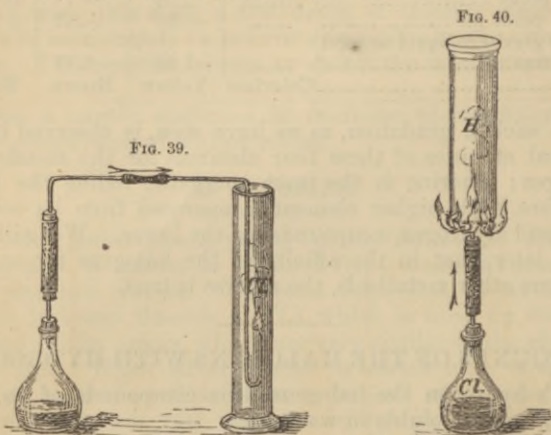
HCl — 36.4. Density — 18.25.

The direct union of chlorine with hydrogen takes place when heated and by the action of direct sunlight or other chemically active rays; in diffused light the action is only gradual, and does not occur at all in the dark. On introducing a flame of hydrogen ignited in the air into a cylinder filled with chlorine (Fig. 39), it will continue to burn in the latter. The opposite, the combustion of chlorine in an atmosphere of hydrogen, may be easily shown in the following experiment (Fig. 40). An inverted cylinder is filled with hydrogen by displacement, the gas is ignited at the mouth, and a tube immediately introduced which will conduct dry chlorine into the cylinder. The burning hydrogen will inflame the chlorine, which will continue to burn in the former. From these experiments, we perceive that combustibility and combustion are only relative phenomena; if hydrogen is combustible in chlorine (or air), so, inversely, is chlorine (or air) combustible in hydrogen. By the term combustion, in



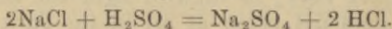
chemistry, is understood every combination of a body (with gaseous aid) which is accompanied by the phenomenon of light.

A mixture of equal volumes of chlorine and hydrogen, made under the above conditions, of the union of the gases,



explodes with very great violence. The product is hydrogen chloride.

The formation of the latter compound succeeds best by allowing sulphuric acid to act upon sodium chloride, when solid sodium sulphate and hydrogen chloride gas will result:—



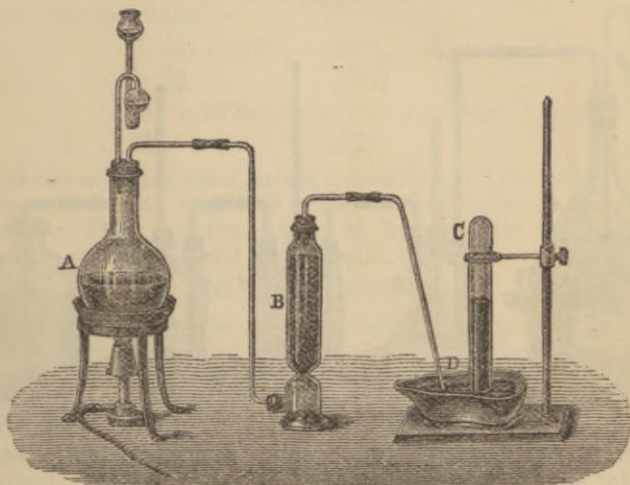
Pour over 5 parts sod. chloride, 9 parts sulphuric acid, somewhat diluted (2 parts), and warm the mixture gently in a flask, A (Fig. 41). The escaping hydrogen chloride is conducted through a Woulff's bottle, containing sulphuric acid to the cylinder B (filled with pumice stone saturated with sulphuric acid), intended to free it from all moisture, and afterwards collected over mercury.

*Physical Properties.* Hydrogen chloride is a colorless gas with a suffocating odor. In moist air it forms dense clouds. Under a pressure of 40 atmospheres (at  $10^\circ\text{C}$ ., or 1 atmosphere at  $-80.3^\circ$ ), it condenses to a liquid, with a specific gravity of 1.27, which does not solidify at  $-110^\circ$  and boils at  $-80.3^\circ$ .

The specific gravity of the gas (density) is 18.25 ( $H = 1$ ), or 1.26 (air = 1).

Hydrogen chloride possesses an acid taste and colors blue litmus paper red; it is, therefore, an acid, and has received the name hydrochloric acid gas. It dissolves very readily in water, and on that account cannot be collected over it. One volume of water at  $0^{\circ} C.$  dissolves 505 volumes, and at ordinary temperatures about 450 volumes of the gas. This great solubility is very nicely illustrated by filling a long glass

FIG. 41.

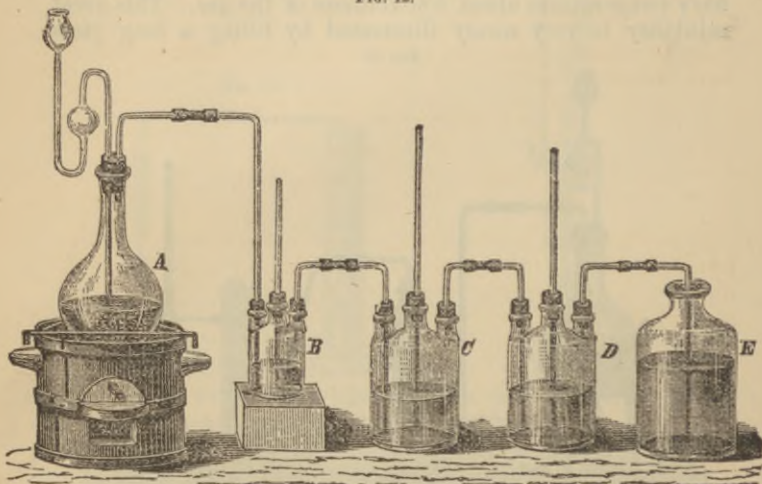


cylinder with the gas and then just dipping its open end beneath water; the latter rushes up into the vessel rapidly, as it quickly absorbs the gas. The aqueous solution of hydrogen chloride, in ordinary language, is known as muriatic or hydrochloric acid (*acidum hydrochloratum*). For its preparation the gas is passed through a series of Woulff bottles (Fig. 42) containing water. The small bottle *B*, in which there is but little water, serves to wash the gas—free it of any mechanically admixed sulphuric acid. The same apparatus may be employed in the manufacture of chlorine water, and is generally used in the saturation of liquids with gases.

A solution saturated at  $15^{\circ} C.$ , contains about 40 % hydrogen chloride, has a specific gravity of 1.2, and fumes in the air.

On the application of heat the gas again escapes, and the temperature of the liquid rises to  $110^{\circ}$  C., when a liquid distills over, containing about 20 % of hydrogen chloride, having a specific gravity of 1.104 and almost corresponds to the formula  $\text{HCl} + 8\text{H}_2\text{O}$ . The composition of the distillate varies somewhat with the pressure. On conducting hydrogen chloride into hydrochloric acid cooled to  $-22^{\circ}$ ,

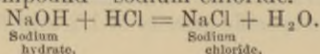
FIG. 42.



crystals of the formula  $\text{HCl} + 2\text{H}_2\text{O}$  separate, which fuse at  $-18^{\circ}$  and then decompose.

Hydrochloric acid finds an extensive industrial application, and is obtained in large quantities, as a by-product, in the soda manufacture.

*Chemical Properties.—Acids—Bases—Salts.* Hydrogen chloride, as well as its solution, possesses all the properties of acids, and can well figure as a prototype of these; it tastes intensely acid, reddens blue litmus paper, and saturates the bases (metallic oxides and hydrates); *i. e.*, such bodies as impart a blue color to red litmus paper. If we add hydrochloric acid to a solution of a base, *e. g.*, sodium hydrate, until the reaction is neutral, we will obtain (besides water) a neutral, solid compound—sodium chloride.

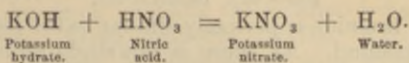


Sodium  
hydrate.

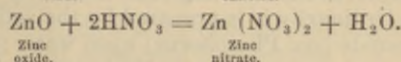
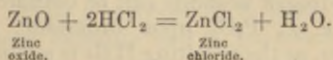
Sodium  
chloride.



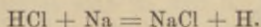
HBr, HI and HFl deport themselves similarly to HCl. These halogen compounds of hydrogen are termed *haloid acids*, to distinguish them from those which, in addition to hydrogen, contain oxygen, hence called *oxygen acids*. The latter conduct themselves like the former, and saturate bases, forming salts and acids:—



In the same manner the acids act upon the basic oxides, to form salts and water:—

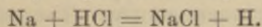


When acids act upon metals, generally, the hydrogen of the former is directly displaced; *salts* and free hydrogen are produced. Thus, by the action of hydrochloric acid upon sodium, its chloride and water result:—

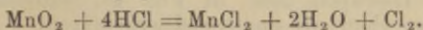


From the cited examples it is manifest that *acids* are such hydrogen compounds as, by the replacement of their hydrogen by metals (by the action of metallic oxides, hydroxides or free metals), yield *salts*. The oxides capable of forming salts by the saturation of acids are called *bases*. Finally, by the term *salts*, we understand such compounds as are analogous to sodium chloride and formed by the mutual action of bases and acids. Salts are distinguished as *haloid salts* and *oxygen salts*. The first have no oxygen and arise in the direct union of the halogens with the metals.

Hydrogen chloride is a very stable compound, suffering only a partial decomposition at 1500° C. Its composition is easily analytically established by the following experiments: Pass hydrochloric acid gas over a piece of sodium, heated in a glass tube, and hydrogen will escape from the latter:—



If manganese superoxide, on the other hand, be heated in it, chlorine will be disengaged:—



If the electric current be permitted to act upon an aqueous solution of hydrochloric acid, the latter will be so decomposed that chlorine separates at the electro-positive and hydrogen at the electro-negative pole.

## 2. HYDROGEN BROMIDE.

HBr = 80.7. Density = 40.3.

Hydrogen bromide is perfectly similar to the corresponding chlorine compound. As there is but slight affinity between Br and H their direct union will only occur at a red heat or in the presence of platinum sponge (see p. 38). Like hydrogen chloride, hydrogen bromide can be obtained by the action of some acids, *e. g.*,  $P_2O_5$ , upon bromides; sulphuric acid would not answer, as the resulting HBr is again partly decomposed by it. Ordinarily it is prepared by the action of phosphorus tri-bromide (see Phosphorus) upon water:—

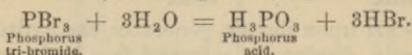


FIG. 43.



Place some water (1 part) in a flask (Fig. 43), gradually admit through the funnel, supplied with a cock, the liquid,  $PBr_3$  (3 parts), and warm gently. The escaping HBr gas is collected over mercury or conducted into water. To free it perfectly from accompanying  $PBr_3$  vapors it is passed through water (the U-shaped tube, in Fig. 43, contains pieces of pumice stone, which are moistened with water).

Instead of employing prepared brom-phosphorus, we may let bromine vapors act upon phosphorus moistened with water. As the action of bromine upon ordinary yellow phosphorus is too energetic, it is more practical to employ red amorphous phosphorus.

To obtain an aqueous solution of the gas, pour 15 parts  $H_2O$  over 1 part amorphous phosphorus, and then add Br (10 parts) drop by drop. Finally the solution is heated, filtered and distilled. From bromides ( $NaBr$ ,  $KBr$ ) hydrogen bromide is obtained by distillation with somewhat dilute sulphuric acid, with addition of phosphorus.

Avery's convenient method to obtain the gaseous  $HBr$  is the following: Heat a mixture of 6 parts sodium sulphite ( $SO_3Na_2$ ), 3 parts bromine and 1 part water.  $HBr$  is at once disengaged.

Hydrogen bromide is a colorless gas, burning strongly in the air. Under great pressure it is condensed to a liquid, boiling at  $-73.3^\circ$ , and solidifying at  $-120^\circ$ . Its density is 40.5 ( $H = 1$ ) or 2.71 (air = 1).

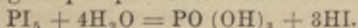
In water the gas is very readily soluble, its saturated solution having a specific gravity of 1.78, and containing 82 %  $HBr$ ; at  $15^\circ$  it contains 49.8 %, and has the specific gravity of 1.515. At  $125^\circ C$  a solution distills over containing 46.8 %  $HBr$ , and closely approximates the formula  $HBr + 5H_2O$ ; its specific gravity is 1.47 at  $14^\circ C$ .

On conducting  $HBr$  into a solution of same cooled to  $-20^\circ$ , crystals of the formula  $HBr + 2H_2O$  separate and melt at  $-11^\circ$ . Chemically,  $HBr$  is the perfect analogue of  $HCl$ ; it is, however, less stable, and suffers a partial decomposition at  $800^\circ C$ .

### 3. HYDROGEN IODIDE.

$HI = 127.5$  Density = 63.7

The attraction of iodine for hydrogen is very slight. Their union (and then only partial) occurs when both elements, in the form of vapor, are conducted over platinum sponge. It cannot be obtained by acting upon iodides with sulphuric acid, because the resulting hydrogen iodide decomposes more easily than the bromide. It is formed, however, similarly to the latter, by acting on phosphorus iodide with water:—

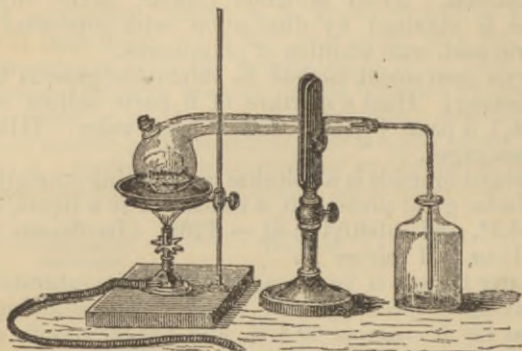


A more convenient procedure, is to warm a mixture of amorphous phosphorus (1 part), iodine (20 parts), and water (15 parts); and an analogous reaction will ensue. Or add a



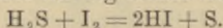
solution of 2 parts iodine in 1 part hydriodic acid, of specific gravity 1.7, drop by drop, to red phosphorus, and aid the reaction by heat. As HI dissolves readily in water, and is decomposed by mercury, we can only collect it by conducting it into a dry flask (Fig. 44), where in consequence of its five-fold greater density, it will displace the air.

FIG. 44.



To get an aqueous solution of HI, take more water, warm the solution, filter, and then distill.

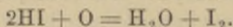
Another method of obtaining HI consists in passing hydrogen sulphide into water having iodine dissolved in it:—



Filter off the separated sulphur and distill the liquid.

Hydrogen iodide is a colorless gas; it fumes strongly in the air; its density is 3.7 ( $\text{H} = 1$ ) or 4.41 ( $\text{air} = 1$ ). Under a pressure of 4 atmospheres (at  $0^\circ$ ) it is condensed to a liquid which solidifies at  $-55^\circ$ . It is easily soluble in water; the solution saturated at  $0^\circ \text{C}$ ., has a specific gravity, 1.99, and fumes strongly in the air. At  $127^\circ$  a solution of 1.56 specific gravity, and containing 57.7% HI distills over, corresponding closely to the formula  $\text{HI} + 5\text{H}_2\text{O}$ .

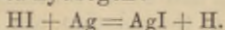
Hydrogen iodide is a rather unstable compound, decomposing at  $180^\circ$ , into hydrogen and iodine. At high temperatures oxygen decomposes it into water and iodine:—



On bringing a flame near a vessel containing a mixture of HI and oxygen, violet iodine vapors will at once fill it. The

same will be noticed when fuming nitric acid is dropped into a vessel containing HI; in this reaction the oxygen of the acid oxidizes the hydrogen and liberates iodine. All oxidizing bodies behave in the same way; the hydrogen iodide abstracts their oxygen and reduces them. The oxygen of the air, even at medium temperatures, gradually decomposes aqueous hydrogen iodide. The solution, at first colorless, becomes brown, owing to separation of iodine, which in the beginning dissolves; subsequently, however, it separates in beautiful crystals.

At ordinary temperatures, mercury and silver decompose HI, with separation of hydrogen:—



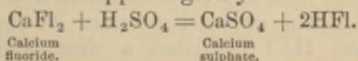
Chlorine and bromine liberate iodine from HI.

This compound is employed as a powerful reducing agent in laboratory work.

#### 4 HYDROGEN FLUORIDE.

H Fl = 20. Density = 10.

It is obtained, like hydrogen chloride, by decomposing fluorides with sulphuric acid. Finely pulverized fluo-rite is mixed with  $\text{H}_2\text{SO}_4$  and heat applied gently:—

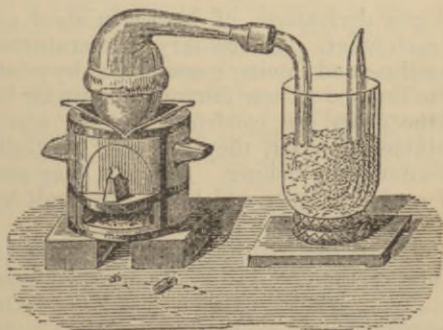


Calcium  
fluoride.

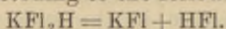
Calcium  
sulphate.

The operation is executed in a lead or platinum retort, as the hydrogen fluoride attacks glass and most of the metals. (Fig. 45). The escaping HFl condenses in the U-shaped

FIG. 45.



receiver containing some water. To get perfectly anhydrous hydrogen fluoride, heat hydrogen potassium fluoride, which then decomposes according to the following equation:—



Anhydrous hydrogen fluoride is a colorless, very mobile liquid, fuming strongly in the air, and attracting moisture with avidity; it boils at  $+19^\circ \text{C}$ ., and has a specific gravity, 0.98 at  $12^\circ$ . To recondense the gas it must be cooled to  $-20^\circ$ .

The concentrated aqueous solution fumes in the air; when heated HFl escapes; the boiling temperature increases regularly until constant at  $120^\circ \text{C}$ ., a solution distills over, whose sp. gr. = 1.15 and whose contents of HFl = 35.37%. The vapors, as well as the solution, are poisonous, extremely corrosive, and produce painful wounds upon the skin.

Hydrofluoric acid dissolves all the metals, excepting lead, gold and platinum, to form fluorides. It decomposes all oxides, even the anhydrides of boric and silicic acids, which it dissolves to form boron and silicon fluorides. Glass, a silicate, is also acted upon; hence the use of the acid for etching glass. To perform the latter operation, coat the glass with a thick layer of wax or paraffin, draw any figure upon it with a pin, and then expose it to the action of the gaseous or liquid HFl. The exposed portions of the glass appear etched; gaseous HFl furnishes a dim, and liquid HFl a smooth, transparent etching.

Vessels of lead, platinum or caoutchouc are employed for the preservation of hydrofluoric acid, as they are not affected by it.

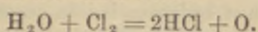
The halogen derivatives of hydrogen show great resemblance to each other. At ordinary temperatures they form strongly smelling and fuming gases, which by pressure can be condensed to liquids. Their fuming in moist air is due to the fact that the gases are condensed by the aqueous vapor. Readily soluble in water, they are only partially expelled from their solution by boiling. As acids they neutralize the bases and form haloid salts, which also can result by the direct union of the halogens with metals.

The densities of the hydrogen haloids exhibit a gradation similar to that of the densities of the halogens (page 46):—

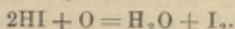
	HFl	HCl	HBr	HI
Density,	10	18.2	40.5	64.



The difference in chemical deportment corresponds to this gradation. Hydrogen fluoride is the most stable, and acts most energetically; chlorine combines with hydrogen in sunlight, bromine only at a red heat, while iodine and hydrogen do not react at all. On the other hand, hydrogen iodide is decomposed at a gentle heat ( $180^{\circ}$ ), into its constituents; the more stable hydrogen bromide at  $800^{\circ}$ , while hydrogen chloride remains unaltered at  $1500^{\circ}\text{C}$ . Corresponding to this we have the very energetic action of fluorine, the tolerably ready action of chlorine upon water, oxygen separating at the same time:—



Iodine does not act upon water. The opposite reaction occurs: oxygen decomposes hydrogen iodide into water and iodine:—

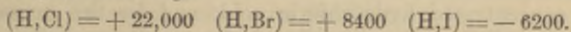


Bromine stands intermediate between chlorine and iodine; in aqueous solution it decomposes water into  $\text{HBr} + \text{O}$ , while a concentrated solution of hydrogen bromide, on the contrary, is partly decomposed by oxygen into water and free bromine.

From all the above it is evident that the affinity of fluorine for hydrogen is the greatest; then follows chlorine and bromine, and finally, as the least energetic element, we have iodine. (See p. 47.)

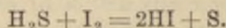
A measure for the chemical affinity of the halogens to hydrogen, as also of the chemical elements and compounds for each other, is the determination of the quantities of heat liberated or absorbed in chemical unions.

The quantity of heat is determined according to heat units or *calories*, and as unit is selected that quantity of heat which is required to raise 1 part of water to  $1^{\circ}\text{C}$ . The quantities of the elements are expressed in numbers corresponding to the atomic weights. Hence, in the union of 35.4 parts chlorine with 1 part hydrogen, 22,000 calories, in the union of 79.7 parts bromine with 1 part hydrogen, 8400 calories are developed, while in the union of 126.5 parts iodine with 1 part hydrogen, 6200 calories are absorbed. This may be more simply expressed by the following:

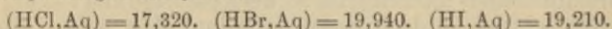


The first two reactions, in which heat is liberated, are exothermic, while the heat absorbing combination of iodine with hydrogen represents an endothermic reaction, which, according to the principle of the greatest heat liberation (p. 17) can only be induced by the addition of external energy (heat). Consequently the thermal relations of the

halogens correspond to their varying chemical affinity, and in them the different deportment of halogen hydrides, in their formation and decomposition, finds complete expression. In similar manner is explained how, from the compounds of the halogens with hydrogen and the metals, iodine is eliminated by bromine and chlorine, and bromine by chlorine. In same manner, bearing in mind the thermal relations in the formation of water, is explained the varying decomposition of the hydrogen haloids by oxygen, and the reverse—that of water by the halogens. To illustrate these interesting relations, let us view the formation of hydrogen iodide, by action of hydrogen sulphide on iodine (p. 54), corresponding to the reaction:—



As in the production of hydrogen iodide, according to the equation, as given above, 12,400 ( $= 2 \times 6,200$ ) calories are absorbed—this rearrangement cannot occur at ordinary temperatures. It does, however, transpire in presence of water, as the heat afforded by the solution of HI in water is sufficient. In the solution of hydrogen haloids, as also of other bodies, in water, a considerable amount of heat is set free, corresponding to the symbols:—



The heat (38,420 C.) set free by the solution of 2 HI in water exceeds the heat of formation of 2HI (12,400 C.) and the decomposition heat of  $\text{H}_2\text{S}$  (9200 C.), so that the reaction can occur even with disengagement of heat.

#### COMPOUNDS OF THE HALOGENS WITH EACH OTHER.

These compounds, resulting from the union of the halogens, like most of those of chemically similar elements, are very unstable.

When chlorine is conducted over dry iodine, the latter being in excess, simple chlorine iodide results, and when the chlorine is in excess there is formed trichlor-iodine.

*Chlorine Iodide*— $\text{ICl}$ —is a red crystalline mass, fusing at  $24.7^\circ \text{C}$ ., and distilling a little above  $100^\circ \text{C}$ . Water decomposes it easily, with formation of iodic acid, iodine and hydrogen chloride.

*Iodine Trichloride*— $\text{ICl}_3$ —is formed upon mixing iodic acid with concentrated hydrochloric acid, and by the action of  $\text{PCl}_5$  upon  $\text{P}_2\text{O}_5$ . It crystallizes in long, yellow needles, and, when heated, suffers decomposition into  $\text{ICl}$  and chlorine (at ordinary pressure, the dissociation commences at  $25^\circ \text{C}$ .); dissolves in little water without alteration; large quantities cause partial decomposition, with formation of iodic acid.

*Bromine Iodide*—IBr—obtained by the direct union of the elements, consists of iodine-like crystals; fusing about 30°.

*Iodine Pentafluoride*—IFl<sub>5</sub>—is produced by the action of iodine upon silver fluoride, and forms a colorless, strongly fuming liquid.

### Weight Proportions in the Union of the Elements. The Law of Constant Proportions. Atomic Hypothesis.

If, in the considered halogen derivatives, as well as in all other chemical compounds, we determine the quantity of the elements (according to methods described in analytical chemistry) we will discover that they are always combined with each other in the same proportions by weight. *In every chemical compound the proportions by weight of the constituents contained in it are invariably the same.* Thus chemical analysis shows the following percentage composition for the halogen derivatives of hydrogen:—

H = 5.3	H = 2.7	H = 1.2	H = 0.8
Fl = 94.7	Cl = 97.3	Br = 98.8	I = 99.2
HF1 = 100.0	HCl = 100.0	HBr = 100.0	HI = 100.0

As experience has shown, H, of all the elements, enters compounds in the least quantity, therefore the latter is chosen as unity, and we calculate those weights of the elements which combine with one part by weight of H. In this manner we find the following proportions for the halogens:—

H = 1	H = 1	H = 1	H = 1
Fl = 19	Cl = 35.4	Br = 79.7	I = 126.5
HF1 = 20	HCl = 36.4	HBr = 80.7	HI = 127.5

Experiments have also established the remarkable fact that the same proportions by weight of the halogens are also obtained by the union of the same with other elements. Thus 19 parts by weight of Fl combine with the following weights of the metals: 23 parts Na, 39 parts K, 32 parts Zn, 31.7 parts Cu, 100 parts Hg and 35.4 parts Cl. 79.7 parts Br and 126.5 parts I combine with exactly the same quantities by weight of the metals. Let us take another example. On bringing copper into the solution of a mercuric salt the former dissolves, while Hg separates out; indeed, 31.7 parts Cu



displace 100 parts Hg. If zinc be brought into the copper solution thus obtained, it will dissolve, while copper separates—and 32 parts of Zn separate 31.7 parts Cu. Furthermore, zinc displaces the hydrogen in acids; from all of them 32 parts Zn separate 1 part H. In all these reactions we observe the same quantities appearing, by weight, of the elements.

These are the remarkable facts fully verified by experiment. Similar facts are formulated in a *rule*, and when a rule comprises a great number of facts—true for all and expressible in numbers—we designate it a *law*. The facts presented above find their expression in the empirical *law of constant proportions*, first proposed by Dalton, and reading: The elements combine with each other in definite proportions by weight, and indeed the proportions by weight of two elements remain the same in their combinations with other elements.

Causes underlie facts. The cause is first expressed in the form of a supposition or *hypothesis*, and when the latter includes a long series of facts, if it is repeatedly substantiated by other phenomena and has acquired a high degree of probability, it is termed a *theory*.

If an hypothesis completely satisfies all the observations to which it refers, it becomes a fact, for the further explanation of which a new hypothesis may be necessary. Conversely, something which long passed as a fact or a theory can be shown to be erroneous, if not any longer consistent with new observations. Hypothesis and that which we designate a fact are distinguished really only by the different degree of probability. If, for example, we make a sight observation we assume the hypothesis that the same has been caused by an external process, the reality of which (in distinction to subjective perceptions) we can only assure ourselves of being certain by repeated observations. The hypothesis of the revolving of the earth, which at first was only a suitable, improbable supposition, proposed for simplifying calculation, has become a fact. The combustion theory of Lavoisier met a like result. Similarly may it deport itself with the supposition of atoms—be it that we comprehend them as material particles or as ether motion.

The law of constant proportions finds its clearest explanation in the *hypothesis of the existence of atoms*. Grecian philosophers even conjectured that matter consisted of indivisible and very small particles—*atoms* (from  $\alpha$ , privative, and  $\tau\omicron\mu\omicron\varsigma$ ,

divisible.) This *a priori* supposition was subsequently repeatedly announced, but Dalton (1804) first gave it an actual confirmation, in that he applied it to the explanation of the law of constant proportions. According to the atomic view, matter consists of extremely small (although not indefinitely small) particles, atoms, which cannot be further divided, either mechanically or chemically. The atoms of different elements possess different weights; all atoms, however, of one element have the same absolute weight and are like each other. By the aggregation of the elementary atoms arise the smallest particles of compound bodies. Upon the basis of this representation is very clearly explained the law of constant proportions; we can comprehend that the quantities of the constituents of a compound should be constant, and that the relative quantities by weight of the elements, as they express the relative weights of the atoms, must in all their compounds be the same.

As yet only the relative atomic weights of the elements have been determined by chemical researches; in these the hydrogen atoms, as they possess the least weight, have been taken as unity. The knowledge of the absolute atomic weight has been, for chemical considerations, until now, unessential. Various physical phenomena allow us to fix, however, even at present, with very great approximate accuracy, the absolute size of the atom. Very different considerations lead to the same conclusion, that the atoms cannot be smaller than the fifty millionth part of a millimeter (Thomson).

If we grant that in the preceding halogen-hydrogen compound one atom of hydrogen is combined with every halogen atom, the conclusion follows, that the found numbers of the ratio express the atomic weights of the halogens. This supposition, however, appears questionable, in view of the more complicated proportions which occur in the union of some elements. Observation shows, to wit, that very frequently two elements unite with each other in not only one, but, indeed, several proportions. For example, 35.4 parts of chlorine combine not only with 31.7 copper and 100 parts mercury but also with 63.4 parts copper and 200 parts mercury. One part, by weight, of hydrogen, combines with 8 to form water, and 16 parts oxygen (to form the so-called hydrogen peroxide); further, with 16 and 32 parts sulphur; oxygen forms five different compounds with nitrogen, according to the following proportions, by weight:—

Nitrogen.		Oxygen.
Nitrous Oxide,	14 parts.	8 parts = $1 \times 8$ .
Nitric Oxide,	14 "	16 " = $2 \times 8$ .
Nitrous Anhydride,	14 "	24 " = $3 \times 8$ .
Nitrogen Dioxide,	14 "	32 " = $4 \times 8$ .
Nitric Anhydride,	14 "	40 " = $5 \times 8$ .

Similar proportions are observed in the union of many other elements. Therefore, they combine with each according to several ratios by weight. As we have noticed in the examples given, the varying quantities of one of the elements (calculating upon the same quantity of the other element), bear a simple ratio to each other; they are mostly multiples of the smallest quantity. These facts are enunciated in the *Law of Multiple Proportions*, also proposed by Dalton (1807), which forms an essential amplification of the law of constant proportions. Based on the atomic hypothesis, these facts are explained by saying the elements can not only unite with each other, atom for atom, but in variable numbers. This considerably complicates the problem of determining the relative atomic weights of the elements, as these are directly dependent upon the conceived number of atoms in a compound. If, for example, in water, one atom of hydrogen is combined with one atom of oxygen, the atomic weight of the latter would = 8 (regarding that of hydrogen as 1). It is just as well possible that water consists of two atoms of H and O, or of one of H and two of O, etc.; in the first case the atomic weight of O would be = 16, in the latter = 4.

Analytical results afford nothing positive for the solution of this difficulty. This was the condition in which, thirty years ago, the question as to the greatness of the atomic weights existed. To establish these correctly, various views were allowed to prevail, none, however, with positive foundation. The question can only be solved upon a new and accurate basis: first and foremost, for that purpose, secure the specific gravities of the chemical compounds in a gaseous or vapor form.

#### Density of Bodies in State of Gas. Volume Ratio in the Union of Gases. Atomic Molecular Theory.

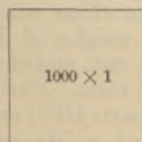
The halogens fluorine, chlorine, bromine and iodine, unite with hydrogen in only one proportion. The supposition, therefore, is, that in the halogen-hydrogen compounds, 1 atom of H is combined with 1 atom of the halogen, the simplest and



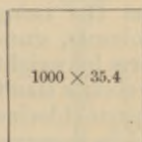
most probable union. Then their weight proportions, derived from analysis, express directly their relative atomic weights. Upon now comparing these atomic numbers (referring to  $H = 1$ , page 59), with those expressing the density in state of gas (also referred to  $H = 1$ ), the astonishing result is that these two series of numbers are identical.

ELEMENTS.	Density. AIR = 1	Density. HYDROGEN = 1	Atomic Weights.
Hydrogen,	0.0693	1	1
Fluorine,	1.31	19	19
Chlorine,	2.44	35.4	35.4
Bromine,	5.39	79.7	79.7
Iodine,	8.71	126.5	126.5

From this similarity of the atomic (combination) weights with the densities, follows the cogent conclusion that *in equal volumes of these elementary gases there is contained the same number of atoms*. Indeed, if in one volume of hydrogen, for example, are contained 1000 atoms of hydrogen, which equal 1000 weight units, and in a like volume of chlorine there are also present 1000 atoms of chlorine, which equal  $1000 \times 35.4$  weight units, then it is evident, that the relation between the atomic weights, and that between the densities (the weights of like volumes) must be the same.



1 Vol. Hydrogen.



1 Vol. Chlorine.

These relations can be expressed by the following rule: *The atomic weights of the halogen elements are proportional or equal to their densities, if referred to the same unit*. Yielding to a too hasty generalization, this was incorrectly followed for all elements.

We arrive at a perfectly similar, but much more general conclusion, by consideration of the physical properties of gases or vapors. The similar deportment of the same under pressure (law of Mariotte and Boyle), their similar expansibility by heat (law of Charles and Dalton, ordinarily the law of Gay-Lussac), only appear comprehensible by the following suppositions. The gases consist of small portions of matter,

which are separated by equally, in proportion to the particles, great distances (those of the centre are alike and suffer like alterations). It immediately follows from this, that *the same number of particles is contained in similar volumes of all gases* (by like temperature and pressure.) The kinetic gas theory, based on the same supposition, explains the similar deportment of gases by the analogous existing force of the smallest gaseous particles.

From the proposition, that in equal volumes an equal number of particles is present, follows directly that their relative weights are proportional to the volume weights or gas densities, and that by determination of the latter, the first are also given. In what ratio these smallest particles (called molecules) stand to the chemically smallest particles (atoms), remains, first of all, undetermined, and is obtained by a comparison of the volume ratios according to which the bodies combine (p. 63). It is, however, even now perceptible, that, at least in case of compound bodies, the smallest gas particles must be sums of atoms, as the same consist of complex atoms.

---

It follows, from the similarity of the atomic weights and the densities, that the halogens must combine with hydrogen in similar volumes, since 1 part by weight of H combines with 35.4 parts by weight of chlorine, etc., and the weights of similar gas volumes stand in the same ratio. Further: 1 part H and 35.4 parts chlorine yield 36.4 parts HCl; one volume of the latter weighs, however, 18.2 ( $H = 1$ , p. 70); consequently, 36.4 parts HCl occupy 2 volumes. Therefore, equal volumes of H and Cl yield a double volume of HCl, or, as ordinarily expressed, 1 volume H and 1 volume Cl yield 2 volumes HCl. In similar manner may be deduced that 1 volume H and 1 volume Br vapor yield 2 volumes HBr; 1 volume H and 1 volume I vapor, 2 volumes HI.

These conclusions are confirmed by the following experiments:—

1. The concentrated aqueous solution of hydrochloric acid is decomposed by the action of the galvanic current, and the chlorine and hydrogen, separated at opposite poles, collected. The electrolysis may be made in an ordinary voltameter (Fig. 46). Better adapted to this purpose is Hofmann's apparatus (Fig. 47). Two glass cylinders, provided at the top with stop-cocks, are connected at the lower end with each other and with a funnel tube; the latter serves to fill the apparatus with liquid; and also, in subsequent additions, to let out the

gases collected in the tubes. The platinum electrodes are fused into the lower part of both tubes. In another form of Hofmann's apparatus (Fig. 48), the electrodes are introduced by means of caoutchouc corks. When the separating gases (in this case the chlorine) attack the platinum, carbon electrodes are substituted for the latter.

To electrolyze hydrogen chloride, fill the apparatus with concentrated hydrochloric acid, which is mixed with ten volumes of a saturated salt solution; close the upper cocks, and connect the electrodes with the poles of the battery. Gases separate in both tubes, and *in equal volumes*; that separated at the positive pole may be proven to be chlorine; the other combustible gas is hydrogen.

This experiment shows that hydrogen chloride decomposes into equal volumes of chlorine and hydrogen. The opposite—the production of HCl by the union of equal volumes of H and Cl—appears from the next experiment:—

FIG. 46.

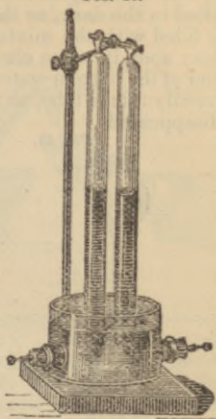
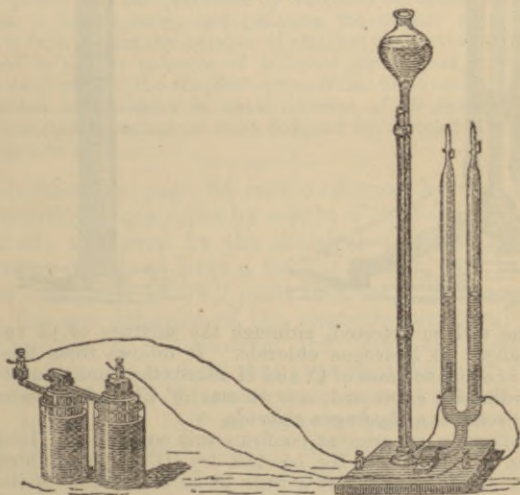


FIG. 47.

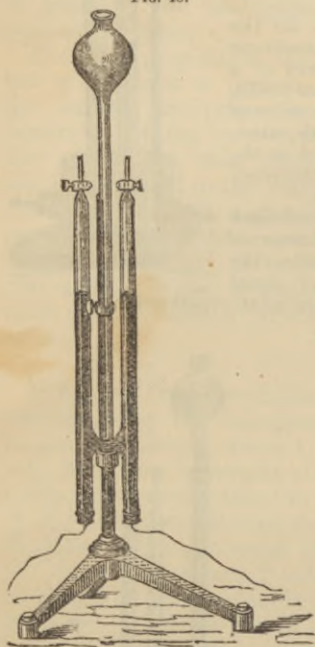


2. Fill a cylindrical glass tube, provided with stop-cocks at both ends (Fig. 49), with equal volumes of chlorine and hydrogen. This is most conveniently done by conducting the gaseous mixture obtained



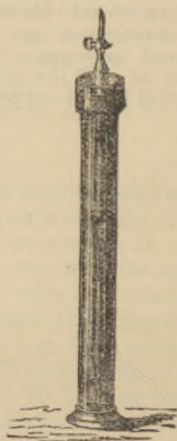
by the electrolysis of HCl into the dry tube. (The tube should be filled in the dark, as the gases combine in daylight.) When the tube is filled with the mixture, sunlight or magnesium light is brought to bear upon it, when chemical union ensues. On immersing the lower end of the tube in water, and opening the lower cock, the water will rapidly fill the tube, as it dissolves; all hydrogen and all chlorine have disappeared.

FIG. 48.



3. The same experiment may be applied in the establishment of another important fact which has reference to the proportion of the volume of the hydrogen chloride to the volumes of its constituents. If the tube filled with equal volumes of Cl and H be opened under Hg, after the explosion, no diminution

FIG. 49.



in volume will be detected, although the mixture of Cl and H has been changed to hydrogen chloride. It follows from this that a mixture of equal volumes of Cl and H affords the same volume of HCl, or, as ordinarily expressed, *one volume of Cl and one volume of H yield two volumes of hydrogen chloride.*

The following experiment confirms this conclusion: Into a bent tube (Fig. 50), filled with Hg, conduct dry HCl and then introduce in the bend of the upper part a little piece of metallic sodium. On heating the latter with a lamp, the HCl is decomposed, the Cl combining with the Na to form sodium chloride, while free hydrogen is separated. Upon measuring the remaining hydrogen it will be found that its volume is exactly the half of the volume of HCl originally in-

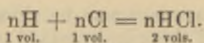
produced. In the same manner may be shown the fact that in two volumes of HBr and HI there is contained one volume of H: From the densities of Br and I vapors follows, further, that the quantities of these elements in gas form combining with one volume of hydrogen also occupy one volume. Hence, *one volume of hydrogen and one volume of bromine vapor yield two volumes of HBr, and one volume of hydrogen and one volume of iodine vapor two volumes of HI.*



The volume ratios in the chemical union of gases were first investigated by Humboldt and Gay-Lussac (1805-1808). The latter derived the two following empirical laws from the experiments: (1) Gases unite according to simple volume ratios; (2) The volume of the resulting body stands in a simple multiple proportion to the volumes of the constituents.

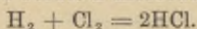
Comparing the fact announced by Gay-Lussac, that simple volume ratios occur in the chemical union of gases, with that discovered by Dalton (p. 60), that the quantities by weight of the combining elements also bear a simple ratio, and granting the atomic constitution of matter, it follows that the number of smallest gas particles (molecules) contained in similar volumes of different gases must bear a simple ratio to each other: the *simplest supposition*, however, would be that this number of molecules in equal volumes of all gases is the same. These important conclusions were deduced by Avogadro in 1811, and by Ampère in 1814.

As deduced on page 64 and confirmed by the described experiments, the quantities by weight of the halogen-hydrogen compounds, expressed by the chemical formulas, HCl, HBr, HI, occupy double as large a volume as one part by weight of H or 35,4 parts Cl, 79,7 parts bromine, 126,5 parts iodine. While the gas densities of the elements are equal to their atomic weights (p. 63) those of the compound bodies, consequently, amount to half that expressed by their formulas. From this it would follow that in equal volumes of compound bodies only half as many atoms or particles are present as in an equal volume of an elementary form of matter. In fact, one volume of H, containing  $n$  atoms of H, combines with one volume of chlorine, which, too, contains  $n$  atoms of Cl.  $n$  parts HCl result, which fill two volumes; therefore, there are only  $\frac{n}{2}$  parts of HCl contained in one volume of HCl:—

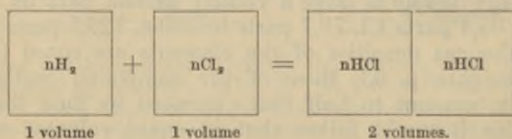


This conclusion contradicts the general postulate (p. 64), derived from the physical properties, viz., that *all* gases, both simple and compound, contain in equal volumes the same number of gaseous particles. This contradiction, which for a long time prevented the adoption of the atomic volume theory in chemical science, is now easily removed by the following supposition of Avogadro, announced in 1811. It is necessary to distinguish two different kinds of particles: *molecules* and *atoms*. The smallest discrete particles in gases are not *atoms*, but *molecules*, which consist of several atoms. That the molecules of compounds consist of atoms, is obvious, as, indeed, the same represent aggregates of atoms, but the elements also form molecules in a free condition, which are composed of several, generally, of *two* atoms. The previously deduced rule (p. 63), that in equal gas volumes of the halogen elements there is contained the same number of atoms, must be formulated somewhat as follows: *In equal volumes of all gases is found the same number of molecules* (law of Avogadro).

The process of the combination of hydrogen with chlorine (and the other halogens) must, therefore, be conceived to be somewhat like the following: 1 molecule of  $\text{H}_2$ , containing 2 atoms of H, acts upon 1 molecule  $\text{Cl}_2$ , also composed of two atoms of Cl, and there result 2 molecules of  $\text{HCl}$ :—

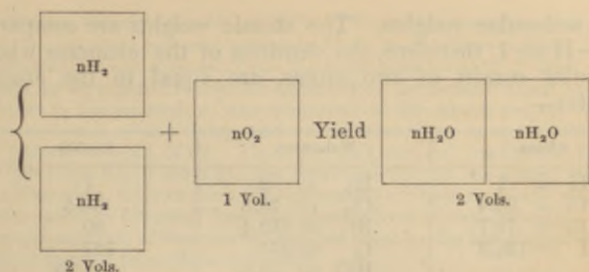


Then it is understood, that hydrogen chloride in an equal volume contains just as many molecules, as  $\text{H}_2$  and  $\text{Cl}_2$ , as is manifest from the following representation:—



In similar manner 2 volumes  $\text{H}_2$  (containing  $2n$  molecules) give with 1 volume oxygen (containing  $n$  molecules), 2 volumes aqueous vapor; consequently,  $2n$  molecules of water. In  $2n$  molecules of the latter ( $\text{H}_2\text{O}$ ) are contained  $2n$  atoms of O; therefore in  $n$  molecules of oxygen,  $2n$  atoms of oxygen—or *one oxygen molecule consists of 2 atoms*.





In the same way it may be deduced that the nitrogen molecule consists of 2 atoms of ( $N_2$ ), the phosphorus molecule, of 4 atoms of ( $P_4$ ), etc., etc.

This peculiar result, following from the law of Avogadro, that the molecules of the elements consist of several atoms, etc., is shown by many other circumstances founded on facts. For example, by the existence of the allotropic modifications of the elements (compare ozone), by the chemical reactions (compare hydrogen peroxide), by the remarkable action of the elements in the moment of their liberation.

Upon p. 43 we said that the oxygen separated from water by chlorine acted much more energetically than free oxygen. Other elements, especially hydrogen, behave similarly in the *moment of formation*—*in statu nascendi*. As viewed by the atomic molecular theory, this may be very easily explained. The free elements (their molecules) are compounds of similar atoms whose chemical affinity has been, of course, always partially satisfied. In the moment of their separation from compounds free atoms appear, which, before they combine to molecules, must act more energetically.

All that has been developed in the preceding statements may be summarized in the following sentences: All bodies are composed of elementary atoms. The latter unite to produce the molecules of the simple and compound bodies. Molecules are the smallest discrete particles existing in a free state. In equal volumes of all gaseous and vapor-forming bodies there is contained the same number of molecules. Therefore, the gas densities bear the same ratio to each other as the molecular weights. The density is generally compared with that of hydrogen = 1, therefore, the gas densities (the specific gravities of gases), of all bodies are one-half

their molecular weights. The atomic weights are compared with—H = 1, therefore, the densities of the elements whose molecules consist of two atoms, are equal to the atomic weights:—

Atoms.	Molecules.	Density.
H = 1	H <sub>2</sub> = 2	1
Cl = 35.4	Cl <sub>2</sub> = 70.8	35.5
Br = 79.7	Br <sub>2</sub> = 159.4	80
I = 126.5	I <sub>2</sub> = 253	127
	HCl = 36.5	18.25
	HBr = 81	40.5
	HI = 128	64
O = 16	O <sub>2</sub> = 32	16
	H <sub>2</sub> O = 18	9
N = 14	N <sub>2</sub> = 28	14
	NH <sub>3</sub> = 17	8.5
P = 31	P <sub>4</sub> = 124	62
	PH <sub>3</sub> = 34	17

A simpler deduction, that the molecules of the elements consist of two or more atoms, is the following: Proceeding from the law of Avogadro, that in like volumes of all gases or vapors an equal number of molecules is contained, this law, or much better, hypothesis, cannot be, as was attempted, proven mathematically, just as little as any other fundamental hypothesis.\*

But it possesses, as basis of the entire later mechanical gas theory, a high degree of probability. It necessarily follows from this law that the molecular weights of all bodies are proportional to the gas densities. Referred to hydrogen as unit, the empirical gas densities of HCl = 18.2, of HBr = 40.3, of HI = 63.7, etc. Analysis shows, however, that 35.4 parts of Cl are in union with 1 part H in HCl, 79.7 bromine in HBr, 126.5 iodine in HI. As the weight of one atom of H is made equal to 1, and 35.4 parts of chlorine are combined with it, the weight of a molecule of hydrogen chloride, as consisting at least of one atom of H and one atom of Cl, must equal at least 36.4; it is, therefore, twice as much as its density, 18.2. Hence the *molecular weights also of all other bodies, as they bear the same ratio as the densities, must also be twice as large as the* (referred to H as unit) *latter*. The hydrogen molecule is = 2, and consists of two atoms, as its atomic weight equals 1. The chlorine molecule weighs 70.8 units, and consists of two atoms (Cl<sub>2</sub>), if we suppose, that the atomic weight = 35.4. Its atomic weight could, however, be only the half (or another sub-multiple) of 35.4; then its molecule would consist of four chlorine atoms (Cl<sub>4</sub> = 70.8 when Cl is made equal to 17.6), and the formula

\* A mathematical proof is only possible upon the basis of another, more general, quantitative hypothesis (or of an axiom), which then on its side is not to be adduced.

of hydrogen chloride would be  $\text{HCl}_2$ . From the densities of the elements in gas form we only ascertain their molecular weights. Their atomic weights are revealed from the molecular weights of their compounds, as we regard the *smallest quantity of the element* which analysis discloses *in the molecule of any compound* as the *atomic weight*. Thus in the molecule of any compound of chlorine there is *never* less than 35.4 parts by weight of Cl. That the thus derived maximum values have not been found too high, but corresponding to the actual relative atomic weights, follows from the agreement of these numbers with the atomic numbers obtained from the specific heat of the elements. The complete certainty of their correctness we reach by the law of periodicity, which is formed from these numbers.

Taking one atom of hydrogen as the unit of weight and volume, then two parts, by weight, of H, or one molecule ( $\text{H}_2$ ), would occupy two volumes. We say, therefore, although incorrectly, that the molecules fill two volumes, and designate the molecular formulas *double volume formulas*. The volume of molecules and atoms is, however, unknown to us; we only know that in like gas volumes there is contained a like number of molecules.

The totality of the convincing suppositions and conclusions deduced from real circumstances forms the atomic-molecular doctrine, which is the foundation of the chemistry of to-day. As this doctrine completely explains the quantitative phenomena arising in the action of the chemical elements upon each other, inasmuch as they have repeatedly been confirmed by entirely opposite phenomena, it is only proper and correct that the doctrine be designated a theory (p. 60).

## OXYGEN GROUP.

In this group are included the elements, oxygen, sulphur, selenium and tellurium. They are perfectly analogous in their chemical department. They unite with two atoms of hydrogen.

### 1. OXYGEN.

$\text{O} = 16^*$   $\text{O}_2 = 32$ .

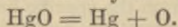
Oxygen (oxygenium) is the most widely distributed element in nature. Found free in the air, in combination it exists in water. It is an important constituent of most of the mineral and organic substances.

\* The correct atomic weight of oxygen referred to  $\text{H} = 1$  is 15.96.



It was first discovered, almost simultaneously, by Priestley, in England, 1774, and Scheele, in Sweden, 1775, as a remarkable body; but Lavoisier, in France, 1774-1781, first explained the important rôle attached to oxygen in processes of combustion, of respiration and of oxidation.

*Preparation.* Heat red mercuric oxide, a compound of mercury with oxygen, in a small glass retort; in this way the oxide is decomposed into mercury and gaseous oxygen:—



The following method is commonly pursued in the chemical laboratory. Potassium chlorate, a compound of potassium, chlorine and oxygen, is heated in a glass retort (Fig. 51) or flask, and thus decomposed into solid potassium chloride and oxygen:—

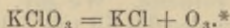
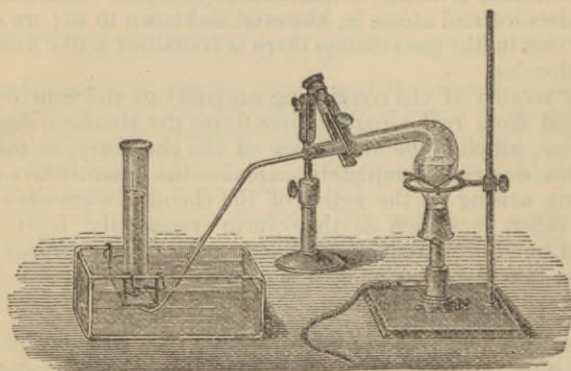
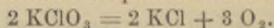


FIG. 51.

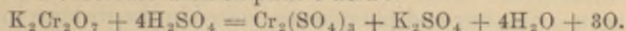


The gas evolution proceeds more regularly and requires a less elevated temperature if the pulverized chlorate be mixed with ferric oxide or manganese peroxide. The liberated oxygen is collected over water.

\* The chemical equations used here and previously are only intended to represent the manner of the reaction and to express the accompanying relative quantities by weight. It should not be forgotten that free atoms do not exist, but that they always occur combined in molecules. Molecularly written the equation would be:—



Very pure oxygen may also be obtained by heating potassium dichromate with sulphuric acid:—



Besides these, many other methods may be employed for the preparation of the gas: *e. g.*, the ignition of manganese and barium super-oxides; the decomposition of sulphuric acid at a high heat; the boiling of a solution of bleaching lime with a cobalt salt, etc., etc. These methods, applied technically, will be considered more thoroughly later.

*Properties.* Oxygen is a colorless, odorless, tasteless gas, which is condensed to a transparent liquid, of specific gravity 0.978, at  $-130^\circ$ , under a pressure of 470 atmospheres. Its density equals 16 ( $\text{H} = 1$ )\*, or 1.1056 ( $\text{air} = 1$ ). One litre of oxygen at  $0^\circ \text{C}$ ., and 700 mm. pressure weighs 1.4336 grams. Only slightly soluble in water; 100 volumes of the latter dissolve, at  $0^\circ$ , 4.1 volumes; at  $15^\circ$ , 2.9 volumes of oxygen. More readily dissolved by absolute alcohol (28 volumes in 100 volumes).

FIG. 52.



FIG. 53.



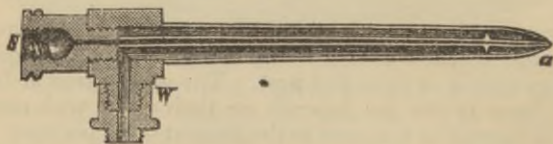
Oxygen combines with all the elements excepting fluorine. With most of them it unites directly, generally accompanied by an evolution of light and heat. The combustion of bodies which burn in the air depends on their union with oxygen, which is present in the same to the amount of 23 per cent. The phenomena of the respiration of animals are also influenced by the oxygen contact of the air—hence the earlier designations of oxygen as inflammable air and vital air. In pure oxygen the phenomena of combustion, as well as those of respiration, proceed more energetically. Ignited charcoal or a

\* Correct density is 15.96.

glowing sliver inflame immediately in oxygen, and burn with a bright light. This test serves for the recognition of pure oxygen. Sulphur and phosphorus ignited in the air burn in it with an intense light (Fig. 52). Even iron is able to burn in the gas. To execute this experiment, take a steel watch spring, previously ignited, attach a match to the end, ignite the same, and then introduce the spring into a vessel filled with oxygen gas (Fig. 53). At once the match inflames and ignites the iron, which burns with an exceedingly intense light and emits sparks. (To protect the vessel from the fusing and glowing globules of iron oxide, cover the bottom with a layer of sand). Iron will burn in any flame if a current of oxygen be conducted into the same.

Oxygen combines with hydrogen to form water. The union occurs at a red heat, by the electric spark or by the action of platinum sponge (p. 38). Hydrogen burns in oxygen with a flame; *vice versa* oxygen must also burn in hydrogen; this may be demonstrated in the same manner as indicated under hydrogen chloride (p. 47). A mixture of hydrogen and oxygen detonates violently; most strongly if the proportions are 1 volume oxygen and 2 volumes hydrogen; such a mixture is known as oxy-hydrogen gas. The explosibility may be shown in a harmless way by the following experiments: Fill a narrow-necked flask of 4-6 ounces, over water,  $\frac{2}{3}$  with hydrogen, and  $\frac{1}{3}$  oxygen; close the opening with a cork, then wrap the flask up in a towel, remove the cork and bring a flame near the opening. A violent explosion ensues, generally with complete breaking of the flask.

Fig. 54.

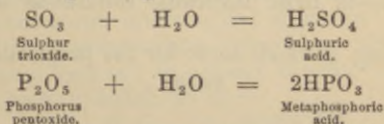


The oxy-hydrogen flame is only faintly luminous; it possesses, however, a very high temperature, answering, therefore, for the melting of the most difficultly fusible substances, *e. g.* platinum. To get a continuous oxy-hydrogen flame, efflux tubes of peculiar construction are employed, Fig. 54; through the outer tube, *W*, hydrogen is brought from a gasometer; through the

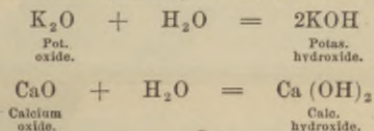


inner the oxygen is conveyed, and the mixture inflamed at *a*. Such a flame impinging on a piece of burnt lime makes the latter glow and emit an extremely bright light—*Drummond's Lime Light*.

The union of oxygen with other substances, is termed *oxidation*. This term, as also the name oxygenium (from *ὀξύς* and *γεννάω*), or acid producer, arises from the fact that sometimes in oxidation acids are formed. This the previously mentioned combustion experiments prove. If the vessels, for instance, in which carbon, sulphur and phosphorus were burned, be shaken up with water, the latter will give an acid taste, and redden blue litmus paper. It was formerly thought that the formation of acids is always conditioned by oxygen. We have, however, already noticed that the haloid acids HCl, HBr, HI, contain no oxygen. Some of the elements yield acids by their union with oxygen, or more correctly *oxides*, which with water form *acids*. Most of these are the metalloids. Thus, from the acid-forming oxides of sulphur and phosphorus the following corresponding acids are derived:—

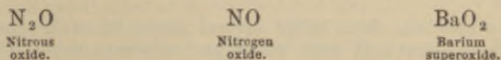


The metals with oxygen mostly yield oxides, which, with water, give *hydroxides* (also hydrates) or *bases*:—



By the alternating action of acids and bases arise the salts (see p. 51).

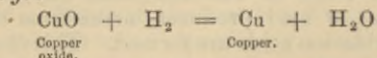
Thirdly, there exist the so-called *indifferent oxides*, which yield neither acids nor bases, with H<sub>2</sub>O, *e. g.*



Oxidation is not only induced by free oxygen or bodies rich in it, but, frequently, also by the halogens; in the latter

case the halogens first decompose the water with the elimination of oxygen, which then oxidizes further (compare p. 42).

The opposite process to oxidation, the removal of oxygen, is called *reduction*. Hydrogen (in statu nascendi), and substances giving it off easily (as HI), have a reducing action. Most of the metallic oxides are, at red heat, reduced by hydrogen, *e. g.* :—



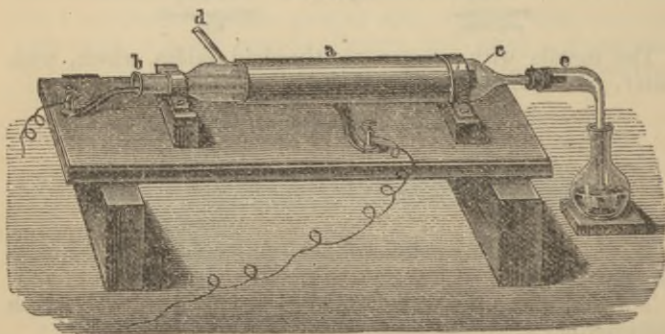
### OZONE, O<sub>3</sub>.

Discovered in 1840, by Schönbein.

Ozone is a peculiar modification of oxygen, characterized by a remarkable odor and great ability to react, therefore, *active oxygen*. It is obtained from oxygen in various ways; it is almost always produced when this gas is liberated, or when it takes part in a reaction, *e. g.*, in all slow oxidations, in every combustion, in the action of electricity upon oxygen or air, in the electrolysis of water. In none of these instances is all the oxygen ever converted into ozone, only a small portion—in most favorable conditions 5-6%—suffers this change.

The following methods serve for the preparation of ozone :

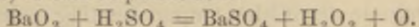
FIG. 55.



1. Into a spacious flask bring several pieces of stick phosphorus, covering them about half with water, and allowing them to stand for some hours. Or conduct oxygen over pieces of phosphorus placed in a glass tube and moistened with water. Ozone is formed in large quantity when a potassium bichromate solution is substituted for water.

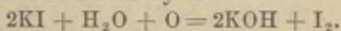
2. Pass the electric spark (from an electrical machine or a Ruhmkorff's coil) through air or oxygen. More advantageous is the so-called silent discharge from a powerful induction current. For this purpose we can employ a Siemen's induction tube (Fig. 55) which consists of a glass tube covered without with tin foil, and in the interior of which is a smaller tube coated within. Between the two tubes the oxygen circulates; the two coatings are in connection with the induction spiral, or the poles of a Holtz electric machine.

3. Gradually add barium peroxide in small portions (or potassium permanganate) to cold sulphuric acid:—



The escaping oxygen is tolerably rich in ozone, and is collected over water.

Ozone possesses a highly penetrating, chlorine-like odor (phosphorus odor), which by prolonged respiration produces bad results. When heated to 230–300° C., it reverts to ordinary oxygen. In pure water it is somewhat soluble; the larger portion of it is, however, converted by the water into oxygen, without formation of hydrogen peroxide. Opposite to oxygen, ozone, especially in a moist state, oxidizes strongly at ordinary temperatures. Phosphorus, sulphur and arsenic are converted into phosphoric, sulphuric and arsenic acids; ammonia is changed to nitrous and nitric acids; silver and lead are converted into the corresponding peroxides; therefore paper moistened with a lead salt is colored brown. Iodine is separated from potassium iodide by it:—



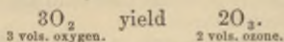
It also oxidizes all organic substances, like caoutchouc; therefore the apparatus used in its preparation must not be constructed of the latter. Solutions of dye stuffs, like indigo and litmus, are decolorized. Very characteristic for ozone is its ability to turn an alcoholic solution of guaiacum tincture blue.

For the detection of ozone the ordinarily so-called potassium iodide starch paper may be used. This is prepared by immersing white tissue paper in a starch solution mixed with potassium iodide. The iodine which the ozone liberates from the potassium iodide blues the starch paper. From the rapidity and the intensity of the coloration the quantity of ozone may be approximately determined. Besides the potassium iodide starch paper, guaiacum tincture and paper saturated with a lead acetate solution may be used to detect the ozone; the first acquires a blue color, the second is browned. Other substances also blue potassium iodized starch and guaiacum, *e. g.*, chlorine, bromine, nitrogen dioxide, etc., etc. To distinguish ozone from these, proceed as follows: Take two strips of violet litmus paper, one of which is saturated with



KI, and expose it to the action of the gas; when  $O_3$  is present potassium will be set free from the KI, and color the violet litmus blue. The second paper serves to show the absence of ammonia.

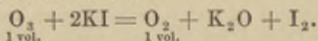
Ozone is formed from pure oxygen, and is nothing more than the latter condensed, the molecules of which consist of 3 atoms of O:—



This is proven by the following experiments: In ozonizing oxygen its volume diminishes; upon heating (whereby ozone is again changed to oxygen), the original volume is reproduced; when ozonized oxygen is brought in contact with oil of turpentine or cinnamon, all the ozone is absorbed and the volume of the gas diminished. Comparing this diminution, corresponding to the ozone volume, with the expansion which an equal volume of ozonized oxygen suffers after the application of heat, we will find (according to Soret) that the first is twice as large as the latter; this indicates that 1 volume of ozone yields  $1\frac{1}{2}$  volumes of oxygen. From this it follows that the specific gravity of ozone must be  $1\frac{1}{2}$  times greater than that of ordinary oxygen, and that if the molecule of O consists of 2 atoms, the molecule of ozone must contain 3 atoms. This conclusion is confirmed by the specific gravity of ozone experimentally derived from the velocity of diffusion. The density of ozone is found to be 24 ( $H = 1$ ); the molecular weight of it, therefore, is  $24 \times 2 = 48$ ; *i. e.*, the molecule of ozone consists of 3 atoms of O.

$$48 = 3 \times 16 = O_3.$$

In the action of ozone upon oxidizable bodies like KI and Hg, a diminution in the volume of the gas does not occur, although all the ozone disappears. From this it would appear that in oxidizing, ozone only acts with one atom of oxygen, while the other two atoms form free oxygen, which occupies the same volume as the ozone:—



As a consequence of this behavior, ozone is also called oxidized oxygen; *i. e.*, free oxygen ( $O_2$ ), which has combined with an additional oxygen atom.

We observe, therefore, that the elementary substance oxygen occurs in free condition in two different forms—*allotropic modifications*—ordinary oxygen ( $O_2$ ) and ozone ( $O_3$ ). We

*shall*  
will learn later that very frequently substances of the same elementary composition possess different physical and chemical properties; such bodies are called *isomerides* and the phenomenon *isomerism*. The isomerism of the elements is known as *allotropy*; this is accounted for (as in the case of oxygen and sulphur) by the different number of atoms in the molecule.

The phenomena of isomerism constitute an important argument for the atomic constitution of matter. If in the chemical union of two bodies the particles of matter would entirely permeate and blend into each other, the existence of isomeric bodies would be scarcely comprehensible. We can therefore only suppose a co-stratification of the atoms, and must consider isomerism as only a varied arrangement of the same. Special allotropy verifies the conclusion drawn from the gas density, that the molecules of the elements are composed of atoms.

We have already seen that ozone is absorbed, not only by turpentine and cinnamon oil, but also by other ethereal oils. These bodies are, in consequence, only very slowly oxidized; the ozone is contained in them in a peculiar, combined condition. In this form it acts upon some bodies like free ozone; in other instances, on the contrary, the oxidizing action is only rendered possible by peculiar bodies which carry the ozone. Such substances are spongy platinum, ferrous sulphate, the blood corpuscles. Thus, for example, old turpentine oil containing absorbed ozone only acts on paper saturated with starch and potassium iodide, if a few drops of the ferrous sulphate solution has been added to it.

As ozone is formed when electricity acts upon air, and indeed, probably, in all oxidation and combustion processes; as, further, potassium iodide starch paper is blued when exposed to the air; it was believed that ozone was a constant constituent of atmospheric air (1-10 milligrams in 100 litres of air); according to recent investigations it is, however, probable that the imagined ozone reactions are frequently produced by hydrogen peroxide.

Antozone, which was regarded as a third peculiar modification of oxygen, probably does not exist.

## COMPOUNDS OF OXYGEN WITH HYDROGEN.

## 1. WATER.

 $H_2O = 18$ . Density = 9.

Water, the combination product of hydrogen with oxygen, is produced in many chemical processes, as, *e. g.*, in the formation of salts from bases and acids (p. 51).

Cavendish was the first (1781) to confirm the formation of water by the combustion of hydrogen. Lavoisier first (1783) determined its quantitative composition. Later (1805), Gay-Lussac showed that water was produced by the union of two volumes of hydrogen with one volume of oxygen.

*Physical Properties.* Chemically pure water is obtained by the distillation of naturally occurring water, which always contains other matter dissolved in it. It appears in all three states of aggregation; in the liquid, gaseous (steam), and solid (ice, snow). When water is cooled it contracts and attains its greatest density at  $+4^\circ C.$ , the maximum contraction. The weight of a cubic centimeter of such water is taken as the unit of weight ( $= 1$  gram). By further cooling the water expands—the opposite of most other bodies; its volume is greater, while the specific gravity decreases. Water is 773 times heavier than air at  $0^\circ$ .

By further cooling water solidifies to ice. The solidification temperature of water, or more correctly the fusing point of ice, is taken as the zero point of Celsius' and Réaumur's thermometric scales. We can, however, reduce still water considerably below the  $0^\circ$  point without its freezing, whilst the *fusing point* of ice, like all other solid bodies, is *constant* (at a definite pressure). In the conversion of water into ice a considerable expansion occurs: 100 vols.  $H_2O$  at  $0^\circ$  yield 107 vols. ice; the specific gravity of the latter is, therefore, 9.3. Ice crystallizes in hexagonal forms, as is distinctly observed in snow flakes.

The various compounds require different quantities of heat to bring them to the same warmth. This capacity for heat is, for water, greater than for all other liquid and solid bodies. It is customary to take the quantity of heat necessary to raise one part by weight of  $H_2O$  from  $0^\circ C.$ , to  $1^\circ C.$ , as the unit of heat, or calorie. In the passage of a liquid to the solid state heat is always set free, while, on the other hand, in the fusion of the solid heat is absorbed. The *latent* heat of



water equals 79 calories; that means, that for the fusion of one part by weight of ice, a quantity of heat is required which is capable of raising one part  $H_2O$  from  $0^\circ$  to  $79^\circ$  C.

When heated water boils and is converted into *steam*, the boiling temperature, like that of all other liquids, depends on the pressure; it is also influenced by the substances dissolved in it; although the temperature of the vapors is constant (at a given pressure). The temperature of the steam escaping from water at the ordinary pressure of 760 mm. is  $= 100^\circ$  of the thermometric scale of Celsius,  $= 80^\circ$  Réaumur.

One volume of water, at  $100^\circ$  C., yields 1696 volumes of vapor of the same temperature. The specific gravity of steam  $= 0.6234$  (air  $= 1$ ), or  $= 9$  (H  $= 1$ ). One litre of aqueous vapor weighs 0.8064 grams.

The vaporization of water, and of other liquids, occurs not only at the boiling point, but also at lower temperatures. The tension of the vapors is measured by the height of the mercurial column.

The following table gives the tension of aqueous vapor for various temperatures:—

Temperature.	Tension.	Temperature.	Tension.
$-20^\circ$ C.	0.93 mm.	$40^\circ$ C.	54.9
$-10^\circ$ C.	2.09 mm.	$60^\circ$ C.	148.8
$0^\circ$ C.	4.6 mm.	$80^\circ$ C.	354.6
$+10^\circ$ C.	9.1 mm.	$100^\circ$ C.	760.0
$20^\circ$ C.	17.4 mm.	$120^\circ$ C.	1491.0

Moist gases, therefore, occupy a larger volume than those which are dry. The above table will answer to reduce the observed volume of a moist gas to its volume when dry, by deducting from the observed atmospheric pressure the tension of steam (in mm.) corresponding to the given temperature.

A definite quantity of heat requisite for the conversion of a liquid into vapor is applied to internal and external work; therefore, it disappears as heat, or becomes latent. The latent heat of the evaporation of water equals 536.5 heat units at  $100^\circ$  C.; *i. e.*, for the conversion of one part of water of  $100^\circ$  C., into vapor of the same temperature, a quantity of heat capable of raising 536.6 parts of  $H_2O$  from  $0^\circ$  to  $1^\circ$  will be absorbed.

In consequence of the evaporation of water, the gases separating from an aqueous solution are always moist. To dry the same, conduct them over such substances as will be able to take up the moisture, *e. g.*, calcium chloride, stick potash, sulphuric acid, phosphorus anhydride (compare page 33).

Many solids abstract moisture from the air without chemically uniting with it: to dry these let them stand in an enclosed space over sulphuric acid (dessicators).

*The Natural Waters.* As water dissolves many solid, liquid and gaseous compounds, all naturally occurring waters contain foreign admixtures. The purest natural water is rain and snow water; it contains upwards of three vols. percentage of gases (oxygen, nitrogen and carbon dioxide), and traces of solids (the ammonium salts of nitrous and nitric acids). If water that has stood exposed to the air be heated, the dissolved gases escape as bubbles.

River and spring waters contain, on an average, in 10,000 parts, from 1-20 parts of solid constituents. Water having present in it much lime and gypsum, is ordinarily known as *hard*, in distinction to *soft* water, which contains very little of these impurities. On boiling lime waters, most of the impurity deposits out. Spring water generally contains in addition larger quantities of carbon dioxide, which imparts to it a refreshing, enlivening taste. Spring waters holding considerable quantities of solid constituents or exhibiting particular healing properties, are called *mineral waters*. These are distinguished as saline waters (containing sodium chloride), bitter waters (containing magnesium salts), sulphur waters (hydrogen sulphide), acidulated waters (saturated with carbon dioxide), chalybeate waters (containing iron), and others.

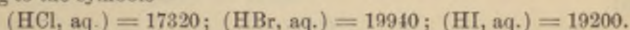
Sea water contains about 3.5 % of salts, of which 2.7 % are sodium chloride.

To purify the natural waters they are filtered (for the removal of mechanical admixtures), and for chemical purposes, distilled (*distilled water*), in apparatus of varying form.

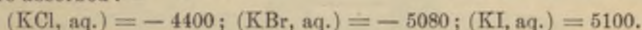
*Solutions.* The phenomena appearing in the dissolving of substances indicate that solutions are not mere mechanical mixtures. In every solution alterations in the temperature of the liquid occur. The solubility of solid and liquid substances increases usually with the temperature, while that of gases diminishes. The quantity of dissolved gas is frequently proportional to the temperature; other gases, on the contrary, which are readily soluble in water, such as the halogen-hydrogen compounds, are exceptions to this rule. Heat does not perfectly expel them from their solution; they distill

over as liquids of definite composition (compare p. 56). When they dissolve, a large quantity of heat is liberated, just as in the case of chemical compounds. Further, in the solution of solids and liquids a contraction is always perceived; the volume of the solution is less than the sum of the volumes of the constituents. These phenomena point to the acceptance of a certain affinity between the dissolving bodies. Therefore, solutions, like *alloys*, are designated *undetermined compounds*, in contrast to the *determined compounds*, which are combined according to constant atomic weight ratios. Among others, this view is confirmed by the fact that frequently definite compounds of bodies with water do exist in solution. Such compounds often separate, unaltered, upon evaporation of the solution; the water present in them is known as *water of crystallization*. It is, however, impossible to draw a sharp line between determined and undetermined compounds, between chemical and physical attraction.

The *thermal phenomena* appearing when solution occurs bear a close relation to chemical affinity. The hydrogen haloids, easily soluble in water, disengage in their solution large quantities of heat corresponding to the symbols—



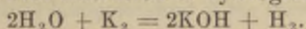
This liberation of heat is explained by the production of the hydrates  $\text{HCl} + 8\text{H}_2\text{O}$ ,  $\text{HBr} + 5\text{H}_2\text{O}$ ,  $\text{HI} + 5\text{H}_2\text{O}$ , which distill over unaltered (p. 56). The slightly soluble, so-called permanent gases do not form such hydrates, and when they dissolve, disengage but little heat. The liquid and solid bodies exhibit a like deportment. These, forming hydrates, liberate heat, while the non-hydrate-forming solid bodies absorb heat in their solution, which at the same time is employed to liquefy them (latent heat of fusion). Thus, in the solution of the halogen compounds of potassium the following quantities of heat are absorbed:—



Upon such an absorption of heat depend the freezing mixtures, to be described later.

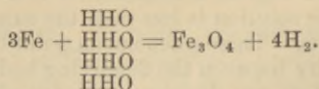
*Chemical Properties of Water.* Water is a neutral substance, *i. e.*, it possesses neither acid nor basic properties. As we have already observed (p. 75), it forms bases with basic oxides and acids with acid-forming oxides.

Despite the fact that the affinity of hydrogen for oxygen is so great, water may, however, be decomposed by many substances. At ordinary temperatures, metals like K, Na and Ca decompose it, with liberation of hydrogen:—

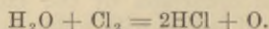




Other metals do not decompose it, except at elevated temperatures. Steam conducted over glowing iron gives its oxygen to the latter, forming ferroso-ferric oxide, while hydrogen is set free:—



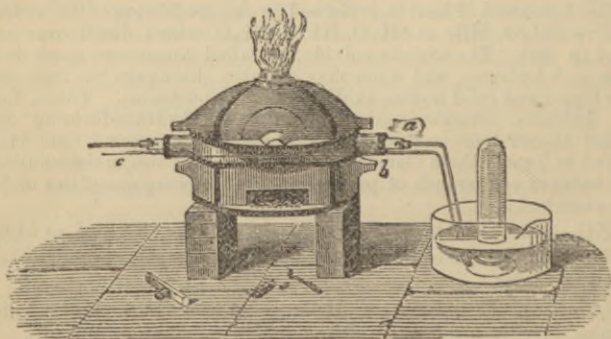
Chlorine in sunlight decomposes water; the decomposition is more rapid when the vapors are conducted through heated tubes:—



The galvanic current separates\* water into its constituents, oxygen and hydrogen; the first collecting at the positive, and the latter at the negative pole. The oxygen thus obtained contains ozone.

The deportment of water at high temperature is very interesting. On pouring molten platinum into cold water, bubbles of oxy-hydrogen gas escape. A similar decomposition of water occurs when it is led through porcelain tubes raised to a white heat.

FIG. 56.



From the observations of Sainte-Claire Deville, it was found that the decomposition of  $\text{H}_2\text{O}$  begins at  $1200^\circ \text{C}$ ., and that it increases, with a rising temperature, and is complete at  $2500^\circ \text{C}$ . Such a partial decomposition increasing with the tempera-

\* Pure water appears not to be decomposed by the galvanic current.

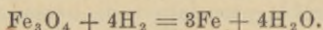
ture is known as *dissociation*. The following experiment illustrates this. Through a porous clay tube, *a*, puttied into a wider, non-permeable porcelain tube, heated to white heat in an oven, pass aqueous vapor, Fig. 56. The water suffers partial decomposition, the lighter hydrogen, which passes through into the porcelain tube more rapidly than the oxygen, escapes through the gas tube *b*. The oxygen escapes, for the most part, through the inner tube at *a*. A part of the same diffuses simultaneously with the hydrogen and reunites with the latter. To avoid this conduct a stream of carbon dioxide through the wider porcelain tube; this will carry out the hydrogen with it. The carbon dioxide will be absorbed by the alkali solution in the collecting vessel, and oxy-hydrogen gas be found in the cylinder. The quantity of the gas increases with the temperature. A platinum tube may be advantageously substituted for the porous clay tube, because only hydrogen will pass through it (p. 36).

Many other compounds, like ozone, ammonium chloride, phosphorus pentachloride, carbon dioxide, etc., suffer a similar partial decomposition at a glowing heat; they are altered to simpler molecules by heat.

The explanation of the *dissociation* phenomena is found in the kinetic theory of gases and heat. According to it, not only have the gas molecules a direct oscillating movement, inasmuch as they, like elastic balls, rebound from each other, but even the atoms in the molecule possess heat vibrations. The velocity of the oscillations of molecules and atoms increases with augmented temperature; it is, therefore, understood that by a determined energy of the oscillations the chemical affinity is overcome and the united atoms are separated from each other. Further, as a consequence of irregular collision, the molecules do not all possess the same velocity at a given temperature; some move more rapidly, others slower; the former are warmer than the latter. Only the sum of the existing forces of all the molecules is a constant quantity at every temperature. The more highly heated molecules, whose number increases with the temperature, therefore, yield to the decomposition. From this we discover that the dissociation is gradual and increases with the temperature. The law of dissociation is expressed by the curve of probability.

Dissociation, *i. e.*, the partial decomposition, increasing with the temperature, explains many chemical processes, previously appearing enigmatical, *e. g.*, the mass action in reversed chemical reactions. We have already said that glowing iron decomposed water with the separation of hydrogen and production of ferrous-ferrie oxide. On conducting H over

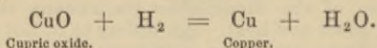
glowing iron oxides the opposite process occurs; the oxygen compound of the iron is reduced and water is formed:—



In the first instance the excess of water acts. Some of its molecules are dissociated; oxygen combines with iron, while the liberated H is carried away by the excess of steam. In the second case, we can suppose that some of the hydrogen molecules are dissociated, the free hydrogen atoms withdraw oxygen from the iron oxide and form water with it, which is removed by the excess of hydrogen, and thus prevented from acting on the reduced iron. In the action of the bodies in an enclosed space at a given temperature there must occur a state of equilibrium, in which  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}$ ,  $\text{H}_2\text{O} + \text{H}_2$  occur simultaneously. Such a state occurs in every dissociation.

### The Quantitative Composition of Water. The Atomic Weight of Oxygen.

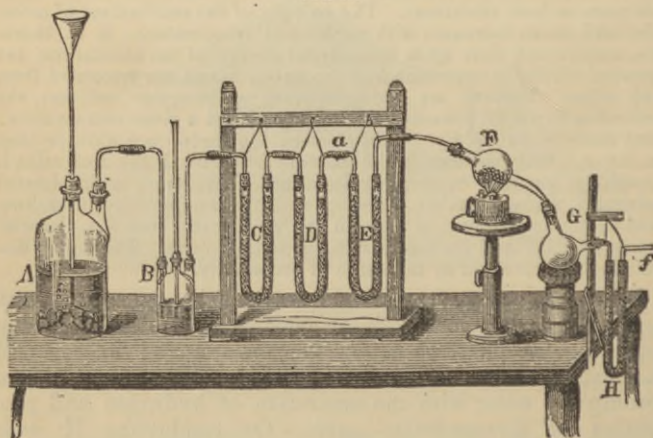
The composition by weight of water is best determined by a synthesis of the same, by reducing cupric oxide with hydrogen:—



Cupric oxide.

Copper.

FIG. 57.





Heat a weighed portion of cupric oxide (containing a definite amount of oxygen), in a stream of pure, dry hydrogen, and weigh the quantity of  $H_2O$  obtained. The operation can be executed in the apparatus represented in Fig. 57. The  $H$  generated in the flask  $A$  is washed in  $B$  and then dried in the tubes  $C$ ,  $D$  and  $E$ , which contain substances that will absorb water. The bulb tube  $F$ , of difficultly fusible glass, contains a weighed amount of cupric oxide, and is heated with a lamp. The water which forms, collects in the bulb  $G$ , and is completely absorbed in the tube  $H$ . Hydrogen is led over the cupric oxide until it is reduced to red metallic copper, then allow to cool, and weigh  $F$  alone and  $G$  and  $H$  together. The loss in weight of  $F$  expresses the quantity of oxygen which, combined with  $H$ , produces water. The increase in weight of  $G$  and  $H$  gives the quantity of water produced. The difference shows the amount of  $H$  in water. Thus we ascertain that in 100 parts by weight of water there are—

11.11	Parts	Hydrogen.
88.81	"	Oxygen.
100.00	"	Water.

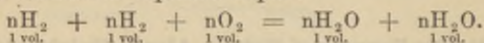
or, 1 part hydrogen and 8 parts oxygen yield 9 parts water.

#### The Molecular Formula of Water. Atomic Weight of Oxygen.

If the molecule of water (like  $HCl$ ) contains 1 atom  $H$  and 1 atom oxygen, then its chemical formula would be  $HO$ , and the atomic weight of oxygen would be = 8. However, such a supposition has not been in any way proved. It would be just as likely that the formula  $HO_2$  might be ascribed to the water molecule; then the atomic weight of oxygen would be 4. According to the formula  $H_2O$  the atomic weight of  $O$  is 16, etc. (see p. 62). The analytical data give no decision. For the determination of the actual atomic weight of oxygen, and therefore also the number of atoms in the molecule, we must direct our attention to the views presented on pages 62-71. In equal volumes of the gases (or vapors) there is an equal number of molecules. The molecular weights, therefore, are proportional to the gas densities, and are equal to double that of the densities referred to  $H = 1$ . The density of steam is 9 ( $H = 1$ ); the weight of the water

molecule is therefore 18. Analysis, however, shows that in 18 parts water 2 parts by weight are hydrogen (= 2 atoms) and 16 weight parts oxygen. According to this the molecule of water contains not more nor less than 2 atoms of hydrogen. That the 16 parts oxygen combined with the latter correspond to *one atom* (that the atomic weight does not equal 8, in which case the molecular formula of water would then be  $H_2O_8$ ), follows from the fact that the analysis of none of the innumerable oxygen derivatives has shown less than 16 parts oxygen in the molecule (see p. 70). *The molecular formula of water, therefore, is  $H_2O = 18$ .* The gas density of oxygen is 16, the molecular weight 32, therefore the *oxygen molecule consists of 2 atoms  $O_2 = 32$ .*

After having thus derived the molecular formula of water and the atomic weight of oxygen, we deduce the following conclusions: (1) 16 parts by weight of *O* occupy the same volume as 1 part by weight of *H*, as 16 parts of the former unite with 2 parts of the latter; from this, in the formation of water 1 *volume* of *O* must combine with 2 *volumes* of *H*. (2) In equal volumes the same number of molecules is contained; *n* molecules *O* unite therefore with 2 *n* molecules of hydrogen ( $H_2$ ); the same yield 2 *n* molecules water; consequently 2 *volumes* of aqueous vapor:—



According to the above, 2 *volumes* of hydrogen and 1 *volume* oxygen condense in their union to 2 *volumes* of aqueous vapor. The same result follows from the gas density of water. As 1 volume of steam weighs 9, 2 weight parts of *H*, however, form with 16 parts by weight of *O*, 18 parts by weight of steam; then this quantity of water in form of vapor must occupy two volumes. Conversely from these volume ratios it is shown that the molecule of oxygen consists of two atoms.

These conclusions are confirmed by the following experiments:—

1. When water is decomposed by the electric current in a voltameter, or more suitably, in Hofmann's apparatus (Fig. 48, p. 66), it will be found that the volume of the separated hydrogen is double that of the oxygen. This can also be proven synthetically. Into an eudiometer tube filled with mercury (see Air), introduce 1 volume oxygen and 2 volumes hydrogen, and let the electric spark pass through the mixture. This will unite the two gases, a small quantity of water forming at the same time; all gas has disappeared, and the tube fills perfectly

with mercury. In place of the eudiometer the following apparatus may be advantageously employed in this experiment (and also in many others Fig. 58). It consists of a V-shaped glass tube, one limb of which, open above, is provided below with an exit tube. The other limb really represents an eudiometer; it is divided into cubic centimeters, having two platinum wires fused into the upper end, and provided with a stop-cock to let out the gases, and thus test them. Fill the tube to the stop-cock with mercury, and run into the eudiometer limb 1 volume O and 2 volumes H. The side exit tube serves to run out the mercury to the same level in both tubes, so that the gases are always measured under the same atmospheric pressure, and thus their volumes are easily compared.

2. To determine the volume of the formed water existing as aqueous vapor, it is only necessary after the explosion to convert it, by heat, into steam. The subjoined

FIG. 58.

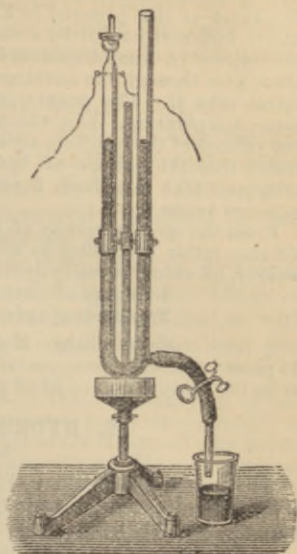
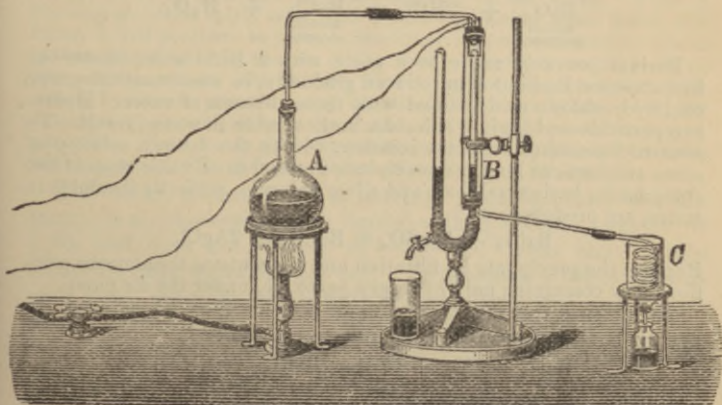


FIG. 59.





apparatus will answer for this purpose (Fig. 59). This is essentially the same as that pictured in Fig. 32, with the eudiometer limb closed above and surrounded by a wider tube. Through the latter conduct the vapors of some liquid boiling above  $100^{\circ}$  C. (aniline). These, then, pass through the envelope B, and are again condensed in the spiral tube C. The quantities of H and O used are heated to the same temperature, their volume noted, the explosion produced, and the volume of the resulting aqueous vapor determined. From this it is found that the volume of hydrogen is  $\frac{2}{3}$  of the volume of the gas mixture; that thus from 3 volumes of oxy-hydrogen gas, 2 volumes aqueous vapor result.

From the specific gravity of hydrogen and of oxygen, and from the volume ratios according to which they combine, the composition by weight, of water, is easily deduced:—

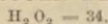
1 volume of oxygen weighs 16 weight parts

2 volumes of hydrogen weigh 2 weight parts

the resulting  $H_2O$  weighs 18 weight parts.

18 parts water, therefore, contain 16 parts oxygen and 2 parts hydrogen, or in 100 parts there are 88.88 parts oxygen and 11.12 parts hydrogen.

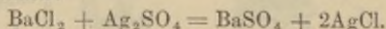
## 2. HYDROGEN PEROXIDE.



In addition to water oxygen forms another compound with hydrogen, known as hydrogen peroxide. It is produced by the action of dilute acids upon certain peroxides, such as those of potassium, calcium and barium. It is most conveniently obtained by the action of hydrochloric acid upon barium peroxide:—

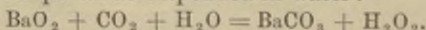


Barium peroxide made to a paste with a little water (better the hydrate—see Barium) is introduced gradually, in small quantities, into cold hydrochloric acid, diluted with three volumes of water. Hydrogen peroxide and barium chloride, both soluble in water, result. To remove the second from the solution, add to the latter a solution of silver sulphate, as long as a precipitate is formed. By this reagent two compounds, barium sulphate and silver chloride, perfectly insoluble in water, are produced:—



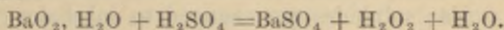
Remove the precipitate by filtration and concentrate the aqueous solution, now containing only hydrogen peroxide, under the air pump.

In making the peroxide carbon dioxide may be allowed to act on barium peroxide suspended in water:—



The insoluble barium carbonate is filtered off and the filtrate concentrated.

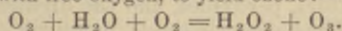
Hydrogen peroxide is most practically obtained by adding moist barium hydrated peroxide (see Barium) to cold dilute sulphuric acid. The reaction occurs according to the following equation :—



When the acid is almost neutralized, filter the solution, and from the filtrate carefully precipitate the slight quantity of free sulphuric acid with a dilute barium hydrate solution, then concentrate the filtrate. Dry commercial hydrate of the peroxide of barium is not applicable for the above.

Further, worthy of remark, is the formation of hydrogen peroxide from water and ozone aided by ether. Ozone is conducted into the latter, and the ozonized liquid shaken with pure water, which dissolves the peroxide that has been produced.

Besides these methods, all dependent on the decomposition of peroxides, others exist for preparing hydrogen peroxide (although in much smaller quantity). Thus, also, it arises in almost all slow oxidations in which ozone is produced at the same time. This simultaneous production of hydrogen peroxide and ozone is explained to some extent by the composition of these bodies. The oxygen molecule splits, in its chemical action, into two atoms of oxygen; one combines with the water, the other with free oxygen, to yield ozone :—

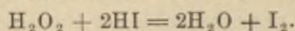


Thus, in the oxidation of moist phosphorus in the air, oxygen is ozonized, while hydrogen peroxide appears in the water. When a glowing platinum spiral is hung in a flask containing some water and ether, it will continue to glow, as the ether vapors burn slowly; ozone is then perceptible in the air of the flask—hydrogen peroxide, however, in the water. On shaking zinc filings or zinc amalgam with water, hydrogen peroxide may be detected in the latter. Oxygen obtained by electrolysis contains ozone, and the water some hydrogen peroxide. Rain water almost invariably contains hydrogen peroxide, which appears to form by the action of sunlight. (Schöne.)

The latter, concentrated as much as possible under the air pump, is a colorless, syrupy liquid, with a specific gravity of 1.45, and does not solidify at  $-30^\circ \text{C}$ .; from mere dilute solutions pure water freezes out. It possesses a bitter, astringent taste, miscible in all proportions with water, and vaporizes in vacuo.

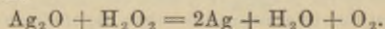
In concentrated solutions hydrogen peroxide is very unstable, and easily decomposed with liberation of oxygen; in more dilute acidulated solutions it may be preserved longer. Decomposition occurs, even at ordinary temperatures; by heat-

ing the point of explosion can be reached. In consequence of this ready decomposition, hydrogen peroxide oxidizes powerfully, since oxygen appears (p. 69) in *statu nascendi*. It converts selenium, chromium and arsenic into their corresponding acids; sulphides are changed to sulphates (PbS to PbSO<sub>4</sub>); from lead acetate solutions the superoxide is precipitated; organic dyestuffs are decolorized and organic tissues decomposed. From hydrogen sulphide sulphur, from hydrogen chloride and iodide, chlorine and iodine are set free:

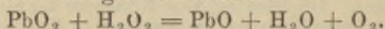


Thus hydrogen peroxide acts in a manner analogous to ozone; in both there exists a slightly bound atom of oxygen, which can readily be transferred to other bodies. Hydrogen peroxide acts very slowly upon a neutral potassium iodide solution, while ozone separates iodine at once; but if platinum-black, ferrous sulphate, or blood corpuscles (see p. 79) be added to the solution, iodine immediately separates out and colors added starch-paste deep blue.

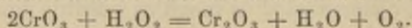
In all these cases the action of hydrogen peroxide is oxidizing. Some substances, on the other hand, are reduced by H<sub>2</sub>O<sub>2</sub>, oxygen separating at the same time; this is true of certain unstable oxides, peroxides, and the highest oxidations of some metals. Thus argentic oxide, mercuric oxide and gold oxide are reduced to a metallic state with an energetic evolution of oxygen:—



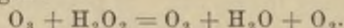
Lead peroxide is changed to lead oxide:—



In presence of acids, the solution of potassium permanganate is decolorized and changed to a manganous salt. In the same way chromic acid and its salts are altered to chromic oxide:—



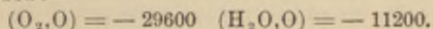
Ozone and hydrogen peroxide decompose themselves into water and oxygen:—



All these reactions can only be explained by supposing that the oxygen atoms (also those of other elements), possess a certain affinity for each other. Those present in other compounds, therefore, separate and unite with each other, and form free oxygen molecules—OO. The conclusion derived from the gas density, viz., that the molecules of the free elements consist of two or more atoms,



is corroborated by these reactions. The unstable union of the one atom of oxygen in ozone and in hydrogen peroxide also finds expression in their thermo-chemical behavior. In the production of ozone from oxygen, as also of hydrogen peroxide from water and oxygen, heat is absorbed:—



Both compounds are endothermic (see p. 57), therefore, little stable, and the one oxygen atom in them is readily capable of reaction. The production of both substances, according to the above symbols, can also only be effected by the addition of external energy. In case of ozone this may be accomplished by electricity, with hydrogen peroxide (in its production from barium superoxide and dilute acids) by heat, which in the formation of the barium salts becomes free.

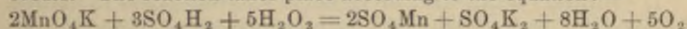
Third and finally, hydrogen peroxide suffers decomposition into water and oxygen by many bodies, especially when the latter exist in a divided condition, and they themselves are not in the least altered. Gold, platinum, silver, manganese peroxide, carbon and others, act in the above way. Such reactions, in which the reacting substances undergo no perceptible changes, are designated *catalytic*. In many cases these may be explained by the previous formation of intermediate products, which subsequently react upon each other. Thus, we can suppose that in the action of silver and gold upon  $H_2O_2$  oxides at first result, which afterwards are reduced in the above mentioned manner, by the hydrogen peroxide.

#### Reactions for the Detection of Hydrogen Peroxide.

$H_2O_2$  decomposes potassium iodide very slowly, but in the presence of iron sulphate, however, iodine at once separates, and is recognized by the blue color it yields with starch paste. In the same way, in the presence of ferrous sulphate guaiacum tincture is at once colored blue and an indigo solution decolorized. The most characteristic test for the peroxide is the following: Introduce some  $H_2O_2$  into a chromic acid solution, add a little ether and shake thoroughly; the supernatant ethereal layer will be colored blue (compare—Chromic acid).

A solution of titanous acid in sulphuric acid (diluted strongly with water), is also a delicate reagent which yields an orange yellow color with hydrogen peroxide.

Quantitatively hydrogen peroxide is determined by oxidation with potassium permanganate (see Manganese). The latter is added to the solution, and acidified with sulphuric acid until a permanent coloration occurs. The reaction takes place according to the equation:—



Or the liquid to be examined (rain water) for hydrogen peroxide is shaken in a stoppered glass with a five per cent. solution of potassium iodide and some starch paste, allowed to stand several hours, and the separated iodine determined, colorimetrically (Schöne).

Hydrogen peroxide occurs in slight quantity in the air and is detected in almost every rain water frequently, also in snow—but not in natural dew and frost. Its quantity varies from 0.05 to 1 milligram in a litre of rain. Its formation in the air is probably induced by the action of ozone upon ammonia, whence ammonium nitrite, hydrogen peroxide and oxygen result (Carius).

Analysis shows that  $H_2O_2$  consists of one part hydrogen and sixteen parts of oxygen; its simplest formula will, therefore, be HO. The difficult volatility of the compound, as well as the above mentioned reactions, let us conceive that the molecule of hydrogen peroxide is more complicated, and is expressed by  $H_2O_2$ . It is supposed that the peroxide is composed of two groups of OH, called *hydroxyl*, combined with each other.

## 2. SULPHUR.

S = 32 S = 64 (above  $1000^\circ$  C.).  $S_8$  = 192 (at  $500^\circ$  C.).

Sulphur is distributed throughout nature, both free and in a combined state. In volcanic regions, like Sicily, it occurs free, and there it forms vast deposits, mixed with gypsum, calcite and marl. The compounds of sulphur with the metals are known as blendes or glances. In combination with oxygen and calcium, sulphur forms calcium sulphate, the widely distributed gypsum. It is also present in many organic substances.

To obtain it, the natural sulphur in Sicily, arranged in heaps and covered with earth, is melted or distilled from earthen retorts. This commercial, crude sulphur, for further purification, is (in the manufactory) again distilled from cast-iron retorts, and when molten, run into cylindrical forms—*stick sulphur*. If the sulphur vapors during distillation are rapidly cooled (which occurs by conducting them into a stone chamber through which cold air circulates), they condense to a fine yellow powder, known as *flowers of sulphur* (*Flores sulphuris*).

By heating the well known pyrites ( $FeS_2$ ) sulphur may be obtained.

Free sulphur forms several allotropic modifications (see page 79).

1. Ordinary octahedral or rhombic sulphur exists in nature in beautiful, well crystallized rhombic octahedra (Figs. 21 and 22, p. 27). It is pale yellow, hard and very brittle; on rubbing, it becomes negatively electrified. Specific gravity 2.05. Difficultly soluble in alcohol and ether; more readily

soluble in hydrocarbons and ethereal oils. The best solvents are sulphur monochloride ( $S_2Cl_2$ ) and carbon disulphide ( $CS_2$ ); 100 parts of the latter at  $22^\circ C.$ , dissolve 46 parts sulphur. By slow evaporation of the solutions sulphur crystallizes in transparent, lustrous, rhombic octahedra, like those occurring naturally. Sulphur fuses at  $111.5^\circ C.$ , ( $113^\circ C.$ ) to a yellow, mobile liquid, which upon further heating becomes dark and thick, and at  $250^\circ C.$ , is so viscid that it cannot be poured from the vessel holding it. Above  $300^\circ C.$ , it again becomes a thin liquid, boils at  $440^\circ C.$ , and is converted into an orange yellow vapor.

2. The *prismatic* or *monoclinic sulphur* results from the rhombic when the latter is heated to its point of fusion; generally on cooling it assumes the monoclinic form (sulphur heated too high crystallizes at  $90^\circ C.$ , in rhombic forms). The monoclinic crystals are best obtained as follows: Fuse sulphur in a clay crucible, allow it to cool slowly until a crust appears on the surface; break this open near the side and pour out the portion yet in a liquid state. The walls of the crucible will be covered with long, somewhat curved, transparent, brownish-yellow needles, or prisms of the monoclinic system. The same are obtained when a solution of sulphur in carbon disulphide, in a sealed tube, is heated to  $100^\circ C.$ , and then gradually allowed to cool; monoclinic crystals at first separate, and later, at low temperatures, rhombic octahedra. The monoclinic crystals separated from the solution are almost colorless and perfectly transparent.

From the supersaturated solution of sulphur in benzene prismatic or octahedral crystals may be obtained as desired, by bringing some of the same into the liquid.

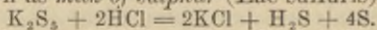
This form of sulphur has a specific gravity of 1.96 and fuses at  $120^\circ$ . Soluble in the same solvent as the rhombic. It is very unstable; the transparent prisms and needles at ordinary temperatures become opaque and pale yellow, specifically heavier (heat is evolved), and pass over into an aggregate of rhombic octahedra retaining the external prismatic form. Stick sulphur deports itself similarly; the freshly moulded sticks are composed of monoclinic prisms, but in time their specific gravity changes and they are converted into the rhombic modification.

3. *Soft, plastic sulphur* appears to consist of two modifications. It is obtained when sulphur melted above  $230^\circ$  is



poured in a thin stream into water; it then forms a soft, fusible mass, of a yellowish-brown color. In a few days it hardens, and is converted into rhombic sulphur. At  $95^{\circ}$  the conversion is instantaneous and accompanied by the evolution of considerable heat. It is only partly soluble in carbon disulphide, leaving behind an amorphous powder—amorphous insoluble sulphur—insoluble in carbon disulphide. Also produced when light acts upon dissolved or fused sulphur, and in the decomposition of the halogen-sulphur compounds by  $H_2O$ . Flowers of sulphur are for the most part insoluble in carbon disulphide.  $100^{\circ} C.$ , will convert the amorphous insoluble sulphur again into the ordinary variety.

On adding hydrochloric acid to polysulphide solutions of potassium or calcium, sulphur separates as a fine, white powder, known as *milk of sulphur* (*Lac sulfuris*):—



This is amorphous, soluble in carbon disulphide, and gradually passes into the rhombic form.

The existence of these various modifications of sulphur, like ozone, may be attributed to the presence of a varying number of atoms in the molecules. This supposition is confirmed by the deportment of sulphur vapor. The vapor density of sulphur at  $500^{\circ} C.$ , has been found to be equal to 96 ( $H = 1$ ). With increase of temperature, from  $700^{\circ} C.$ , up, the vapor density steadily diminishes, becoming constant at  $900^{\circ} C.$ , and equalling 32; the molecular weight, therefore, is 64. As now the atomic weight of S (as we will see) = 32, it follows that at  $1000^{\circ} C.$ , the molecules of S consist of two atoms ( $S_2 = 64 = 32 \times 2$ ). At  $500^{\circ}$ , however, when the vapor density = 96, molecular weight equalling 192, the molecule consists of six atoms ( $S_6 = 6 \times 32 = 192$ ). According to this the hexatomic sulphur molecules dissociate (see p. 85) on further heating, and fall into normal diatomic molecules; the dissociation beginning at  $700^{\circ}$  and being complete at  $1000^{\circ} C.$  As, then, the sulphur molecules in vapor formed at very high temperatures consist of two atoms and at lower of six atoms, we can take for granted that the molecules in liquid and solid condition are more complicated, and that the various allotropic modifications of sulphur are influenced by the number of atoms contained in the molecules. Just like sulphur, other solid metalloids, *e. g.*, selenium, phos-

phorus, arsenic, carbon, silicon, occur in different modifications. Up to this time we have no means of ascertaining the size of the molecular elements in liquid and solid conditions; there is much, however, which favors the idea of these elements in free condition consisting of complex atomic groups.

*Chemical Properties.* In its chemical behavior sulphur is very similar to oxygen, and its compounds have the same constitution as the corresponding oxides. It unites directly with most of the elements. Heated to  $260^{\circ}$  in the air, it inflames and burns with a pale bluish flame, giving sulphur dioxide ( $\text{SO}_2$ ). Nearly all the metals combine with sulphur to form sulphides. By rubbing mercury, flowers of sulphur and water together, black mercury sulphide is obtained. A moist mixture of iron filings and sulphur glows after a time. Cu and Fe burn in sulphur vapor. The sulphides are analogous to the oxides, exhibit similar reactions, and possess, for the most part, a similar composition, as is seen from the following formulas:—

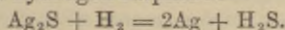
$\text{H}_2\text{O}$ ,	Water.	$\text{H}_2\text{S}$ ,	Hydrogen sulphide.
$\text{KOH}$ ,	Pot. hydrate.	$\text{KSH}$ ,	Pot. sulphhydrate.
$\text{BaO}$ ,	Barium oxide.	$\text{BaS}$ ,	Barium sulphide.
$\text{CO}_2$ ,	Carbon dioxide.	$\text{CS}_2$ ,	Carbon disulphide.
$\text{CO}_3\text{K}_2$ ,	Pot. carbonate.	$\text{CS}_3\text{K}_2$ ,	Pot. sulpho-carbonate.

## COMPOUNDS OF SULPHUR WITH HYDROGEN.

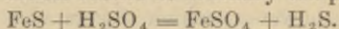
### 1. HYDROGEN SULPHIDE.

$\text{H}_2\text{S}$  = 34. Density = 17.

In nature hydrogen sulphide occurs principally in volcanic gases and in the so-called sulphur waters. It is always produced in the decomposition of organic substances containing sulphur, and also in the reduction of alkaline sulphates by decomposing carbon compounds. It may be formed directly from its constituents, although in small quantity, if hydrogen gas be conducted through boiling sulphur, or if sulphur vapors, together with hydrogen, be conducted over porous substances (pumice stone, bricks) heated to  $500^{\circ}$  C. Many sulphides are reduced upon ignition in a stream of hydrogen, with separation of hydrogen sulphide:—

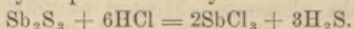


For its production acids are allowed to act upon sulphides. Ordinarily iron sulphide with diluted sulphuric acid is employed; the action occurs at ordinary temperatures:—



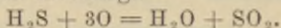
The operation is performed either in Kipp's apparatus (p. 33) or in the one pictured in Fig. 30.

Hydrogen sulphide thus obtained contains admixed hydrogen, in consequence of metallic iron existing in the sulphide. Perfectly pure hydrogen sulphide is obtained by heating antimony sulphide with hydrochloric acid:—



*Properties.* Hydrogen sulphide is a colorless gas, having an odor similar to that of rotten eggs; inhaled in large quantities it has a stupefying effect, and is very poisonous. At medium temperatures it condenses under a pressure of 14 atmospheres (under ordinary pressure at  $-74^\circ$ ) to a colorless liquid of specific gravity 0.9, which at  $-85^\circ \text{C}$ ., solidifies to a white crystalline mass. Its density equals 17 ( $\text{H} = 1$ ) or 1.177 ( $\text{air} = 1$ ). Water dissolves 3-4 times its volume of gas, the solution possessing all the properties of gaseous hydrogen sulphide, and hence called hydrogen sulphide water.

Ignited in the air the gas burns with a blue flame, water and sulphur dioxide resulting:—

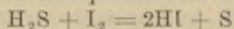


With insufficient air access, or when the flame is cooled by the introduction of a cold body, only hydrogen burns, while sulphur separates out in a free condition. In aqueous solution hydrogen sulphide is decomposed by the oxygen of the air at ordinary temperatures, sulphur separating as a fine powder:—



For this reason hydrogen sulphide becomes turbid upon exposure to the air.

The halogens behave like oxygen; the hydrides of the halogens are formed with separation of sulphur:—



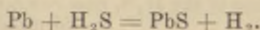
This reaction serves for the production of hydrogen iodide (p. 54).

As hydrogen sulphide has a great affinity for oxygen, it withdraws the latter from many of its compounds, hence

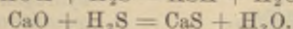
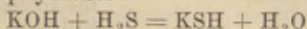


acting as a reducing agent (p. 76). Thus chromic, manganese and nitric acids are reduced to lower stages of oxidation. On pouring fuming nitric acid into a dry vessel containing hydrogen sulphide, the mixture will ignite with a slight explosion.

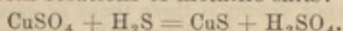
Hydrogen sulphide possesses weak acid properties, reddens blue litmus paper, forms salt-like compounds with bases, and is, therefore, termed hydrosulphuric acid. Nearly all the metals liberate hydrogen from it, yielding metallic sulphides:—



With the oxides and hydroxides of the metals  $\text{H}_2\text{S}$  yields sulphides and sulphhydrates:—



Sulphides, therefore, like the compounds of the halogens with the metals, may be viewed as the salts of hydrosulphuric acid. The sulphides of almost all the heavy metals are insoluble in water and dilute acids; therefore they are precipitated by  $\text{H}_2\text{S}$  from solutions of metallic salts:—



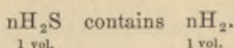
The precipitates thus obtained are variously colored (copper sulphide, black; cadmium sulphide, yellow; antimony sulphide, orange), and answer for the characterization and recognition of the corresponding metals. Paper saturated with a lead solution is at once blackened by  $\text{H}_2\text{S}$ , lead sulphide being formed—sensitive test for  $\text{H}_2\text{S}$ .

#### Molecular Formula of Hydrogen Sulphide. Atomic Weight of Sulphur.

The analysis of hydrogen sulphide shows that it consists of one part hydrogen and sixteen parts sulphur. If the molecular formula of hydrogen sulphide were  $\text{HS}$ , the atomic weight of sulphur would be sixteen (compare p. 87). The great analogy of the sulphur compounds, with those of oxygen (p. 97), permits us to accept a formula for the former similar to those of the latter. The molecular formula of hydrogen sulphide would, therefore, be  $\text{H}_2\text{S}$ , and the atomic weight of sulphur would equal 32. Hence the gas density of hydrogen sulphide must be  $\frac{34}{2} = 17$  ( $\text{H} = 1$ ), or 1.177 (air = 1), which is also confirmed by direct experiment. Conversely, it follows from the gas density that the molecular weight of hydrogen sulphide = 34. As, then, according to analysis, there are in thirty-four parts of the same, two parts hydrogen, the molecule will contain two atoms of hydrogen. That the thirty-two parts, sulphur combined with them correspond to *one* atom of sulphur

follows, because in the molecule of no sulphur compound have there been found less than thirty-two parts of that element (see p. 87).

From the molecular formula  $H_2S$ , further, we conclude that the contained hydrogen in one volume hydrogen sulphide, in free condition, occupies the same volume:—

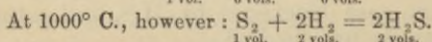
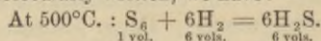


This conclusion is experimentally verified as follows: In a bent glass tube filled with mercury (Fig. 60), introduce dry hydrogen sulphide gas; then in the bent portion place a piece of tin, which is heated by a lamp. The sulphur of the  $H_2S$ , now combines with the metal to



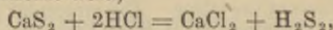
form solid tin sulphide, while hydrogen is set free; its volume is exactly equal to the volume of the employed hydrogen sulphide. The quantity of sulphur, 32 parts, in vapor form, at 1000 C., when the density is 32 (p. 96) combined with hydrogen (2 parts) will equal exactly half the volume of the hydrogen; at 500° C., how-

ever, when the vapor density is three times as great, it will equal 1 volume of the hydrogen. 1 volume  $H_2S$ , therefore, consists of  $\frac{1}{3}$  volume H and  $\frac{2}{3}$  volume sulphur vapor (at 500°), or as ordinarily expressed, 2 volumes  $H_2S$  consist of 2 volumes H and  $\frac{1}{3}$  volume sulphur vapor. Molecularly written, we have:—

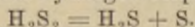


## 2. HYDROGEN PERSULPHIDE.

Just as hydrogen peroxide is formed by the action of acids upon some superoxide, so hydrogen persulphide may be obtained from metallic persulphides. Calcium persulphide is most suitable, and when its aqueous solution is poured into aqueous hydrochloric acid,



a yellow, oily, disagreeable liquid, insoluble in water, separates. It decomposes gradually at medium temperatures, more rapidly on warming, into hydrogen sulphide and sulphur:—



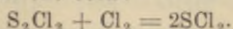
It is generally thought that  $H_2S_2$  is analogous to  $H_2O_2$ , and is hydrogen disulphide containing excess of sulphur dissolved

in it. As, however, the calcium supersulphide used represents a mixture of  $\text{CaS}_2$ ,  $\text{CaS}_3$  and  $\text{CaS}_5$ ; it is probable that the oily liquid is a mixture of  $\text{H}_2\text{S}_2$ ,  $\text{H}_2\text{S}_3$  and  $\text{H}_2\text{S}_5$ . We must at least conclude that  $\text{H}_2\text{S}_3$  is present in it, because it unites with strychnine to form a crystalline compound.

### COMPOUNDS OF SULPHUR WITH THE HALOGENS.

Sulphur and chlorine unite to form three compounds:  $\text{SCl}_2$ ,  $\text{SCl}_4$  and  $\text{S}_2\text{Cl}_2$ .

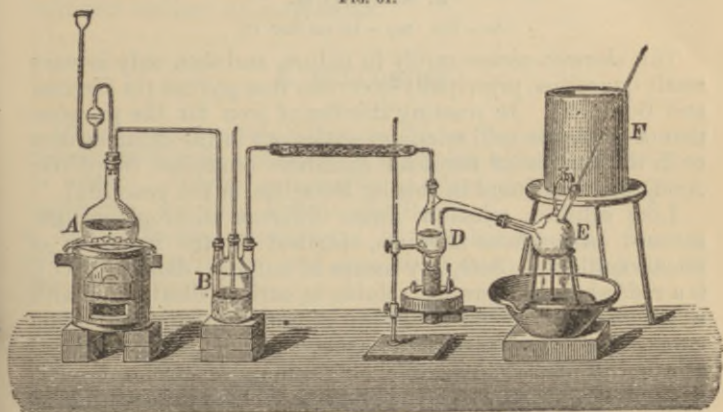
*Sulphur Dichloride*— $\text{SCl}_2$ —produced when  $\text{S}_2\text{Cl}_2$  is saturated with chlorine in the cold:—



The excess of chlorine is removed by conducting a stream of  $\text{CO}_2$  through it.

A dark, red colored liquid, with a specific gravity 1.62; boils at  $64^\circ \text{C}$ ., with partial decomposition into  $\text{S}_2\text{Cl}_2$  and  $\text{Cl}_2$ ; the dissociation commences at ordinary temperatures.

FIG. 61.



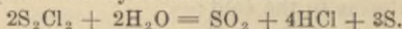
*Sulphur Tetrachloride*— $\text{SCl}_4$ —only exists at temperatures below  $0^\circ \text{C}$ . It is formed by saturating  $\text{SCl}_2$  with  $\text{Cl}$  at  $30^\circ \text{C}$ ., and readily decomposes into  $\text{SCl}_2$  and  $\text{Cl}_2$ ; the dissociation commences at  $-20^\circ \text{C}$ ., and is complete at  $+6^\circ$ . It yields crystalline compounds with some chlorides, *e. g.*,  $\text{SnCl}_4$ ,  $\text{AsCl}_3$ ,  $\text{SbCl}_3$ .



The most stable of the sulphur chlorides is

*Sulphur Mono-chloride*— $S_2Cl_2$ —formed when chlorine is conducted over molten sulphur. (Fig. 61.) It distills over and condenses in the receiver *E*; the product is redistilled, to purify it.

Sulphur mono-chloride is a reddish-yellow liquid with a sharp odor, provoking tears, having a specific gravity of 1.68, and boiling at  $139^\circ C$ . Its vapor density equals 67 ( $H = 1$ ) corresponding to the molecular formula  $S_2Cl_2 = 135$ . Fumes strongly in the air, and by water is decomposed into sulphur dioxide, sulphur and hydrochloric acid:—



Sulphur mono-chloride readily dissolves sulphur and serves in the vulcanization of caoutchouc. Bromine forms analogous compounds with S.  $S_2Br_2$  is a red liquid, boiling at  $190-209^\circ C$ . Iodine, upon gentle warming, unites with S to form  $S_2I_2$ .

### 3. SELENIUM.

Se = 79.5.  $Se_2 = 159$  (at  $1400^\circ C$ ).

This element occurs rarely in nature, and then only in very small quantities, principally in certain iron pyrites (in Sweden and Bohemia). In roasting this ore of iron for the preparation of sulphuric acid selenium settles out in the chimney dust or in the deposit of the lead chambers (compare Sulphuric Acid), and was found in this by Berzelius, in the year 1817.

Like sulphur, selenium forms different allotropic modifications. *Amorphous selenium*, obtained by the reduction of selenium dioxide ( $SeO_2$ ) by means of sulphur dioxide ( $SO_2$ ), is a reddish-brown powder, soluble in carbon disulphide, with a specific gravity 4.26. From carbon disulphide selenium crystallizes in brownish-red crystals. From the brownish-red solution of potassium selenide on standing exposed to the air, leafy black selenium crystals separate, which are isomorphous with sulphur. Upon suddenly cooling fused selenium it solidifies to an amorphous, glassy, black mass, with a specific gravity of 4.28, and is also soluble in carbon disulphide. When selenium (amorphous) is heated to  $97^\circ C$ ., its temperature suddenly rises above  $200^\circ C$ .; it is converted into a crystalline, dark gray mass with a specific gravity 4.8. It possesses metallic lustre, conducts electricity, and is insoluble in carbon

disulphide. The crystalline, insoluble modification is obtained by slowly cooling the molten selenium.

Selenium melts at  $217^{\circ}$ , and boils toward  $700^{\circ}$ , converting itself into a dark yellow vapor. The vapor density diminishes regularly with increasing temperature (similar to sulphur), becoming constant at  $1400^{\circ}\text{C}$ . Then it equals 79.5; the molecular weight is, therefore, 159, *i. e.* the molecule of selenium at  $1400^{\circ}\text{C}$ ., consists of two atoms ( $2 \times 79.5 = 159$ .)

Selenium is a perfect analogue of sulphur. In the air it burns with a reddish blue flame, forming  $\text{SeO}_2$  and emitting a peculiar odor resembling rotten horse-radish. In concentrated sulphuric acid selenium dissolves with a green color, forming selenious acid.

*Hydrogen Selenide* —  $\text{H}_2\text{Se}$  — produced like hydrogen sulphide, is a colorless, disagreeable smelling gas with poisonous action. In the air the aqueous solution becomes turbid and free selenium separates.

With chlorine selenium forms  $\text{SeCl}_4$  and  $\text{Se}_2\text{Cl}_2$  perfectly analogous to the sulphur compounds;  $\text{SeCl}_4$  is a solid and sublimes without decomposition.

---

#### 4. TELLURIUM.

Te — 128.\*

Of rare occurrence, either native or in combination with metals; with gold and silver in sylvanite, with silver and lead in altaite. Occurs principally in Transylvania, Hungary, California, Virginia, Bolivia and Brazil.

The tellurium precipitated by sulphurous acid from a solution of tellurous acid (see this) is a black powder of specific gravity 5.928.

According to its physical properties tellurium is a metal. It is silver white, of a perfect metallic lustre, and conducts electricity and heat. It crystallizes in rhombohedra, having a specific gravity 6.25. Fuses at  $500^{\circ}$  and vaporizes in a stream of hydrogen. Heated in the air it burns, with a bluish-gray flame, to tellurium dioxide ( $\text{TeO}_2$ ).

---

\* The atomic weight of tellurium, formerly taken as = 128, has been determined to be 126.8; from the law of periodicity, to be presented later, it, however, seems, with much certainty, that the same will yet be found to be somewhat lower (indeed, some less than that of iodine — 126.5).

The vapor density of tellurium at 1380° C., has been discovered to be about 126, corresponding to the molecular formula  $\text{Te}_2$ .

Hydrogen telluride  $\text{H}_2\text{Te}$ , is a colorless, very poisonous gas, with disagreeable odor. With chlorine tellurium yields two compounds  $\text{TeCl}_2$  and  $\text{TeCl}_4$ ; with bromine it gives  $\text{TeBr}_2$  and  $\text{TeBr}_4$ .

### Summary of the Elements of the Oxygen Group.

The elements oxygen, sulphur, selenium and tellurium form a natural group of chemically similar bodies. Especially marked is the similarity of the last three, while oxygen, possessing the lowest atomic weight, stands somewhat apart. Among the halogens, fluorine exhibits a similar deportment; it departs somewhat from its analogues, chlorine, bromine and iodine. Like the latter, the elements of the oxygen group present a gradation in their properties corresponding to their atomic weights:—

	O.	S.	Se.	Te.
Atomic weights,	16	32	79.5	126.8.

With the increase in the atomic weight there occurs a simultaneous condensation of substance, the volatility diminishes, while the specific gravity, the point of fusion and boiling increase, as seen in the following table:—

	Oxygen.	Sulphur.	Selenium.	Tellurium.
Specific gravity,	.....	1.95-2.07	4.2-4.8	6.2.
Melting point,	.....	111.5°	217°	500°.
Boiling point,	.....	420°	700°	White heat.
Gas density,	16	32	79.5	.....

Oxygen is a difficultly coercible gas, while the others, at ordinary temperatures, are solids. We must, however, bear in mind that sulphur, selenium and tellurium in free state are probably composed of larger complex atomic groups (see p. 96).

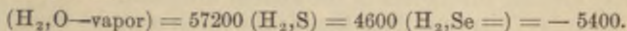
Further, with rising atomic weight the metalloidal passes into a more metallic character. Tellurium exhibits the physical properties of a metal; even selenium in its crystalline modification possesses metallic properties. In chemical deportment, however, the metalloidal character shows scarcely any alteration. All four elements unite directly, at elevated temperatures, with two atoms of hydrogen, to form volatile gaseous compounds having an acid nature; only the oxy-



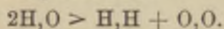
gen derivative—water—is liquid at ordinary temperatures and shows a neutral reaction. At a glowing heat the hydrogen compounds are decomposed into their elements. The affinity of hydrogen for oxygen is greatest; therefore,  $H_2S$ ,  $H_2Se$  and  $H_2Te$  are decomposed in aqueous solution by the air.

A measure for the chemical affinity of the elements of the oxygen group is afforded, as in the case of the halogens (p. 57), by their thermo-chemical department. By the union of 2 parts hydrogen with 16 parts oxygen to steam of  $100^\circ$  ( $H_2O$ —vapor), 57200 calories are disengaged. By the condensation of steam to water of  $100^\circ$  9600 additional ( $= 18 \times 536.5$ ) calories become free (latent heat of evaporation, p. 81), and by the cooling of water for each 1 degree C., further also 18 calories; so, on the whole, by the production of 1 molecular weight of water from its elements, 69000 calories\* are disengaged.

The heat disengagement is less in the formation of hydrogen sulphide, while in case of hydrogen selenide it is even absorbed, corresponding to the symbols:—



The previously mentioned fact, viz., the decomposition of  $H_2S$ ,  $H_2Se$ , and also of  $H_2Te$ , by oxygen, is then explained according to the idea of the greatest liberation of heat. We see, consequently, that here, as also with the halogens, the chemical affinity of the homologous elements successively diminishes with increasing atomic weight (decrease of negative character). It must, however, be borne in mind, that the heat liberation represents no direct measure for the affinity of the free atoms. If, for example, water be produced, corresponding to the molecular equation  $2H_2 + O_2 = 2H_2O$ , the hydrogen and oxygen molecules must first be broken up into individual atoms, for which a definite quantity of heat is necessary (heat of decomposition). The directly observed heat disengagement of 57200 calories only indicates that the energy of hydrogen to oxygen ( $2H, O$ ) is so much greater than the energy of the elementary molecules.



As the solid sulphur molecules consist of a greater number of atoms, it is probable their heat of decomposition is greater than that of the diatomic oxygen molecules, so that the energy of  $2H$  to  $S$  certainly is more than 4600 calories. From this decomposition of the molecules standing in connection with the absorption of heat, is explained why in every reaction, for its introduction and continuation, definite thermal conditions are necessary; that, for example, sulphur and hydrogen unite first at more elevated temperature, and then only partially.

That, indeed, in the breaking of the molecules, heat is absorbed, follows, among others, from the fact that, in the process of combustion, in nitrogen oxide more heat will be set free than in oxygen ( $O_2$ ). All the energy masses derived from thermal data are, therefore, only

\* 68360 calories, according to Thomsen.

relative; it is only in the most recent times that it has become possible to calculate the heat of decomposition of the carbon molecules, and, consequently, the real chemical energy of the carbon atoms (Thomsen).

### NITROGEN GROUP.

Here belong nitrogen, phosphorus, arsenic, antimony and bismuth. The latter possesses a decidedly metallic character. With three atoms of hydrogen these elements, bismuth excepted, yield gaseous derivatives.

#### 1. NITROGEN.

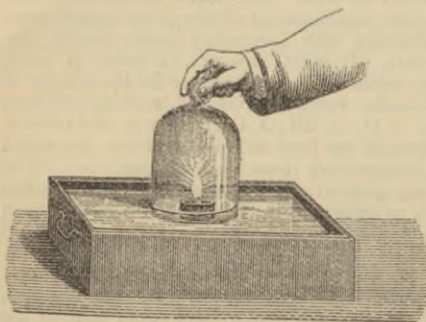
N = 14. N<sub>2</sub> = 28.

Free, it exists in the air, of which it constitutes  $\frac{4}{5}$  and oxygen the remaining  $\frac{1}{5}$ . Combined, it is principally contained in the ammonium and nitric acid compounds, as well as in many organic substances of the animal kingdom.

To isolate nitrogen from the air the latter must be deprived of its second constituent. This is effected by such bodies as

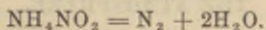
are capable of absorbing oxygen without acting upon the nitrogen. It is most simply brought about by the combustion of phosphorus. Several pieces of the latter are placed in a dish swimming on water, then ignited, and a glass bell jar placed over them (Fig. 62). In a short time, when all the oxygen is

FIG. 62.



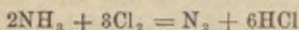
absorbed from the air, the phosphorus will cease burning; the phosphorus pentoxide produced dissolves in water, and the residual gas consists of almost pure N; its volume will equal four-fifths of the air taken. Another procedure consists in conducting air through a glowing tube filled with copper turnings; the copper unites with the oxygen and pure nitrogen escapes. At ordinary temperatures the removal of O from the air may be accomplished by the action of phosphorus, a solution of pyrogallic acid and other substances.

A very convenient course for the direct preparation of nitrogen is the following. Heat ammonium nitrite in a small glass retort; this decomposes the salt directly into water and nitrogen:—

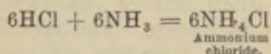


In place of ammonium nitrite a mixture of potassium nitrite and  $\text{NH}_4\text{Cl}$  may be used; by double decomposition upon warming, these salts yield potassium chloride and ammonium nitrite ( $\text{KNO}_2 + \text{NH}_4\text{Cl} = \text{NH}_4\text{NO}_2 + \text{KCl}$ ), which decomposes further. As potassium nitrite usually contains free alkali, to combine the same, some potassium bichromate is added. Practically the solution consists of 1 part potassium nitrite, 1 part ammonium nitrate, and 1 part potassium bichromate, in 3 parts water, and then boiled; to free the liberated nitrogen from every trace of oxygen, the gas is conducted over glowing copper.

The action of chlorine upon aqueous ammonia produces nitrogen. The chlorine combines with the H of the ammonia, forming  $\text{HCl}$ , which, with the excess of  $\text{NH}_3$  forms ammonium chloride. The nitrogen that was in combination with the hydrogen is set free. The following equations express the reactions:—



and



The apparatus pictured in figure 36, page 40 will serve to carry out the experiment. The disengaged chlorine is conducted through a Woulff wash bottle containing ammonia water, the free nitrogen being collected over water.

In this experiment the greatest care should be exercised that an excess of chlorine is not conducted into the solution, because its action upon the ammonium chloride will cause the formation of an exceedingly explosive body (nitrogen chloride,  $\text{NCl}_3$ ) separating in oily drops.

*Properties.* Nitrogen is a colorless, odorless, tasteless gas, which condenses at  $-130^\circ$  and a pressure of 280 atmospheres. Its density = 14 ( $\text{H} = 1$ ) or 0.9695 (air = 1). Water dissolves about 2% by volume. In its chemical department it is extremely inert, combining directly with only a few elements, and entering chemical reaction but slowly. It does not support combustion or respiration; a burning candle is extinguished in nitrogen; animals are suffocated in it. This is not due to the activity of the N, but to absence of O—a substance which cannot be dispensed with in combustion and



respiration. The presence of N in the air moderates the strong oxidizing property of the pure oxygen.

### THE ATMOSPHERE.

The air, or the envelop encircling the earth, consists principally of a mixture of nitrogen and oxygen; in addition it always contains, but in slight and variable quantities, aqueous vapor, carbon dioxide and traces of other substances, as accidental constituents. The pressure exerted by the air is measured by a column of mercury which holds it in a state of equilibrium; the height of the barometric column at the sea level and  $0^{\circ}$  C., equals, upon an average, 760 millimeters. As 1 c.c. of mercury weighs 13.596 grams, 76 c.c. will equal 1033.7 grams, and the last number would indicate the pressure which the column of air exercises upon one square centimeter of the earth's surface.

1 c.c. air weighs (at  $0^{\circ}$  C. and 760 mm. pressure), 0.001295 grams; 1000 c.c., therefore, or one litre, would weigh 1.295 grams. As one litre of  $H_2O$  weighs 1000 grams, air is consequently 773 times lighter than water. Air is 14.46 times heavier than hydrogen. The specific gravities of the gases and vapors were formerly referred to air ( $= 1$ ); compared with  $H = 1$ , they are, therefore, 14.46 times greater than before.

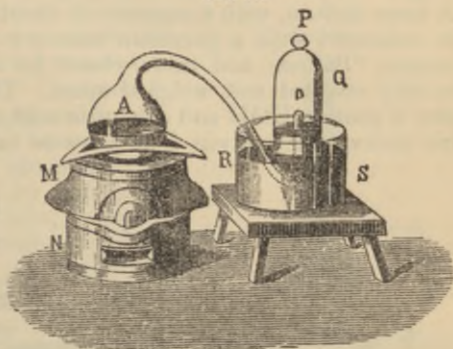
*Remarks.* From these data, with the aid of the specific gravity derived from the molecular weights, the absolute weight of definite volumes of all gases may be readily determined, a problem frequently presented for solution in practice. One litre of air weighs 1.295 grams, one litre of hydrogen 0.0896 grams. To ascertain the weight of a litre of any other gas or vapor, its specific gravity referred to air  $= 1$  must be multiplied by 1.295, or if compared with  $H = 1$  by the factor 0.0896.

*History.* In ancient times air, like fire and water, was regarded as an element. In the beginning of the seventeenth century it became known that by combustion and respiration in an enclosed space a portion of the air disappeared, and that the part remaining was no longer suitable for the support of the above processes; hence to it was ascribed the name *destroyed air*; to the first *fire air*. In the second half of the eighteenth century Scheele, in Sweden, and Priestley, in England, found that when, to the so-called *destroyed air* (nitrogen), a certain amount of the gas, set free by heating mercuric oxide (oxygen), was added, a mixture resulted possessing all the properties of atmospheric air. Although thus both constituents of air were separately won and by their mixture air again regenerated, yet at that time

views regarding the nature of both ingredients and the nature of combustion and oxidation processes prevailed which, throughout, were perfectly false. It was believed that combustion and oxidation were destructive processes; that the combustible and oxidizable bodies enclosed within themselves a peculiar substance, called *phlogiston*, which, in combustion and oxidation, escaped as fire and heat (phlogiston theory of Stahl, 1723). These erroneous opinions were explained and corrected by Lavoisier (in 1774) by the following celebrated experiment bearing upon the composition of the air: A glass

sphere, provided with a long, twice bent neck (Fig. 63), was filled with a weighed quantity of mercury. The open end of the neck dipped into a mercury trough, *RS*, and was closed completely by a glass bell jar. Then the balloon *A* was heated for some days at a temperature near the boiling point of mercury. By this means the mercury absorbed the oxygen of the air contained in *A* and the bell jar *P*, forming mercuric oxide. In the course

FIG. 63.



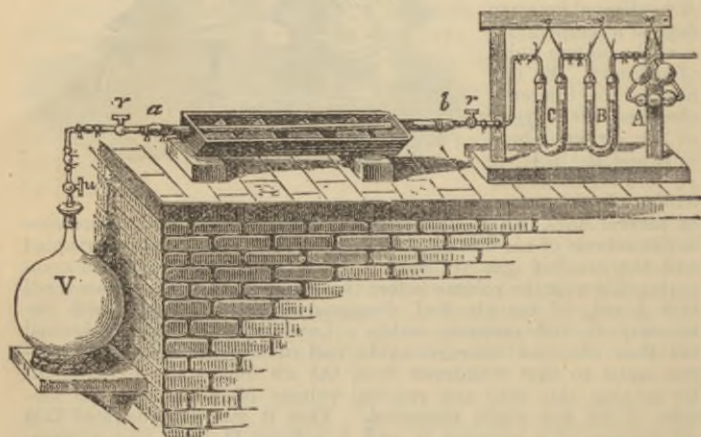
of several days, when, upon further heating, no additional decrease in the volume of air was observable, the experiment was interrupted and the residual gas volume in *A* and *P* measured. Upon comparing this with the volume before the experiment, it was discovered that  $\frac{1}{5}$  vol. of the air had disappeared and combined with the mercury to red mercuric oxide. Lavoisier now strongly ignited the thus obtained mercuric oxide, and obtained a volume of oxygen equal to that withdrawn from the air during the experiment. By mixing this with the residual volume of *N* the original volume of air was again recovered. Thus it was demonstrated that air consists of  $\frac{4}{5}$  volumes *N* and  $\frac{1}{5}$  volume *O* gas. The elementary character of nitrogen was first established by Lavoisier, in 1787. It was called azote (from ζώη life and ἀ privative), by him. The symbol *Az*, derived from azote, is used in France and England for nitrogen. The name nitrogenium (from which the symbol *N*) was given to nitrogen because it was a constituent of saltpetre (nitrum).

The above experiment served Lavoisier for another important deduction. As he determined the weight, both of the employed mercury and the resulting mercuric oxide, he discovered that the weight increase was exactly equal to that of the oxygen withdrawn from the

air, and by glowing the mercuric oxide the same weight of oxygen was again separated. Thus was it demonstrated that the process of oxidation was the union of two bodies (not a decomposition), and that the weight of a compound body equals the sum of the weights of its constituents; the principle of the indestructibility of matter.

*Quantitative Composition of Air.* Its composition is expressed by the quantity of oxygen and nitrogen contained in it, as its remaining admixtures are more or less accidental and variable. Boussingault and Dumas determined the accurate weight composition of the air by the following experiment: A large balloon, with a capacity of about 20 litres (Fig. 64), is connected with a porcelain tube *ab* filled with metallic copper. Balloon and tubes, closed by stop-cocks, are previously emptied and weighed apart. The bent tubes *A*, *B* and *C* contain KOH and sulphuric acid, and serve to free the air undergoing analysis from aqueous vapor, carbon dioxide

FIG. 64.



and other impurities. The porcelain tube, filled with copper, is heated to a red heat, and by carefully opening the stop-cocks *n*, *r* and *r'* a slow current of air is allowed to enter the empty balloon *V*. The impurities are given up in the bent tubes, and all the oxygen absorbed by the ignited *Cu*, forming cupric oxide, so that only pure nitrogen enters *V*. Now close the cocks and weigh the balloon and porcelain tube. The increase in weight of the latter represents the quantity of



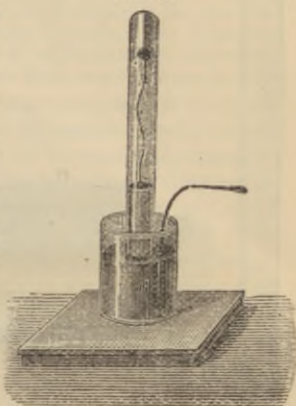
oxygen in the air; the increase in  $V$  the quantity of *nitrogen*. In this manner we find that in 100 parts by weight, of air, there are contained—

Nitrogen.....	76.87 parts by weight.
Oxygen.....	23.13 " " "
	100.00 " " "

As we know the specific gravity of nitrogen (14) and of oxygen, we can readily calculate the volume composition of air from that, in parts by weight, and can also determine its specific gravity (14.46).

Directly, the volume composition of air may be found by means of the absorptiometer. The latter is a tube carefully graduated, and sealed at one end. This is filled with mercury, and air, whose volume is determined by reading off the divisions on the tube, permitted to enter. Now introduce up into the tube, through the mercury, a platinum wire having a ball of phosphorus attached to the end (Fig. 65), (or a ball of coke saturated with an alkaline solution of pyrogallic acid). The phosphorus absorbs the oxygen of the air, and only nitrogen remains, whose volume is read off by the graduation.

FIG. 65.



The *eudiometric method* affords greater accuracy. It is dependent upon the combustion of the oxygen with hydrogen in an eudiometer. The latter is an absorptiometer, having two platinum wires fused in its upper end (Fig. 66). Into the eudiometer are introduced 100 volumes of air and 100 volumes of hydrogen, and the electric spark then passed through the wires (Fig. 67). All the oxygen in the air combines with a portion of the hydrogen to form water. On cooling, the aqueous vapor condenses and a contraction in volume occurs. Upon now measuring the volume of the residual gas, with regard to all corrections (see below), we will discover that the same equals 137.21 volume units; consequently, of the 200 employed volumes of gas, 62.79 volumes

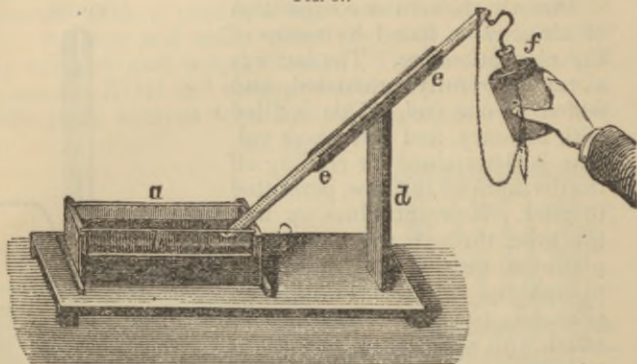
FIG. 66.



disappeared in the formation of water. As water results from the union of 1 volume of oxygen and 2 volumes of hydrogen, therefore, the 100 volumes of air employed in the analysis contained  $\frac{62.79}{3} = 20.93$  volumes of oxygen. From this the air consists of

79.07	volumes Nitrogen,
20.93	" Oxygen.
100.00	" Air.

FIG. 67.



*Measuring Gases.* The volume of gases is influenced by pressure, temperature, and the moisture contained in them. The volume of dry gases, at 760 mm. barometric pressure and  $0^{\circ}$  C., is accepted as the normal volume. If a gas has been measured under any other conditions, it must be reduced to the normal volume. According to the law of Boyle and Mariotte, the volumes of the gases are inversely proportional to the pressure; therefore, if the volume of the gas at pressure  $h$  has been found equal to  $V$ , its volume by 760 mm. equals  $\frac{Vh}{760}$ .

According to Gay-Lussac's law, all gases expand in proportion to the temperature. Their coefficient of expansion is  $\frac{1}{273} = 0.003665$ ; *i e.*, one volume of gas at  $0^{\circ}$  occupies at  $1^{\circ}$  the volume 1.000365. If  $V_t$  represents the observed gas volume at  $t^{\circ}$ ,  $V_0$ , however, its volume at  $0^{\circ}$ , then

$$V_o = \frac{V_t}{1 + 0.003665.t} *$$

and, considering the pressure,

$$V_o = \frac{V_h}{760(1 + 0.003665.t)}$$

Further, the gas volume is enlarged by moisture, as the tension of the aqueous vapor opposes the atmospheric pressure. The moisture may be removed by introducing into the gas a ball of coke saturated with sulphuric acid, which dries it. More convenient, however, is to make the correction of the gas volume in the following manner: Water is brought in contact with the gas to be measured, in order to perfectly saturate it with aqueous vapor; now measure the gas and calculate its normal volume from the above formula, after deducting from the observed pressure  $h$  the number of millimeters corresponding to the tension of the aqueous vapor for the given temperature (p. 81).

While formerly it was supposed that everywhere upon the earth's surface, as also in the highest attainable media, the air contained the same relative quantity of oxygen and nitrogen, it is at present proven, by accurate investigations, that variations to 0.5 % occur. These are dependent upon the wind currents; and it also appears that in the tropics a stronger oxygen absorption occurs than in the polar regions (v. Jolly). From this invariability in composition one might conclude that air is a chemical compound of oxygen and nitrogen.

This supposition is, however, opposed by the following circumstances. All chemical compounds contain their constituents in atomic quantities, which in the case of air is not so. In the mixing of nitrogen and oxygen, to form air, neither the separation nor absorption of heat occurs, which is always observed in chemical compounds. Further, the air absorbed by water or other solvents possesses a composition different from the atmospheric; this depends upon the dissimilar solubility of nitrogen and oxygen in water. The air expelled from water by heating consists of 34.9 volumes oxygen and 65.1 volumes nitrogen (Bunsen). From this, air is not a chemical compound, but a mechanical mixture of its two constituents.

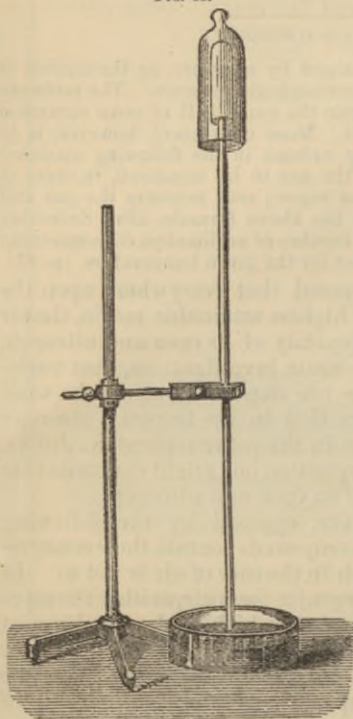
The great constancy in composition of the air depends on the mutual diffusion of the gases. As the gas molecules possess a direct progressive movement, they distribute themselves, without limitation, into space, and intermingle regularly among each other. *The velocity of*

\*  $V_o = V_t - V_o \cdot 0.00366t$ , consequently  $V_o + V_o \cdot 0.00366t = V_t$  and  $V_o (1 + 0.00366t) = V_t$ .



*the diffusion of gases is approximately inversely proportional to the square root of their densities*—the law of the diffusion of gases. The density of hydrogen = 1; the density of oxygen = 16; therefore, hydrogen diffuses 4 times more rapidly than oxygen. The unequal

FIG. 68.



diffusion of gases may be perceived if they are allowed to pass through very narrow apertures, or through porous partitions. The following experiment very clearly illustrates this: In the open end of an unglazed clay cylinder (as used in galvanic elements) there is putted a glass tube about one meter long, its open end terminating in a dish containing water (Fig. 68); the cylinder and tube are filled with air. Over the porous cylinder is placed a wider vessel filled with hydrogen. The latter presses almost four times faster into the cylinder than the air escapes from it; the air in the tube and cylinder are displaced and rise in the water in bubbles. When the separation of gas ceases, tube and cylinder are almost filled with pure hydrogen. On removing the larger hydrogen vessel the gas will escape much more rapidly into the external air than the latter can enter the cylinder; the internal pressure will therefore be weaker than the external, and water ascends in the glass tube.

In addition to N and O, air constantly contains aqueous vapor and carbon dioxide in very small quantities. The presence of the former can readily be recognized by the fact that cold bodies in moist air are covered with dew. Its quantity depends on the temperature and corresponds to the vapor tension of water (see p. 81). 1 c.c. of air perfectly saturated with aqueous vapor contains 22.5 grams water at 25° C.; on cooling to 0° 17.1 grams of these separate as rain. Generally the air contains only 50-70 % of the quantity of vapor

necessary for complete saturation. The amount of moisture in it is either determined according to physical methods (hygrometer), or directly by weighing. To this end a definite quantity of air is conducted through a tube filled with calcium chloride or sulphuric acid, and its increase in weight determined.

To detect the carbon dioxide in the air, conduct a portion of the latter through solutions of barium or calcium hydrates, and a turbidity will ensue. To determine its quantity, pass a definite and previously dried amount through a weighed calcium hydrate tube, and ascertain its increase in weight. 10,000 parts of atmospheric air contain, ordinarily, from 2-6 parts carbon dioxide.

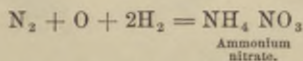
Besides the four ingredients just mentioned, air mostly contains, although in small quantities, ozone, hydrogen peroxide, and ammonium salts (ammonium nitrite). Finally, air, especially in its lower layers, contains microscopic germs of lower organisms, whose presence influences the processes of the decay and fermentation of organic substances.

## COMPOUNDS OF NITROGEN WITH HYDROGEN.

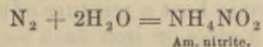
### AMMONIA.

$\text{NH}_3$  = 17. Density = 8.5.

Ammonia occurs in the air in combination with some acids, in natural waters and in the earth, only, however, in small quantities. The formation of ammonia by the direct union of nitrogen and hydrogen occurs under the influence of the silent electric discharge. Its compounds are frequently produced under the most varying conditions. Thus, by the action of the electric spark upon moist air ammonium nitrate is formed:—

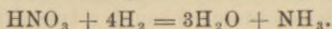


By the evaporation of water in the air small quantities of ammonium nitrite result:—



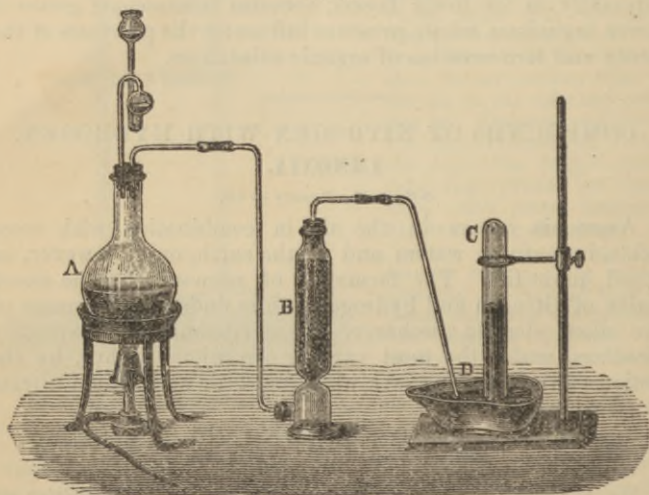
The same salt is formed in every combustion in the air; by the rusting of iron and in the electrolysis of water. The white vapors which moist phosphorus forms in the air, consist

of ammonium nitrite. Further, ammonium salts are produced in the solution of many metals in nitric acid, in consequence of a reduction of the acid by the liberated hydrogen:—

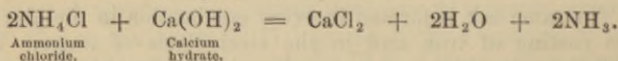


A fruitful source for ammonia production is the decomposition of nitrogenous organic substances and their dry distillation. Formerly, up to the preceding century, the bulk of the technically most important ammonium salt, ammonium chloride, was obtained by the distillation of camel's dung (in Egypt in the oasis of Jupiter Ammon—hence the name *Sal ammoniacum*). At present ammonia is almost exclusively prepared by the dry distillation of stone coal, as a bye-product in illuminating gas, by combining ammonia separating from the latter with sulphuric or hydrochloric acid.

FIG. 69.



To prepare ammonia heat a mixture of ammonium chloride and slaked lime in a glass or iron flask:—





The disengaged ammonia gas is collected over mercury, as it is readily soluble in water (Fig. 69). For perfect drying conduct it into a vessel filled with burnt lime ( $\text{CaO}$ ). Calcium chloride is not applicable here for drying, as it enters into combination with the gas. In consequence of its levity, ammonia, like hydrogen, may be collected by displacing the air in inverted vessels.

*Physical Properties.* Ammonia is a colorless gas with a suffocating, characteristic odor. Its density is 8.5 ( $\text{H} = 1$ ), or 0.591 (air = 1). Under a pressure of 6.5 atmospheres (at  $10^\circ\text{C}$ .), or by cooling to  $-40^\circ\text{C}$ ., it condenses to a colorless, mobile liquid, with a specific gravity of 0.613 at  $0^\circ$ , which solidifies at  $80^\circ$ .

Ammonia gas may be condensed, just like chlorine. Take ammonium silver chloride ( $\text{Ag Cl } 2\text{NH}_3$ ), obtained by conducting ammonia over silver chloride, and fuse it in a tube with a knee-shaped bend (Fig. 70). The limb containing the compound is now heated in a water bath, while the other limb is cooled. The compound is decomposed into silver chloride and ammonia, which condenses in the cooled limb.

Ammonia gas is exceedingly readily soluble in water, with the liberation of heat. One part of water at  $0^\circ$  and 760 mm. pressure absorbs

1050 volumes ( $= 0.817$  parts by weight); at  $15^\circ$  730 volumes of ammonia. When a long glass tube, closed at one end and filled with ammonia, has its open end placed in water, the latter rushes up into the tube as into a vacant space; a piece of ice melts rapidly in the gas. The aqueous solution possesses all the properties of the free gas, and is called *Liquor ammonii caustici*. The specific gravity of the solution is so much less, the larger the quantity of ammonia present. The solution saturated at  $14^\circ$  contains about 30%  $\text{NH}_3$ , and has a specific gravity of 0.897. Upon warming, all the gas escapes.

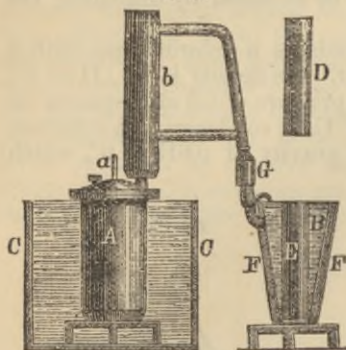
The condensed liquid ammonia, upon evaporation, absorbs a great amount of heat and answers, therefore, for the artificial production of

FIG. 70.



cold and ice in Carrè's apparatus. The simplest form of the latter is represented in Fig. 71. The iron cylinder *A* is filled about half with a concentrated aqueous ammonia solution, and is connected, by means of the tubes *a* and *b*, with the conical vessel *F*, in the middle of which is the empty cylindrical space *E*. The entire internal space of *A* and *F*

FIG. 71.



is hermetically shut off. *A* is heated upon a charcoal fire until the thermometer *a*, in it, indicates  $130^{\circ}\text{C}$ ., while *F* is cooled with water. In this way the gaseous ammonia is expelled from the aqueous solution in *A*, passes through *b*, in which most of the water runs back and condenses in *B*, of the receiver *F*, to a liquid. The cylinder *A* is removed from the fire, cooled with water, and the vessel *D*, constructed of thin sheet-metal and filled with water, placed in the cavity *E*, which is surrounded with a poor conductor, *e. g.*, felt. The ammonia condensed in *B* evaporates, and is reabsorbed by the water in *A*.

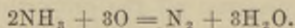
By this evaporation a large quantity of heat, withdrawn from *F* and its surroundings, becomes latent; the water in *D* freezes.

The method of Carrè for the artificial production of ice has acquired great application in the arts; in recent times, however, it is being more and more replaced by the method of Windhausen. The latter depends upon the expansion of compressed air.

*Chemical Properties.* By a glowing heat and continued action of the electric spark, ammonia is decomposed into nitrogen and hydrogen. On conducting ammonia gas over heated sodium or potassium, the nitrogen combines with these metals and hydrogen escapes:—



In the air ammonia will not burn; in oxygen, however, it burns with a yellow flame:—



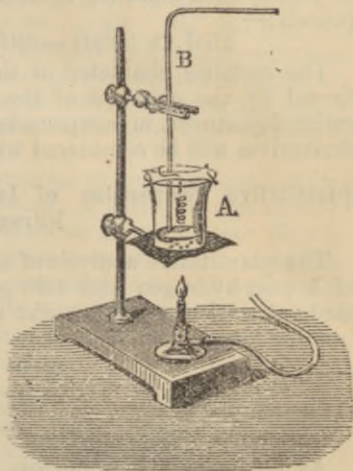
Ammonium nitrite and nitrogen dioxide are formed simultaneously. A mixture of ammonia and oxygen burns, when ignited, with explosion.

To show the combustion of  $\text{NH}_3$  in  $\text{O}$ , proceed as follows: A glass tube, through which ammonia is conducted, is brought into a vessel with oxygen, bringing the opening of the latter

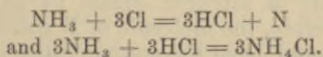
near a flame at the moment of the introduction of the glass tube. In contact with oxygen, the ammonia gas ignites and continues to burn in it.

The following experiment (of Kraut) very conveniently shows the combustion of ammonia. Place a somewhat concentrated ammonia solution in a beaker glass, heat over a lamp until an abundant disengagement of ammonia vapors occurs, and then, by means of a tube dipping into the liquid, run in oxygen gas. Upon approaching the mixture with a flame, it ignites with a slight explosion. The ignition may be induced without a flame, by sinking a glowing platinum spiral into the mixture (Fig. 72); here explosion also occurs. Simultaneously, the glass at first is filled with white vapors of ammonium nitrite ( $\text{NH}_4\text{NO}_2$ ); later, when oxygen predominates, red vapors of nitrogen dioxide ( $\text{NO}_2$ ) and nitrous acid ( $\text{HNO}_2$ ) appear.

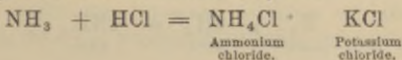
FIG. 72.



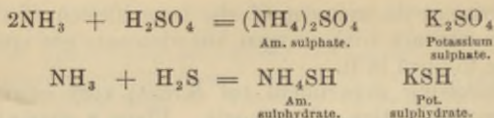
If chlorine gas be conducted into the vessel with ammonia, it immediately ignites and continues to burn in the latter, at the same time forming fumes of ammonium chloride ( $\text{NH}_4\text{Cl}$ ). The chlorine combines with the hydrogen of the ammonia to yield hydrochloric acid, which, with the excess of ammonia, produces



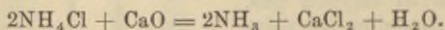
In gaseous form, as well as in solution, ammonia possesses strongly basic properties; it blues red litmus paper, neutralizes acids, forming salt-like compounds with them, which are very similar to the salts of the alkalis—sodium and potassium. The following illustrates the similarity:—







In these ammonia derivatives  $\text{NH}_4$  plays the rôle of the metal potassium. Hence the group  $(\text{NH}_4)$  has been designated *Ammonium* and its compounds, *ammonium salts*. By the action of strong bases ammonia is set free from the ammonium compounds:—



The metallic character of the ammonium group is confirmed by the existence of the ammonium amalgam and its entire deportment in compounds. Therefore, the ammonium derivatives will be considered with the metals.

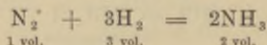
#### Quantitative Composition of Ammonia. Atomic Weight of Nitrogen.

The quantitative analysis of ammonia shows that it consists of 1 part hydrogen and 4.66 parts nitrogen; hence we conclude that the atomic weight of N is a multiple of the last number (see p. 62).

H = 1	2H = 2	3H = 3
N = 4.66	N = 9.33	N = 14
NH = 5.66	NH <sub>2</sub> = 11.33	NH <sub>3</sub> = 17

As the density of ammonia equals 8.5 ( $\text{H} = 1$ ), then its molecular weight = 17. In 17 parts of ammonia are contained 3 parts, and, therefore, 3 atoms, of hydrogen. That the 14 parts nitrogen united with them correspond to *one* atom of N is a consequence, as never less than 14 parts of N are present in the molecular weight of any nitrogen derivative. The density of nitrogen equals 14 and its molecular weight 28; therefore, the molecule of N consists of two atoms ( $\text{N}_2$ ). This is found from the volume ratios occurring in the formation of ammonia (see below).

From the molecular formulas  $\text{NH}_3$  and  $\text{N}_2$  follows, further, that 1 vol. N and 3 vols. H form 2 vols. ammonia gas, or that 2 vols.  $\text{NH}_3$  decompose into 3 vols.  $\text{H}_2$  and 1 vol.  $\text{N}_2$ , corresponding to the molecular equation:—



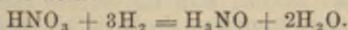
The following experiments prove these conclusions:—

1. Decompose an aqueous ammonia solution, mixed with sulphuric acid to increase its power of conductivity, in a Hofmann's apparatus (Fig. 47), by the galvanic current. Hydrogen will separate at the negative and nitrogen at the positive pole; the former will have three times the volume of the latter.

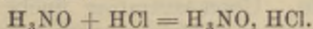
2. The electric (induction) sparks are permitted to strike through dry ammonia gas enclosed in an eudiometer, or the apparatus represented in Fig. 58 (p. 89). In this way the ammonia is decomposed into nitrogen and hydrogen, whose volume is twice as large as that of the ammonia employed. That 3 vols. H are present in the mixture for each 1 vol. N is easily shown by the volumetric method, by burning the H with oxygen (p. 111).

The volume ratios in the formation of ammonia confirm the conclusion drawn from the density of nitrogen (see above), that the molecule of the latter consists of two atoms. In two volumes of ammonia there are  $2n$  molecules of  $\text{NH}_3$ , therefore,  $2n$  atoms of N. The nitrogen contained in these 2 volumes of  $\text{NH}_3$  in a free condition occupies 1 volume, which contains  $n$  molecules and therefore  $2n$  atoms of N.

**Hydroxylamine.**  $\text{NH}_3\text{O} = \text{NH}_2\text{OH}$ . This compound, very analogous to ammonia, was discovered (Lossen) in the reduction of ethyl nitrate by zinc and hydrochloric acid. It is produced, too, by the action of tin upon dilute nitric acid, and by tin and hydrochloric acid upon all the oxygen compounds of nitrogen. In all these reactions it is the hydrogen eliminated by the tin which, in *statu nascendi*, reduces the nitric acid:—

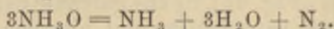


The hydroxylamine remains in solution in combination with nitric acid. Like ammonia, hydroxylamine unites directly with acids, to form salts:—

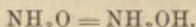


It cannot be obtained in free condition, as it is very unstable. On adding to the aqueous solution of the sulphate of hydroxylamine sufficient barium hydrate to remove all the sulphuric acid, an aqueous solution of the base is obtained, which, like the ammonia solution, possesses strongly

basic properties, and blues red litmus paper. The solution is, however, very unstable, and readily decomposes into water, ammonia and nitrogen:—

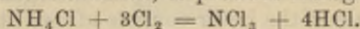


Owing to its great similarity to ammonia, it is supposed that hydroxylamine represents ammonia in which, 1 H is replaced by the hydroxyl group OH; therefore the name hydroxylamine:—



### COMPOUNDS OF NITROGEN WITH THE HALOGENS.

**Nitrogen Chloride.**  $\text{NCl}_3$ . As we have seen, nitrogen is liberated when chlorine acts upon excess of ammonia; when, however, the chlorine is in excess, it acts upon the previously formed ammonium chloride, to produce nitrogen chloride:—



For the preparation of a small quantity of nitrogen chloride, dip a flask filled with chlorine, open end down, into an aqueous ammonium chloride solution, warmed to  $30^\circ$ . The chlorine is absorbed, and heavy oil drops separate, which are best collected in a small leaden dish.

Nitrogen chloride is an oily, yellow liquid, with a disagreeable odor; its specific gravity equals 1.65. Of all chemical compounds this is the most dangerous, as it, by the slightest contact with many substances, frequently decomposes without any perceptible external cause, accompanied by an extremely violent explosion.

The formation and explosibility of nitrogen chloride may be harmlessly illustrated in the following manner: Decompose a saturated ammonium chloride solution with the electric current. Nitrogen chloride rising in small drops from the liquid will separate at the positive pole. Upon covering the surface of the solution with a thin layer of turpentine oil, each drop, as it comes in contact with the latter, will explode.

**Nitrogen Iodide.** Upon saturating finely divided iodine powder with ammonium hydrate, or upon pouring an alcoholic solution of iodine into ammonium hydrate, a brownish black substance is obtained, which is extremely explosive. Its explosibility may be shown without danger in the following manner: The precipitate is collected on a filter, washed with water, the filter opened out and torn into small pieces,



which are then allowed to dry; upon the slightest disturbance these pieces explode with a violent noise. According to the method of preparation the compound possesses the composition  $\text{NH}_2\text{I}$  or  $\text{NI}_3$ ; it is regarded as ammonia in which the hydrogen is partly or entirely replaced by iodine.

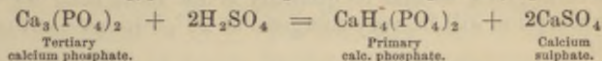
## 2. PHOSPHORUS.

P — 31.  $\text{P}_4$  — 124. Density — 62.

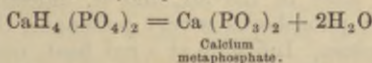
This element does not occur free in nature, owing to its very great affinity for oxygen. The phosphates, especially calcium phosphate, are widely distributed. By the disintegration of the minerals containing phosphates the latter pass into the soil, are absorbed by plants, and remain in their ash. In the animal kingdom calcium phosphate occurs in the bones.

Brand and Kunkel, in Hamburg (1669), first obtained phosphorus by the ignition of evaporated urine. In 1769, Scheele, in Sweden, demonstrated its isolation from bones. Its name is derived from its power of giving light in the dark — *φωσφόρος*, *i. e.*, light-bearer.

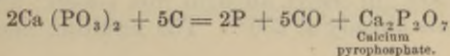
To obtain phosphorus from bones the latter are burned, thereby destroying all organic admixtures and leaving bone ashes, which consist principally of tertiary calcium phosphate  $(\text{PO}_4)_2\text{Ca}_3$  (see Phosphoric acid). The ashes are now heated with  $\frac{2}{3}$  of their weight of sulphuric acid, the tri-phosphate thus becoming primary calcium phosphate, and gypsum (cal. sulphate) resulting as a bye-product:—



The gypsum, which is very difficultly soluble in water, is separated from the readily soluble primary phosphate by filtration; the solution is mixed with charcoal, evaporated in leaden pans, and the residue raised to a red heat. This converts the primary phosphate, with loss of water, into calcium metaphosphate:—



The ignited residue is then raised to a white heat, in retorts of infusible clay. The carbon partly reduces the metaphosphate to phosphorus, by forming carbon oxide gas with oxygen, and half of the phosphorus contained in the metaphosphate remains as calcium pyrophosphate:—



The liberated phosphorus escapes in vapor, and is collected under water in receivers of peculiar construction, and there condensed. To remove mechanically admixed impurities the phosphorus is again distilled from retorts and fused under water; it is then moulded into sticks.

The *crystalline* or *yellow* phosphorus obtained by distillation is a waxy, transparent, slightly yellow-colored substance, with specific gravity of 1.83 at 10° C. At ordinary temperatures it is soft and tough; at 0° it becomes brittle. Fuses under water at 44° and boils at 290° C. By the action of sunlight it becomes yellow and is coated with a non-transparent, reddish-white layer. In water, phosphorus is insoluble; slightly insoluble in alcohol and ether; very readily soluble in carbon disulphide. From the latter solution it crystallizes in forms of the isometric (rhombic dodecahedra) system. Exposed to the air, it readily oxidizes to phosphorous acid ( $H_3PO_3$ ); the white vapors which arise contain ammonium nitrite ( $NH_4NO_2$ ), ozone and hydrogen peroxide. Its odor resembles that of ozone. In the air it phosphoresces at night. Also shines in other gases, but only in such as contain oxygen. It appears the phosphorescence is influenced by the formation and combustion of the self-inflammable phosphine, as all substances which destroy the latter also prevent and put an end to the former. It is noteworthy that in pure oxygen the oxidation of phosphorus occurs first at 27°. If the oxygen be diluted by removal over an air pump or the addition of neutral gases, so that its quantity is not more than 40%, the absorption will be very energetic at 20°, but cease entirely at 70°.

Another modification—the *red* or *amorphous phosphorus*—possesses properties entirely different from the ordinary variety. It is a reddish-brown amorphous powder, of specific gravity 2.14; insoluble in carbon disulphide, non-phosphorescent, does not alter in the air, and is, indeed, very stable. While ordinary phosphorus is very poisonous, this variety is perfectly harmless. Infusible at a red heat, not even under strong pressure, and vaporizes very slowly (above 260°), and only partially, the vapors passing over into ordinary phosphorus.

To prepare the red, the first variety is heated for some minutes to 300°, in closed, air-tight iron vessels; a slow conversion occurs already at 250°. The resulting mass is then

treated with carbon disulphide or sodium hydrate, to withdraw, unaltered, ordinary phosphorus. If some iodine be added to the ordinary phosphorus, the change will occur below  $200^{\circ}$ .

A third modification—*metallic phosphorus*—is formed, if the amorphous variety be heated in a glass tube, free of air, to  $530^{\circ}$ . Microscopic needles then sublime into the upper, less heated portion of the tube. More easily obtained if phosphorus be heated with lead, in a closed tube, to a red heat. The molten metal dissolves the phosphorus, which, on cooling, separates in black, metallic, shining crystals. Metallic phosphorus possesses the specific gravity 2.34, vaporizes with difficulty, and is less active than the amorphous variety.

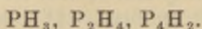
Two green lines characterize the spectrum of phosphorus. On conducting hydrogen gas over a small piece of it, heated in a glass tube, the escaping gas burns with a bright green flame, in consequence of the phosphorus it contains. When ordinary phosphorus is distilled with water, some passes over with the steam and, in the dark, phosphoresces. This procedure serves for the detection of phosphorus in poisoning with this substance.

The density of P equals 62 ( $H = 1$ ), or 4.42 (air = 1); the molecular weight is, therefore, 124. As the atomic weight of P is 31, it follows that the molecule in form of vapor consists of 4 atoms:  $P_4 = 124 (31 \times 4)$ . We saw that the sulphur molecule at  $500^{\circ}$  consists of 6 atoms ( $S_6$ ), at  $900^{\circ}$  of 2 atoms ( $S_2$ ). Such a dissociation does not, however, occur with phosphorus; even at  $1040^{\circ}$  its vapor density remains unaltered.

When burned in oxygen or in air, phosphorus forms the pentoxide ( $P_2O_5$ ). The ordinary variety inflames at  $40^{\circ}$ , and also by gentle friction; the amorphous not below  $260^{\circ}$ . Even under water the first burns with a bright flame. To this end heat some pieces of P in a flask with water, until they fuse, and conduct a current of oxygen through the water. Phosphorus combines with Cl, Br and I very energetically at ordinary temperatures; by throwing a small piece of it into a vessel containing dry chlorine gas it at once inflames. The red only reacts with the halogens after applying heat. With most of the metals phosphorus unites on warming, and throws out some metals from solutions of their salts. From a silver nitrate solution, it precipitates silver and phosphorus-argentide ( $PAg_3$ ); this solution, therefore, answers as a counter-irritant in phosphorus burns.



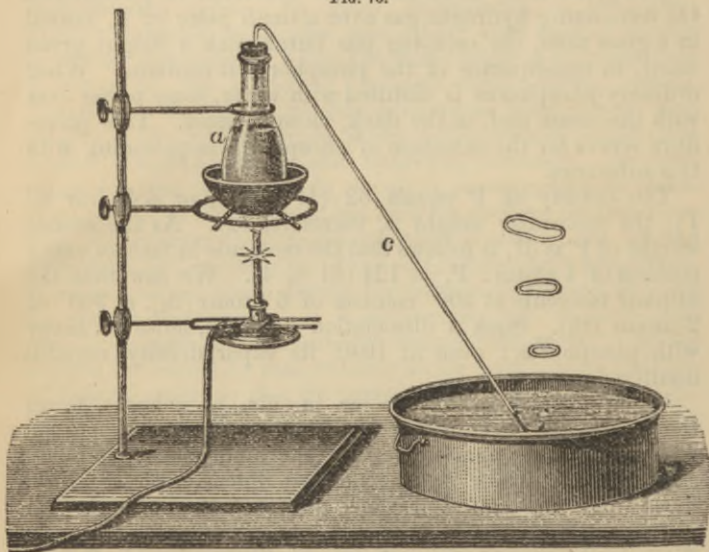
## COMPOUNDS OF PHOSPHORUS WITH HYDROGEN



On warming yellow phosphorus with potassium or sodium hydrate, spontaneously inflammable hydrogen phosphide is produced.

The liberated gas mixed with air in a closed vessel explodes violently, hence, to make it, proceed as follows: Fill a glass flask almost full of aqueous KOH, add a few pieces of P, and heat over a lamp (Fig. 73). When the liberation of gas commences, and the air in the neck of the flask has been expelled, close the same with the cork of

FIG. 73.

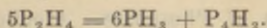


the delivery tube, the other end of which dips under *warm* water, to prevent any obstruction arising in it from phosphorus that has been carried over and solidified by cooling. Each bubble rising from the liquid inflames in the air, and forms white cloud-rings which ascend.

The gas thus produced consists of gaseous phosphine ( $\text{PH}_3$ ) and hydrogen, with which is mixed a small quantity of a liquid substance ( $\text{P}_2\text{H}_4$ ), whose presence imparts the spontaneous inflammability to the gas. On conducting the latter through a cooled tube, the liquid phosphine ( $\text{P}_2\text{H}_4$ ) is con-

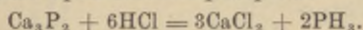
densed to a liquid, and the escaping gas no longer inflames spontaneously. Similarly the liquid compound may be isolated if the gas, is conducted through alcohol or ether, by which the compound  $P_2H_4$  is absorbed.

**Liquid Phosphine**,  $P_2H_4$ , separated from the gas by cooling, presents a colorless, strongly refracting liquid, insoluble in water, and boiling at  $30^\circ$ . Inflames spontaneously in the air, and burns with great brilliancy to phosphorus pentoxide and water. Its presence in combustible gases, such as hydrogen, marsh gas, and  $PH_3$ , gives to them their spontaneous inflammability. In contact with some compounds, like carbon and sulphur, and by the action of sunlight, it decomposes into gaseous and solid phosphine:—

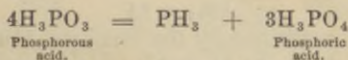


**Solid Phosphine**,  $P_4H_2$ , is a yellow powder inflamed at  $160^\circ$  or by a blow. Formed in the decomposition of calcium phosphide by hydrochloric acid.

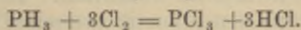
**Gaseous Phosphine**,  $PH_3$ , may be formed, in addition to the manner previously described, by the action of water or hydrochloric acid upon calcium phosphide:—



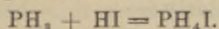
Further, by the glowing of phosphorous and hypophosphorous acid:—



A colorless gas with a disagreeable, garlic-like odor, and somewhat soluble in alcohol. Its density is 17 ( $H = 1$ ), or 1.185 ( $air = 1$ ). Pure—freed of  $P_2H_4$ —it ignites at  $100^\circ C$ . Oxidizing agents convert it again into the spontaneously inflammable variety, owing to the production of  $P_2H_4$ . It is extremely poisonous. By heat and the action of the electric current  $PH_3$  decomposes into phosphorus and hydrogen. Mixed with chlorine it explodes violently, with production of phosphorus tri-chloride and hydrogen chloride:—

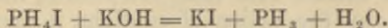


Like ammonia, gaseous hydrogen phosphine possesses faint alkaline properties, and combines with hydrogen iodide and bromide to yield compounds similar to ammonium chloride:—



With HCl it combines at 30°–35°, or at the ordinary temperature under a pressure of 20 atmospheres. The group PH<sub>4</sub>, figuring in the rôle of a metal in these compounds, is analogous to ammonium (p. 120), and termed *Phosphonium*.

**Phosphonium iodide, PH<sub>4</sub>I.** It is best prepared by the decomposition of phosphorus di-iodide (PI<sub>2</sub>), by a slight quantity of water. It sublimes in colorless, shining, cube-like rhombohedra; fumes in the air, and, with water, decomposes into PH<sub>3</sub> and HI. Decomposed by potassium hydrate it yields pure hydrogen phosphide, which is not spontaneously inflammable:—

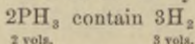


### Molecular Formula of Phosphine. Atomic Weight of Phosphorus.

Analysis of gaseous phosphine shows that it consists of 1 part hydrogen and 10.33 parts phosphorus. Were its molecular formula PH the atomic weight of P would be 10.33. The great analogy of phosphine, with NH<sub>3</sub>, as also all the P compounds with those of N, argues, however, for the formula PH<sub>3</sub>. The atomic weight of P, therefore, is 31 (= 3 × 10.33), and the molecular weight of the gaseous phosphine is 34:—

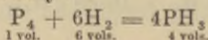
$$\begin{array}{r} \text{H}_3 = 3 \\ \text{P} = 31 \\ \hline \text{PH}_3 = 34 \end{array}$$

This view is confirmed by the density. Corresponding to the formula, it must be  $\frac{3}{2} = 17$ , which follows from direct experiment. Further, from the formula PH<sub>3</sub>, it follows that in 2 volumes of the gas 3 volumes of hydrogen are present:—



Or in 1 volume are contained 1½ volumes hydrogen. On decomposing the gas in an eudiometer by the passage of electric sparks, it will be found that the volume increases 1½ times; the gas consists, then, of pure hydrogen, while phosphorus separates in a solid condition. As the phosphorus molecule in gaseous condition is composed of 4 atoms, the phosphorus (31 parts) separated from 2 volumes PH<sub>3</sub>, in vapor form, will fill ½ volume; hence in 2 volumes of PH<sub>3</sub> 3 volumes of H and ½ volume phosphorus vapor are present:—

Or, written molecularly:—



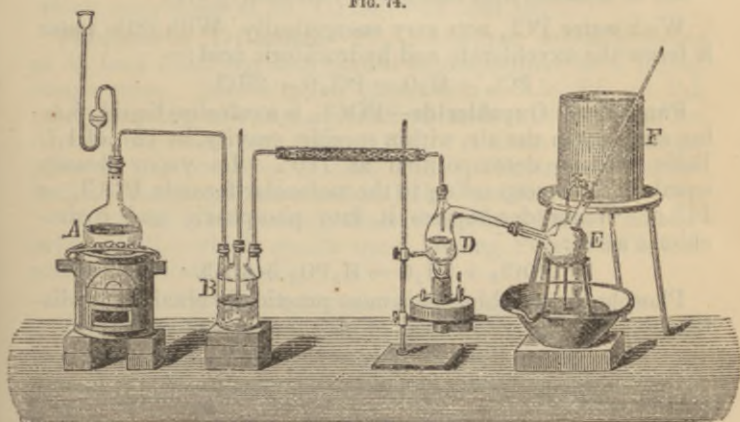


## COMPOUNDS OF PHOSPHORUS WITH THE HALOGENS.

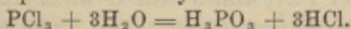
Phosphorus combines directly with the halogens, to yield compounds of the forms  $PX_3$  and  $PX_5$ , in which X indicates an halogen atom.

**Phosphorus Trichloride**—*Phosphorous Chloride*— $PCl_3$ . Conduct dry chlorine gas over phosphorus gently heated in the retort *D* (Fig. 74). The phosphorus ignites in the stream of gas and distills over as trichloride, which is collected in the receiver *E* and condensed. The product is purified by a second distillation. It is a colorless liquid, boiling at  $74^\circ$

FIG. 74.



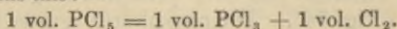
C., and has a sharp, peculiar odor. Its specific gravity equals 1.616 at  $0^\circ$ . It fumes strongly in the air, decomposing with moisture to phosphorous and hydrochloric acids:—



The vapor density of the trichloride equals 68.7 ( $H = 1$ ), corresponding to the molecular formula  $PCl_3 = 137.5$ .

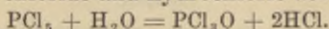
**Phosphorus Pentachloride**—*Phosphoric Chloride*— $PCl_5$ . Produced by the action of an excess of chlorine upon the liquid trichloride. It is a solid, crystalline, yellowish-white compound. Fumes strongly in the air and sublimates by heating, without fusion, but with partial decomposition, into trichloride and chlorine.

At lower temperatures (in an atmosphere of chlorine) the vapor density of the pentachloride has been found to be 104.2, corresponding to the molecular formula  $\text{PCl}_5$  ( $2 \times 52.1 = 104.2$ ). At increased temperatures the vapor density steadily diminishes, a gradual decomposition occurs—dissociation (p. 85) of the molecules  $\text{PCl}_5$  into the molecules  $\text{PCl}_3$  and  $\text{Cl}_2$ . At  $236^\circ$  the dissociation is complete, and then equals the vapor density 52.2; *i. e.*, the vapor then fills double as large a volume as at a lower temperature. The breaking up of  $\text{PCl}_5$  into  $\text{PCl}_3$  and  $\text{Cl}_2$  explains this:—

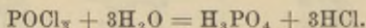


That, in fact, such a decomposition of the penta- into trichloride and chlorine does occur, is, among other things, proven by the originally colorless vapor, gradually assuming the yellow color of chlorine with increasing temperature. The decomposition products— $\text{PCl}_3$  and  $\text{Cl}_2$ —may be separated from each other by diffusion (p. 114).

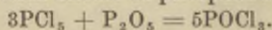
With water  $\text{PCl}_5$  acts very energetically. With little water it forms the oxychloride and hydrochloric acid:—



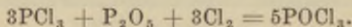
**Phosphorus Oxychloride**— $\text{POCl}_3$ , is a colorless liquid, fuming strongly in the air, with a specific gravity, at  $12^\circ$ , of 1.7. Boils without decomposition at  $110^\circ$ . Its vapor density equals 72.7, corresponding to the molecular formula  $\text{POCl}_3 = 145.5$ . Water decomposes it into phosphoric and hydrochloric acids:—



Phosphorus oxychloride is most practically obtained by distillation of  $\text{PCl}_5$ , with excess of phosphorus pentoxide:—



Or chlorine gas is conducted into a mixture of  $3\text{PCl}_3$  and  $\text{P}_2\text{O}_5$ :—



Particularly interesting is the production of it by conducting ozonized air through phosphorus chloride (Remsen). In the same manner  $\text{PCl}_3$  unites with S when heated to  $130^\circ$ , to form *phosphorus sulpho-chloride*— $\text{PSCl}_3$ —an oily liquid, sinking in water, which with the latter decomposes into  $\text{SH}_2$ ,  $\text{ClH}$  and  $\text{PO}_3\text{H}$ .

The bromine and iodine phosphorus compounds are perfectly analogous to the chlorine derivatives. They are obtained by uniting the constituents in the proportions by weight expressed by their formulas. As the union is exceedingly ener-

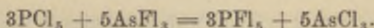
getic, it is best to proceed as follows: Dissolve the phosphorus in carbon disulphide, add gradually the calculated amount of Br or I, and then distill off the volatile carbon disulphide.

**Phosphorus Tribromide**  $\text{PBr}_3$ , is a colorless liquid, boiling at  $175^\circ$ , and having a specific gravity of 2.7. The **pentabromide**, formed by gradual addition of  $2\text{Br}$  to  $\text{PBr}_3$  is a yellow, crystalline substance, which by heat fuses, and breaks up into  $\text{PBr}_3$  and  $\text{Br}_2$ . Water decomposes both compounds, as it does the corresponding chlorides. **Phosphorus oxy-bromide** ( $\text{POBr}_3$ ), is a colorless crystalline mass, fusing at  $45^\circ$ , and boiling at  $195^\circ$ .

**Phosphorus Chlor-bromide**,  $\text{PCl}_3 \text{ Br}_2$  is produced by the union of  $\text{PCl}_3$  with  $\text{Br}_2$  in the cold. A yellowish red mass, which decomposes at  $35^\circ \text{C}$ ., into  $\text{PCl}_3$  and  $\text{Br}_2$ .

**Phosphorus Tri-iodide**— $\text{PI}_3$ , forms red crystals, fusing at  $55^\circ$  and distilling, with partial decomposition, at a higher temperature. The so-called phosphorus iodide,  $\text{PI}_2$ , or  $\text{P}_2\text{I}_4$  (corresponding to  $\text{P}_2\text{H}_4$ ), crystallizes in beautiful orange red crystals or prisms, and fuses at  $110^\circ$ . A little water decomposes it into phosphorous acid,  $\text{PH}_3 + \text{HI}$ , and the last two bodies form *phosphonium iodide*,  $\text{PH}_4\text{I}$  (p. 128).

Of interest is the recently discovered **Phosphorus Pentafluoride**— $\text{PF}_5$ —which results upon heating  $\text{PCl}_3$  or  $\text{PCl}_5$  with arsenic trifluoride,  $\text{AsF}_3$ .



It is a colorless gas, fuming in moist air, which, with water, breaks up into phosphoric acid and hydrogen fluoride. Its density is 63, corresponding to the molecular formula  $\text{PF}_5 = 126$ .

Remarkable is the fact that, while phosphorus pentaiodide could not be obtained, the stability of the compounds,  $\text{PBr}_5$ ,  $\text{PCl}_5$ ,  $\text{PF}_5$ , gradually increases with diminution of the atomic weight of the combined halogens.

### 3. ARSENIC.

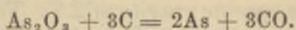
As = 75.  $\text{As}_4 = 300$ . Vapor density, 150.

Arsenic is a perfect analogue of phosphorus, but possesses a somewhat metallic character. Free, it is similar to metals.

Arsenic is found free in nature. More frequently in combination with sulphur (realgar, orpiment), with oxygen (arsenolite,  $\text{As}_2\text{O}_3$ ), and with metals (mispickel,  $\text{FeSAs}$ ,



cobaltite,  $\text{CoAsS}$ ). To prepare it, heat mispickel with some iron; when free, arsenic will sublime. Or, in the customary way of isolating metals from their oxides, heat the trioxide (arsenolite) with charcoal:—

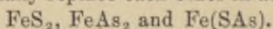


Arsenic appears in two modifications. The *amorphous arsenic* is an almost lustreless, black mass, with a specific gravity 4.71. It is brittle and can be easily pulverized. *Crystallized arsenic*, obtained by continuous heating to  $210\text{--}220^\circ$ , forms steel gray hexagonal rhombohedra, with strongly metallic lustre; its specific gravity equals 5.7.

Arsenic volatilizes at  $180^\circ$  without previously fusing; under strong pressure and in a sealed tube it is fusible. Its vapor possesses a lemon-yellow color. The vapor density is 150 ( $\text{H} = 1$ ), the molecular weight, therefore, 300. As its atomic weight equals 75, it follows that its gas molecule, like that of phosphorus, consists of four atoms ( $\text{As}_4 = 300 = 4 \times 75$ ).

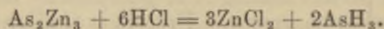
Arsenic does not change in dry air. Heated, it burns with a blue colored flame and disseminates the garlic-like odor of arsenic tri-oxide ( $\text{As}_2\text{O}_3$ ). It combines directly with most elements. Powdered arsenic projected into chlorine gas inflames. With the metals it yields arsenides.

It is remarkable that arsenic, which belongs to the nitrogen group and generally forms entirely differently constituted compounds from sulphur, is analogous to the latter in its metallic combinations. Thus the sulphides and arsenides have similar formulas, and in them sulphur and arsenic can mutually replace each other in atomic ratios, *e. g.*

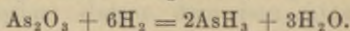


### COMPOUNDS OF ARSENIC WITH HYDROGEN.

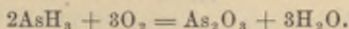
**Arsine**,  $\text{AsH}_3 = 78$ . Like nitrogen and phosphorus, arsenic furnishes a gaseous compound containing 3 atoms of hydrogen. It is obtained pure by the action of dilute sulphuric acid or hydrochloric acid upon an alloy of zinc and arsenic:—



It also results in the action of nascent H (zinc and sulphuric acid), upon many arsenic compounds, like the tri-oxide:—

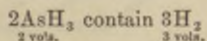


Arsine is a colorless gas, of strong, garlicky odor, and extremely poisonous action, and at  $-40^{\circ}$  is condensed to a liquid. Its density equals 39 ( $H = 1$ ), or 2.69 (air = 1). Ignited it burns with a blueish white flame, with the evolution of white fumes of arsenic tri-oxide:—



By gentle glowing or by the electric spark it is decomposed into arsenic and hydrogen. On conducting the gas through a heated tube the arsenic deposits itself behind the heated part as a metallic coating (*arsenic mirror*). On holding a cold object, *e. g.*, a piece of porcelain, in the flame of the gas the arsenic forms a black deposit (arsenic spots). In its chemical behavior arsine is very similar to  $PH_3$ , possesses, however, scarcely any more basic properties, and does not furnish any derivatives with the halogens.

According to analysis, arsine consists of 1 part by weight of hydrogen and 25 parts arsenic. If, owing to its analogy to  $PH_3$ , we ascribe to it the formula  $AsH_3$ , then the atomic weight of arsenic would be 75 ( $3 \times 25$ ), and the molecular weight of  $AsH_3 = 78$ . Hence the density must be  $\frac{78}{2} = 39$ , which is confirmed by experiment. From the formula it follows that 3 volumes of hydrogen are contained in 2 volumes  $AsH_3$ :—

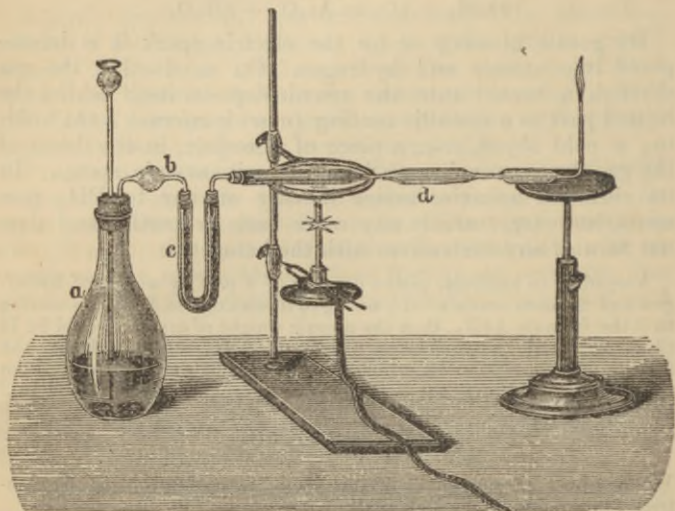


We may become convinced of this by decomposing the gas by electricity in an eudiometer (see p. 128).

*Marsh's Method for the Detection of Arsenic.* Resting upon the above described method of forming  $AsH_3$  and its characteristic properties, arsenic may be readily detected in the following manner—a task which, owing to the poisonous nature of this element, is important: Hydrogen is generated in a flask *a* (Fig. 75), by action of dilute sulphuric acid upon zinc, and through the funnel tube is then introduced some of the solution to be examined for arsenic. The liberated gas, a mixture of hydrogen and arsine, is dried in the calcium chloride tube *c* and escapes through the difficultly fusible glass tube *d*, which is at various places drawn out into narrow parts. Upon igniting the escaping hydrogen (after all the air has been previously expelled from the vessel, as otherwise oxy-hydrogen gas will be present) it will burn, providing  $AsH_3$  is present, with a bluish-white flame and dissemination of white vapor. The dark arsenic spots are obtained by holding a cold porcelain

dish in the flame. If the tube *d* be heated (as shown in Fig 75), an arsenic mirror is formed upon the adjoining contraction of the tube. The slightest traces of arsenic may be detected by this method.

FIG. 75.



Besides the ordinary arsine,  $\text{AsH}_3$ , the existence of  $\text{As}_2\text{H}_4$  and  $\text{As}_4\text{H}_2$ , corresponding to the liquid and solid phosphines ( $\text{P}_2\text{H}_4$  and  $\text{P}_4\text{H}_2$ ) might be expected. The first is not known, but derivatives of it are, which, in place of hydrogen, contain hydrocarbon groups, such as cacodyl  $\text{As}_2(\text{CH}_3)_4 = (\text{CH}_3)_2\text{As}-\text{As}(\text{CH}_3)_2$ . Nitrogen affords similar compounds— $(\text{CH}_3)_2\text{N}-\text{NH}_2$  and  $(\text{CH}_3)\text{NH}-\text{NH}_2$ , which are derived from diamine ( $\text{N}_2\text{H}_4 = \text{H}_2\text{N}-\text{NH}_2$ ) not known in a free condition.

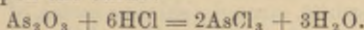
The solid arsine  $\text{As}_4\text{H}_2$  is obtained by the action of nascent hydrogen upon arsenic compounds in presence of nitric acid. It forms a red-brown powder, which decomposes when heated.

#### COMPOUNDS OF ARSENIC WITH THE HALOGENS.

These are perfectly analogous to the corresponding phosphorus compounds, and are the result of the direct union of their constituents; however, the compounds with the formula  $\text{AsX}_3$  (see p. 129) are not known. The metallic character of arsenic appears in the fact that arsenic chloride, like other

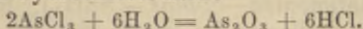


metallic chlorides, may be obtained by the action of hydrochloric acid upon the oxide:—



Upon boiling a solution of  $\text{As}_2\text{O}_3$  with strong  $\text{HCl}$ , arsenic chloride is set free.

**Arsenic Trichloride**— $\text{AsCl}_3$ . A colorless, oily liquid, fuming in the air and having a specific gravity of 2.2. It solidifies at  $-30^\circ$  and boils at  $134^\circ$ . The vapor density equals 90.7 ( $\text{H} = 1$ ), corresponding to the molecular formula  $\text{AsCl}_3 = 181.5$ . In a small quantity of  $\text{H}_2\text{O}$  the chloride dissolves without change; much water converts it into oxide and hydrochloric acid:—



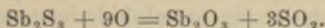
**Arsenic Tribromide**,  $\text{AsBr}_3$ , is a white crystalline mass, fusing at  $20^\circ$ , and boiling at  $220^\circ \text{C}$ . The **Tri-iodide**,  $\text{AsI}_3$ , forms red crystals; the **Trifluoride**,  $\text{AsFl}_3$ , is a liquid, fuming strongly in the air. It results in the distillation of  $\text{AsCl}_3$  or  $\text{As}_2\text{O}_3$  with calcium fluoride and sulphuric acid.

#### 4. ANTIMONY.

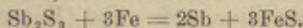
Sb — 122.

The metallic character which appeared with arsenic, exhibits itself more distinctly with antimony, which at the same time retains its complete analogy with the metalloidal elements, arsenic and phosphorus. As far as concerns its physical properties, it is already entirely metallic.

Antimony (Stibium) occurs in nature, principally in union with sulphur, as stibnite,  $\text{Sb}_2\text{S}_3$ , and with sulphur and metals, almost always accompanied by arsenic, in many ores. To prepare it, stibnite is roasted in a furnace, *i. e.*, heated with air access, whereby sulphur burns and antimony trioxide remains:—



The residual oxide is ignited together with carbon, which causes a reduction to metal (general procedure for the separation of metals). Antimony may also be obtained by heating its sulphide with iron, which combines with the sulphur:—



The resulting commercial crude antimony is further purified in the laboratory by fusing it with nitre, whereby admixed

arsenic, sulphur and lead are removed. Chemically pure antimony is obtained by reducing the pure oxide.

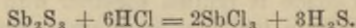
It is a silver-white, strongly shining metal, of leafy crystalline structure; specific gravity 6.715. Like arsenic it crystallizes in rhombohedra, is very brittle, and may be easily broken. Fuses at  $430^{\circ}$ , and distills at a white heat. It is not altered in the air at ordinary temperatures; upon heating it burns with a blue flame, with production of white vapors of antimonious oxide,  $Sb_2O_3$ . Like phosphorus, it combines directly with the halogens; powdered antimony inflames in chlorine gas. It is insoluble in hydrochloric acid; by nitric acid it is oxidized to antimonious oxide.

**Hydrogen Antimonide**—*Stibine*—( $SbH_3$ ), produced like arsine, and very similar to the latter; thus far only obtained mixed with hydrogen. A colorless gas of peculiar odor, which ignited, burns with a greenish-white flame, and separation of white vapors of antimonious oxide. A red heat decomposes it into antimony and hydrogen. In Marsh's apparatus (Fig. 75, p. 134) it gives, like  $AsH_3$ , an antimony mirror and spots. The mirror is distinguished from that of arsenic by its black color, lack of lustre, its insolubility in a solution of sodium hypochlorite ( $NaClO$ ); further, by its slight volatility in a current of hydrogen.

When a solution of  $SbCl_3$  is decomposed by the galvanic current, metallic antimony, strongly impregnated with hydrogen, separates. This is more readily obtained if antimony be made the negative electrode in the galvanic decomposition of water. When heated (or on breaking the rod) such antimony throws off the hydrogen with explosion (compare palladium hydride).

## COMPOUNDS OF ANTIMONY WITH THE HALOGENS.

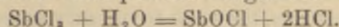
**Antimonous Chloride**—*Trichloride*— $SbCl_3$ , results from the action of chlorine upon the metal or its sulphide; better by the solution of the oxide or sulphide in strong hydrochloric acid:—



This solution is evaporated to dryness and the residue distilled.

A colorless, crystalline, soft mass (*Butyrum Antimonii*), fusing at  $73^{\circ}$  and boiling at  $223^{\circ}$ . Its vapor density equals  $114.2^{\circ}$  ( $H = 1$ ), corresponding to the molecular formula,

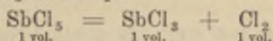
$\text{SbCl}_3 = 228.5$ . In the air it attracts water and deliquesces. Dissolved without alteration by water acidified with hydrochloric acid. Much water decomposes it; the solution becomes turbid and a white powder—algar red—separates:—



The composition of this powder varies with the conditions under which it is formed, and generally corresponds to the formula 2 ( $\text{SbOCl}$ ),  $\text{Sb}_2\text{O}_3$ . Pure **Antimony Oxychloride**,  $\text{SbOCl}$ , obtained by heating  $\text{SbCl}_3$  with alcohol, presents colorless crystals and is further decomposed by water.

While the metallic chlorides are not decomposed by water at ordinary temperatures, yet, in the ready decomposition of the halogen derivatives of antimony, is exhibited the partial metalloidal character of this element.

**Antimonic Chloride—Pentachloride—** $\text{SbCl}_5$ , results from the action of excess of chlorine upon antimony or the trichloride. Forms a yellowish liquid which fumes in the air, becomes crystalline when cold and fuses at  $6^\circ$ , and crystallizes in three different forms. Heat partially decomposes it, like  $\text{PCl}_5$ , into  $\text{SbCl}_3$  and  $\text{Cl}_2$ :—



Water changes it to pyroantimonic acid ( $\text{H}_4\text{Sb}_2\text{O}_7$ ), and hydrochloric acid.

**Antimony Tribromide—** $\text{SbBr}_3$ —is a white, crystalline substance, fusing at  $94^\circ$  and distilling at  $270^\circ$ . The **Triiodide**,  $\text{SbI}_3$ , is a red compound, *crystallizing* in three distinct forms.

To the group, nitrogen, phosphorus, arsenic and antimony, belongs yet bismuth, which gives rise to similarly constituted compounds, *e. g.*,  $\text{BiCl}_3$ ,  $\text{BiI}_3$ ,  $\text{BiOCl}$ . The metallic character, however, of bismuth considerably exceeds its metalloidal. Thus it does not unite with hydrogen, and the oxide ( $\text{Bi}_2\text{O}_3$ ), similarly constituted to the acid-forming  $\text{As}_2\text{O}_3$ , possesses only basic characters. Therefore, we will consider bismuth and its derivatives with the metals.

**Vanadium.**

Vd = 51

**Niobium.**

Nb = 95

**Tantalum.**

Ta = 182

In close relation to the phosphorus group stand three rare elements, vanadium, niobium and tantalum. They yield de-



rivatives very much like those of P; possess, however, a more metallic character, and do not combine with hydrogen. They exhibit many characteristics similar to those of chromium, iron and tungsten, with which, in their naturally occurring compounds, they are frequently associated (compare the Periodic System of the elements).

**Vanadium** occurs in nature principally in the form of salts of vanadic acid (vanadium lead ore) and in some iron ores. It is very difficult to prepare it in a pure state, and is a white-gray, metallic, lustrous powder, of specific gravity 5.5. It is difficultly fusible, and does not change in the air. Heated, it burns to  $Vd_2O_5$ .

**Vanadium Trichloride**— $VdCl_3$ —forms red plates, which readily deliquesce in the air; it is not volatile.

**Vanadium Oxychloride**— $VdOCl_3$ —results from heating a mixture of  $Vd_2O_3$  and C in chlorine gas, forming a lemon-yellow liquid, of specific gravity 1.84, and boiling at  $120^\circ$ . It fumes strongly in the air and with water (analogous to phosphorus oxychloride), it decomposes into vanadic acid and hydrochloric acid. Its vapor density equals 85 ( $VdOCl_3 = 173$ ).

**Vanadium Oxide**— $Vd_2O_3$ —is a black powder obtained by heating  $Vd_2O_3$  in hydrogen. It combines with O, to form  $Vd_2O_5$ .

**Vanadium Pentoxide**— $Vd_2O_5$ —or vanadic anhydride, is a mass obtained by fusing the naturally occurring vanadates with nitre, etc. It is soluble in the alkalis, yielding with the metals salts of *Vanadic*  $H_3VdO_4$ , and *metavanadic* acids  $HVdO_3$  (compare Oxygen compounds of P). All these compounds are analogously constituted to those of P. In addition to these, vanadium forms other compounds, constituted analogously to those of sulphur and chromium. To these belong  $VdCl_2$  (dichloride), the tetrachloride  $VdCl_4$ , vanadious oxide  $VdO$ , vanadium dioxide  $VdO_2$  and  $VdOCl_2$ . The tetrachloride  $VdCl_4$  is a red-brown liquid, boiling at  $154^\circ$ ; its vapor density equals 96 ( $VdCl_4 = 192$ ). Niobium and tantalum are not known in a free state. The chlorides  $NbCl_3$  and  $TaCl_3$  are volatile and decomposed by water. The oxides  $Nb_2O_5$  and  $Ta_2O_5$  form, with bases, salts of niobic ( $H_3NbO_4$ ) and tantalic ( $H_3TaO_4$ ) acids.

### Tabulation of the Elements of the Nitrogen Group.

The elements belonging here—nitrogen, phosphorus, arsenic, antimony and bismuth—present similar graded differences in their physical and chemical properties, like the elements of the chlorine and oxygen group, and this gradation is intimately related to the atomic weights. With the increase of the latter the substance condenses, the fusibility and volatility decrease, and the metallic character becomes more prominent:—

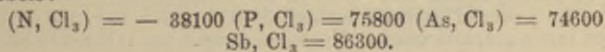
	N	P	As	Sb
Atomic weight,	14	31	75	122.
Specific gravity,	...	1.8-2.1	4.7-5.7	67.
Fusion point,	...	44°	red-white heat	...
Vapor density,	0.972	4.32	10.3	...

With exception of metallic bismuth, the first four elements form gaseous compounds with three atoms of hydrogen.

Ammonia ( $\text{NH}_3$ ) possesses strongly basic properties, and combines with all acids to yield ammonium salts; phosphine ( $\text{PH}_3$ ) combines with  $\text{HBr}$  and  $\text{HI}$  to form salt-like compounds.  $\text{AsH}_3$  and  $\text{SbH}_3$  no longer show basic properties. There are, however, compounds of arsenic and antimony, as well as of the two preceding elements, with hydrocarbons (*e. g.*,  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ ), which are analogously constituted to the hydrides, and very similar to them in character. These compounds ( $\text{As}(\text{CH}_3)_3$  and  $\text{Sb}(\text{CH}_3)_3$ ) which will be described in organic chemistry, possess basic properties and yield salts corresponding to those of ammonium.

The oxygen derivatives of these elements exhibit a similar gradation. With increase of atomic weight corresponding to the addition of metallic character, the oxides, which in the lower series form strong acids, acquire a more basic nature.

The thermal relations of the elements of the nitrogen group are as yet but little investigated. In the production of one molecular weight of ammonia gas from hydrogen and nitrogen ( $\text{H}_3\text{N}$ —gas) 11890 calories are set free; the union, however, occurs almost only in an indirect way. It is very probable that the heat disengagement of  $\text{PH}_3$ ,  $\text{AsH}_3$  and  $\text{SbH}_3$  is gradually a less one, for which the increasing decomposition of the same would argue. On the opposite hand, in the formation of the chlorides with increase of atomic weights and metallic character the heat disengagement successively increases, corresponding to the symbols:—



The great instability of the halogen derivatives of nitrogen finds explanation in the remarkable heat absorption taking place in their formation.

## CARBON GROUP.

Here belong the two non-metals, carbon and silicon, and the metal *Tin*. These unite, each, with four atoms of hydrogen and four of the halogens.

### 1. CARBON.

C — 12.

Free carbon occurs in nature as the diamond and graphite. It constitutes the most important ingredient of all the so-called organic substances originating from the animal and plant kingdoms, and is especially contained in the fossilized products arising from the slow decomposition of plant matter—in turf, in brown coal, stone coal and in anthracite. In combination with hydrogen it forms the so-called mineral oils—petroleum and asphaltum. It occurs, further, as carbon dioxide ( $\text{CO}_2$ ) in the air and in the form of carbonates (marble, calcite, dolomite), comprises many minerals and entire rock formations.

In free condition it is found in different allotropic modifications, which may be referred to the three principal varieties: diamond, graphite and amorphous carbon. In all these forms it is a solid, even at the highest temperatures, non-fusible and non-volatile substance, which is only explainable by the supposition that its free molecules are composed of a large number of atoms of elementary carbon combined with each other. (See p. 97.) As far as concerns their chemical deportment, all the modifications of carbon are very stable and little capable of chemical reaction. When burned, all yield carbon dioxide.

1. The diamond occurs in alluvial soils in certain districts (in India, Brazil and South Africa); less frequently in micaceous schist. It has great lustre, strong power of refraction, and the greatest hardness of all substances. It crystallizes in forms of the regular system, mostly rhombohedra, seldom in octahedra. Ordinarily it is perfectly colorless and transparent, sometimes, too, colored by impurities. Its specific gravity equals 3.5. Only in the strongest heat, between the poles of a powerful galvanic battery, does it soften any, and is converted into a graphitic mass. Heated in oxygen gas, it burns to carbon



dioxide. By the action of a mixture of nitric acid and potassium chlorate it is scarcely at all attacked.

2. The fact that graphite heated with nitric acid and potassium chlorate yields graphitic acid—and oxidized by potassium permanganate to mellitic acid—is characteristic. Native graphite is found in the oldest rock formations, and of especially good quality at Altai, in Siberia. It occurs, too, at many places in the United States, in considerable quantities. Occasionally it appears crystallized in six-sided forms, mostly, however, as an amorphous, grayish-black, glistening, soft mass, used in the making of lead pencils. The specific gravity is 2.25. It conducts heat and electricity well. When away from air contact it does not alter, even at the highest temperatures. Heated in an oxygen atmosphere it usually burns, with more difficulty than the diamond, to carbon dioxide, leaving a residual ash of 2-5 per cent. For the purification of the poorer, more impure kinds of graphite, the latter is pulverized, and heated with a mixture of  $KClO_3$  and  $H_2SO_4$ ; the product is washed with water and the residue glowed (Brody's Graphite).

Artificially, graphite may be obtained by fusing amorphous carbon with iron; on cooling the latter a portion of the dissolved carbon separates in hexagonal, shining leaflets.

3. *Amorphous carbon* is produced by the carbonization of organic (containing carbon) substances, and is found in a fossilized state. Nitric acid and potassium chlorate in the cold convert it into brown substances soluble in water. The purest amorphous carbon is soot, which is obtained by the imperfect combustion of resins and oils (like turpentine) rich in carbon. *Gas carbon*, also called metallic carbon, which deposits in the manufacture of gas in the glowing tubes, is very hard, possessing metallic lustre, and conducting electricity well, hence used in galvanic batteries. *Coke*, resulting from the ignition of stone coal, forms a sintered mass, conducting heat and electricity well. *Charcoal* is very porous and can absorb many gases and vapors. 1 vol. of it absorbs 90 vols.  $NH_3$ , 55 vols.  $H_2S$ , and 9 vols.  $O$ ; at  $100^\circ$  and under the air-pump the absorbed gases are again liberated. Charcoal will also take up many odorous substances and decaying matter, hence employed as a disinfectant. *Animal charcoal*, obtained by the carbonization of animal matter (bones, blood, etc.), possesses in a high degree the power of removing many coloring substances from their solutions; hence it serves, in the laboratory and practice, for the decolorization of dark solutions.

All these varieties of carbon contain, in smaller or larger quantities, nitrogen, hydrogen and mineral substances, which, in combustion, remain behind, as ash. Hydrochloric acid will withdraw almost all the mineral constituents.

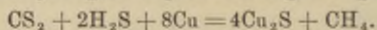
The fossil coal varieties, stone coal, lignite, turf, are the products of a peculiar, slow decay of wood fibre, which gradually separates oxygen and hydrogen, and enriches itself in carbon. Fossil coal contains 90 per cent., brown coal, 70 per cent., of carbon. The fossil coal richest in carbon, the last product of the alteration, is *anthracite*, which has lost all its organic structure, and contains 96-98 per cent. of carbon.

## COMPOUNDS OF CARBON WITH HYDROGEN.

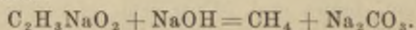
With hydrogen, carbon forms an unlimited number of compounds, into which, also, all other elements, especially oxygen and nitrogen, can enter. These carbon compounds have been termed *organic compounds*, because formerly they were exclusively obtained from vegetable and animal organisms, and the idea was entertained that they were produced by the influence of forces other than those producing the mineral substances. At present, the most carbon derivatives are artificially prepared from the elements by simple synthetic methods; we are aware that they do not essentially differ from mineral substances. Hence the description of the carbon compounds must be arranged in the general system of chemical bodies. This, however, is not readily executed without sacrificing the review of a defunct system. The carbon compounds are so numberless, and possess so many peculiarities, that, from didactic reasons, it appears necessary to treat them apart from the other compounds, in a separate portion of chemistry, which we, pursuing the old custom, term organic chemistry. In opposition to this, the chemistry of *all other bodies* is designated *Inorganic Chemistry*. Hence, only the simplest carbon compounds will be considered here.

It is only under the influence of the electric arc that the direct union of carbon and hydrogen, whereby acetylene ( $C_2H_2$ ) results, may be effected. All other hydrocarbons are obtained indirectly, in various ways.

**Methane**—*Marsh Gas*— $CH_4$ . This simplest hydrocarbon, containing but one atom of carbon, is formed in the decay of organic matter under water (in swamps and coal mines), and escapes in large quantities in many regions of the earth (thus at Baku, on the Caspian Sea). Synthetically, it may be formed, among other methods, by conducting vapors of carbon disulphide and hydrogen sulphide over glowing copper filings:

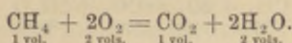


For its preparation heat a mixture of sodium acetate with sodium hydrate:—



Methyl is a colorless, odorless gas, insoluble in water; it has not yet been condensed. Ignited, it burns with a faintly

luminous flame. With two volumes of oxygen (or 10 vols. of air) it gives a violently explosive mixture (fire damp of the miners):—



#### Molecular Formula of Methyl. Atomic Weight of Carbon.

The quantitative analysis of methyl shows that for every 1 part of hydrogen in it there are 3 parts carbon. Were the formula CH (analogous to hydrochloric acid) then the atomic weight of carbon would be 3. If it corresponded to the formula of water (H<sub>2</sub>O) then carbon would equal 6, etc., (see (p. 87):—

H = 1	2H = 2	3H = 3	4H = 4
C = 3	C = 6	C = 9	C = 12
CH = 4	CH <sub>2</sub> = 8	CH <sub>3</sub> = 12	CH <sub>4</sub> = 16

In this case the analysis yields (as in former instances) no conclusive answer. We cannot either derive the atomic weight of C from its vapor density, as it is not volatile, but it may be arrived at from the density of methane. The latter equals 8 (H = 1) hence the molecular weight is 16. In 16 parts by weight of methyl there are 4 parts by weight, hence 4 atoms of hydrogen and 12 parts carbon. The atomic weight of C is, then, presuming that only one atom of it is present in methane, 12:—

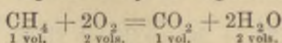
4 atoms hydrogen	H <sub>4</sub> = 4
1 atom carbon	C = 12
Methyl molecule	CH <sub>4</sub> = 16

That indeed the atomic weight of carbon is 12, is proven by the fact that of all its innumerable derivatives not one contains less than 12 parts, by weight, of this element. It follows, with certainty, from the periodic system of elements (p. 70).

From the formula CH<sub>4</sub> it follows that in 1 volume methane, 2 volumes of hydrogen are present, (CH<sub>4</sub> contains 2H<sub>2</sub>).  
1 vol. 2 vols.  
 This is indirectly proven by the combustion of methyl with oxygen in a eudiometer (see p. 111). Four atoms of hydrogen yield two molecules of H<sub>2</sub>O; 1 atom of C gives 1 mole-

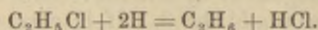


cule  $\text{CO}_2$ . Hence the volume relation in the combustion of  $\text{CH}_4$  in oxygen is expressed by the equation:—



In two volumes of aqueous vapor there are 2 volumes of hydrogen; hence in one volume  $\text{CH}_4$ , 2 volumes of H. The result of the eudiometric analysis confirms these conclusions.

**Ethyl— $\text{C}_2\text{H}_5$ .** Formed when hydrogen *in statu nascendi* acts upon ethyl chloride:—



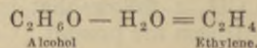
Or by the action of potassium or sodium upon methyl iodide:—

$$2\text{CH}_3\text{I} + \text{Na}_2 = \text{C}_2\text{H}_6 + 2\text{NaI}_2.$$

This is a colorless gas, insoluble in water, which ignited burns with a feebly luminous flame. Its density equals 15 ( $\text{H} = 1$ ) or 1.036 ( $\text{air} = 1$ ) corresponding to the molecular formula  $\text{C}_2\text{H}_6 = 30$ .

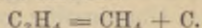
Besides methyl ( $\text{CH}_4$ ) and ethyl ( $\text{C}_2\text{H}_6$ ) there exists a long series of hydrocarbons of the general formula  $\text{C}_n\text{H}_{2n+2}$ , (*e. g.*,  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$ ,  $\text{C}_5\text{H}_{12}$  etc.) in which each member differs from the preceding and next following by 1 C and 2 H ( $\text{CH}_2$ ). Bodies belonging to such a series greatly alike in their chemical behavior are termed *homologues*. In addition to this series of *saturated* hydrocarbons exist others, with less quantity of hydrogen, and which, by the addition of the latter, pass into the *saturated*, and may hence be termed *unsaturated*. The first *unsaturated* series is composed according to the formula  $\text{C}_n\text{H}_{2n}$ , the second according to  $\text{C}_n\text{H}_{2n-2}$ , etc. The lowest member of the series  $\text{C}_n\text{H}_m$  is ethylene (see Chemical Structure p. 162).

**Ethylene— $\text{C}_2\text{H}_4$ .** Formed in the destructive distillation of wood, stone coal and many carbon compounds, hence contained in illuminating gas. Most easily obtained by the action of sulphuric acid upon alcohol, whereby the acid withdraws  $\text{H}_2\text{O}$  from the alcohol:—



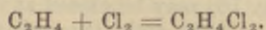
It is a colorless gas, of weak, ethereal odor, condensing at  $-110^\circ$  to a liquid. Density equals 14 ( $\text{H} = 1$ ) or 0.978 ( $\text{air} = 1$ ), corresponding to the molecular formula  $\text{C}_2\text{H}_4 = 28$ . It

burns with a bright, luminous flame, at first being decomposed into marsh gas and free carbon:—



The  $CH_4$  burns and heats the particles of coal in the flame to incandescence; these then are consumed to carbon dioxide ( $CO_2$ ).

The unsaturated compound, ethylene, unites directly with two atoms of chlorine and bromine:—



The resulting compounds  $C_2H_4Cl_2$  and  $C_2H_4Br_2$  are oily liquids; hence the name olefiant gas, for ethylene.

The lowest member of the second unsaturated series is  $C_2H_2$ .

**Acetylene**— $C_2H_2$ —is produced in the dry distillation of many carbon compounds, and is present in coal gas, whose peculiar penetrating odor is due to this. Density = 13 (H = 1) corresponding to the formula  $C_2H_2 = 26$ . It combines directly with 2 and 4 atoms of chlorine and bromine.

The three hydrocarbons above considered, methyl ( $CH_4$ ), ethylene ( $C_2H_4$ ), and in slight amount ( $C_2H_2$ ), constitute, together with H and carbonous oxide ( $CO$ ), ordinary illuminating gas, produced in the dry distillation of stone, brown coal or wood. The illuminating power is influenced by its quantity of ethylene and acetylene (and their homologues).

### THE NATURE OF FLAME.

We are aware that every chemical union which occurs in a gaseous form and accompanied by the evolution of light is designated combustion. In this we observe that some bodies, like sulphur and phosphorus, when burned in the air or in some other gas, yield a flame. These are those substances which, at the temperature of combustion, are converted into gases or vapors. Carbon burns without a flame, with only a glow, because it is non-volatile. The carbon compounds, wood, stone coal and lard, are, indeed, not even volatile, but burn with a flame, because under the influence of heat they develop combustible gases. Flame is, therefore, nothing more than a combustible gas heated to glowing, and which is continually formed anew. We observed, too, that the com-

bustibility was only a relative phenomenon; if hydrogen burns in oxygen and chlorine, conversely oxygen and chlorine burn in hydrogen (p. 47). Illuminating gas burns in the air, therefore air (its oxygen) burns in the former.

This may be demonstrated in the same manner as in the case of chlorine and hydrogen. The relative combustibility and the so-called return of the flame may be very plainly illustrated by means of the following contrivance. An ordinary lamp globe (Fig. 76) may be closed at its lower end with a cork, through which enter two tubes; the narrow tube, *a*, somewhat contracted at its end, is connected with a gas stop-cock; the other tube, *b*, (best a cork borer) is about 5 mm. wide, and communicates with the air. The gas issuing from the tube *a* is ignited, and the chimney is then dropped over the not too large flame; it continues to burn along quietly, as sufficient air enters through the wide tube *b*. Upon increasing the supply of gas, the flame becomes larger, the globe constantly fills more with illuminating gas, while air is crowded out; now the gas flame is extinguished, and upon the wider tube, *b*, an air-flame appears, as the entering air continues to burn farther in the atmosphere of illuminating gas. The excess of

FIG. 76.

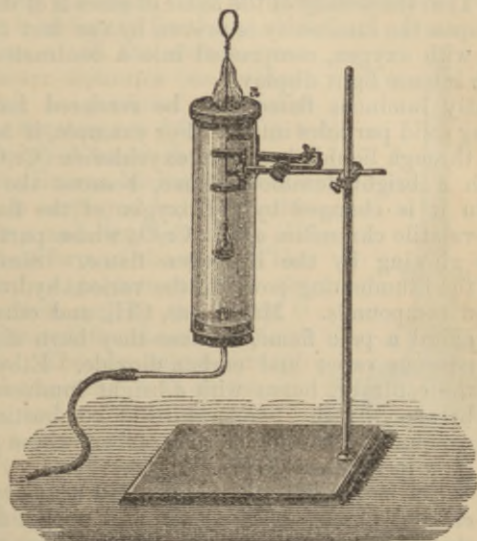


the latter pouring out from the upper portion of the globe may be ignited, and we then have above a gas flame, while within the globe we have an air flame. On lessening again the gas flow, the air flame will distribute itself, extend to the exit of the tube *a*, and then upon the latter will appear again the gas flame, while the flame above the globe is extinguished. In this, at will, we may repeat the return process of flames. That the air in the air flame actually burns, may be plainly proven if we introduce a small gas flame, *c*, through the wide metallic tube, *b*; the little flame will continue to burn in the air flame, but will be extinguished, if it be introduced higher up into the atmosphere of illuminating gas.



Ordinarily we designate only such bodies as combustible which, because they are capable of combining with oxygen, burn in an atmosphere of oxygen or of atmospheric air. If we imagine, however, an atmosphere of hydrogen, or illuminating gas, then, in such an one, bodies rich in oxygen must be combustible. In fact, nitrates, chlorates, etc., burn in an atmosphere of gas with production of an oxygen flame. This may readily be demonstrated, as follows: An argand lamp chimney (Fig. 77) is closed at its lower end by a cork, bearing a gas-conducting tube. The gas, issuing above, through the

FIG. 77.



opening of the sheet covering, *a*, is ignited. Now the substance (potassium or barium chlorate, etc.) is introduced into a flame by means of an iron spoon provided with a handle, heated to the temperature of decomposition (disengagement of oxygen), and the spoon then plunged through the opening into the gas atmosphere. The substance now burns with brilliant disengagement of light, as the resulting oxygen flame is brightly colored by the vaporizing and reduced metallic salts.

The brilliancy or luminosity of a flame is influenced by the

nature of the substances contained in it, also by its temperature and density. Glowing gases, especially in dilute condition, shine very faintly *per se*. Thus hydrogen, ammonia, and methyl burn with a pale flame. Even sulphur burns in the air with a slightly luminous flame. If, on the contrary, sulphur or phosphine be permitted to burn in oxygen, or arsenic and antimony in chlorine gas, an intense display of light follows. This depends on the fact that the flame is not diluted by the nitrogen of the air, therefore is more condensed, develops a higher temperature, and the combustion products ( $\text{SO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{PCl}_3$ ) or the evaporating substances are not immediately gasified. That the density of the flame of gases is of important influence upon the luminosity is proven by the fact that also hydrogen, with oxygen, compressed into a contracted space, burns with intense light display.

A slightly luminous flame may be rendered intense by introducing solid particles into it. For example, if hydrogen be passed through liquid chromium oxychloride ( $\text{Cr}_2\text{O}_2\text{Cl}_2$ ) it burns with a bright luminous flame, because the volatile  $\text{Cr}_2\text{O}_2\text{Cl}_2$  in it is changed by the oxygen of the flame into solid, non-volatile chromium oxide,  $\text{Cr}_2\text{O}_3$ , whose particles are heated to glowing by the hydrogen flame. Similarly is explained the illuminating power of the various hydrocarbons and carbon compounds. Marsh gas,  $\text{CH}_4$ , and ethyl,  $\text{C}_2\text{H}_5$ ,

FIG. 78.



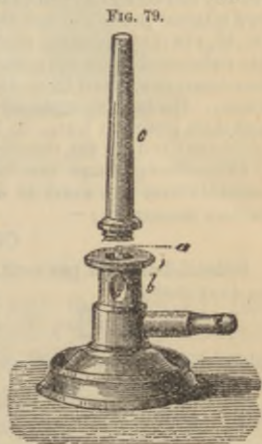
afford a pale flame, because they burn directly to aqueous vapor and carbon dioxide. Ethylene, on the contrary, burns with a bright luminous flame, because, by the temperature of combustion, it decomposes first into  $\text{CH}_4$  and carbon, whose particles glow in the flame. (See p. 150.)

Let us consider the flame of an ordinary stearin candle: On approaching the wick with a flame the stearin melts, is drawn up by the fibres and converted into gaseous hydro-carbons, which ignite, and by chemical union with the oxygen of the air, produce the flame. In the latter, three distinct zones may be perceived. In the inner non-volatile zone, *a a'* (Fig. 78), are contained unaltered gases, which, owing to lack of air access, cannot burn. If the lower end of a thin glass tube be inserted here the gases will rise in it, and may be ignited at the upper end. In the middle, brightly luminous part,

*f e g*, a partial combustion of these occurs; ethylene  $C_2H_4$  breaks up into  $CH_4$  and  $C$ : the first burns completely, while the  $C$  is heated to a white glow, as not sufficient oxygen is present for its combustion. The presence of carbon particles in the luminous part may be easily proven by placing in it a cold body, like a wire net; it will at once be coated with soot.

Finally, in the outer, only very feebly luminous and almost invisible mantle, *b c d*, of the flame, which is completely surrounded by air, the perfect combustion of all the carbon to carbon dioxide occurs.

An entirely identical structure is possessed by the ordinary illuminating gas flame. By bringing as much air or oxygen into it as is necessary for the perfect combustion of all the carbon, none of the latter separates (see below), and there is produced a faintly luminous but very hot flame. Upon this principle is based the construction of the Bunsen burner, the flame of which is employed in laboratories for heating and ignition. Fig. 79 represents a form of the same. The upper end, *e*, is screwed into the lower portion, and in the figure is only separated for the sake of explanation. The gas enters through the narrow opening, *a*, from the side gas tube, and mingles with air in the tube *e*, which makes its entrance through the openings of the ring *b*.



In this way only a slightly non-luminous but intensely heating flame is obtained. On closing the openings in *b*, the air is cut off, and the gas burns at the upper end of the tube *e*, with a bright, strongly smoking flame. The non-luminous flame contains excess of oxygen, and hence oxidizes—*oxidizing flame*. It is employed to effect oxidation reactions. The luminous flame, on the other hand, is reducing in its action, and is designated the *reduction flame*, because the glowing carbon in it abstracts oxygen from many substances.

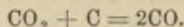
Upon the same occurrences depends the construction and application of the ordinary and the gas blowpipe, which, however, at present, in most cases, are replaced by gas burners.



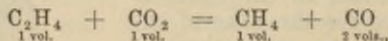
The non-luminosity of the Bunsen burner flame, due to addition of air, depends on a more complete combustion of the separated carbon or of the yet undecomposed hydrocarbons. The flame, in consequence, is smaller, more intense, and the combustion extends itself even to the inner cone of the flame. The non-luminosity becomes more difficult in case of pure oxygen, as the flame is then not diluted by nitrogen, therefore it is far smaller, the temperature much higher, and the flame gases are more condensed.

Another variety of non-luminosity of hydrocarbon flames is induced by the admixture of inactive gases, like nitrogen and carbon dioxide. By this means the flame is enlarged and the combustion, as in the luminous flame, takes place only in the outer cone. In consequence of the dilution there are present fewer combustible particles in an equal space, and therefore can be more completely consumed by the more readily intruding oxygen of the air; further, the temperature is lowered and attains probably not the decomposition temperature of ethylene ( $C_2H_4$ ) in the adjoining, continually renewing inner cone. Also by simple extension of an illuminating flame upon a plate it may be rendered non-luminous, since then the air comes in contact with a larger flame plane. On heating a gas made non-luminous by admixture of nitrogen, and then letting it burn, its flame illuminates as the increased temperature may induce the decomposition of ethylene.

In rendering flame non-luminous by carbon dioxide we must also consider that the same is converted, by the particles of carbon, into carbon monoxide:—



Indeed, but a few per cent. of  $CO_2$  in a gas flame suffices to decrease its luminosity,



while the presence of nitrogen is far less detrimental.

Every substance requires for its ignition a definite temperature—*temperature of ignition*. When a substance is once ignited it generally burns further, because by the heat of combustion more particles are raised to the temperature of ignition. By rapid cooling (*e. g.*, by introduction of a piece of metal into a small flame) every flame may be extinguished. By holding a metallic net over the opening of a gas lamp, from which gas issues, and igniting the same above the wire (Fig. 80), the latter, being a good conductor of heat, cools the flame so much that it is incapable of igniting the gas below the gauze. Upon this phenomenon depends the construction of Davy's safety lamp, which is used in coal mines, to avoid ignition of the fire-damp (Fig. 81). It is an ordinary oil lamp surrounded and shut off from the air by a metallic wire gauze. On bringing a lighted lamp of this sort into an explo-

FIG. 80.

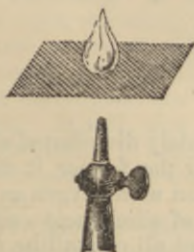
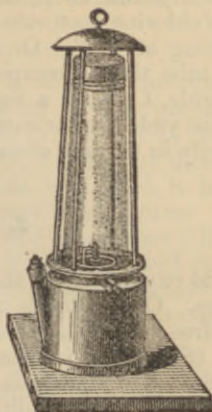


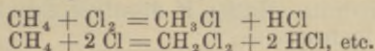
FIG. 81.



sive mixture, or into a combustible gas (*e. g.*, in a large jar, in which ether is present), the gas penetrating into the lamp will burn, but the combustion will not extend to the external gases.

### COMPOUNDS OF CARBON WITH THE HALOGENS.

Carbon does not combine directly with the halogens; the compounds result, however, by the action of the halogens upon the hydrocarbons. We have seen that chlorine and bromine act upon water, ammonia,  $\text{H}_2\text{S}$ ,  $\text{PH}_3$ , etc., in such a manner as to unite with the hydrogen to hydrogen chloride, etc., while the other element is either set free or is also united with the chlorine. Chlorine and bromine act similarly upon the hydrocarbons; here hydrogen, atom after atom is displaced by chlorine, forming  $\text{HCl}$  and chlorine derivatives:—



Such a process is termed *substitution*, and the products *substitution products*. In this way we obtain from methyl,  $\text{CH}_4$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  (**chloroform**) and finally  $\text{CCl}_4$ , **carbon tetrachloride**. The last compound is a colorless, ethereal liquid, boiling at  $77^\circ$ . Vapor density equals 77 ( $\text{H} = 1$ ), corresponding to the molecular formula  $\text{CCl}_4 = 154$ . The chlorides of carbon are not decomposed by water.

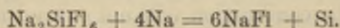
The compound  $C_2Cl_6$ , ethyl hexachloride, obtained by the action of chlorine upon ethyl,  $C_2H_6$ , is a crystalline mass, fusing and boiling at  $182^\circ$ . On conducting the vapors through a red-hot tube they decompose into  $C_2Cl_4$  and  $Cl_2$ . *Ethylene tetrachloride*,  $C_2Cl_4$ , is a liquid, boiling at  $122^\circ$  C. Bromine and iodine yield similar compounds; they will be treated more extensively in organic chemistry.

## 2. SILICON.

Si = 28.

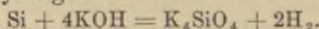
Next to oxygen this is the most widely distributed element in nature. Owing to its affinity for the former it does not occur in free condition. In combination with oxygen as silicon dioxide ( $SiO_2$ ), and in form of salts of silicic acid (silicates) it comprises many minerals and almost all crystalline rocks.

Obtained in a free condition by heating the silicon fluoride ( $SiF_4$ ), or sodium-silicon fluoride ( $Na_2SiF_6$ ) with metallic sodium:—



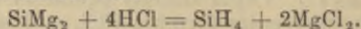
The ignited mass is treated with water, which dissolves the sodium fluoride and leaves the silicon as a brown, non-lustrous, *amorphous* powder. Heated in the air it burns to silicon dioxide ( $SiO_2$ ).

Another modification—the *crystalline silicon*—is obtained by fusing a mixture of  $Na_2SiF_6$ , sodium and zinc. The separated silicon dissolves in the molten zinc, and on cooling, deposits out in crystals, which remain on dissolving the metal in hydrochloric acid. In this form the metal exhibits black, strongly lustrous octahedrons, of specific gravity, 2.49, and of very great hardness. Upon ignition in the air or oxygen it is not oxidized; it is not attacked by acids. On boiling it with a sodium or potassium hydrate solution it dissolves, forming a silicate and liberating hydrogen:—



Heated in chlorine gas, silicon burns to the chloride.

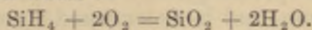
**Hydrogen Silicide**— $SiH_4$ —the analogue of  $CH_4$ , forms like arsine by dissolving an alloy of silicon and magnesium in dilute hydrochloric acid:—



The escaping hydride contains admixed hydrogen, has a



disagreeable odor, ignites spontaneously in the air, and burns to the dioxide and water:—



Entirely pure silicide, free of H, is obtained by heating a compound,  $\text{SiH}(\text{O}.\text{C}_2\text{H}_5)_2$ , belonging in the province of organic chemistry. It only ignites in the air at ordinary pressure upon warming; if, however, the gas, by diminution of pressure or by the addition of H, is diluted, it becomes spontaneously combustible at ordinary temperatures. Glowing heat decomposes the hydride into amorphous silica and hydrogen. Mixed with chlorine it inflames and probably forms substitution products similar to those of methyl ( $\text{CH}_4$ ). Pure hydrogen silicide condenses, at  $-5^\circ$  and 70 atmospheres, to a liquid.

**Silicon Chloride**— $\text{SiCl}_4$ —results from the action of chlorine upon silicon, or by conducting chlorine over a mixture of the dioxide and carbon (Fig. 82):—

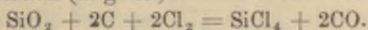
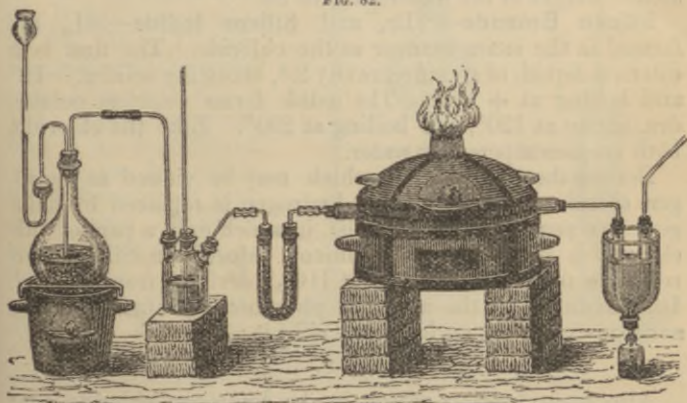
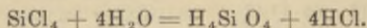


FIG. 82.



The mixture is placed in a porcelain tube, which is heated to a red heat in a charcoal furnace. The chlorine generated in the flask is washed in a three-necked bottle and dried in a glass tube filled with calcium chloride. While carbon or chlorine do not act upon the  $\text{SiO}_2$ , the reaction or their simultaneous action is induced by the mutual supporting affinities of carbon for oxygen and of chlorine for silicon.

The silicon chloride which distills over is a colorless liquid, having a specific gravity of 1.52, and boiling at  $57^{\circ}$ . In the air it fumes, and is decomposed by water into silicic and hydrochloric acids:—



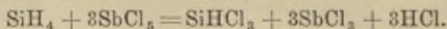
This compound may be employed in determining the atomic weight of silicon. Analysis shows that in it, for 35.4 chlorine, there are seven parts of silicon. Supposing, from the great analogy of the silicon compounds to those of carbon, that its formula is  $\text{SiCl}_4$ , the atomic weight of the silicon would be 28.

$$\begin{array}{r} \text{Si} = 28 \\ \text{Cl}_4 = 141.6 \quad (4 \times 35.5) \\ \hline \text{SiCl}_4 = 169.6 \end{array}$$

This supposition is confirmed by the vapor density of the compound. This equals 85 ( $\text{H} = 1$ ), hence the molecular weight is  $2 \times 85 = 170$ . Since, according to the analysis, there are 142 parts chlorine in 170 parts of silicon chloride, the atomic weight of the metal must be 28.

**Silicon Bromide**— $\text{SiBr}_4$  and **Silicon Iodide**— $\text{SiI}_4$ , are formed in the same manner as the chloride. The first is a colorless liquid, of specific gravity 2.8, becoming solid at  $-12^{\circ}$  and boiling at  $+153^{\circ}$ . The iodide forms colorless octahedra, fusing at  $120^{\circ}$ , and boiling at  $290^{\circ}$ . Like the chloride, both are decomposed by water.

Besides these compounds, which may be viewed as hydrogen silicide, in which all the hydrogen is replaced by halogens (see page 151), others exist, in which only a part of this element is replaced. Thus, **silicon chloroform**,  $\text{SiHCl}_3$  corresponds to the chloroform ( $\text{CHCl}_3$ ) derived from methyl. It is produced by the action of phosphorus pentachloride, or antimony chloride, on hydrogen silicide:—

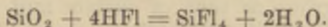


Also upon heating silicon in dry hydrogen chloride gas: in this instance a mixture of  $\text{SiCl}_4$  and  $\text{SiHCl}_3$  results. These compounds may be separated by fractional distillation. Silicon chloroform is a colorless liquid, of specific gravity 1.6, and boils at  $35-37^{\circ}$ . The vapor density equals 67.7 ( $\text{H} = 1$ ), corresponding to the molecular formula,  $\text{SiHCl}_3 = 135.5$ . It fumes in the air, and with water decomposes into silicic and hydrochloric acids.

Very similar to silicon chloroform are the bromoform,  $\text{SiHBr}_3$ , and the iodoform,  $\text{SiHI}_3$ , which correspond to the analogous compounds obtained from carbon.

The compound  $\text{Si}_2\text{I}_6$ , analogous to  $\text{C}_2\text{Cl}_6$ , is known. From all these data we observe the great analogy between silicon and carbon.

**Silicon Fluoride**,  $\text{SiFl}_4$ , is formed when  $\text{HFl}$  acts upon  $\text{SiO}_2$  :—



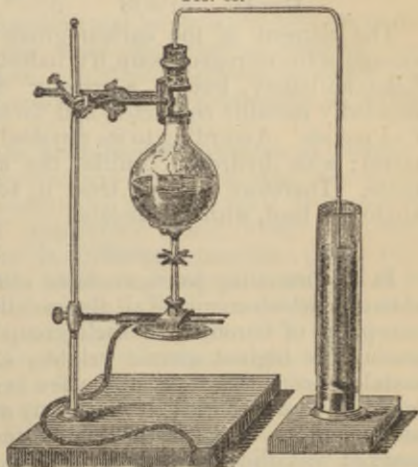
To prepare it, a mixture of fluorite and powdered glass, or sand ( $\text{SiO}_2$ ), is warmed with sulphuric acid; by the action of the  $\text{H}_2\text{SO}_4$  upon the fluorite hydrogen fluoride (p. 55) is disengaged, which then reacts upon the silicon dioxide, in the manner indicated in the above equation. The liberated gas

is collected over mercury. It is colorless, has a disagreeable odor, and fumes strongly in the air. Its vapor density is 3.57 (air = 1), or 52, ( $\text{H} = 1$ ), corresponding to the molecular formula  $\text{SiFl}_4 = 104$ . Very characteristic is its deportment with water, by which it is decomposed into silicic acid ( $\text{H}_4\text{SiO}_4$ ) and hydrogen silico-fluoride:  $3\text{SiFl}_4 + 4\text{H}_2\text{O} = \text{H}_4\text{SiO}_4 + 2\text{H}_2\text{SiFl}_6$ . For the execution of this method,

conduct the  $\text{SiFl}_4$  formed, through a glass tube, into a vessel containing water (Fig. 83). Gelatinous silicic acid separates out, and the gaseous  $\text{SiH}_2\text{Fl}_6$  remains dissolved in the water. As the separating silicic acid may readily obstruct the opening of the glass tube, the latter is allowed to project a slight distance into mercury. By filtration the solid silicic acid is separated from the aqueous solution.

**Hydrogen Silico-Fluoride**— $\text{H}_2\text{SiFl}_6$  (or  $2\text{HFl}, \text{SiFl}_4$ ) is only known in aqueous solution. Upon evaporating at a low

FIG. 83.





heat it decomposes into  $\text{SiF}_4$  and  $2\text{HF}$ . In its chemical department it is an acid similar to the hydrogen-halogen acids. Its aqueous solution reddens blue litmus paper, dissolves many metals, and saturates bases, forming salts with them, in which two hydrogen atoms are replaced by metal.

The potassium and barium salts are insoluble in water.

To the same group as that of carbon and silicon belongs, as regards its chemical nature,  $\text{TiN}=\text{Sn}=118$ , which forms perfectly analogous compounds, like  $\text{SnCl}_4$ ,  $\text{SnBr}_4$ ,  $\text{SnF}_4$ . It bears the same relation to these elements as antimony to those of the nitrogen group. This fact is plainly visible in the atomic weights:—

N = 14	P = 31	As = 75	Sb = 122
C = 12	Si = 28	.....	Sn = 118

The element of the carbon group corresponding to the arsenic of the nitrogen group, if it indeed does exist, is unknown. Like antimony, but to a greater degree, tin exhibits a decidedly metallic character, and forms the transition to the real metals. According to its physical properties tin is a true metal: with hydrogen (unlike the metalloids) it does not unite. Therefore we will treat it, together with its higher analogue, lead, with the metals.

In the preceding pages we have considered four groups of elements, which comprise all the so-called metalloids (with the exception of boron). In each group the last members, possessing the highest atomic weights, exhibit already distinct metallic properties, especially when in a free condition. This is plainly the case with tin, antimony and arsenic. Tellurium and selenium, also (in the crystalline modification) possess marked metallic appearance; finally, iodine has a metallic lustre. With addition of metallic character diminishes, on the other hand, the affinity for hydrogen; such compounds of iodine, tellurium, antimony and arsenic are very unstable and readily decompose into their constituents; finally, tin and bismuth do not combine with hydrogen.

The remarkable relations between the atomic weights of the elements of the four groups in which, at the same time, the deportment of the elements finds its expression, are perceived from the following table:—

C = 12.	N = 14.	O = 16.	Fl = 19.
Si = 28.	P = 31.	S = 32.	Cl = 35.4.
.....	As = 75.	Se = 79.	Br = 79.7.
Sn = 118.	Sb = 122.	Te = 125.	I = 126.5.

These relations will find more consideration in the examination of the *Periodic System of the Elements*.

### ATOM AND MOLECULE.

In the study of the hydrogen derivatives of the elements of the four previously mentioned groups, we arrived at the establishment of the following formulas:—

CH <sub>4</sub> .	NH <sub>3</sub> .	OH <sub>2</sub> .	FlH.
SiH <sub>4</sub> .	PH <sub>3</sub> .	SH <sub>2</sub> .	ClH.
.....	AsH <sub>3</sub> .	SeH <sub>2</sub> .	BrH.
.....	SbH <sub>3</sub> .	TeH <sub>2</sub> .	IH.

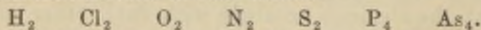
As these possess a fundamental importance, and serve for the derivation of further, more important conclusions and generalizations, we again introduce together, here, all the actual relations and considerations in connection, upon the basis of their deduction.

The fact, proven by the analysis and synthesis of chemical bodies, that the elements combine with each other according to constant multiple proportions, explains itself most simply by the supposition of elementary atoms, which can combine among themselves in different quantity (page 59). The existence of isomeric bodies can only be concluded from the atomic constitution of matter. To determine the number of atoms in a compound, and, therefore, also, the true relative atomic weights of the elements, the experimental combining weights, however, offer no footing (page 79); the question can only be solved upon a basis of other actual relations. The specific gravity of bodies in the gaseous and vapor form, and the volume relations according to which the gases combine, serve best for this task.

The physical properties of the gases and vapors lead to the supposition that they consist of very small discrete particles, molecules, which are separated from each other by relatively large but like distances, and that, therefore, in equal volumes of all gases an equal number of molecules is contained. Hence molecules are the smallest particles of matter—masses which occur separated in gases. Their relative weights, therefore, are directly expressed by their relative gas densities

(page 70). Molecules of compound bodies are composed of atoms; therefore, the relative atomic weights may be derived from the molecular weights. *The atomic weight is the smallest quantity of an element which is contained in the molecular weight of any one compound.* Although the atomic weights of the above considered elements have been deduced from a small number of compounds, yet all further investigations have confirmed the observation that these elements are not contained in a smaller quantity in any molecule. Thus oxygen is present in all molecules, in at least 16 parts by weight; nitrogen not less than 14; carbon not less than 12; if the smallest quantity of hydrogen contained in a molecule, *i. e.*, an atom, equals 1.

From a comparison of the densities of the elements with those of their derivatives we concluded (p. 68)—upon the basis, that in equal volumes of gases the same number of molecules is contained—that the molecules of the elements consist of two or more atoms. Thus the molecules of hydrogen, the halogens, oxygen, nitrogen, are composed of two atoms; the sulphur molecules at 500° of six atoms; the molecules of phosphorus and arsenic of four atoms:—



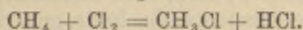
The molecular quantities of all bodies in the gaseous state occupy equal volumes. Referring the densities (specific gravities) to hydrogen as unit ( $=1$ ), the molecular weights are double the densities, and conversely, the latter are half the molecular weights (p. 69). The existence of allotropic modifications of the elements confirms (p. 78) the hypothesis that the molecules of the elements are composed of several atoms. In the gaseous condition the allotropy is known only in the case of oxygen and sulphur. Ordinary oxygen has two atoms, ozone three; the sulphur molecule, at 1000°, contains two atoms; at 500°, however, six atoms. Although we possess no means of determining the molecular size of the solid elements, yet there are many indications that the free elements occurring in several modifications, like P, As, C, and Si, consist of larger complex atoms. Further, the energetic action of the elements in the moment of their formation (see p. 69) argues for their complexity when free.

The phenomena of the so-called *status-nascens* find, in the majority of cases, their explanation in the thermo-chemical processes accompanying them. If, *e. g.*, in the action of zinc upon nitric acid,

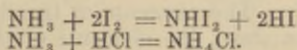


where, in accordance with the analogy with other acids, hydrogen must be set free, the same does not occur, but the nitric acid is reduced to ammonia and nitrogen oxides—while free hydrogen does not exert any action on nitric acid—then it is the heat disengaged by the formation of zinc and ammonium nitrate, which, in accordance with the principle of greatest heat liberation, represents the true cause of the reaction. By this, however, the supposition that the free atoms act more energetically than the molecules is not refuted; it finds an additional confirmation in thermo-chemistry.

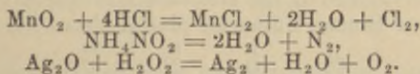
The determination of the density is the simplest means of ascertaining the molecular quantity; but we have another, a pure chemical procedure, leading to the same end. As molecules are the smallest quantities which can exist in a free condition, it is very probable the same quantities appear in the chemical reactions. Indeed, the study of the latter brings us the same molecular quantities as are derived from the densities. For example, the compound  $\text{CH}_3\text{Cl}$  results when chlorine acts upon marsh gas; we hence infer that in the molecule of the latter hydrocarbon, four atoms of H are present:—



From ethylene— $\text{C}_2\text{H}_4$ —we obtain  $\text{C}_2\text{H}_5\text{Cl}$ ; its composition, therefore, cannot be expressed by the simpler formula  $\text{CH}_2$ . With iodine ammonia yields  $\text{NHI}_2$ ; with hydrogen chloride  $\text{NH}_4\text{Cl}$ :—



Both reactions lead to the formula  $\text{NH}_3$ . In the same manner the compound nature of the elementary molecules is disclosed; in all accurately determined reactions we perceive that hydrogen, the halogens, oxygen, nitrogen, invariably act or separate out with two atoms, as is observed from the following equations:—



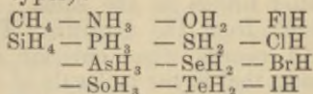
This chemical method for obtaining the molecular value is, although less simple, so much more general than the one depending on the determination of the densities, inasmuch as it finds application in the case of the non-volatile bodies. Thus, for example, the composition of hydrogen peroxide is expressed by the formula  $\text{HO}$ ; the methods of its production

and chemical rearrangements point, however, with great probability, to the doubled molecular formula  $H_2O_2$ .

Hence the most varied relations carry us to the same conclusions as to the existence and the magnitude of the atoms and molecules. The atomic-molecular formulas used to-day in chemistry are only the expression of actual relations; they are entirely independent of speculative abstractions, but forcibly call out these.

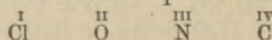
### The Quantivalence of the Elements. Chemical Structure.

From the above derived molecular formulas of the hydrogen compounds, arose further important generalizations. We have the four following groups of hydrogen compounds (forms of combination or types):—

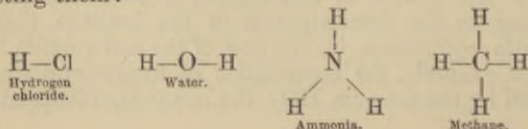


In each group, step by step, with increasing atomic weight, the affinity of the elements for hydrogen diminishes. Yet the number of hydrogen atoms which are combined with an atom of the other elements is constant for each group. Hence, to each element, in its relation to hydrogen, we must ascribe a particular function of affinity, called *quantivalence*, *valence* or *atomicity*. The elements of the fluorine group are univalent or monatomic; the elements of the oxygen group *diatomic* or *bivalent*; nitrogen and its analogues, *triatomic*; carbon and silicon, finally, are *tetratomic* elements—if we accept the quantivalence of hydrogen as the *unit of valence*. The halogens, combining with *one* atom of hydrogen, possess *one affinity unit*; oxygen combines with two hydrogen atoms, and possesses, therefore, *two* affinity units, etc.

The quantivalence of the elements is frequently designated by the lines or Roman numerals placed above the symbols:—

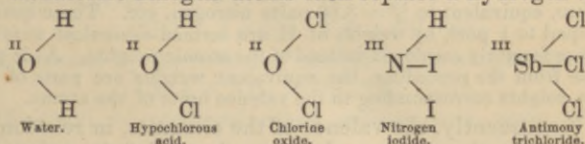


The mutual union of affinity units is indicated by a line connecting them:—

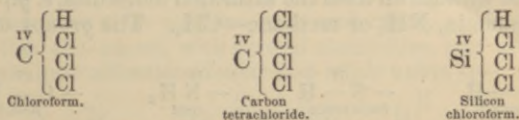


In these formulas the atoms of oxygen, of nitrogen, of carbon—indeed, of all the monatomic elements—represent, as it were, the nuclei to which the hydrogen atoms attach themselves; their valence units are, as it were, the points of attachment for the valence unit of hydrogen.

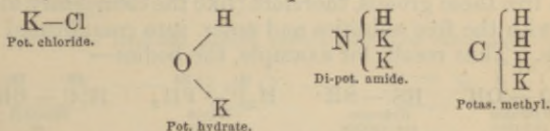
In these molecules the hydrogen atoms can now be replaced or substituted by other elements (p. 151). According to this the monatomic halogen atoms each replace a hydrogen atom.



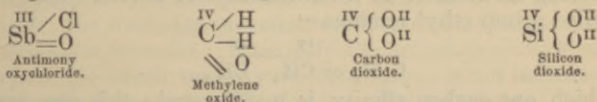
Instead of the lines we can more conveniently employ brackets:—



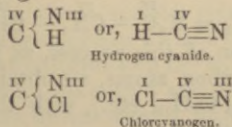
By the replacement of hydrogen by the monatomic metal potassium, we arrive at the compounds—



The diatomic elements, like oxygen, sulphur, replace two hydrogen atoms in the compounds of that element:—



Finally, triatomic nitrogen can replace three atoms of hydrogen, or of the halogen:—

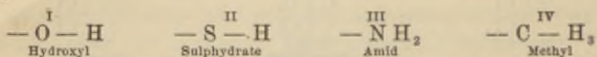




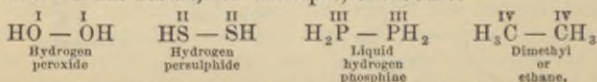
In all these compounds the quantivalence peculiar to the elements appears.

Like valence is designated with the word *equivalencce*. 1 atom of chlorine is equivalent to an atom of hydrogen: 35.4 parts, by weight, of chlorine are, then, equivalent to 1 part, by weight, of hydrogen. 1 atom oxygen is equivalent to 2 atoms of hydrogen; consequently, 2 parts, by weight, of hydrogen, are equivalent to 16 parts, by weight, of O, or 1H to 8 parts of oxygen. Further, 1 atom of N, or 14 parts, is equivalent to 3 atoms or 3 parts hydrogen; 1 part hydrogen is, therefore, equivalent to  $\frac{1}{3} \times 14 = 3.66$  parts nitrogen, etc. These quantities, equal to 1 part, by weight, of H are termed *equivalent weights*, and were formerly employed instead of the atomic weights. As is perceptible from the preceding, the equivalent weights are parts of the atomic weights corresponding to the valence units of the atoms.

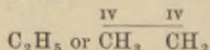
If, consequently, the valence of the elements, in relation to hydrogen (as also to other elements), has a definite value, the question naturally arises—what will result, if an atom of hydrogen be withdrawn from the saturated molecules, *e. g.*, water,  $H_2O$ , ammonia,  $NH_3$  or methane— $CH_4$ . The *groups* or *residues*—



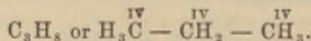
can plainly not exist in a free condition, as one affinity-unit of the elements, having higher atomicity is not saturated. When free these groups, therefore (like the elementary atoms), unite with the free affinities and enter into complicated compounds. Thus result, for example, the bodies—



To such combination carbon is particularly inclined. Removing an atom of H from dimethyl or ethane ( $C_2H_6$ ) the so-called group ethyl remains—

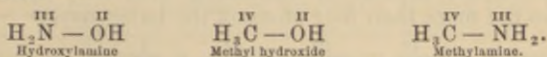


in which one carbon affinity is unsaturated; this can again unite with the methyl group  $CH_3$ . The resulting compound is—

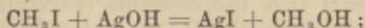


By the continuation of this process, as it were, of a chain-like union of the carbon atoms, we obtain a whole series of hydrocarbons ( $C_4H_{10}$ ,  $C_5H_{12}$ , etc.), with the general formula  $C^nH_{2n+2}$  (compare page 144).

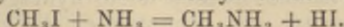
Not only similar residues or groups combine, but also dissimilar:—



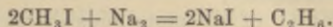
Such combinations are generally effected by reactions of double decomposition. Thus methyl hydroxide (wood spirit) results from the action of methyl iodide ( $\text{CH}_3\text{I}$ ) upon silver hydrate ( $\text{AgOH}$ ):—



methylamine by the action of methyl iodide and ammonia:—

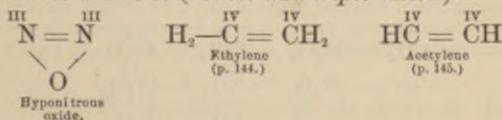


Dimethyl is produced when sodium acts upon methyl iodide:—

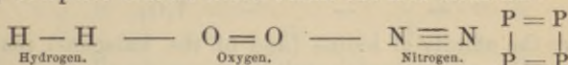


By the withdrawal of sodium the methyl groups are liberated, and these then combine with each other.

Further the atoms, with several atomicities, can unite with two and three affinities (*double* and *triple* union):—

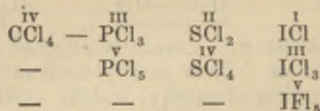


By complete mutual union result the free elements:—



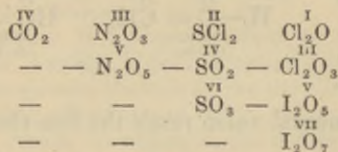
This manner of joining or combination of the atoms in the molecule, not with their entire mass, but with single affinities, is designated *chemical constitution* or *chemical structure* of compounds; the formulas representing them are called *constitution* or *structural formulas*. Naturally the actual position of atoms in space (of which we have no knowledge) is not indicated by the chemical structure. The fundamental principle of chemical structure consists in this, that *the affinity of an atom unites itself with the affinity of another atom*. The following circumstances, however, complicate these simple relations: Among the elements of the nitrogen group we saw that P and N combine with 3 and 5 atoms of chlorine and the halogens; that sulphur, selenium and tellurium take up 2 and 4 atoms of chlorine and bromine; that iodine unites with 1 and 3 atoms of chlorine

and five of fluorine. Only the tetratomic elements, carbon and silicon, are capable of combining with four hydrogen, and also not more than four atoms of the halogens:—



Hence, it appears that the elements (excepting carbon) in their relation to chlorine (and to the halogens) do not express such a constant balance as they do to hydrogen. P and its analogues appear tri- and pent-atomic; the elements of the sulphur group, di- and tetra-atomic; iodine finally appears mon-, tri- and pent-atomic.

This higher affinity of the metalloids shows itself more distinctly and universally in the more stable oxygen derivatives. In the elements of the four previously considered groups we are acquainted with the following oxygen compounds, in which the members of each group afford perfectly analogous compounds:—

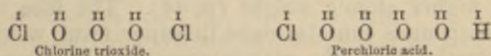


Here the affinity of iodine (and of the halogens) reaches seven, and the elements of the sulphur group six affinities. The elements of the nitrogen group are, both in their relation to chlorine and oxygen, not more than pentatomic. Carbon finally extends, both to H as to Cl and O, not more than four affinities. These relations are more apparent, as we will see, in the hydroxyl derivatives of the oxides and the acids. Hence we conclude, *that the equivalence is not an absolute property belonging per se, to and for the elements solely (like the atomic weights) but that it appears as a relative function of the mutual action of the various elements.* In general we can distinguish the *hydrogen valence* and the *halogen or oxygen valence*. For all elements the hydrogen valence is *constant*: for Cl = 1, for O = 2, for N = 3, for C = 4. As regards oxygen, the *quantivalence* of the most of the elements appears to be *variable*; and indeed it varies, as visible from the above given formulas, for



the Cl group from 1 to 3 to 5 and to 7; for the elements of the S group from 2 to 4 to 6; for P and its analogues from 3 to 5. The regular increase of maximum valence from C = 4 to Cl = 7 argues the actual occurrence of a change of valence whether we ascribe a variable valence to the elements or accept the maximum as the true measure, and regard the lower compounds as *unsaturated*, is entirely immaterial, as we possess no conception upon the nature of valence. Later we will discover that this alteration of valence finds full expression and generalization in the periodic system of the elements, which is based upon the grouping of the elements according to their atomic weights.

In the manner just represented the idea of quantivalence is viewed purely from an empirical standpoint. Another opinion prevails, which, denying the alterability, regards the *valence as an absolute constant property of the elementary atoms*. According to this idea, the true valence, or atomicity, is only derivable from the hydrogen compounds; the halogens are absolutely monatomic, the elements of the O group diatomic, and those of the N group triatomic, etc. To carry out the constant atomicity, for all the compounds different suppositions are made. To explain the oxygen compounds a linking union of the diatomic oxygen atoms, in the same manner as the union of the C atoms in carbon compounds, is assumed, visible from the following:—



Chlorine trioxide.

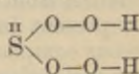
Perchloric acid.



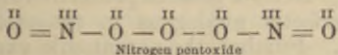
Sulphur dioxide.



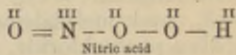
Sulphur trioxide.



Sulphuric acid.



Nitrogen pentoxide

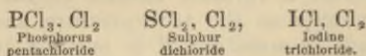


Nitric acid

Hence it would appear that the oxygen atoms can unite without end, in a chain-like manner, similar to the C atoms in the carbon compounds. However, there actually occurs a maximum combining affinity of different groups for oxygen, which varies regularly from group to group (for Cl = 7, for S = 6, for N = 5, for C = 4). Consider it as we may, on the supposition of constant affinity, the reason for the different number of linking O atoms must be based on the nature of the other element. The circumstance, then, that the highest oxides or their hydrates ( $\text{HClO}_4$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ) are more stable than the lower (p. 176), argues decidedly against the chain-like union of the oxygen atoms, as occurs in the unsaturated peroxides.

To explain other compounds according to the constant atomicity theory, a difference between *atomic* and *molecular* compounds is noted.

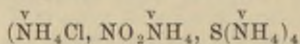
The former are such as can be explained by constant atomicity. All others are regarded as molecular compounds, resulting from the addition of two or more entire molecules, upon the basis of newly supposed molecular affinities. Thus the compounds  $\text{PCl}_5$ ,  $\text{SCl}_4$ ,  $\text{ICl}_3$  are viewed as addition products from atomic combinations with chlorine molecules:—



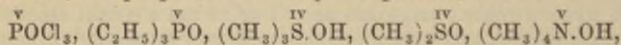
It was thought that a proof that these bodies were differently constituted from the real atomic compounds, was seen in the fact that when vaporized they decomposed into simpler derivatives; the molecular compounds were not regarded as capable of existing as such in the gaseous state. We saw, however, that the decomposition of the molecules  $\text{PCl}_5$ ,  $\text{SCl}_4$  is only gradual, increasing with the temperature, and that they do exist undecomposed, at lower temperature, in a vapor form (compare p. 130). True atomic compounds, like  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  frequently separate into simpler molecules, in their conversion into gas (compare Sulphuric Acid).

Especially demonstrating for the pentavalence of phosphorus is the, at ordinary temperatures, gaseous pentafluoride,  $\text{PF}_5$ , also, that iodine affords a volatile pentafluoride,  $\text{IF}_5$ . It is noteworthy that, generally, the metalloids with the lower halogens (fluorine and chlorine) yield more stable and higher compounds than with bromine and iodine, which possess a higher atomic weight (p. 44). The idea that molecular compounds can also exist in vapor form, would mark their distinction from the atomic compounds as purely arbitrary—not present in the nature of the bodies themselves. Other gaseous compounds also exist, which in no light can be regarded as molecular. Thus, the usually tetratomic or hexatomic tungsten ( $\text{WCl}_4$ ,  $\text{WOCl}_4$ ) forms a gaseous pentachloride,  $\text{WCl}_5$ , and molybdenum, perfectly analogous to tungsten, yields a pentachloride,  $\text{MoCl}_5$ . Further, the pentatomic vanadium ( $\text{VdOCl}_3$ ) gives rise to a gaseous tetrachloride,  $\text{VdCl}_4$ .

The salts of ammonia, according to the theory of constant atomicity, are not regarded as ammonium compounds



(page 120), but as addition products of ammonia with acids— $\text{NH}_3$ ,  $\text{HCl}$ ,  $\text{NH}_3$ ,  $\text{NO}_3\text{H}$ ,  $(\text{NH}_3)_2$ ,  $\text{SO}_4\text{H}_2$ —whereby the analogy of the same with metallic salts appears enigmatical. Further, the properties of many compounds, like



and others, can scarcely be interpreted by the constant valence theory. The existence, also, of potassium permanganate,  $MnO_4K$ , is not compatible with a constant di- or tetravalence of manganese.

Indeed, up to the present, the acceptance of molecular additions could not be entirely dispensed with, especially for the so-called water of crystallization compounds; the proposed effort, however, successfully continues to derive all such compounds on the basis of higher quantivalence of the elements. While, of course, the constant valence theory comprises only the so-called atomic compounds, the extended valence idea draws all others into the circle of generalizations.

Before all, we must be mindful that the nature of chemical union and the cause of the valence of the atoms is entirely unknown to us, and that, therefore, neither the idea of a variable, nor yet of a constant quantivalence constitutes a final explanation. So long as we do not possess an hypothesis upon the real causes, our task can only confine itself to collecting the varying combination relations of atoms into single points of view. The supposition of a constant valence, which formerly was given preference as the simpler, has shown itself as insufficient. Because it maintains real differences, where such are not perceptible, it departs from the ground of induction. The idea of a variable valence, considering all facts, is not prejudicial. Indeed, it finds a pregnant analogy in the department of hydrocarbon radicals. By elimination of hydrogen from the border molecules (as  $C_2H_6$ ) arise radicals or groups of increasing valence ( $C_2H_5$ ,  $C_2H_4$ ,  $C_2H_3$ ,  $C_2H_2$ , . . . . .), just as the valence increases from fluorine to carbon ( $Fl = 19$ ;  $O = 16$ ;  $N = 14$ ;  $C = 12$ ). The group  $C_2H_3$ , however, is di- and tetravalent; the group  $C_2H_2$ , mono- and trivalent. Everything, however, indicates that the chemical elements do not represent final individuals, but are composed of one or several primary substances.

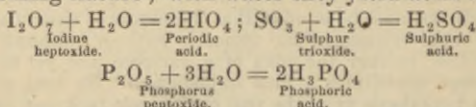
The principles of chemical structure, above presented, show themselves most distinctly, and with regularity, in carbon. The constitution of the innumerable varieties of carbon compounds explains itself by the tetratomic nature of the carbon atoms, and their ability to combine themselves with each other by a simple affinity. In other, the so-called inorganic compounds, the valence and structure relations are more complicated, and are far less investigated, but even in them so many regularities show themselves that thereby the actual material is greatly simplified, and is made more comprehensible. The theory of valence and structure is the first attempt to refer the facts underlying the law of multiple proportions to the functions of the elementary atoms. As this doctrine only comprises actual relations, it cannot be negated, but only further developed.



The platform of the theory of atomicity and structure was laid down by A. Kekulé, (1857-1859). It constitutes a representation and further development of the type theory of Gerhardt, at the basis of which lies, unrecognized, the idea of the different valence of the atoms.

### OXYGEN COMPOUNDS OF THE METALLOIDS.

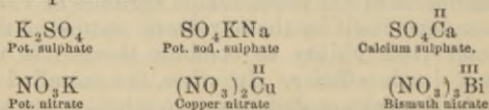
Almost all the oxygen derivatives of the metalloids are of an acid-forming nature; with water they yield acids:—



Conversely, these oxides may be formed by the removal of water from the acids; therefore, they are ordinarily termed *anhydrides* of the corresponding acids;  $\text{I}_2\text{O}_7$ —anhydride of periodic acid;  $\text{SO}_3$  as sulphuric-anhydride;  $\text{P}_2\text{O}_5$  as phosphoric anhydride, etc.

By the replacement of the hydrogen of the acids by metals salts arise. According to the number of hydrogen atoms replaceable by metals, acids are distinguished as *monobasic*, *dibasic*, *tribasic* or monohydric, dihydric, trihydric, etc.

Like the metalloids the metals are of various atomicities; the monatomic metals (Na, K, Ag,) replace each *one* hydrogen atom; those of greater atomicity replace more. Therefore the metals of higher atomicity can unite several residues. From this the importance *e. g.*, of the following chemical formulas is explained:—



The salts of sulphuric acid are called *sulphates*, those of nitric acid, *nitrates*, those of phosphoric acid, *phosphates*, etc. The symbols of the metals are indifferently written at the beginning or end of the chemical formulas of the salts; in the second case we mean to indicate that the metal atoms are in union with the oxygen.

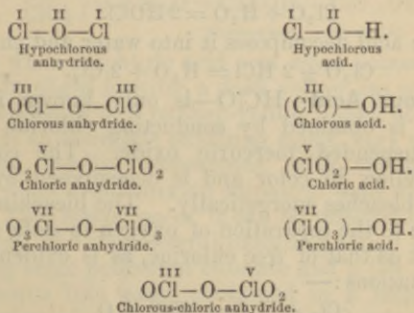
## OXYGEN COMPOUNDS OF THE HALOGENS.

Excepting fluorine, all the halogens combine with oxygen to form anhydrides and acids entirely analogously constituted, although not all the members are known for each halogen. The acids have *one* atom of hydrogen replacable by metals, and hence are *monobasic*. Chlorine forms the following anhydrides and acids:—

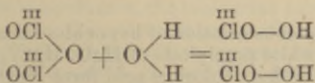
Anhydrides.	Acids.
$\text{Cl}_2\text{O}$	$\text{HClO}$ —Hypochlorous acid.
$\text{Cl}_2\text{O}_3$	$\text{HClO}_2$ —Chlorous acid.
$(\text{Cl}_2\text{O}_4)$	$\text{HClO}_3$ —Chloric acid.
$(\text{Cl}_2\text{O}_7)$	$\text{HClO}_4$ —Perchloric acid.

The anhydrides  $\text{Cl}_2\text{O}_5$  and  $\text{Cl}_2\text{O}_7$  (corresponding to the compounds  $\text{I}_2\text{O}_5$  and  $\text{I}_2\text{O}_7$ ) are unknown. The compound  $\text{Cl}_2\text{O}_4$  exists and must be regarded as a mixed anhydride of chlorous and chloric acid.

The following formulas express the chemical structure of these compounds:—

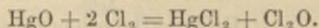


In the acids we assume the presence of the monotomic group OH (hydroxyl or water residue) in which hydrogen, by action of metals or bases, can be replaced by metals. The acid groups ( $\text{ClO}_2$  or  $\text{ClO}_3$ ) combined with hydroxyl are called *acid residues* or *radicals*. In the anhydrides two acid radicals are united by an oxygen atom; by the action of water they decompose into 2 molecules of acid:—



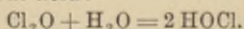
The salts of perchloric acid are called *perchlorates*; those of chloric acid, chlorates; those of chlorous acid, chlorites; those of hypochlorous acid, hypochlorites.

**Hypochlorous Oxide**— $\text{Cl}_2\text{O}$ —Hypochlorous anhydride, is produced by conducting dry chlorine gas, in the cold, over precipitated and dried mercuric oxide:—

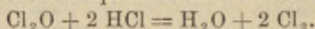


The disengaged gas is condensed in a bent glass tube, cooled by a freezing mixture.

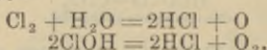
Hypochlorous oxide is a red brown liquid, resembling chlorine, boiling at  $+20^\circ$ , and passing into a yellow vapor. The vapor density is 43.5 ( $\text{H} = 1$ ), corresponding to the formula,  $\text{Cl}_2\text{O} = 87$ . The oxide is very unstable, and in the course of a few hours decomposes, yielding chlorine and oxygen. It has strong oxidizing and bleaching properties. Dissolves in water to hypochlorous acid:—



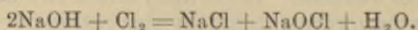
Hydrochloric acid decomposes it into water and chlorine:—



**Hypochlorous Acid**— $\text{HClO}$ —is only known in aqueous solution. It is obtained by conducting chlorine into water containing suspended mercuric oxide. The concentrated solution is yellow in color and is decomposed by light. It oxidizes and bleaches energetically. The bleaching action of this acid, due to the separation of oxygen in *statu nascendi*, is twice as great as that of free chlorine, as is evident from the following equations:—



The acid itself is very feeble and incapable of decomposing carbonates. Its salts (Bleaching powder, see Chloride of Lime) are formed by the action of chlorine, in the cold, upon strong bases:—



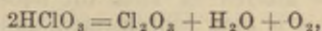
Upon heating their solutions with dilute nitric acid the free acid distills over.

On shaking the aqueous solution of hypochlorous acid with mercury, there is produced a white precipitate of  $\text{HgO}$ ,  $\text{HgCl}_2$ , soluble in hydrochloric acid (salts of hypochlorous acid form  $\text{HgO}$ ). This behavior



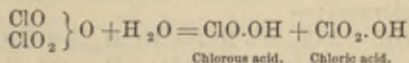
serves to distinguish hypochlorous acid from chlorine, which under like circumstances forms  $\text{Hg}_2\text{Cl}_2$ , insoluble in hydrochloric acid (Reaction of Wolter).

**Chlorine Trioxide**— $\text{Cl}_2\text{O}_3$ —Chlorous anhydride. This results from the deoxidation of chloric acid, as *e. g.*, when a mixture of  $\text{KClO}_3$ , nitric acid and reducing substances like arsenic trioxide is warmed—



a yellowish green gas escapes, which can be condensed at  $-20^\circ$ . Chlorine trioxide is a reddish-brown liquid, boiling about  $0^\circ$  and decomposing rapidly. Its vapors, when heated to  $50^\circ$ , explode with violence. In water the oxide is soluble, forming *chlorous acid*  $\text{ClO}_2\text{H}$  or  $\text{ClO}\cdot\text{OH}$ , unknown in a free condition. With alkalis it yields salts called chlorites.

**Chlorine Tetroxide**— $\text{Cl}_2\text{O}_4$ —is the mixed anhydride of chloric and chlorous acid, as water and the alkalis, decomposing it into these two acids:—



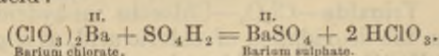
Chlorous acid.      Chloric acid.

It forms when sulphuric acid acts upon potassium chlorate ( $\text{KClO}_3$ ); by slight heating, a dark yellow gas escapes, which, at  $-20^\circ$  condenses to a reddish-yellow liquid, boiling at  $+9^\circ$ . The oxide is an energetic oxidizing agent, very unstable, and, in daylight, readily decomposes, with violent explosion. Hence, we must avoid mixing sulphuric acid with potassium chlorate. The formation of it can be effected in a perfectly harmless way, and its powerful oxidizing action be illustrated, by throwing some potassium chlorate and a few pieces of yellow phosphorus into water, contained in a measuring glass, then, by means of a pipette, allowing sulphuric acid to touch the bottom of the tube, drop by drop. By the action of the tetroxide, which is disengaged, the phosphorus will burn under water with a brilliant light.

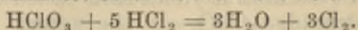
When concentrated sulphuric acid is added to a mixture of potassium chlorate and sugar, violent combustion occurs.

The vapor density of the oxide is 33.7 ( $\text{H}=1$ ); the gaseous molecules, therefore, possess the formula  $\text{ClO}_2$  ( $=67.5$ ). It is very probable, that, at lower temperature, the molecules have a double formula,  $\text{Cl}_2\text{O}_4$ ; this is confirmed by the manner in which water decomposes it, and by its perfect analogy with nitrogen tetroxide, for which a dissociation of the molecules  $\text{N}_2\text{O}_4$  into  $\text{NO}_2$  has been proven.

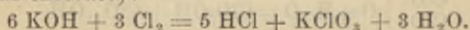
**Chloric Acid**— $\text{HClO}_3$ , or  $\text{ClO}_2\cdot\text{OH}$ —is obtained by decomposing an aqueous solution of barium chlorate, by means of sulphuric acid:—



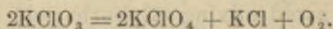
The barium sulphate separates as a white insoluble powder, and can then be filtered off from the aqueous solution of chloric acid. This is then concentrated, under an air-pump, until the specific gravity is 1.28; when about 40 % chloric acid is present; it is oily and, when warmed to  $40^\circ$ , decomposes into chlorine, oxygen and perchloric acid,  $\text{HClO}_4$ . The concentrated aqueous solution oxidizes strongly; sulphur, phosphorus, alcohol and paper are inflamed by it. Hydrochloric acid eliminates chlorine from the acid and its salts:



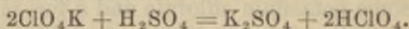
The chlorates are produced, together with chlorides, by the action of chlorine, in the heat, upon many bases (compare Potassium chlorate):—



**Perchloric Acid**— $\text{HClO}_4$ , or  $\text{ClO}_3\cdot\text{OH}$ . Of all the oxygen derivatives of chlorine this is the most stable. As previously stated, it forms by the decomposition of chloric acid; more easily obtained from its salts. Upon heating potassium chlorate to fusion, oxygen escapes and potassium perchlorate results:—

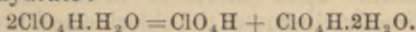


Upon warming the perchlorate with four parts sulphuric acid, perchloric acid distills over:—

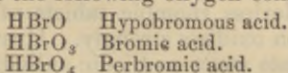


Pure, the acid is a mobile, colorless liquid, fuming strongly in the air; its specific gravity is 1.78 at  $15^\circ$ . It boils at  $110^\circ$ . It cannot be preserved, since after a few days it decomposes with violent explosion. In contact with phosphorus, paper, carbon and other organic substances, it also explodes. Upon the skin it produces painful wounds. Dissolves in water with hissing and with one molecule of the solvent forms the crystalline hydrate  $\text{HClO}_4 + \text{H}_2\text{O}$ , fusing at  $50^\circ$ ; the crystals fume in the air and gradually deliquesce. The second hydrate— $\text{HClO}_4 + 2 \text{H}_2\text{O}$ —is a thick, oily liquid, resembling sulphuric acid, and boiling unchanged at  $208^\circ$ . Also obtained by evaporation of the aqueous solutions of

perchloric and chloric acids. When the crystalline hydrate is distilled it breaks up into anhydrous perchloric acid and the second hydrate:—



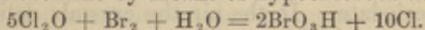
Bromine yields the following oxygen compounds:—



The corresponding anhydrides are not known. The acids are perfectly analogous to the corresponding chlorine compounds.

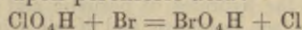
**Hypobromous Acid**— $\text{HBO}$ —is formed when bromine water acts upon mercuric oxide; the aqueous solution can be distilled in vacuo, and possesses all the properties of its chlorine analogue.

**Bromic Acid**— $\text{BrO}_3\text{H}$ . Bromates are formed by the action of bromine, in the heat, upon the aqueous solution of the alkalies or of barium hydrate; from the barium salts the acid may be obtained in aqueous solution by liberation by means of sulphuric acid. More practically is the acid procured by the action of bromine upon silver bromate or oxidation of bromine by means of hypochlorous acid:—



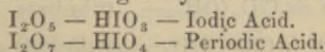
The aqueous solution may be concentrated in vacuo until its quantity reaches 50.6%  $\text{BrO}_3\text{H}$  and then closely corresponds to the formula  $\text{BrO}_3\text{H} + 7\text{H}_2\text{O}$ . When heated it breaks up into bromine, oxygen and water.

**Perbromic Acid**— $\text{BrO}_4\text{H}$ —is said to be formed in the action of bromine vapor upon perchloric acid:—

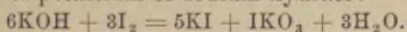


and perfectly similar to the latter.

Iodine forms the following anhydrides and acids.

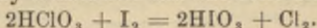


**Iodic Acid**— $\text{HIO}_3$ . Its salts (iodates) are formed similarly to those of chloric and bromic acids, by dissolving iodine in a hot solution of potassium or sodium hydrate:—

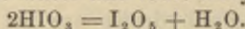




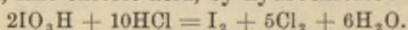
The free acid can be obtained by the oxidation of iodine with strong nitric acid, or by the aid of chlorine; further, by the action of iodine upon chloric or bromic acids, whereby the iodine directly eliminates the chlorine and bromine:—



Upon evaporating the aqueous solution the free iodic acid crystallizes in colorless rhombic tablets of specific gravity 4.63. The solution oxidizes strongly. Heated to  $170^\circ$  iodic acid decomposes into water and iodic anhydride:—



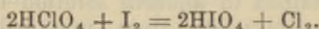
Decomposed, like chloric acid, by hydrochloric:—



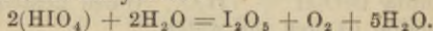
By reducing agents ( $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{HI}$ ) it is reduced to iodine. Similar decompositions are sustained by periodic acid.

**Iodic Anhydride**— $\text{I}_2\text{O}_5$ —forms a white crystalline powder, which dissolves in water to iodic acid. At  $300^\circ$  it decomposes into iodine and oxygen.

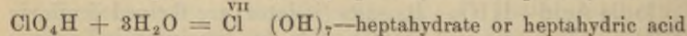
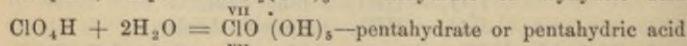
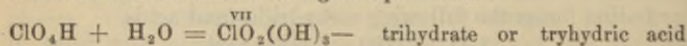
**Periodic Acid**— $\text{HIO}_4$ . Produced by the action of iodine upon perchloric acid:—



Upon the evaporation of the aqueous solution, the acid crystallizes out with two molecules of water ( $\text{HIO}_4 \cdot 2\text{H}_2\text{O}$ —compare Sod. periodate). In the air the crystals deliquesce, fuse at  $130^\circ$ , and at a higher temperature decompose into water and periodic anhydride, the latter readily breaking up into oxygen and iodic anhydride:—

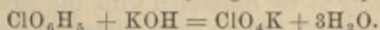


The existence of the hydrates of periodic and perchloric acids, as also of many others (see Sulphuric and Nitric acids), which formerly we were accustomed to view as molecular compounds (p. 165), are interpreted at present by the acceptance of hydroxyl groups, directly combined with the element of higher equivalence:—

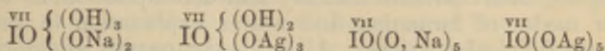


The extreme hydrates ( $\text{Cl}(\text{OH})_7$  and  $\text{I}(\text{OH})_7$ , in which all seven affinities of the halogen atom are attached to hydroxyl groups, are not known, but probably exist in aqueous solution. As they give up water

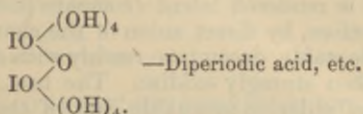
and one atom of O, becoming simultaneously united with two bonds to the halogen, they yield the lower hydrates—even to the monohydrate  $\text{ClO}_2\text{OH}$ . Just as in the monohydrate, perchloric acid is monobasic in the polyhydrates, since but *one* hydrogen atom is replaced by metals :



On the other hand, periodic acid ( $\text{IO}_3\text{OH}$  is not only monobasic, but as a pentahydrate ( $\text{IO}(\text{OH})_5$ ) can, similar to the polybasic acids, also furnish polymetallic salts, as—



Salts also exist which are derived from condensed polyiodic acids, as—



(Compare disulphuric, dichromic acid, etc.)

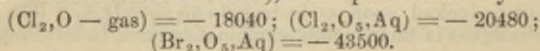
The existence of such salts plainly indicates that the hydrates of acids must be looked upon as hydroxyl-compounds, and that iodine and the halogens in their highest combinations are, in fact, heptads.

The oxygen compounds of the halogens in some respects display a character exactly opposite to the hydrogen derivatives. While the affinity of the halogens with reference to hydrogen diminishes with increasing atomic weight from Fl to I (see page 56), the degrees of affinity for oxygen is the exact reverse. Fluorine is not capable of combining with oxygen; the chlorine and bromine compounds are very unstable and in free condition generally not known; the iodine derivatives, on the contrary, are the most stable. In accord with this is the fact that in the higher oxygen compounds chlorine is liberated directly by bromine, and bromine by iodine, while in the hydrogen and metallic compounds of the halogens the direct reverse—that iodine and bromine are removed by chlorine—is the case.

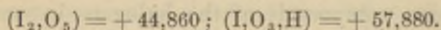
Further, the oxygen compounds exhibit the remarkable peculiarity, that their stability increases with the addition of oxygen. The lowest acids  $\text{HClO}$ ,  $\text{HBrO}$ ,  $\text{HClO}_2$ , are very unstable, even in their salts; they possess a very slight acid character, and are, too, separated from their salts by carbon dioxide. The most energetic and most stable are the highest

acids,  $\text{HClO}_4$ ,  $\text{HBrO}_3$ ,  $\text{HIO}_3$ , in which the higher valence of the halogens appears. The corresponding oxygen compounds of the sulphur and nitrogen groups are perfectly similar—a property scarcely to be connected with the supposition of a linking grouping of the oxygen atoms (according to the constant atomicity theory, see p. 165).

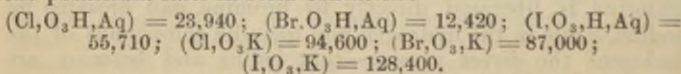
The peculiar behavior of the oxygen compounds of the halogens, their variable stability and decomposition, as also their modes of formation, find nearer explanation in their thermo-chemical relations. All oxide compounds of chlorine and bromine are endothermic, *i. e.*, in their production from the elements heat is rendered latent (compare p. 57). They do not result, therefore, by direct union of the elements; further, they are little stable, decompose readily with elimination of oxygen, and then strongly oxidize. The heat, appearing in the formation of chlorine monoxide, and of the hypothetical pentoxides,  $\text{Cl}_2\text{O}_5$  and  $\text{Br}_2\text{O}_5$  (in their production from the elements and solution in water), corresponds to the symbols:—



In the formation of iodine pentoxide and iodic acid, heat is liberated:—



This explains its stability in comparison with the chlorine and bromine compounds, also the direct production of iodic acid by the oxidation of iodine. When the pentoxides are compared with each other, it is seen that, in the formation of bromine pentoxide,  $\text{Br}_2\text{O}_5$ , the most heat is rendered latent—the affinity of bromine for oxygen, consequently, is the lowest, that of iodine the greatest. The same is also evident from the heat produced from acids, in dilute aqueous solution, or of the potassium salts in solid condition:—

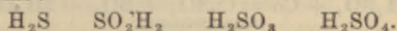


From this is understood, that chlorine and bromine are separated by iodine, with formation of iodic acid, from chloric and bromic acids, while bromine does not act upon chloric acid. Later, we will see that also in the group of sulphur and of phosphorus, the middle members, selenium and arsenic, exhibit a less liberation of heat in their oxygen compounds—their affinity, therefore, is slighter.

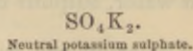
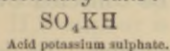


## 2. OXYGEN COMPOUNDS OF THE ELEMENTS OF THE SULPHUR GROUP.

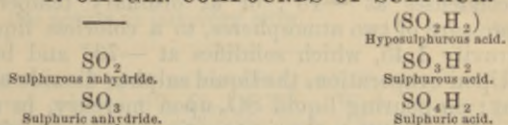
The elements sulphur, selenium and tellurium combine with two atoms of H, and yield oxygen acids, which also contain 2 H atoms:—



In these acids 1 and 2 atoms of H can be replaced by metals; hence they are *dibasic*. By replacement of one atom of H are formed the so-called *acid* or *primary salts*, while, by the replacement of both hydrogen atoms are obtained the *neutral* or *secondary salts*:—

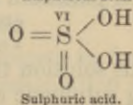
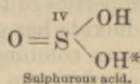
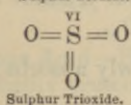
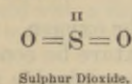


### 1. OXYGEN COMPOUNDS OF SULPHUR.



In addition to these, so to speak, normal compounds, exist still others, more complicated, which will be studied later.

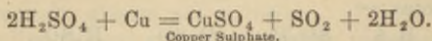
The structure of these derivatives may be expressed in the following formulas:—



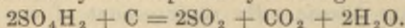
**Sulphur Dioxide**,  $\text{SO}_2$ , or sulphurous anhydride, is formed by burning sulphur or sulphides in the air:— $\text{S} + \text{O}_2 = \text{SO}_2$ .

\* The structure of sulphurous acid must probably be expressed by the formula,  $\text{H}-\overset{\text{IV}}{\text{SO}}_2-\text{OH}$ , according to which 1 atom of H is connected with sulphur, but the other is contained as hydroxyl. This appears from the carbon derivatives of sulphurous acid. Probably, in compounds, both structural cases exist, as two isomeric series of neutral ethers of the acid are known.

The combustion may also be effected by the action of metallic oxides (copper oxide, manganese peroxide) which give up their oxygen readily. It is most conveniently prepared for laboratories by heating sulphuric acid with mercury or copper :—



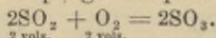
The acid is similarly decomposed by heating it with carbon :—



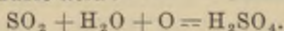
By this method we get a mixture of carbon and sulphur dioxides, which are separated with difficulty. Owing to its solubility in water, sulphur dioxide must be collected over mercury.

It is a colorless gas, with a suffocating odor. Its density is 32 (H = 1), corresponding to the molecular formula  $\text{SO}_2 = 64$ . It condenses at  $-15^\circ$ , or at ordinary temperatures under a pressure of two atmospheres, to a colorless liquid, of specific gravity 1.45, which solidifies at  $-76^\circ$  and boils at  $-10^\circ$ . Upon evaporation, the liquid sulphur dioxide absorbs much heat; on pouring liquid  $\text{SO}_2$  upon mercury, in a clay crucible and accelerating the evaporation by blowing air upon it, the metal will solidify. Water dissolves, with liberation of heat, 50 volumes of sulphur dioxide gas, which is again set free upon application of heat. The solution shows all the chemical properties of the free gas.

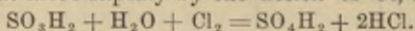
Sulphur dioxide has great affinity for oxygen. In dry condition the gases combine; if their mixture be conducted over feebly heated platinum sponge\* sulphur trioxide results :—



In aqueous solution the dioxide slowly absorbs O from the air, forming sulphuric acid :—



The oxidation of the aqueous sulphur dioxide to sulphuric acid proceeds more rapidly by the action of Cl, Br and I :—



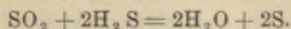
In consequence of the affinity of the halogen for hydrogen and of sulphurous acid for oxygen the decomposition of a

\* Instead of platinum sponge, platinized asbestos may be applied; this is obtained by immersing asbestos in a platonic chloride solution, then in ammonium chloride, and afterwards drying and igniting.

molecule of water is here effected. On adding sulphurous acid to a dark-colored iodine solution, the latter is decolorized.

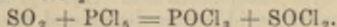
Similarly, sulphurous anhydride and its solution withdraw oxygen from many compounds rich in that element; hence it deoxidizes strongly, and passes over into sulphuric acid. Thus chromic acid is reduced to oxide, and the red solution of permanganic acid is decolorized with formation of manganous salts. Many organic coloring substances, like those of flowers, are decolorized by it. Upon this property rests its application in the bleaching of wools and silks, which are strongly attacked by the ordinary chlorine bleaching agents (p. 43).

By stronger reducing agents the dioxide may be deoxidized, thus by  $H_2S$  sulphur is separated out:—

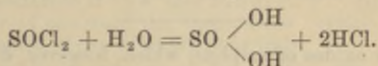


If, however, both gases are strongly diluted by other neutral gases, the action is but very slow.

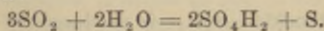
A mixture of equal volumes  $SO_2$  and  $Cl_2$  unite in direct sunlight to thionyl chlorine  $SO_2Cl_2$  (p. 188). When sulphur dioxide acts upon warmed phosphoric chloride, there is formed with the oxychloride the compound  $SOCl_2$ :—



**Chlorthionyl**— $SOCl_2$ —may be viewed as sulphur dioxide in which one atom of O is replaced by two atoms of chlorine. It is a colorless liquid with a sharp odor, and boils at  $78^\circ$ . Water decomposes it into hydrogen chloride and sulphurous acid:—



**Sulphurous Acid**— $H_2SO_3$ —is not known in free condition, but is probably present in the aqueous solution of  $SO_2$ . On cooling the concentrated solution to  $0^\circ$ , colorless cubical crystals separate with the composition  $(SO_2 + 15H_2O)$  or  $(SO_3H_2 + 14H_2O)$ . Upon longer standing of the aqueous solution, especially in sunlight, sulphur separates with formation of sulphuric acid:—

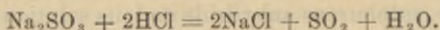


Sulphurous acid is dibasic and forms two series of salts; the primary ( $KHSO_3$ ) and secondary ( $K_2SO_3$ ).

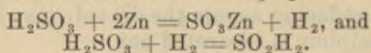
*Sulphites.* These are obtained by saturating solutions of bases with  $SO_2$ . When sulphurous acid is separated out of its



salts by stronger acids it decomposes into its anhydride and water:—

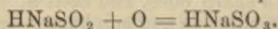


**Hydrosulphurous Acid**— $\text{H}_2\text{SO}_2$ . On adding zinc to the aqueous solution of sulphurous acid the metal dissolves without liberation of hydrogen. A yellow solution is obtained, which decolorizes indigo and litmus solutions energetically. Schützenberger has shown that this property is due to the hydrosulphurous acid contained in the solution, formed there by the action of the H set free by the zinc upon a second molecule of  $\text{SO}_2\text{H}_2$ :—



The pure aqueous solution is obtained by the decomposition of its salts. Its solution has an orange yellow color, reduces powerfully, bleaches and soon decomposes with separation of sulphur. The bleaching action of this lowest oxygen compound of sulphur reminds us of a similar behavior of the lower oxygen derivatives of chlorine and bromine.

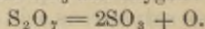
The salts are more stable than their acid. The sodium salt is obtained by the action of zinc filings upon a solution of primary sodium sulphite, and has the formula  $\text{HNaSO}_2$ ; the second atom of hydrogen (as in the case of hypophosphorous acid ( $\text{H}_2\text{PO}_2$ )) cannot be replaced by metals. Hence the acid is monobasic, and its structure may be expressed by the formula  $\text{HSO}^{\text{IV}}, \text{OH}$ . The solutions of the salts absorb oxygen from the air and are converted into sulphites:—



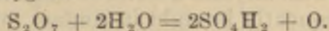
Two peculiar oxides of sulphur, which, however, do not afford any corresponding acids and salts, but resemble the peroxides more, are sulphur sesquioxide and sulphur heptoxide.

**Sulphur Sesquioxide**— $\text{S}_2\text{O}_3$ . Obtained by solution of flowers of sulphur in anhydrous sulphuric anhydride; separates out in blue drops, which solidify to a malachite-like mass. It decomposes gradually, more rapidly on warming, into  $\text{SO}_2$  and sulphur. It is violently broken up by water, with formation of sulphur,  $\text{SO}_2$ ,  $\text{SO}_4\text{H}_2$  and polythionic acids. In concentrated sulphuric acid it dissolves with a blue color.

**Sulphur Heptoxide**— $\text{S}_2\text{O}_7$ —is produced by the action of the silent discharge of an electric stream of great tension upon a mixture of  $\text{SO}_2$  and oxygen, and separates in oily drops, which solidify to a crystalline mass at  $0^\circ$ . Upon standing, especially upon warming, it gradually decomposes into  $\text{SO}_3$  and oxygen:—



It fumes strongly in the air, and with water decomposes into sulphuric acid and oxygen:—



Its solution in concentrated sulphuric acid is tolerably stable. The same arises, too, in the electrolysis of sulphuric acid, and by addition of  $\text{H}_2\text{O}_2$  to strongly cooled sulphuric acid.

**Sulphur Trioxide**— $\text{SO}_3$ —or sulphuric anhydride, is produced, as previously described, by the union of  $\text{SO}_2$  and oxygen, aided by platinum black; or when  $\text{SO}_2$  and air are conducted over glowing oxide of iron (Wöhler). It is most conveniently obtained by warming fuming (Nordhausen) sulphuric acid (p. 186); the escaping white fumes are condensed in a chilled receiver. Sulphur trioxide exists in two different (polymeric) modifications. In the one form, obtained by cooling the vapors, there is produced a white, matted, silky mass which, after fusion, crystallizes in long, colorless prisms; it fuses at  $16^\circ$  and boils at about  $46^\circ$ . The vapor density agrees with formula  $\text{SO}_3$ . By keeping it below  $25^\circ$  it passes in another so-called solid modification, which does not fuse until above  $50^\circ$ , and passes into the liquid variety.

According to later investigations of Weber both modifications are not pure anhydride, but hydrous. The pure anhydride he obtained from the ordinary asbestos-like variety, by repeated, careful distillation in a closed tube. It is a readily mobile liquid, of specific gravity 1.940 at  $16^\circ$ , which solidifies to long, transparent, needles, like salt-petre. The crystals fuse at  $14.8^\circ$  and boil at  $46.2^\circ$ . By the addition of a small quantity of moisture the transparent crystals pass into the asbestos-like needles of the ordinary anhydride.

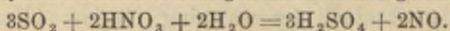
Sulphuric oxide fumes strongly in the air, and attracts moisture with avidity. When thrown on water it dissolves with hissing, to form sulphuric acid ( $\text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$ ).

When the vapors are led through heated tubes they are decomposed into  $\text{SO}_2$  and oxygen.

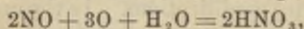
**Sulphuric Acid**— $\text{H}_2\text{SO}_4$ . This acid has long been known and is extensively applied in technology, etc. Besides the reaction first mentioned, it arises in the oxidation of sulphur by nitric acid. Formerly it was obtained by heating ferrous sulphate ( $\text{FeSO}_4$ ); at present, however, it is almost exclusively manufactured in large quantities, after the so-called English lead chamber process. This method is based upon the conversion of  $\text{SO}_2$  into  $\text{SO}_4\text{H}_2$ . Sulphur or pyrite ( $\text{FeS}_2$ ) is

roasted in ovens, and the disengaged  $\text{SO}_2$  immediately conducted, together with air, into a series of large leaden chambers in which it is frequently brought in contact with nitric acid and steam. By the combined action of these substances (sulphur dioxide, nitric acid, oxygen of the air and water) sulphuric acid is formed in the chambers and collected upon the floor of the same.

The lead chamber process is very complicated, being influenced by the quantity of the reacting substances and the temperature, and is even not yet entirely explained. It is most simply represented as follows: in the presence of water, the nitric acid oxidizes the  $\text{SO}_2$  to sulphuric acid, whereby it is reduced to nitrogen oxide or nitrogen dioxide:—



The oxygen of the air (which entered the chambers simultaneously with the  $\text{SO}_2$ ) and the steam convert the  $\text{NO}$  again into nitric acid:—



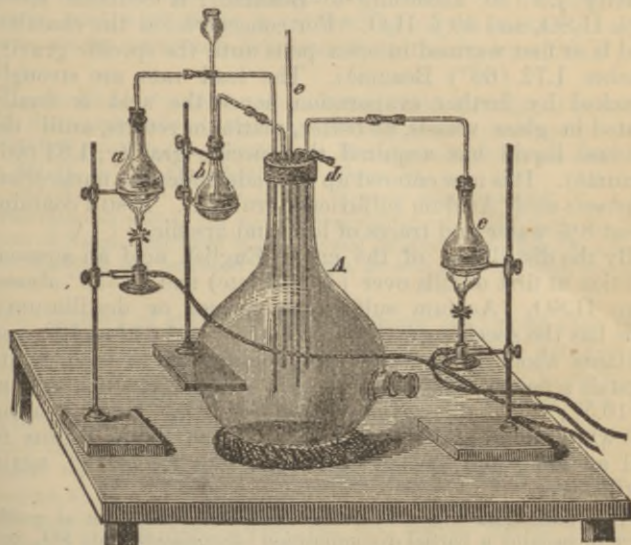
and this converts a fresh portion of  $\text{SO}_2$  into sulphuric acid. In this manner apparently one and the same quantity of nitric acid, by sufficient air access and water, changes an unlimited amount of  $\text{SO}_2$  into sulphuric acid; the nitrogen oxide (and other oxides of nitrogen) acts, as it were, as oxygen bearer. In truth, in this process, in addition to the  $\text{NO}$ , small quantities of  $\text{N}_2\text{O}$  and  $\text{N}$  are formed from the nitric acid, and these not being oxidized by the air, escape, with excess of the latter, out of the chambers. For the continuation of the process, the regular addition of a definite amount of nitric acid is required.

In practice, by means of the escaping nitrogen and excess of air, the active nitrogen oxides ( $\text{N}_2\text{O}_3$  and  $\text{NO}_2$ ) are carried along and withdrawn from the action. To avoid further loss of saltpetre thus occasioned, the escaping brown gases are aspirated by the so-called Gay-Lussac tower. The same is constructed from lead sheets, and filled with pieces of coke, over which concentrated sulphuric acid constantly trickles. The latter completely absorbs the nitrogen oxides  $\text{N}_2\text{O}_3$  and  $\text{NO}_2$ , with formation of nitrosylsulphuric acid (see p. 199). From the acid collected at the bottom of the tower—the so-called nitroso acids, the nitrogen oxides can be regained and made useful in the production of sulphuric acid in the chambers. This takes place, at present, in the so-called *Glover tower*, which, made of lead plates and fire-proof bricks, is inserted between the sulphur ovens and lead chambers. In this the nitroso-acid (diluted with the previously obtained chamber acid) is allowed to run over fire-brick, while the hot gases of combustion of the sulphur ovens stream against it. In this way the hot gases are cooled to the required temperature (70–80), from the acid chamber water evaporates, and, at the same time, the nitrogen oxides are set free (see p. 200) and carried into the lead chambers. Hence, the Glover tower serves, not only for complete utilization of the nitrogen oxides, but also for the concentration of the chamber acid.

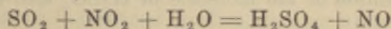


The chamber process may be illustrated by the following laboratory experiment: A large glass flask (Fig. 84) *A* replaces the lead chamber; in its neck are introduced, by means of a cork, several glass tubes, serving to conduct the various gases. In *a*  $\text{SO}_2$  is developed by heating a mixture of  $\text{H}_2\text{SO}_4$  and Hg or copper strips. The flask *b* contains some dilute nitric acid and copper turnings, from which is

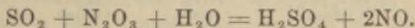
FIG. 84.



evolved (NO). In *c* water is boiled, to afford steam. Through *d* air enters, while the excess of gases escapes through *e*. By the meeting of (NO) with the air red fumes of nitrogen dioxide ( $\text{NO}_2$ ) and nitrogen trioxide ( $\text{N}_2\text{O}_3$ ) arise, and these in presence of water change the sulphur dioxide to sulphuric acid:—



and



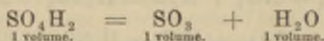
The regenerated nitrogen oxide yields  $\text{NO}_2$  with the oxygen of the air, and this converts another portion of  $\text{SO}_2$  into sulphuric acid. In time aqueous sulphuric acid collects upon the bottom of the vessel. If at first only  $\text{SO}_2$ , NO and air enter without the steam, there is produced (by aid of the moisture of the air) the compound  $\text{SO}_2 \begin{cases} \text{NO}_2 \\ \text{OH}^2 \end{cases}$  (the so-called nitrosulphonic acid) which covers the walls of the vessel with a white crystalline sublimate (comp. p. 200). These crystals, known as

lead chamber crystals, also form in the technical manufacture of sulphuric acid, when an insufficient quantity of water is conducted into the chambers. Water decomposes them into sulphuric acid and nitrogen oxide.

The acid collecting in the chambers (chamber acid) possesses, when the operation has been properly conducted, the specific gravity 1.5 (50° according to Beaumè); it contains about 60%  $\text{H}_2\text{SO}_4$  and 40%  $\text{H}_2\text{O}$ . For concentration the chamber acid is at first warmed in open pans until the specific gravity reaches 1.72 (60° Beaumè). The lead vats are strongly attacked by further evaporation, hence the acid is finally heated in glass vessels, or better, platinum retorts, until the residual liquid has acquired the specific gravity, 1.83 (66° Beaumè). It is now entered up on trade under the name *crude sulphuric acid* (*Acidum sulfuricum crudum*). It still contains about 8% water and traces of lead and arsenic.

By the distillation of the crude English acid an aqueous solution at first distills over ( $\frac{1}{3}$  distillate) and at 330° almost pure  $\text{H}_2\text{SO}_4$  (*Acidum sulfuricum purum* or *destillatum*). This has the specific gravity 1.854 at 0° or 1.842 at 12°, and contains about 1.5% water. On cooling this to -35° white crystals separate, which by repeated recrystallization fuse at +10.5°; this is the *anhydrous acid*,  $\text{H}_2\text{SO}_4$ . Upon heating this white fumes of  $\text{SO}_3$  escape at 40°; the liquid begins to boil at 290°, and at 330° the acid, with 1.5%  $\text{H}_2\text{O}$ , again distills over.

From these data it is obvious that sulphuric acid, even at gentle warmth, sustains a partial decomposition (dissociation) into  $\text{SO}_3$  and  $\text{H}_2\text{O}$ , which, upon cooling, again unite to sulphuric acid. The dissociation is complete at a boiling temperature, as seen from the vapor density, which has been found to be 24.5. The normal vapor density, corresponding to the molecular formula  $\text{H}_2\text{SO}_4 = 98$ , must be equal to 46 ( $\frac{98}{2}$ ); the empirically found formula, half as large, is explained by the decomposition of the molecule of  $\text{H}_2\text{SO}_4$  into the molecules  $\text{SO}_3$  and  $\text{H}_2\text{O}$ .

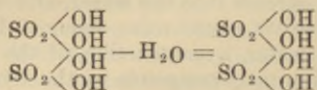


Concentrated sulphuric acid is a thick, oily liquid. On cooling, the ordinary English sulphuric acid (containing 8% water), to 0°, large six-sided prisms of the hydrate  $\text{SO}_4\text{H}_2 + \text{H}_2\text{O}$  separate; these fuse at +8.5°, and give up water at 205°. The *second hydrate*,  $\text{SO}_4\text{H}_2 + 2\text{H}_2\text{O}$ , corresponding to the maximum contraction, has the specific gravity 1.62, and yields water at 195°. The concentrated acid possesses an ex-



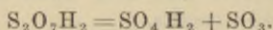


**Pyrosulphuric or Disulphuric Acid**— $\text{H}_2\text{S}_2\text{O}_7$ . On withdrawing one molecule of water from two of the acid there results the compound  $\text{S}_2\text{O}_7\text{H}_2$ , whose formation and structure may be represented by the following formula:—



As this contains two hydroxyl groups it is a dibasic acid; besides, however, it reveals, from its formation, an *anhydride* character. Later we will observe that almost all polybasic acids as phosphoric acid  $\text{PO}(\text{OH})_3$ , silicic acid  $\text{SiO}(\text{OH})_2$ , chromic acid  $\text{CrO}_2(\text{OH})_2$  are capable, by condensation of several molecules, with elimination of water, of forming like derivatives which bear the name *Poly-* or *Pyro-acids*.

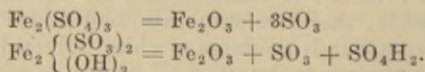
The disulphuric acid is contained in the so-called *fuming* or *Nordhausen sulphuric acid* (*Acidum sulfuricum fumans*), which is obtained by heating dehydrated ferrous sulphate—green vitriol ( $\text{FeSO}_4$ ). It is a thick, oily, strongly fuming liquid, of specific gravity, 1.85–1.9. On cooling this, large, colorless crystals of  $\text{H}_2\text{S}_2\text{O}_7$  separate; these fuse at  $35^\circ$ . On warming it breaks up into sulphuric acid and sulphur trioxide, which volatilizes:—



Conversely, the disulphuric acid dissolves  $\text{SO}_3$  and can become sulphuric acid.

The production of fuming sulphuric acid depends on this: it may be regarded as a solution of  $\text{SO}_3$  (or  $\text{S}_2\text{O}_7\text{H}_2$ ) in excess of sulphuric acid.

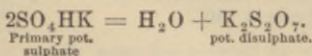
Technically, fuming sulphuric acid is obtained from pyrites ( $\text{FeS}_2$ )—(at present only in Bohemia). By weathering of the pyrites in the air ferrous sulphate and ferric oxide arise. The first can be dissolved out with water. The solution is evaporated and roasted in a reverberatory furnace, whereby the ferrous salt is changed to ferric salts. The latter are then distilled from earthen retorts, when sulphuric acid and the trioxide pass over and are collected in the receivers:—



The residue, consisting of red ferric oxide, finds application as colcothar (caput mortuum) in polishing and as a paint.

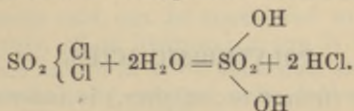
Recently, the method of Winkler has been employed to obtain solid fuming sulphuric acid  $\text{H}_2\text{S}_2\text{O}_7$ . The mixture of  $\text{SO}_2 + \text{O}$ , obtained by the heating of English sulphuric acid (p. 184) and absorption of steam produced at same time by sulphuric acid in a coke tower, is conducted over glowing platinized asbestos (p. 178) and the resulting  $\text{SO}_3$  taken up by concentrated sulphuric acid.

With water disulphuric acid yields sulphuric acid. Its salts may be obtained by heating the primary salts of the latter acid:—

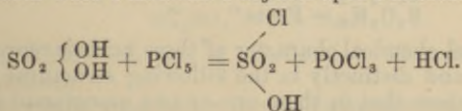


By further warming, these decompose into  $\text{SO}_3$ , and sulphates:  $\text{S}_2\text{O}_7\text{K}_2 = \text{SO}_4\text{K}_2 + \text{SO}_3$ ; hence these reactions may serve for the formation of  $\text{SO}_3$ .

**Sulphuric Acid Chlor-anhydride.** Under the name of halogen anhydrides we understand the derivatives resulting from the replacement of OH in hydroxides by halogens. Conversely, the chlor-anhydrides, by the action of water, pass into the corresponding acids:—



The ordinary method for the preparation of the chloranhydrides consists in permitting  $\text{PCl}_5$  to act on the acids. Sulphuric acid has two hydroxyl groups; therefore it can furnish two chloranhydrides. The first,  $\text{SO}_2 \left\{ \begin{array}{l} \text{Cl} \\ \text{OH} \end{array} \right.$ —sulphuryl hydroxy-chloride or chlorsulphonic acid—results when 1 molecule  $\text{PCl}_5$  acts upon 1 molecule  $\text{H}_2\text{SO}_4$ :—



The resulting  $\text{POCl}_3$  acts further upon 2 molecules  $\text{SO}_4\text{H}_2$ , with formation of phosphorous and chlorsulphonic acids.

It is formed, too, by the direct union of  $\text{SO}_3$  with  $\text{HCl}$ . It is most practically prepared by conducting chlorine gas through  $\text{SO}_4\text{H}_2$  (15 parts) and allowing  $\text{PCl}_3$  (7 parts) to gradually drop in. Or  $\text{HCl}$  gas is led into solid fuming sulphuric acid ( $\text{S}_2\text{O}_7\text{H}_2$ ), so long as absorption occurs, and then distilled (Otto).

Chlorsulphuric acid is a colorless, strongly fuming liquid, of specific gravity 1.776 at 18°, which boils at 152°. The salt  $\text{SO}_2 \begin{cases} \text{Cl} \\ \text{OK} \end{cases}$  results from the union of  $\text{SO}_3$  with  $\text{HCl}$ .

The *second chloranhydride*  $\text{SO}_2\text{Cl}_2$ , or sulphuryl-chloride\* forms when  $\text{PCl}_5$  acts upon  $\text{SO}_3$ ; by heating  $\text{SO}_3\text{HCl}$  to 180°:  $2\text{SO}_3\text{HCl} = \text{SO}_2\text{Cl}_2 + \text{SO}_4\text{H}_2$ ; and also by the direct union of  $\text{SO}_2$  with  $\text{Cl}_2$  in sunlight. A colorless, suffocating, strongly fuming liquid of specific gravity, 1.66 results. It boils at 77°. Water decomposes both these anhydrides into sulphuric and hydrochloric acids.

Thionyl chloride— $\text{SOCl}_2$ —(p. 179), may be regarded as a chloranhydride of sulphurous acid. The chloranhydride ( $\text{S}_2\text{O}_5\text{Cl}_2$ ) of disulphuric acid is known. It boils at 146°.

**Amid Derivatives of Sulphuric Acid.** When  $\text{NH}_3$  acts on  $\text{SO}_3$ , the compound  $\text{SO}_3\cdot 2\text{NH}_3$  arises, which is to be regarded as ammonium sulphamate  $-\text{SO}_2 \begin{cases} \text{NH}_2 \\ \text{O.NH}_4 \end{cases}$ . It is a white powder, which may be crystallized from water; the solution is not precipitated by barium salts. When ammonia acts upon  $\text{SO}_2 \begin{cases} \text{OH} \\ \text{Cl} \end{cases}$  the ammonium salt of disulphimid-acid  $\text{HN} \begin{cases} \text{SO}_2, \text{OH} \\ \text{SO}_2, \text{OH} \end{cases}$  forms; this is tribasic, as all three H atoms can be replaced by metals.

### POLYTHIONIC ACIDS.

By this name (from *θειον*, sulphur,) is understood the complex acids of sulphur, containing 2 or more atoms of the latter. The following are known:—

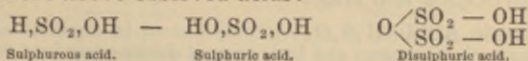
$\text{S}_2\text{O}_3\text{H}_2$	— Thiosulphuric acid.
$\text{S}_2\text{O}_6\text{H}_2$	— Dithionic Acid.
$\text{S}_3\text{O}_6\text{H}_2$	— Tri “ “
$\text{S}_4\text{O}_6\text{H}_2$	— Tetra “ “
$\text{S}_5\text{O}_6\text{H}_2$	— Penta “ “

The general chemical character of these acids is represented most simply and distinctly in the following structural formulas. We suppose that in them one or two monatomic groups,  $\text{SO}_3\text{H}$  or  $-\overset{\text{VI}}{\text{SO}_2}-\text{OH}$ , are contained, in which one affinity of sulphur is unsaturated. This is known as the *sulpho* group; it is also present in organic sulpho-acids, and corresponds to the acid forming carbon group,  $\text{COOH}$ , known as

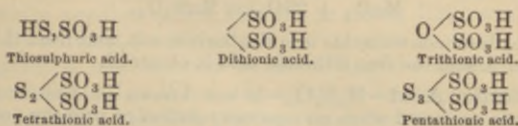
\* The group combined with 2OH in  $\text{H}_2\text{SO}_4$  is known as sulphuryl.



carboxyl. From this group, (written in another form,) are derived the above observed acids:—

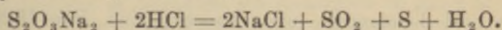


The following structural formulas express the polythionic acids:—

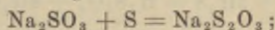


The last three acids may be viewed as derivatives of the hydrogen sulphides,  $\text{SH}_2$ ,  $\text{S}_2\text{H}_2$ , and  $\text{S}_3\text{H}_2$ , in which both H atoms are replaced by two monatomic sulpho groups. In thiosulphuric acid, only 1H-atom is replaced by *sulpho*; the dithionic acid, on the other hand, results by the direct union of two sulpho groups, with their free affinities.

**Thiosulphuric acid**,  $\text{H}_2\text{S}_2\text{O}_3 = \text{SO}_2 \begin{array}{l} \langle \text{OH} \\ \text{SH} \end{array}$ , generally known as *hyposulphurous acid*, can be considered sulphuric acid in which the oxygen of an hydroxyl group is replaced by sulphur. It is not known in a free condition, since as soon as it is freed from its salts by stronger acids, it decomposes instantaneously into  $\text{SO}_2$ , S and  $\text{H}_2\text{O}$ :—

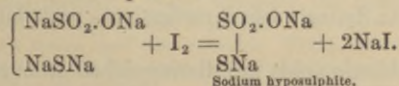


Its salts, called *hyposulphites*, are of practical importance (compare sodium hyposulphite). They form by the direct addition of sulphur to sulphites:—



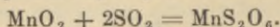
similar to the formation of sulphates by the addition of O to the sulphites.

Particularly interesting is the formation of thiosulphuric acid by the action of iodine upon a mixture of sodium sulphite and sodium sulphide:—



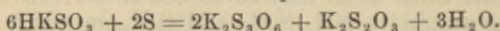
Conversely sodium hyposulphite is split up by sodium amalgam into  $\text{SO}_3\text{Na}_2$  and  $\text{Na}_2\text{S}$ .

**Dithionic Acid**— $\text{H}_2\text{S}_2\text{O}_6$ —is only known in aqueous solution. By concentration in vacuo and by heating it decomposes into sulphuric acid and sulphur dioxide. Its manganese salt results from the action of sulphur dioxide upon  $\text{MnO}_2$  suspended in water.

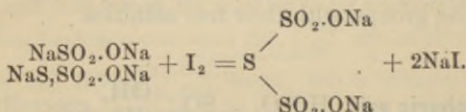


Barium hydrate converts this into the barium salt, and from this aided by sulphuric acid the free dithionic acid is obtained.

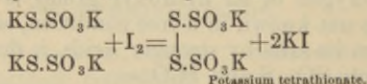
**Trithionic Acid**— $\text{H}_2\text{S}_3\text{O}_6$ —is not known in free condition. Its salts are produced when an aqueous solution of primary potassium sulphate is warmed with flowers of sulphur:—



Separated from its salts by other acids it decomposes into  $\text{H}_2\text{SO}_4$ ,  $\text{SO}_2$  and S. Of great interest is its production by the action of iodine upon a mixture of sodium sulphite and hyposulphite:—

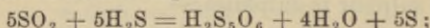


**Tetrathionic Acid**— $\text{H}_2\text{S}_4\text{O}_6$ . When iodine acts upon solutions of hyposulphite its salts are produced.

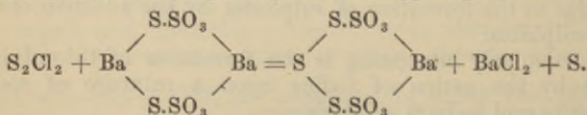


The free acid decomposes, upon concentration, into  $\text{H}_2\text{SO}_4$ ,  $\text{SO}_2$  and 2S.

**Pentathionic Acid**— $\text{H}_2\text{S}_5\text{O}_6$ —results when  $\text{H}_2\text{S}$  is conducted into an aqueous solution of sulphur dioxide:—



further, by the action of  $\text{S}_2\text{Cl}_2$  upon barium hyposulphite:—



According to Spring's late investigations, pentathionic acid does not exist.

The polythionic acids are distinguished from sulphuric acid by the solubility of their barium salts.

## 2. Oxygen Derivatives of Selenium and Tellurium.

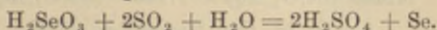
$\text{SeO}_2$   
Selenious dioxide.

$\text{SeO}_3\text{H}_2$   
Selenious acid.

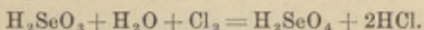
$\text{SeO}_3$   
Selenic trioxide.

$\text{SeO}_4\text{H}_2$   
Selenic acid.

**Selenium Dioxide**— $\text{SeO}_2$ —or selenious anhydride, is produced when selenium burns in the air or in oxygen, forming long white needles, which sublime at about  $320^\circ$  without fusing. In water it readily dissolves to selenious acid,  $\text{H}_2\text{SeO}_3$ . The latter is also formed by dissolving the metal in concentrated nitric acid. When the solution is evaporated it crystallizes in large, colorless prisms, which decompose, on heating, into the anhydride and water. Sulphurous oxide reduces selenious acid, with separation of free selenium:—



**Selenic Acid**— $\text{H}_2\text{SeO}_4$ —is obtained by conducting chlorine gas into an aqueous solution of selenious acid.



The solution may be concentrated until it attains a specific gravity of 2.96, when it becomes an oily liquid, similar to sulphuric acid, and containing 95 per cent.  $\text{H}_2\text{SeO}_4$ . If the solution be heated above  $280^\circ$ , the acid breaks up into  $\text{SeO}_2, \text{O}$  and  $\text{H}_2\text{O}$ . The anhydride of the acid is unknown.

The salts of selenic acid are known as *selenates*, those of selenious acid as *selenites*.

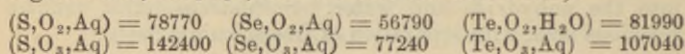
The derivatives of tellurium are analogous to those of selenium. The dioxide— $\text{TeO}_2$ —results from burning tellurium, and forms a white crystalline mass, fusing at a red heat and subliming. In water it is almost insoluble.

**Tellurous Acid**— $\text{H}_2\text{TeO}_3$ —is produced when the metal is dissolved in concentrated nitric acid. Water will precipitate it from such a solution as a white amorphous powder. On warming, it readily breaks up into  $\text{TeO}_2$  and water.

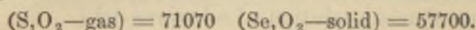
**Telluric Acid**— $\text{H}_2\text{TeO}_4$ . Upon fusing tellurium or its dioxide with saltpetre, potassium tellurate is formed, from which, by means of sulphuric acid, telluric acid is obtained. From aqueous solutions it crystallizes in large, colorless prisms, with 2 molecules of  $\text{H}_2\text{O}$  ( $\text{H}_2\text{TeO}_4 + 2\text{H}_2\text{O}$ ), which are expelled at  $100^\circ \text{C}$ ., and the acid becomes a white powder. Water dissolves the latter with difficulty and exhibits only a slightly acid reaction. Carefully heated, the acid breaks up into water and the trioxide  $\text{TeO}_3$ , which is a yellow mass insoluble in  $\text{H}_2\text{O}$ , and upon further application of heat decomposes into  $\text{TeO}_2$  and oxygen.



The affinity of the elements of the oxygen group for the halogens appears, the reverse of that of the halogens with hydrogen, to gradually increase with rise of atomic weight from oxygen to tellurium successively;  $\text{OCl}_2$  is very unstable and is formed with heat absorption,  $\text{SCl}_2$  and  $\text{SCl}_4$ , only exist at lower temperatures, while  $\text{SeCl}_4$ ,  $\text{TeCl}_2$  and  $\text{TeCl}_4$  even exist as gases. On the contrary, the thermal relations in the formation of the oxygen compounds indicate that in them the affinity of selenium is the least, as is the case with bromine in the halogen group (p. 176). This follows from the heat disengagement in the formation of the acids  $\text{RO}_3\text{H}_2$ , and also the higher acids,  $\text{RO}_4\text{H}_2$  (from the elements and water):—



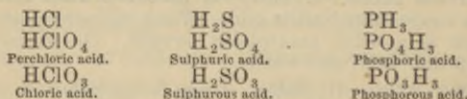
The same is seen in the formation of the anhydrous dioxides:—



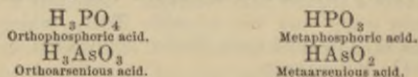
Of course in all these compounds the affinity of selenium to oxygen is the least, and in it the reduction of selenious by sulphurous acid, and the slight stability of selenic acid find explanation.

### 3. Oxygen Derivatives of the Elements of the Nitrogen Group.

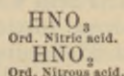
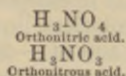
The halogens combine with one atom of hydrogen and also afford oxygen acids containing one atom of the former. The elements of the sulphur group contain two atoms of H in the hydrogen derivatives and oxygen acids. Corresponding to this the elements of the N group combining with 3 atoms of H, form acids which, too, contain 3 atoms.



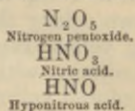
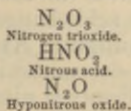
The acids containing three atoms of H, designated *normal* or *Ortho-Acids* (as  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{AsO}_4$ ,  $\text{H}_3\text{AsO}_3$ ) can yield monobasic acids by the removal of one molecule of water. Such derivatives, having one atom of H, are called *meta-acids*:—



These meta-acids of phosphorus and arsenic are less stable than the ortho-acids and pass into the latter by the absorption of water. The ortho-acids of N, on the other hand, are less stable and only exist in some salts. The ordinary acids and salts of N belong to the meta-series and contain one atom of H (or metal):

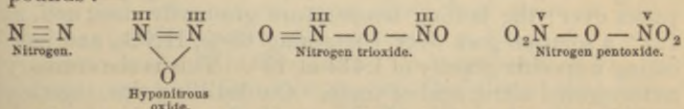


### 1. OXYGEN DERIVATIVES OF NITROGEN.

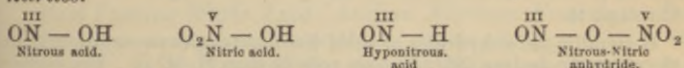


Besides these compounds there exist further: Nitrogen tetroxide ( $\text{N}_2\text{O}_4$ ), the mixed anhydride of nitrous and nitric acids, and two oxides, nitrogen dioxide ( $\text{NO}_2$ ) and nitrogen oxide ( $\text{NO}$ ), which do not yield acids.

The following formulas express the structure of these compounds:—

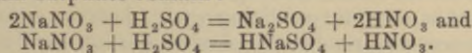


The salts of nitric acid are called *nitrates*; those of nitrous, *nitrites*.



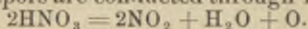
**Nitric Acid**— $\text{HNO}_3$ —This acid occurs in nature only in the form of salts,—potassium, sodium and calcium saltpetre (compare these)—which have resulted from the decay of nitrogenous organic substances in the presence of strong bases (the alkalis). Sometimes present in the air as ammonium salt. The free acid is formed in very slight quantity by continuously conducting the electric sparks through moist air.

To prepare nitric acid heat potassium or sodium nitrate with sulphuric acid, by which operation nitric acid will distill over and sodium sulphate remain:—



The process may be conducted in the distillation apparatus figured (page 44). The quantity, by weight, of sodium nitrate and sulphuric acid corresponding to the second equation must be employed, since, with less acid to complete the reaction, a higher temperature is requisite, and, in consequence, the formed nitric acid will be partially decomposed.

Pure anhydrous nitric acid is a colorless liquid of specific gravity 1.54 at 0°, fuming in the air and at -40°, solidifying to a crystalline mass. At medium temperatures it undergoes a partial decomposition (like H<sub>2</sub>SO<sub>4</sub>) into water, oxygen and nitrogen dioxide NO<sub>2</sub>, which dissolves in the acid, with a yellowish-brown color; the colorless acid changes upon standing, becoming yellow rapidly in sunlight. At 86° the acid commences boiling, with partial decomposition; the first portions are colored yellow by the dissolved nitrogen dioxide, while subsequently, some aqueous acid distills over. Nitric acid is completely decomposed into nitrogen dioxide, oxygen and water, when its vapors are conducted through red hot tubes:—



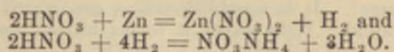
The acid mixes in all proportions with water. Upon distilling the dilute aqueous solution, at first only pure water passes over; the boiling temperature gradually rises, and, at 121°, a solution goes over, containing 68% HNO<sub>3</sub>, and indicating a specific gravity of 1.414 at 15°. This is the ordinary concentrated nitric acid of trade. On distilling this, together with 5 parts sulphuric acid, almost anhydrous acid is obtained, which is freed of contained NO<sub>2</sub>, by conducting a stream of air through it.

Generally, the anhydrides of acids distill at temperatures lower than the acids themselves (SO<sub>3</sub> is more volatile than H<sub>2</sub>SO<sub>4</sub>). The higher boiling point of the aqueous acid, in relation to the anhydrous, is probably explained by the fact that, in the solution, the hydrate, HNO<sub>3</sub> + H<sub>2</sub>O, *i. e.*, the normal nitric acid (NO<sub>4</sub>H<sub>3</sub>) = NO(OH)<sub>3</sub>, compare page 193, is present. The solution boiling at 121°, however, contains more water than corresponds to this hydrate (just as distilled sulphuric acid contains water), so that it can be regarded as a mixture of the trihydrate (NO(OH)<sub>3</sub>) and pentahydrate (N(OH)<sub>5</sub>).

Nitric acid is a very powerful acid, oxidizing or dissolving almost all metals (gold and platinum excepted). Nearly all the metalloids, like sulphur, phosphorus and carbon, are converted by it into their corresponding acids. Especially does the acid act as a strong oxidizing agent, destroys organic coloring substances and readily decolorizes a solution of indigo. In

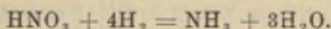


so doing, the nitric acid itself is deoxidized to the lower oxidation products of nitrogen (NO and NO<sub>2</sub>). Some substances even reduce the acid to ammonia. Thus, for example, in bringing zinc into nitric acid the metal is dissolved without the liberation of hydrogen. The latter at once, *in statu nascenti*, acts upon the excess of acid and reduces it to ammonia, which forms an ammonium salt with the acid; hence, in solution, we have ammonium nitrate in addition to the zinc nitrate:—



If the aqueous nitric acid be more dilute (containing more than 10 % NO<sub>3</sub>H), the same is reduced by zinc and other metals, not to ammonia, but to the nitrogen oxides N<sub>2</sub>O, NO, N<sub>2</sub>O<sub>3</sub> and N<sub>2</sub>O<sub>4</sub>.

The reduction of nitric acid to ammonia by nascent hydrogen occurs more easily in alkaline solution. On treating such a solution of nitrates with zinc or aluminum filings, all the N of the nitric acid is converted into ammonia:—



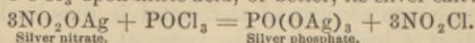
By the action of tin upon nitric acid there is formed hydroxylamin, together with ammonia (p. 121).

Nitric Acid—NO<sub>2</sub>OH—as also its hydrates NO(OH)<sub>3</sub> and N(OH)<sub>4</sub> (p. 194), form almost exclusively only salts with 1 aeq. of the metals of the form NO<sub>3</sub>Me; these are called nitrates, and are all soluble in water.

**Red Fuming Nitric Acid** (*Acidum Nitricum Fumans*) is the name given a nitric acid containing much nitrogen dioxide in solution. It is obtained by the distillation of 2 molecules HNO<sub>3</sub> with 1 molecule sulphuric acid (see above), or, simpler, by the distillation of commercial nitric acid with much sulphuric acid. Generally it has the specific gravity 1.5–1.52 and solidifies at — 40° to a crystalline mass. It possesses greater oxidizing power than the colorless nitric acid.

A mixture of 1 volume nitric acid and 3 volumes concentrated hydrochloric acid is known as *aqua regia*, as it is able to dissolve gold and platinum, which neither of the acids alone is capable of doing. The powerful oxidizing action of the mixture depends upon the presence of free chlorine and both chlorine derivatives (NO<sub>2</sub>Cl and NOCl), which may be considered the chloranhydrides of nitric and nitrous acids.

**Nitroxyl Chloride**— $\text{NO}_2\text{Cl}$ —the chloranhydride of nitric acid, results from the union of  $\text{NO}_2$  with chlorine, and also, according to the ordinary method of forming chloranhydrides (see p. 187), by the action of  $\text{PCl}_5$  or  $\text{POCl}_3$  upon nitric acid, or better, its silver salt:—



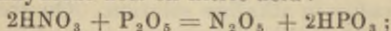
It is a yellowish liquid, boiling at  $+5^\circ$ . With water it breaks up into nitric and hydrochloric acids.

**Nitrosyl chloride**— $\text{NOCl}$ —is produced when hydrochloric acid acts upon nitric acid, and also by the union of  $\text{NO}$  (2 vols.) with chlorine (1 volume). It is a reddish-yellow gas which below  $0^\circ$  condenses to a liquid. With water it forms nitrous and hydrochloric acids:—

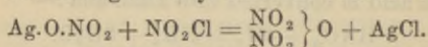


It may, therefore, be looked upon as the chloranhydride of nitrous acid— $\text{NO.OH}$ .

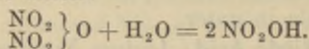
**Nitrogen Pentoxide**— $\text{N}_2\text{O}_5$ —nitric anhydride, arises when phosphoric anhydride acts on nitric acid:—



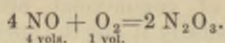
further by conducting nitroxyl chloride over silver nitrate:—



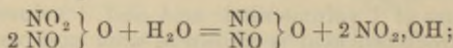
It forms colorless, rhombic prisms, fusing at  $30^\circ$  and boiling with partial decomposition at  $47^\circ$ . It is very unstable, decomposing readily into  $\text{N}_2\text{O}_4$  and  $\text{O}$  and sometimes exploding spontaneously. With water it yields  $\text{HNO}_3$  and evolves much heat by the union:—



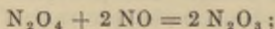
**Nitrogen Trioxide**,  $\text{N}_2\text{O}_3$ , nitrous anhydride, is formed by the direct union of nitrogen oxide (4 vols.) with oxygen (1 vol.) about  $-18^\circ$ :—



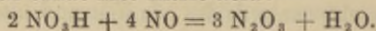
And by mixing liquid nitrogen tetroxide,  $\text{N}_2\text{O}_4$ , with a little water:—



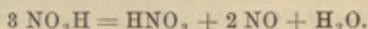
further by introduction of nitrogen oxide into liquid nitrogen tetroxide:—



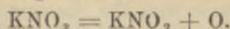
and of nitrogen oxide into nitric acid:—



It is a dark blue liquid, boiling at  $0^\circ$  with partial decomposition into  $\text{NO}$  and  $\text{NO}_2$ ; both gases combine again by cooling to  $\text{N}_2\text{O}_4$ . The trioxide mixes with a little cold water, forming, probably, nitrous acid ( $\text{HNO}_2$ ); by more water, and when warm, it is decomposed to nitric acid and nitrogen oxide gas:—



**Nitrous Acid**,  $\text{HNO}_2$ , is not known in a free state. Its salts are obtained by glowing the nitrates:—

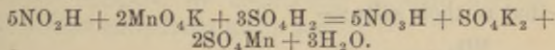


The withdrawal of oxygen is rendered easier if oxidizable metals, *e. g.*, lead, be added to the fusion.

On adding sulphuric acid to the nitrites, brown vapors are disengaged; these consist of  $\text{NO}_2$  and  $\text{NO}$ . We may suppose that the nitrous acid, at first liberated, is broken up into water, and the trioxide, which, as we have above seen, decomposes into  $\text{NO}_2$  and  $\text{NO}$  very readily. Similar reddish-brown vapors are obtained if nitric acid of specific gravity 1.3–1.35 be permitted to act upon starch or arsenious oxide ( $\text{As}_2\text{O}_3$ ). On cooling, these vapors condense to a liquid, which at medium temperatures is green, and probably consists of  $\text{N}_2\text{O}_4$  and  $\text{N}_2\text{O}_3$ . When the green liquid is warmed, vapors escape, which, on cooling, condense to a blue liquid, consisting principally of  $\text{N}_2\text{O}_4$ .

The nitrous acid separated out in the solution and its decomposition products— $\text{NO}_2$  and  $\text{NO}$ —are strong oxidizers, setting iodine free from the soluble iodides. In other cases, however, they exhibit a reducing action; thus *e. g.*, the acidified red solution of potassium permanganate is decolorized by the addition of nitrites.

In very dilute solution the action proceeds according to the following equation:—



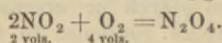
**Nitrogen Tetroxide**— $\text{N}_2\text{O}_4$ , or *nitrogen dioxide*  $\text{NO}_2$  (formerly called *hyponitric acid*) really constitutes two compounds. The former only exists at low temperatures; on warming, it suffers a gradual decomposition into the simpler molecules  $\text{NO}_2$  which upon cooling recombine to  $\text{N}_2\text{O}_4$ . We meet here the interest-



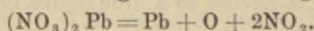
ing case of dissociation, occurring even at a medium temperature.  $N_2O_4$  is colorless, while  $NO_2$  is colored red-brown: it appears, therefore, with increasing temperature the color, corresponding to the increasing dissociation of the complex molecules  $N_2O_4$ , gradually becomes darker.

The theoretical vapor density of  $N_2O_4$  (molecular weight = 92) equals 46, while that of  $NO_2$  (46) = 23. At the boiling temperature ( $26^\circ$ ) of the liquid compound the experimental vapor density has been found = 38; from this, by calculation, we find that at this temperature 20 per cent. of the molecules  $N_2O_4$  decompose into the molecules  $NO_2$ . Hence we conclude that the dissociation of the compound  $N_2O_4$  commences already in the liquid state, which is confirmed by the yellow coloration appearing at  $0^\circ$ . Sulphuric acid, as we saw (p. 184), exhibits a similar dissociation in liquid condition. With rising temperature the density of the vapor steadily diminishes, becomes constant finally at  $150^\circ$  and equals 23. Then all the molecules ( $N_2O_4$ ) are decomposed into the simpler molecules  $NO_2$ ; at the same time, at this temperature the dark coloration of the vapors attains its maximum.

Nitrogen tetroxide is formed by the union of two volumes of nitrogen oxide with one volume of oxygen:—

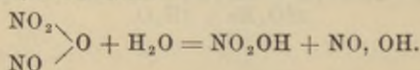


We can get it more conveniently by heating dry lead nitrate, which decomposes according to the following equation:—



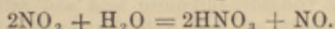
The escaping vapors condense in the cooled receiver to liquid  $N_2O_4$ .

The varying molecular composition of nitrogen tetroxide at lower and higher temperatures manifests itself also in its chemical reaction. We saw that by the action of a little cold water, the tetroxide is decomposed into nitrogen trioxide and nitric acid (p. 197). With excess of cold water, and also with an aqueous solution of alkalies, it forms nitric and nitrous acids—that is, their salts:—



Both reactions plainly indicate that the liquid tetroxide represents the *mixed oxide* of nitric and nitrous acid; similarly, the compound  $Cl_2O_4$  constitutes the mixed oxide of chloric and chlorous acid (p. 171).

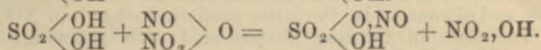
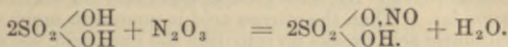
Warm water converts the tetroxide into dioxide  $\text{NO}_2$ , which in turn yields nitric acid and nitrogen oxide—



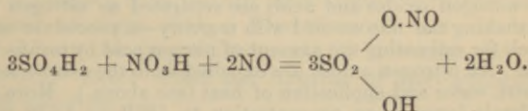
The tetroxide and dioxide have strong oxidizing properties; many substances burn in their vapors; iodine is set free from the soluble metallic iodides by them.

**Nitrosylsulphuric Acid**,  $\text{SO}_2\text{NH} = \text{SO}_2 \begin{cases} \text{O, NO.} \\ \text{OH.} \end{cases}$  This com-

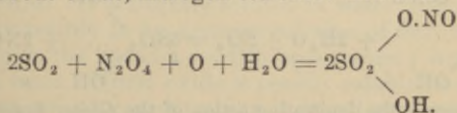
ound, also termed nitrosulphonic acid, which, as intermediate product in the technical manufacture of sulphuric (see p. 182), is important, and also for the analytical determination of the nitrogen oxides, is produced by conducting nitrogen trioxide and tetroxide into concentrated sulphuric acid:—



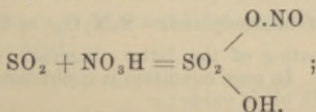
Nitrogen monoxide— $\text{NO}$ —is not absorbed by pure sulphuric acid, but will be if the same contain nitric acid:—



Further, the nitrosylsulphuric acid results from the action of sulphurous oxide, nitrogen tetroxide and little water:—

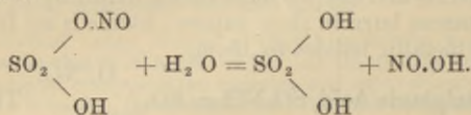


Most easily obtained by conducting sulphur dioxide into strongly cooled anhydrous nitric acid:—



there results a thick magma, which may be dried upon porous earthen plates under the desiccator.

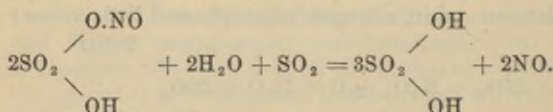
Nitrosylsulphuric acid forms a leafy or granular crystalline, colorless mass (chamber acid crystals p. 184), which fuse about  $73^\circ$  and decompose into the trioxide, sulphuric acid and nitrogen trioxide. In moist air it deliquesces, and with water breaks up into sulphuric and nitrous acids:—



and the latter further partly into nitric acid and nitrogen oxide.

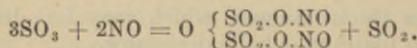
In concentrated sulphuric acid nitrosylsulphuric acid dissolves without any change; the solution called *nitroso acid*, produced also in the sulphuric acid manufacture in the Gay-Lussac tower, is very stable and may be distilled without decomposition. When diluted with water it remains at first unaltered, until the specific gravity of the solution reaches 1.55–1.50 ( $51\text{--}48^\circ\text{B}$ ); then escape, especially on warming, all the nitrogen oxides. When the nitroso acid is poured in much water, the nitrososulphuric acid breaks up into (like the pure acid, see above) sulphuric and nitrous acids; the latter partially further into  $\text{NO}_3\text{H}$  and  $2\text{NO}$ . Therefore in titrating nitrous acid with permanganate of potassium ( $\text{MnO}_4\text{K}$ . See p. 197) we only get the results corresponding to nitrososulphuric acid, if the latter be poured into the permanganate (Lunge.)

All the nitrogen oxides and acids are separated as nitrogen oxide ( $\text{NO}$ ) by shaking the nitroso-acid with mercury—a procedure serving equally well for estimating the amount of nitroso acid by means of the nitrometer. All nitrogen oxides are expelled from the *nitroso acid* by dilution with water and application of heat (see above.) More easily and completely (even upon concentration to  $58^\circ\text{B} = 1.679$  specific gravity) occurs the action of sulphur dioxide:—



Upon this depends the denitrating action of the *Glover tower*—see p. 182.

The anhydride of nitrosulphonic— $\text{S}_2\text{N}_2\text{O}_9 = \text{O} \left\{ \begin{array}{l} \text{SO}_2\cdot\text{O.NO} \\ \text{SO}_2\cdot\text{O.NO} \end{array} \right.$  is produced in the heating of the latter (together with  $\text{SO}_4\text{H}_2$  and  $\text{N}_2\text{O}_3$ —see p. 199). In pure condition it is obtained by saturation of sulphur trioxide with nitric oxide:—

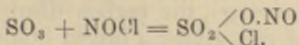




It is a crystalline, colorless mass, fusing at  $217^{\circ}$  and boiling without decomposition about  $360^{\circ}$ . Much water decomposes it, the same as nitrosylsulphuric acid.

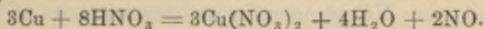
The chloranhydride of nitrosulphonic acid,  $\text{SNO}_4\text{Cl} = \text{SO} \begin{matrix} \text{O.NO} \\ \text{Cl} \end{matrix}$ ,

is formed by the union of sulphur trioxide with nitrosylchloride:—



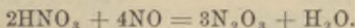
White leaflets, decomposed by heat into its components, and with water breaks up into sulphuric, hydrochloric and nitrous acids.

**Nitric Oxide**—NO. When different metals are dissolved in somewhat diluted nitric acid this oxide is formed, inasmuch as the hydrogen *in statu nascendi* at first liberated reduces another portion of the acid. It is most conveniently obtained by pouring dilute nitric acid (specific gravity 1.2) upon copper filings:—

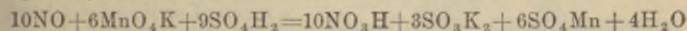


The action begins in the cold. A colorless gas escapes, which, however, immediately forms brown vapors when it comes in contact with the air, as it unites with the oxygen of the latter to form  $\text{NO}_2$ . Therefore all the air must be expelled from the generating vessel by NO and the gas collected over water when the interior of the apparatus has become colorless.

Nitric oxide is a colorless gas, of specific gravity 15 (H = 1) or 1.039 (air = 1), which can be condensed by cold and pressure. It is slightly soluble in water, dissolving, however, very readily in an aqueous solution of ferrous salts, and imparting to the liquid a reddish-brown color; heat expels it from the same. Nitric oxide is readily soluble in nitric acid. According to its concentration it is colored brown, yellow, green and blue, as nitrogen trioxide is formed:—



Potassium permanganate oxidizes it, like nitrous acid (p. 197), to nitric acid:—

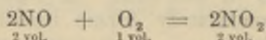


As nitric oxide contains 57% oxygen, it is capable of sustaining the combustion of some substances, but to bring about the previous separation of oxygen from the nitrogen re-

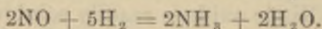
quires energetic reaction. Hence, phosphorus continues to burn in this gas, while a sulphur flame, developing only a slight heat, is extinguished; glowing charcoal does the same, while an energetically burning splinter will continue to burn in it. On shaking a few drops of readily volatile carbon disulphide into a cylinder filled with NO, and bringing a flame to the mouth of the vessel, the carbon disulphide vapors will quietly burn in the gas, giving a bright luminous flame, emitting strong actinic rays; in this combustion, the C and S of the CS<sub>2</sub> unite with the oxygen of the nitric oxide.

On determining the quantity of heat disengaged in the combustion of phosphorus, carbon or other substances in NO gas, it will be discovered that the same is greater (about 21600 calories), than that which is developed by the combustion of these bodies in oxygen. This can only be explained upon the theory that less heat is necessary for the separation of NO into N and O, than for the separation of the molecules of combined oxygen atoms—an additional proof that the molecules of free oxygen (as of other elements) consist of atoms.

With oxygen, NO at once forms brown vapors of nitrogen dioxide:—



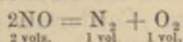
With less oxygen nitrogen trioxide is produced, (p. 196). Just as with oxygen so with chlorine, NO combines to nitrosylchloride NOCl (p. 196), and the compound, NOCl<sub>2</sub>, which is, as yet, little investigated; with bromine, it unites to form NOBr<sub>3</sub>. At a red heat NO becomes NO<sub>2</sub> and N. With hydrogen and moderate heat, it forms water and nitrogen: NO + H<sub>2</sub> = N + H<sub>2</sub>O; a mixture of both gases burns with a white flame. On conducting NO and H together over platinum sponge, water and ammonia are produced:—



The volumetric analysis of nitric oxide gas may be easily executed as follows: Fill a bent glass tube (Fig. 85) over mercury with NO gas; introduce in the same a piece of sodium and heat the latter with a lamp. The sodium combines with the oxygen, and free nitro-

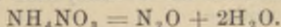


gen separates; the volume of the latter always equals half the volume of the employed nitric oxide gas, which would follow from the formula NO:—

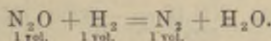


The molecular formula of the oxide is NO = 30, as its vapor density is 15 (H = 1). NO, NO<sub>2</sub> and chlorine dioxide, ClO<sub>2</sub> (p. 171), present an apparent anomaly as regards the common laws regulating the valence of the elements. Ordinarily, the quantivalence changes from an odd number to an odd, and from an even to an even number (p. 165). Nitrogen usually is pentatomic and triatomic; in the cited compounds it appears di- and tetra-tomic. This abnormal behavior of N finds a partial explanation in the position it occupies in the periodic system of the elements.

**Nitrous Oxide**—*Hyponitrous Oxide*—N<sub>2</sub>O—is formed when zinc or tin acts upon dilute nitric acid. It may be best obtained by heating ammonium nitrate, which at about 170° breaks up directly into water and nitrous oxide:—



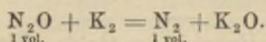
This compound is a colorless gas, of sweetish taste and slight odor. Its density is 22 (H = 1), or 1.52 (air = 1), corresponding to the molecular formula N<sub>2</sub>O = 44. In cold water it is tolerably soluble (1 volume H<sub>2</sub>O dissolves at 0° 1.305 volumes N<sub>2</sub>O); therefore it must be collected over water or mercury; cooled to 88°, or under a pressure of 30 atmospheres at 0°, it condenses to a colorless liquid of specific gravity 0.937. By evaporation of the liquid in the air its temperature diminishes to —100°, and solidifies to a crystalline, snowy mass. If the aqueous nitrous oxide be evaporated under an air pump its temperature falls to —140°; the lowest which has been attained. Although this oxide contains less oxygen than nitric oxide, it supports the combustion of many bodies more readily than the latter, because more easily decomposed into oxygen and nitrogen. A glimmering chip inflames in it, as in oxygen; phosphorus burns with a bright luminous flame, while one of sulphur is extinguished. The liquid nitrous oxide behaves like the gas; a glowing coal thrown on its surface burns with a bright light. A mixture of equal volumes of nitrous oxide and hydrogen explodes like detonating gas, only less violently:—



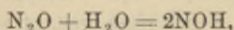


From oxygen, to which it is very similar, nitrous oxide may be distinguished by its not affording brown vapors with nitric oxide, as is the case with the former. It is not capable of combining with oxygen. Conducted through a glowing tube it is converted into nitrogen and oxygen. Inhaled in slight quantity it has an exhilarating effect, therefore termed *laughing gas*.

Its volume composition may be determined in the same manner as with nitric oxide, viz.: by heating a definite volume of the gas with potassium. Then we learn that from a volume of  $N_2O$  an equal volume of nitrogen will be separated—corresponding to the molecular formula:—



**Hyponitrous Acid**— $NOH = O = \overset{III}{NH}$ . As nitrous and nitric acids correspond to nitrogen trioxide and pentoxide, so may hyponitrous oxide be regarded as the anhydride of the recently discovered hyponitrous acid:—

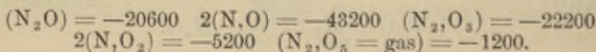


although the latter is not formed by the hydration of  $N_2O$ . On the contrary, hyponitrous acid, by removal of water by sulphuric acid, yields nitrous oxide.

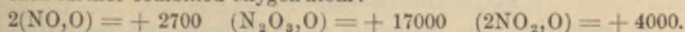
The acid is got in aqueous solution by decomposition of its silver salt  $AgNO$  by means of hydrochloric acid. Dissolved in water it is colorless, reacts strongly acid and is tolerable stable. It liberates iodine from potassium iodide and reduces a permanganate solution. With silver nitrate the silver salt is again precipitated.

The silver salt  $AgNO$  is obtained by action of sodium amalgam upon a solution of potassium nitrite, neutralization with acetic acid and precipitation by silver nitrate. It is a light yellow, amorphous powder, not altered by the light. Heated above  $110^\circ$  it decomposes with explosion. Soluble in dilute sulphuric acid, and upon neutralization with ammonium hydrate it is reprecipitated. By concentrated sulphuric acid it, as well as the solution of the free acid, is decomposed, with liberation of  $N_2O$ .

In their thermo-chemical department is found the explanation of the varying department of the oxygen compounds of nitrogen, their little stability, and oxidizing properties, as well as their mode of formation. All nitrogen oxides are endothermic compounds, *i. e.*, they are produced from their elements with heat absorption (compare p. 176) corresponding to the symbols;—

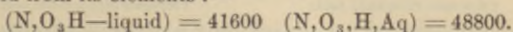


Proceeding from nitric oxide (NO), we observe from the above numbers that the formation of the higher oxides from it occurs with heat disengagement and, indeed, the latter becomes regularly less for each further combined oxygen atom:—



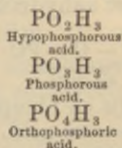
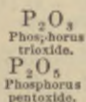
A similar decrease in heat disengagement, according to multiple proportion, is also observed in other compounds. The great absorption of heat in nitrous oxide ( $\text{N}_2\text{O} = 21000$ ), with which also its difficult condensability agrees, is to be interpreted by the fact that the affinity of N for O is weaker than that of the oxygen atoms in the molecule of oxygen (compare p. 202).

Heat disengagement, on the contrary, occurs in the production of nitric acid from its elements:—

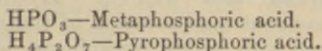


This explains the relative stability of nitric acid.

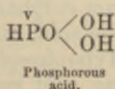
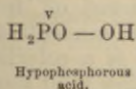
## 2. OXYGEN COMPOUNDS OF PHOSPHORUS.



From orthophosphoric acid the two following anhydride acids (compare p. 192) are derived:—

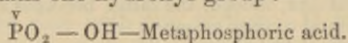


The structure of these compounds is expressed by the following formulas:—

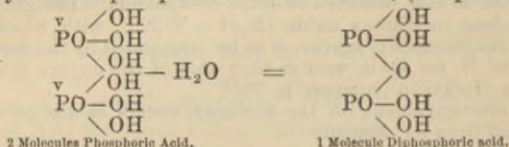


In hypophosphorous acid two atoms of hydrogen are directly combined with pentatomic phosphorus, while the third atom forms an hydroxyl group with oxygen. The former, by the action of bases, is easily replaced, and, therefore, hypophosphorous acid is a *monobasic acid*. Phosphorous acid contains one atom of H united to P and two hydroxyl groups; therefore, it is *dibasic*. Finally, phosphoric acid has three hydroxyl groups, and forms three series of salts. By the elimination of one molecule of  $\text{H}_2\text{O}$  from  $\text{H}_3\text{PO}_4$ , metaphosphoric acid re-

sults—an anhydride, which, at the same time, is a monobasic acid, as it contains one hydroxyl group:—

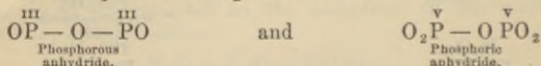


On removing one molecule of  $\text{H}_2\text{O}$  from two molecules  $\text{H}_3\text{PO}_4$ , pyro- or diphosphoric acid is formed, (see p. 186):—



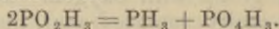
Pyrophosphoric acid contains four hydroxyl groups, hence is tetrabasic.

Finally, if, from two molecules of phosphorous acid, or phosphoric acid, all the H atoms be removed, in the form of water, two perfect anhydrides are produced:—



The salts of phosphoric acid are termed *phosphates*; those of phosphorous acid, *phosphites*, and of hypophosphorous acid, *hypophosphites*.

**Hypophosphorous Acid— $\text{H}_3\text{PO}_2$ .** Hydrogen phosphide escapes when a concentrated solution of sodium or potassium hydrate is warmed with yellow phosphorus, leaving behind in solution, a salt of hypo-phosphorous acid. The free acid may be separated from the barium salt by means of sulphuric acid; the insoluble barium sulphate being filtered off from the aqueous solution of the acid, and the latter concentrated under the air-pump. Hypophosphorous acid is a colorless, thick liquid, with a strong acid reaction. Below  $0^\circ$  it sometimes solidifies to large white leaflets, which fuse at  $+17.4^\circ$ . Heat converts it, with much foaming, into hydrogen phosphide and phosphoric acid:—

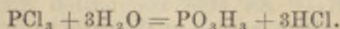


It readily absorbs oxygen, becoming phosphoric acid, hence acts as a powerful reducing agent. It reduces sulphuric acid to sulphur dioxide, and even to sulphur. From their solutions it precipitates many of the metals; from copper sulphate it separates the hydride— $\text{Cu}_2\text{H}_2$ .

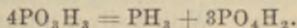


The acid is monobasic. Its salts are easily soluble in water and absorb oxygen from the air, thus becoming phosphates. Heated in dry condition they set free the hydride of P and are converted into pyrophosphates; some also yield metallic phosphides.

**Phosphorous Acid**— $\text{H}_3\text{PO}_3$ —is formed at the same time with phosphoric acid in the slow oxidation of P in the air. The decomposition of the trichloride by water gives it more conveniently:—



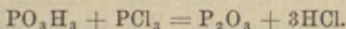
By evaporation of this solution under the air pump the phosphorous acid becomes crystalline. The crystals are readily soluble in water and deliquesce in the air. It fuses at  $70^\circ$  and decomposes on further heating into  $\text{PH}_3$  and phosphoric acid:—



In the air the acid absorbs oxygen and changes to phosphoric acid. Hence it reduces strongly and precipitates the free metals from many of their solutions. In presence of water the halogens oxidize it to phosphoric acid. It is a dibasic acid, forming two series of salts, in which 1 and 2 atoms\* of H are replaced by metals.

In the air the phosphites do not oxidize, excepting by means of oxidizing agents. When heated they generally decompose into hydrogen and pyrophosphates.

**Phosphorus Trioxide**— $\text{P}_2\text{O}_3$ —*Phosphorous anhydride*, results from passing a slow, dry air current over gently heated phosphorus; further, by the action of the trichloride upon phosphorous acid:—



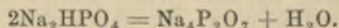
It forms white, voluminous flocks, which readily sublime and possess a garlic-like odor. Water dissolves the oxide, forming phosphorous acid. From the air it attracts oxygen and moisture very energetically, yielding phosphoric acid.

\*Therefore, the structural formula  $\text{HPO}(\text{OH})_2$  is assigned to this acid. There appears to exist another phosphorous acid, at least in compounds, to which the formula  $\text{P}(\text{OH})_3$  belongs.

**Phosphoric Acid**— $\text{PO}_4\text{H}_3$ , or *Orthophosphoric acid*, is formed when the pentoxide is dissolved in hot water, and by the decomposition of the penta- or oxy-chloride ( $\text{POCl}_3$ ) by water (see p. 130). It may be obtained by decomposing bone ash ( $\text{PO}_4$ )<sub>2</sub>Ca<sub>3</sub> with sulphuric acid, or, better, by oxidizing yellow phosphorus with nitric acid. The aqueous solution is evaporated to dryness in a pewter dish. The anhydrous acid consists of colorless, hard, prismatic crystals, which in the air deliquesce to a thick, acid liquid. Phosphoric acid is tribasic, forming three series of salts called *acid* ( $\text{PO}_4\text{H}_2\text{K}$ ), *neutral* ( $\text{PO}_4\text{HK}_2$ ) and *basic* ( $\text{PO}_4\text{K}_3$ ). As this designation does not entirely correspond with the behavior of the salts to litmus, it is more rational to term them *primary*, *secondary* and *tertiary*; or to speak of them according to the number of hydrogen atoms replaced by metals, as *e. g.*, monopotassium phosphate ( $\text{H}_2\text{KPO}_4$ ), dipotassium ( $\text{K}_2\text{HPO}_4$ ) and tripotassium ( $\text{K}_3\text{PO}_4$ ) phosphate.

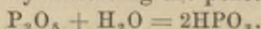
The tertiary phosphates, excepting the salts of the alkalis, are insoluble in water. With a silver nitrate ( $\text{AgNO}_3$ ) solution soluble phosphates give a *yellow* precipitate of tri-silver phosphate  $\text{PO}_4\text{Ag}_3$ .

**Pyrophosphoric Acid**— $\text{H}_4\text{P}_2\text{O}_7$ —(structure p. 206) is formed by the continuous heating of orthophosphoric acid to 200–300°, until a portion of it in ammonium hydrate does not yield a yellow but pure white precipitate with silver nitrate. The sodium salt is easily obtained by heating di-sodium phosphate:—



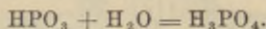
The acid presents a white crystalline appearance, and is readily soluble in water. In solution at ordinary temperatures it slowly, by warming rapidly, takes up water, and like all anhydrides, passes into the corresponding acid—orthophosphoric acid. It is tetrabasic. Its salts are very stable and are not altered by boiling with water; warmed with acids they become salts of the ortho-acid. The soluble salts give a *white* precipitate,  $\text{Ag}_4\text{P}_2\text{O}_7$ , with silver nitrate.

**Metaphosphoric Acid**— $\text{HPO}_3$  or  $\text{PO}_2\text{OH}$ —results from heating the ortho- or pyro- acid to 400°. It can be more conveniently obtained by dissolving the pentoxide in cold water:

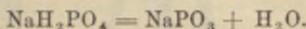


A glassy, transparent mass (*Acidum phosphoricum glaciale*) which fuses on heating and volatilizes at higher temperature

without suffering any change. It deliquesces in the air and dissolves with ease in water. (The commercial glassy phosphoric acid contains sodium and magnesium phosphate and dissolves with difficulty in water.) The solution coagulates albumen; this is a characteristic method of distinguishing the meta- from the ortho- and pyro- acids. In aqueous solution the acid changes gradually, by boiling rapidly, into the ortho- acid:—



It is a monobasic acid. Its salts, the metaphosphates, are readily obtained by the ignition of the primary salts of the ortho- acid:—



Boiling the aqueous solutions of these salts converts them into the ortho-primary salts. With silver nitrate the soluble *metaphosphates* give a white precipitate,  $\text{AgPO}_3$ .

In addition to the ordinary salts of metaphosphoric acid, various modifications of the same exist; these are derived from the polymeric meta-acids,  $\text{H}_2\text{P}_2\text{O}_6$ ,  $\text{H}_3\text{P}_3\text{O}_9$ ,  $\text{H}_4\text{P}_4\text{O}_{12}$ , etc. These acids arise from the corresponding polyphosphoric acids, which are formed by the union of  $n$  molecules of the ortho acid, with the separation of  $n - 1$  molecules of water (p. 186), just as the meta acid is formed from the ortho. Boiling their solutions converts all the above into primary orthophosphates.

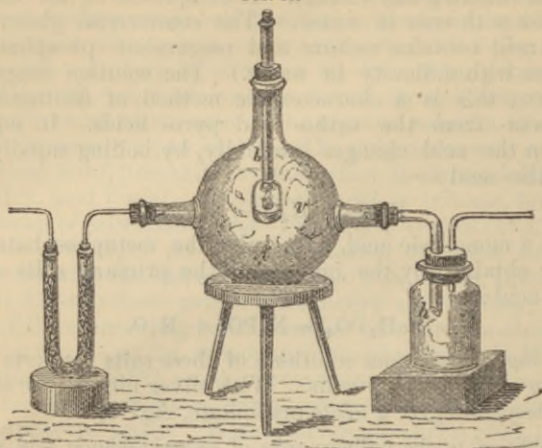
**Phosphorus Pentoxide**— $\text{P}_2\text{O}_5$  or *Phosphoric anhydride*, is formed by burning phosphorus in a current of oxygen or dry air. The following procedure serves for the preparation of it (Fig. 86):—

In the glass balloon A a piece of P placed in an iron dish attached to *ab* is burned. The necessary amount of air is drawn through the vessel by means of an aspirator; to dry it perfectly it passes first through the bent tube containing pieces of pumice stone moistened with sulphuric acid. After the phosphorus has been consumed, fresh pieces of it are introduced into the little dish through *ab*, and the upper end of the tube closed with a cork. The  $\text{P}_2\text{O}_5$  formed collects partly in A and partly in the receiver.

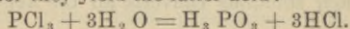
Phosphorus pentoxide forms a white, voluminous, flocculent mass, which is fixed. It attracts moisture energetically and deliquesces in the air. With hissing it dissolves in cold water to metaphosphoric acid. Owing to its great affinity for water it serves as an agent for drying gases, and also for the withdrawal of water from many substances.



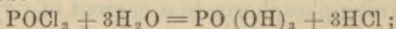
FIG. 86.



**Chlor-Anhydrides of the Acids of Phosphorus.** The halogen derivatives of P considered on page 129 may be viewed as the halogen anhydrides of phosphorous and phosphoric acids (p. 187). The compounds  $\text{PCl}_3$ ,  $\text{PBr}_3$  and  $\text{PI}_3$  are derived from phosphorous acid, because with water they yield the latter acid:—

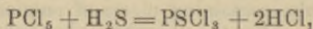


The compounds  $\text{POCl}_3$ ,  $\text{POBr}_3$  are the halogen anhydrides of phosphoric acid:—



while  $\text{PCl}_5$  and  $\text{PBr}_5$  correspond to the normal hydroxide  $\text{P}(\text{OH})_5$ , which has not been obtained in a free condition.

Analogous to the oxychloride— $\text{POCl}_3$ —is the compound  $\text{PSCl}_3$ . It is obtained by the action of  $\text{PCl}_5$  upon hydrogen sulphide and some metallic sulphides:—



a reaction very similar to that occurring in the formation of phosphorus oxychloride. *Phosphorus sulphochloride*— $\text{PSCl}_3$ —is a colorless liquid, fuming in the air and boiling at  $124^\circ$ . Water decomposes it into phosphoric and hydrochloric acids and hydrogen sulphide.

### COMPOUNDS OF PHOSPHORUS WITH SULPHUR.

With sulphur phosphorus forms a number of compounds which are obtained by direct fusion of P with S. As the union of ordinary P with S occurs usually with violent explo-

sion, to produce these compounds red phosphorus should be employed.

The compounds  $P_2S_3$  and  $P_2S_5$ , analogously constituted to  $P_2O_3$  and  $P_2O_5$ , are solid crystalline substances, melting at higher temperatures and subliming without decomposition. Water changes them to hydrogen sulphide and the corresponding acids, phosphorous and phosphoric. They combine with metallic sulphides to compounds (*e. g.*,  $PS_4K_3$ ) which are analogously constituted to the salts of phosphoric acid (see sulpho-salts of arsenic).

At ordinary temperatures,  $P_2S$  and  $P_4S$  are liquids, which inflame readily in the air.

Besides the preceding, other phosphorus derivatives containing N exist. These have been little studied and, at present, offer little interest. Such compounds are  $PN_2H$  (phospham),  $PNO$ ,  $PNCl_2$ . On allowing ammonia to act upon  $POCl_3$ , there arise, by replacement of Cl by the group  $NH_2$  (amido) the so-called amid derivatives:  $POCl_2NH_2$ ,  $POCl(NH_2)_2$  and  $PO(NH_2)_3$ .

### 3. OXYGEN DERIVATIVES OF ARSENIC.

$As_2O_3$   
Arsenic trioxide.

$AsO_3H_3$   
Arsenious acid.

$As_2O_5$   
Arsenic pentoxide.

$AsO_4H_3$   
Arsenic acid.

**Arsenic Trioxide**,  $As_2O_3$ , or *Arsenious anhydride*, occurs in nature as arsenic "bloom." It is produced by the burning of arsenic in oxygen or in the air, and by the oxidation of the metal with dilute nitric acid. On a large scale it is obtained metallurgically, as a bye-product in the roasting of ores containing arsenic. The trioxide which is thus formed volatilizes and is collected in walled chambers, in which it condenses in the form of a white powder (white arsenic, poison flour). To render it pure, it is again sublimed in iron cylinders, and obtained in form of a transparent, amorphous, glassy mass (arsenic glass), the specific gravity of which equals 3.69. Upon preservation, this variety gradually becomes non-transparent and porcelanous, acquires a crystalline structure, and its specific gravity increases to 3.74. Upon dissolving this oxide in hot hydrochloric acid, it crystallizes on cooling, in shining, regular octahedra. At the same time, the interesting phenomenon is observed, that the solution of the glassy variety upon crystallizing phosphoresces strongly in the dark, while

the porcelainous does not exhibit this property. Arsenic trioxide crystallizes in similar forms of the regular system, when its vapors are rapidly cooled, but upon cooling slowly, it assumes the shape of rhombic prisms; therefore, it is dimorphous. Heated in the air, it sublimes above  $218^{\circ}$ , without fusing; by higher pressure, however (in sealed tubes), it melts to a liquid which, upon solidifying, is glassy.

The vapors of  $As_2O_3$  have the vapor density 198 ( $H = 1$ ). Corresponding to formula  $As_2O_3$  ( $= 198$ ) the vapor density should be  $\frac{198}{2} = 99$ . From the experimentally determined vapor density, which is doubly as great, it follows that the gaseous molecules of the trioxide possess the double formula  $As_4O_6$ . Before we noticed that the molecule of free arsenic also consists of four atoms ( $As_4$ ); in arsenic trioxide this complex arsenic group, consequently, is retained; while in arsine ( $AsH_3$ ), and arsenious chloride ( $AsCl_3$ ) the molecules contain but 1 atom of arsenic.

The trioxide dissolves with difficulty in water; the solution possesses a sweetish, unpleasant, metallic taste, exhibits but feeble acid reaction and is extremely poisonous. Very soluble in acids and forms salts, probably, with them; at least, on boiling a solution of  $As_2O_3$  in strong hydrochloric acid arsenious chloride,  $AsCl_3$ , volatilizes. From this and its feeble acid nature we perceive an indication of the basic character of the trioxide corresponding to the already partially metallic nature of arsenic (see p. 139).

Nascent hydrogen converts the trioxide into arsine ( $AsH_3$ ); heated with charcoal it is reduced to the metallic state. Upon heating  $As_2O_3$  in a narrow glass tube with C, the reduced arsenic deposits as a metallic mirror on the sides. Oxidizing agents convert it into arsenic acid.

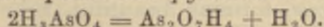
**Arsenious Acid**— $H_3AsO_3$ —corresponding to  $As_2O_3$ , is not known in a free condition. It probably exists in the aqueous solution, but upon evaporation the anhydride separates out. In its salts (*arsenites*) it is tribasic and affords mostly tertiary derivatives:  $Ag_3AsO_3$ ,  $Mg_3(AsO_3)_2$ . The alkali salts, soluble in water, absorb oxygen from the air and serve as powerful reducing agents, they themselves becoming arsenates.

Other salts derived from the meta-arsenious acid,  $HAsO_2$ , also exist.

**Arsenic Acid**— $H_3AsO_4$ —is obtained by the oxidation of arsenic or its trioxide with concentrated nitric acid or by means of chlorine. Upon evaporating the solution rhombic



crystals of the formula  $H_3AsO_4 + \frac{1}{2}H_2O$  separate out; these deliquesce on exposure. They melt at  $100^\circ$ , lose their water of crystallization and yield orthoarsenic acid  $H_3AsO_4$ , which heated to  $140-180^\circ$  passes into *pyroarsenic acid*— $H_4As_2O_7$ :—



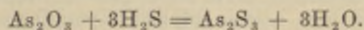
At  $200^\circ$  this again loses water and becomes *Meta-arsenic acid*— $HAsO_3$ . With water the last two acids become ortho again; hence the latter is perfectly analogous to phosphoric acid.

At a red heat the meta-arsenic acid loses all its water and becomes *Arsenic Pentoxide*— $As_2O_5$ , a white, glassy mass. Very strong ignition breaks this up into  $As_2O_3$  and  $O_2$ ; in contact with water it gradually changes to arsenic acid.

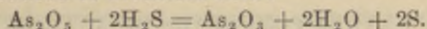
Orthoarsenic acid is readily soluble, and is a strong tribasic acid. Its salts—the arsenates—are very similar to the phosphates and are isomorphous with them. With the soluble salts silver nitrate gives a reddish-brown precipitate of trisilver-arsenate,  $Ag_3AsO_4$ ,

#### COMPOUNDS OF ARSENIC WITH SULPHUR.

Like phosphorus, arsenic, upon fusion with sulphur, yields several compounds. In these derivatives is shown the metallic nature of arsenic, because they, according to the common method of forming the metallic sulphides, can be obtained by the action of hydrogen sulphide upon the oxygen derivatives of arsenic:—



**Arsenic Trisulphide**— $As_2S_3$ —is precipitated from solutions of arsenious acid or its salts by hydrogen sulphide, as a lemon-yellow amorphous powder. Also from solutions of arsenic acid we get the trisulphide (at same time mixed with S), as it is at first reduced to arsenious acid:—

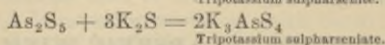
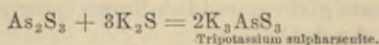


This compound is readily prepared by fusing  $As_2O_3$  with sulphur. In nature it occurs as *auripigment*, in the form of a brilliant, leafy, crystalline mass of gold-yellow color, of specific gravity 3.4. On fusing artificially prepared arsenic trisulphide it solidifies to a similar yellow mass, the specific gravity of which equals, however, 2.7. In water and acids the trisulphide is insoluble, dissolves readily in ammonium hydrate and the alkalies.

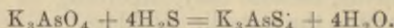
**Arsenic Pentasulphide**— $\text{As}_2\text{S}_5$ —separates from the solution of sodium sulph. arseniate,  $\text{Na}_3\text{AsS}_4$  (see below), upon the addition of acids, as a bright yellow powder.

The **Arsenic Disulphide**— $\text{As}_2\text{S}_3$ —also exists. It occurs in nature as *Realgar*, forming beautiful, ruby-red crystals, of specific gravity 3.5. These, as powder, find application as a pigment. It is prepared artificially by fusing As with S.

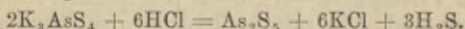
**Arsenic Sulpho-Salts.**—Owing to the similarity of sulphur to oxygen we may anticipate for arsenic (as also for other elements) the existence of sulphur acids corresponding to the oxygen acids, *e. g.*, sulpharsenious acid,  $\text{H}_3\text{AsS}_3$ , and sulpharsenic acid,  $\text{H}_3\text{AsS}_4$ . However, these acids are unknown in a free state, although their salts, known as *sulphides* and *sulpho-salts*, are found, and they, too, correspond perfectly with the oxygen salts. Just as the latter arise by the union of metallic oxides with acid oxides, so are formed the sulpho-salts by the combination of alkaline sulphides with the oxides of sulphur derivatives:—



For the preparation of these sulpho-salts, arsenic sulphide is dissolved in the aqueous solution of potassium or sodium sulphide, or hydrogen sulphide is conducted through the alkaline solution of the oxygen salts:—



The sulpho-salts of the alkalis and ammonium are easily soluble in water and, on evaporating the solution, generally separate in crystals. Acids decompose them, arsenic sulphide separating out and hydrogen sulphide becoming free:—



Antimony, carbon, tin, gold, platinum and some other metals form sulpho-salts similar to those of arsenic (and also phosphorus).

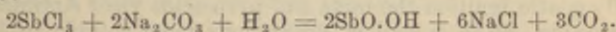
#### 4. OXYGEN COMPOUNDS OF ANTIMONY.

The oxygen derivatives of antimony are in constitution analogous to those of arsenic:  $\text{Sb}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_5$ . In them is expressed more distinctly the metallic nature of antimony, which we observed appearing also in the halogen derivatives. The lowest oxygen compound does not possess acid, but almost solely basic properties; only forms salts with acids, hence called *Antimony oxide*. The normal hydrate  $\text{H}_3\text{SbO}_3$ , corres-

ponding to arsenious acid,  $H_3AsO_3$ , is not known. An hydrate  $SbO_2H$  or  $SbO.OH$ , analogous to meta-arsenious acid, does exist; it deports itself like a base.

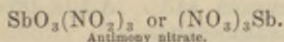
The higher oxidation product, the pentoxide  $Sb_2O_5$ , on the contrary, has an acid nature and forms salts with the bases. The hydrate,  $SbO_4H_3$  or ortho-antimonic acid and its salts have not been obtained. The known salts are derived from pyro-antimonic acid,  $H_4Sb_2O_7$  and meta-antimonic acid,  $HSbO_3$ : these exist in a free condition.

**Antimony Oxide**— $Sb_2O_3$ —is obtained by burning the metal in the air or by oxidizing it with dilute  $HNO_3$ . By sublimation it may be obtained in two different crystal systems, in regular octahedra and in rhombic prisms. Arsenic trioxide also crystallizes in the same forms; therefore the two compounds are isomorphous. On adding sodium carbonate to the solution of the trichloride a white precipitate of antimony hydrate or antimonious acid,  $HSbO_2$ , separates out:—



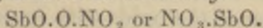
Boiling changes the hydrate to oxide. The latter and the hydrate are soluble in sodium and potassium hydrate, very probably, forming salts ( $NaSbO_2$ ) which decompose upon evaporating the solution. In this behavior is perceived also the acid nature of antimony hydrate, therefore it has received the name of antimonious acid.

The acid forms salts with acids which are derived either from the normal hydrate,  $H_3SbO_3$ , or from the hydrate,  $HSbO_2 = SbO.OH$ . In the salts of the first kind we have 3 hydrogen atoms of the hydrate replaced by acid radicals, or, what is the same, a triatomic antimony atom displacing 3 atoms of hydrogen of the acids:—



Antimony nitrate.

In the second variety of antimony salts derived from the hydrate,  $SbO.OH$ , hydrogen is replaced by a monatomic acid residue, or the hydrogen of the acid is substituted by the monatomic group,  $SbO$ , known as *antimonyl*:—



Antimonyl nitrate.

Of these salts may be mentioned the following:—

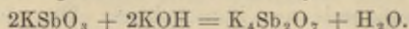
**Antimony Sulphate**— $(SO_4)_2Sb_2$ —which separates when a solution of the oxide in sulphuric acid is cooled.



**Antimonyl Sulphate**— $\text{SO}_4(\text{SbO})_2$ —is formed when antimony oxide is dissolved in somewhat dilute sulphuric acid and on cooling crystallizes in fine needles. Water decomposes both, forming basic salts; hence the basic nature of antimony oxide is slight.

**Antimonic Acid**— $\text{HSbO}_3$ —or more correctly *Metantimonic acid*, is formed upon warming antimony with concentrated nitric acid, and is a white powder, almost insoluble in water and in nitric acid, but reddens blue litmus paper. It is a weak monobasic acid, the salts of which are mostly insoluble.

If antimony pentachloride be mixed with much water **Pyroantimonic Acid**,  $\text{H}_4\text{Sb}_2\text{O}_7$ , separates as a white powder. Its salts are formed by the fusion of antimonic acid or metaantimonates with potassium or sodium hydrates:—



Hydrochloric acid precipitates pyroantimonic acid from the solutions of these salts.

By gentle ignition the meta and pyro-acids yield **Antimony Pentoxide**,  $\text{Sb}_2\text{O}_5$ , a yellow, amorphous mass, soluble in hydrochloric acid. By heating the oxygen compounds for some time with air access, they are converted into the oxide,  $\text{Sb}_2\text{O}_5$ , which can be viewed as antimonyl antimoniate,  $\text{SbO}_3.\text{SbO}$ , or as a mixed anhydride  $\left. \begin{array}{l} \text{SbO}_2 \\ \text{SbO} \end{array} \right\} \text{O}$ . It is a white powder, becoming yellow when heated and non-volatile.

#### COMPOUNDS OF ANTIMONY WITH SULPHUR.

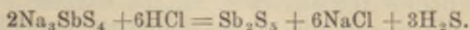
These are perfectly analogous to the S compounds of arsenic and form sulphosalts with alkaline sulphides corresponding to the oxygen salts. Acids precipitate antimony sulphide from the sulphosalts.

**Antimony Trisulphide**— $\text{Sb}_2\text{S}_3$ —is found in nature as stibnite, in radiating crystalline masses of dark gray color and metallic lustre: specific gravity = 4.7. When heated it melts and sublimes. The artificial sulphide obtained by precipitating a solution of the oxide with hydrogen sulphide is an amorphous red powder. Fused it solidifies to a mass exactly like stibnite. The sulphide dissolves in concentrated HCl, upon warming, to form antimony trichloride.

The compound  $\text{Sb}_2\text{S}_2\text{O}$ , occurring in nature as red stibnite,

can be artificially prepared, and serves as a beautiful red color, under the name of *antimony cinnabar*. *Kermes minerale*, employed in medicine, is formed by boiling antimony sulphide with a sodium carbonate solution, and is a mixture of  $Sb_2S_3$  and  $Sb_2O_3$ .

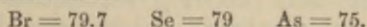
**Antimony Pentasulphide**— $Sb_2S_5$ —or gold sulphur (*sulfur auratum*) is precipitated by  $H_2S$  from acid solutions of antimonious acid; more conveniently obtained by the precipitation of sodium sulphantimoniate  $Na_3SbS_4$  with hydrochloric acid:—



It is an orange-red powder, like the trisulphide; it decomposes on being heated into  $Sb_2S_3$  and  $S_2$ . In strong hydrochloric acid it dissolves with separation of sulphur and hydrogen sulphide to antimony trichloride.

**Sodium Sulphantimoniate**— $Na_3SbS_4$  (Schlippe's salt) results from boiling pulverized  $Sb_2S_3$  with sulphur and sodium hydrate. Upon concentrating the solution, it crystallizes in large, yellow tetrahedra containing 9 molecules  $H_2O$  ( $SbS_4 \cdot Na_3 + 9H_2O$ ): exposed to the air it becomes covered with a brown layer of  $Sb_2S_3$ . It serves principally for the preparation of the officinal gold sulphur.

The affinity of the elements of the nitrogen group to hydrogen diminishes successively with increase of atomic weight, agreeing with the addition of metallic character, while the affinity to chlorine, concluding from the thermo-chemical relations, in general increases (compare p. 139). However, the heat disengagement in the formation of  $AsCl_3$  is somewhat less than that in the case of  $PCl_3$ , from which the non-existence of the compounds  $AsX_5$  (see p. 134) finds a partial explanation. The slight affinity of arsenic expresses itself yet more distinctly in the oxygen compounds, just as in the case of the halogen and oxygen group (p. 176), the arsenic corresponding to bromine and selenium—



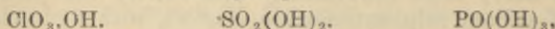
shows, in the formation of its compounds, a less development of heat:—

$(N_2O_4, H_3, Aq) = 117400$	$(N_2O_5 \cdot Aq) = 29800$
$(P_2O_4, H_3, Aq) = 305300$	$(P_2O_5) = 363800$
$(As_2O_4, H_3, Aq) = 215200$	$(As_2O_5) = 219400$

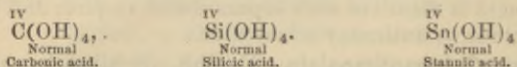
Phosphoric acid is, therefore, more stable and more energetic than nitric and arsenic acids; nitric acid oxidizes phosphorus and arsenic to phosphoric and arsenic acids. The latter acid is readily reduced to arsenious acid.

#### 4. Oxygen Derivatives of the Elements of the Carbon Group.

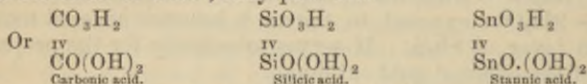
According to analogy with the hydroxyl derivatives of the elements of the three first groups:—



we may conclude the existence, for the tetratomic elements—carbon, silicon and tin, of the following normal hydroxides, corresponding to the halogen compounds,  $\text{CCl}_4$ ,  $\text{SiCl}_4$ , and  $\text{SnCl}_4$ :—



These normal hydrates or acids have but little stability, and exist mostly only in some derivatives. By the separation of a molecule of water, they pass into

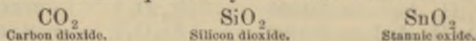


These hydroxyl derivatives deport themselves toward the normal just as the meta-acids of the elements of the N-groups do to the ortho-acids (see p. 192). They constitute the ordinary acids of the tetratomic elements, carbon, silicon and tin, and are, as they contain 2 hydroxyl groups, dibasic.

Carbon is the lowest member of this group, with the least atomic weight. Among the elements of the other three groups corresponding to it, are: nitrogen, oxygen and fluorine:—



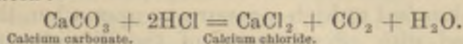
Fluorine and oxygen do not afford any oxygen acids. The normal nitrogen acid,  $\text{NO}(\text{OH})_3$ , is very unstable, and passes into the meta-acid,  $\text{HNO}_3$ . Corresponding to this is, also, the normal carbonic acid ( $\text{C}(\text{OH})_4$ ) not capable of existing. Indeed, the meta or ordinary carbonic acid,  $\text{H}_2\text{CO}_3$ , is also very unstable and decomposes, when separated from its salts, at once into water and carbon dioxide,  $\text{CO}_2$ . Even silicic and stannic acids break up readily into water and their oxides:—





## 1. OXYGEN COMPOUNDS OF CARBON.

**Carbon Dioxide**— $\text{CO}_2$ —or carbonic anhydride (generally called carbonic acid). It is produced when carbon or its compounds are burned in air or oxygen. Found free in the air (in 100 volumes, upon average, 0.05 volumes  $\text{CO}_2$ ), in many mineral springs (acid springs), and escapes in large quantities from the earth in many volcanic districts. It is prepared on a large scale by burning coke; in the laboratory it may be most conveniently obtained by the decomposition of calcium carbonate (marble or chalk) with dilute hydrochloric acid:—



Carbon dioxide is a colorless gas, of sweetish odor and taste. Its gas density equals 1.524 (air = 1), or 22 ( $\text{H} = 1$ ), corresponding to the molecular formula,  $\text{CO}_2 = 44$ . Owing to its weight, the gas may be collected by displacement of air, and may be poured from one vessel into another filled with air. Under a pressure of 36 atmospheres (at  $0^\circ \text{C}$ .), carbon dioxide condenses to a mobile, colorless liquid, not miscible with water, and boiling at  $-78^\circ$ . The specific gravity of the liquid carbon dioxide is 0.99 at  $-10^\circ$ , at  $0^\circ$  0.94. Hence, it expands more equally than even all gases, although, ordinarily, the coefficient of expansion of liquids is less than that of gases. Similar deportment is observed in the case of other bodies compressible, under pressure, to liquids.

Above  $32.5^\circ$  carbon dioxide cannot be condensed, by any pressure, to a liquid, although it may be reduced to a smaller volume than that which the liquid  $\text{CO}_2$  would equal. In the same way all other coercible gases show a *critical point in temperature* at which they are no longer able to be condensed to liquids. \* \* \* \* That the so-called permanent gases (as H, N, NO, O) could not formerly be condensed was due to the fact that they were compressed at temperatures lying above their critical points.

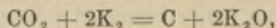
When liquid carbon dioxide stands exposed to the air so much heat is absorbed by the evaporation of a portion of it that the remainder solidifies to a white, snow-like mass. Solid carbon dioxide is a bad conductor of heat and evaporates but slowly. It can, therefore, although its temperature is  $-78^\circ$ , be taken up in the hand and even introduced into the mouth without danger, as it is always encircled by a gaseous layer, and thus not in immediate contact with the skin; upon pressing it hard, however, between the fingers it causes a pain-

ful blister. By the evaporation of solid carbon dioxide under the air pump its temperature is lowered to  $-130^{\circ}$  C. (compare p. 192).

Water dissolves its volume of the gas at  $14^{\circ}$ ; at  $0^{\circ}$  it takes up 1.79 vols. For every pressure this proportion remains constant, *i. e.*, at every pressure the same volume of gas is absorbed. As gases are condensed in proportion to the pressure, the quantity of absorbed gas is also proportional to the former. Hence 1 volume  $H_2O$  absorbs (at  $14^{\circ}$ ) and two atmospheres 2 volumes, at 3 atmospheres 3 volumes, etc., of carbon dioxide—measured at ordinary pressure. The quantity of gas absorbed at high pressure escapes when the latter is diminished with effervescence of the liquid; upon this depends the sparkling of soda water and champagne, which are saturated with  $CO_2$  under higher pressure. Every naturally occurring water, especially spring water, holds  $CO_2$  in solution, which imparts to it a refreshing taste.

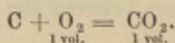
As the product of a complete combustion carbon dioxide is not combustible, and is unable to support the combustion of most bodies; a glimmering chip is immediately extinguished in it. In similar manner it is non-respirable. Although it is not poisonous, in the true sense of the word, yet the admixture of a few per cent. of  $CO_2$  to the air makes it suffocating, as it retards the separation of the same gas from the lungs.

By continued action of the electric sparks it is decomposed into carbonous oxide ( $CO$ ) and oxygen; upon heating to  $1300^{\circ}$  it suffers a partial decomposition (dissociation) into  $CO$  and  $O$ . Also decomposed when conducted over heated  $K$  or  $Na$ , with separation of carbon; the potassium combines with oxygen to form potassium dioxide:—



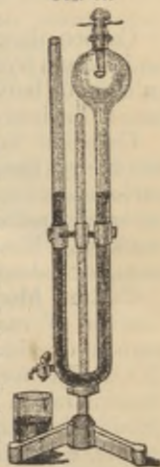
which, with excess of  $CO_2$ , forms potassium carbonate ( $K_2CO_3$ ).

The composition of carbon dioxide is readily determined by burning a weighed quantity of pure carbon (diamond or graphite) in a current of oxygen, and ascertaining the weight of the resulting gas. From the formula  $CO_2$  it follows that in one volume of it an equal volume of  $O$  is contained. We may satisfy ourselves of this by burning  $C$  in a definite volume of  $O$ ; after cooling there is obtained an equal volume of carbon dioxide:—



The experiment is most practically executed by aid of the apparatus of Hofmann pictured in Fig. 87. The spherical shaped expansion of the eudiometer limb of the V tube is closed by means of a glass stopper, through which two copper wires pass. The one wire bears a combustion spoon at its end, upon which the carbon to be burned lies, while the other wire terminates in a thin piece of platinum, which is in contact with the carbon. For the performance of the experiment the air is expelled from the globe limb by means of a rapid current of oxygen, the stopper placed in air tight, the mercury level noted and the copper wires connected with the poles of an induction stream of 3-4 Bunsen elements, which induces the burning of the carbon. As the volume of the enclosed gas is greatly expanded by the heat developed, it is advisable, in order to avoid the jumping out of the stopper, to previously, by running out mercury, reduce the pressure of the gas to two-thirds. A practical modification of this apparatus consists in having the usual cylindrical eudiometer limb provided with two side tubes, in which carbon electrodes can be inserted.

FIG. 87.

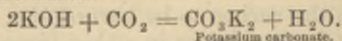


*The Physiological Importance of Carbon Dioxide.* The gas is present in the atmosphere and is inhaled by the plants. The chlorophyll grains in the green parts of the plant decompose carbon dioxide in sunlight, with a partial separation of oxygen; from the residue, by the mutual action of water and ammonia is formed the limited quantity of carbon compounds peculiar to plants. The respiration and life process of animals are essentially the reverse of the above. These absorb through the lungs the oxygen of the air, which, influenced by the blood corpuscles, oxidizes the substances present in the blood, and in this manner shapes the life process. The final products of the oxidation are carbon dioxide and water, which are exhaled. The absorption of O by animals and its separation by plants, as also the reverse course of  $\text{CO}_2$ , are about alike, so that the quantities of O and  $\text{CO}_2$  in the air show no appreciable alteration.

In dry condition carbon dioxide, like all anhydrides, exhibits neither basic nor acid reaction. In aqueous solution it colors blue litmus paper a faint red; upon drying the latter, the red disappears, in consequence of the evaporation of the carbon dioxide.



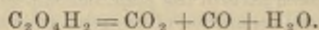
We may then regard it as probable that free *carbonic acid*  $H_2CO_3$  is contained in the aqueous solution, which, however, decomposes readily into the dioxide  $CO_2$  and water. The salts of carbonic acid are formed by the action of carbon dioxide upon the bases:—



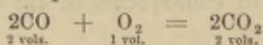
Carbon dioxide is therefore easily absorbed by potassium and sodium hydrate. On conducting it through a solution of calcium or barium hydrate there is produced a white precipitate of barium or calcium carbonate— $CaCO_3$ .

Carbonic acid is dibasic, forming primary (acid) and secondary (neutral) salts,  $CO_3HK$  and  $CO_3K_2$ , called also *carbonates*. As the acidity of carbonic acid is only slight the secondary salts formed from strong bases exhibit a basic reaction. Most acids expel the weak carbonic acid from its salts, with decomposition into carbon dioxide and water.

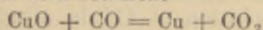
**Carbon Monoxide**— $CO$ —produced in the imperfect combustion of carbon by insufficient access of air, and when carbon dioxide is conducted over red hot coals:  $CO_2 + C = 2CO$ . The forms of apparatus described, p. 221 serve for the demonstration of this volume relation. The monoxide is produced further, by glowing carbon with different metallic oxides, *e. g.*, zinc oxide:  $ZnO + C = Zn + CO$ . For its preparation oxalic acid is warmed with sulphuric acid; the latter withdraws water from the former and the residue breaks up into carbon dioxide and monoxide:—



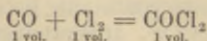
The disengaged mixture of gases is conducted through an aqueous solution of sodium hydrate, by which the  $CO_2$  is absorbed, the monoxide passing through unaltered. Pure monoxide may be prepared by heating yellow prussiate of potassium (see Iron) with 9 parts  $H_2SO_4$ . The resulting gas is colorless and odorless, and can only be condensed with difficulty. Its specific gravity is 14 ( $H = 1$ ), corresponding to the molecular formula  $CO = 28$ . It is almost insoluble in water, but is dissolved readily by an ammoniacal solution of cuprous chloride ( $CuCl$ ). Ignited, it burns in the air with a faintly luminous flame, to carbon dioxide. With air or oxygen it affords an explosive mixture:—



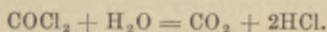
In consequence of its oxidation it is capable of reducing most metallic oxides at a red heat—



Burning bodies are extinguished by it. Inhaled, it acts very poisonously, even in slight quantity, as it expels the oxygen of the blood. The carbon vapor developed in heated ovens closed too soon, is carbon monoxide. As an unsaturated compound, this oxide, like ethylene, unites directly with 2 atoms of chlorine, to yield carbon oxychloride, or phosgene gas  $\text{COCl}_2$ :—



This is obtained by bringing together equal volumes of CO and  $\text{Cl}_2$  in direct sunlight, or, better, by conducting CO into  $\text{SbCl}_3$ . It is a colorless, suffocating gas, of specific gravity 49.4 ( $H = 1$ ), agreeing with the molecular formula  $\text{COCl}_2 = 98.8$ . Water decomposes it into hydrogen chloride and carbon dioxide:—



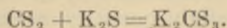
#### COMPOUNDS OF CARBON WITH SULPHUR.

**Carbon Disulphide.**  $\text{CS}_2$  is formed like the dioxide, by the direct union of carbon and sulphur, if vapors of the latter are led over glowing carbon; the escaping disulphide vapors are condensed in a cooled receiver. It forms a colorless, mobile liquid, of characteristic odor, and refracts light strongly. Its specific gravity equals 1.27. It is very volatile and burns with a blue flame, to carbon dioxide and sulphurous acid. The mixture of the vapors with oxygen explodes violently when ignited.



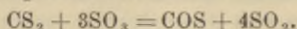
In nitrous oxide the vapors burn with a bright, blinding flame. On blowing a strong current of air upon carbon disulphide in a porcelain capsule (which conducts heat poorly), so much warmth is absorbed by the evaporation, that the residual liquid solidifies to a white, snow-like mass. Carbon disulphide is insoluble in water; it mixes, in every proportion, with alcohol and ether. It dissolves iodine with a violet red color, and serves as an excellent solvent for sulphur, phosphorus, caoutchouc and the fatty oils.

Carbon disulphide may be viewed as the anhydride of *sulphocarbonic acid*— $\text{H}_2\text{CS}_3$ . The salts of these acids are obtained by the solution of  $\text{CS}_2$  in alkaline sulphides (see sulphosalts p. 214):—

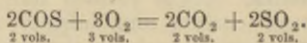


On adding hydrochloric acid to the solutions of these salts the sulphocarbonic acid separates as a reddish-brown oil. This decomposes readily.

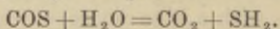
The sulphur compound corresponding to CO is not known: \* there exists, however, one containing both oxygen and sulphur—*Carbon oxysulphide*, COS. It is produced (in small quantity) when a mixture of sulphur vapors and carbon monoxide gas is passed through red hot tubes and by heating carbon disulphide with sulphuric oxide:—



Most readily obtained from potassium sulphocyanide—CN.SK—see organic chemistry—by the action of dilute sulphuric acid. It is a colorless gas, with an odor reminding one of carbon dioxide and hydrogen sulphide. It is present in some sulphur springs. It is very readily inflammable and burns with a blue flame:—



It is decomposed at a red heat into CO and sulphur. Soluble in an equal volume of water, decomposing gradually into the dioxide and hydrogen sulphide:—



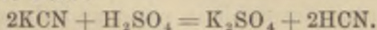
**Cyanogen Compounds.** Of the innumerable compounds of C treated in organic chemistry, we will here mention only those of cyanogen, as they are of importance in inorganic chemistry.

Nitrogenous carbon compounds heated with potassium hydrate yield potassium cyanide—CNK—which with iron forms the so-called yellow prussiate of potassium,  $\text{K}_4\text{Fe}(\text{CN})_6$ . From these two compounds all the other cyanogen derivatives may be prepared. They all contain the group CN, called

\* Upon standing in sunlight  $\text{CS}_2$  is said to break up into S and CS—a chestnut-brown powder of specific gravity 1.66.

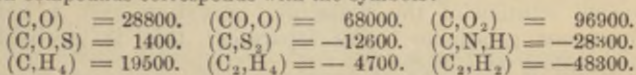


*cyanogen*. In it we have a triatomic nitrogen atom combined with a tetratomic carbon atom; the fourth affinity of the latter is not saturated:  $\overset{\text{III}}{\text{N}} \equiv \overset{\text{IV}}{\text{C}} -$ : it is similar, therefore, to the groups OH,  $\text{NH}_2$ ,  $\text{CH}_3$ , and is a monatomic radical. In chemical behavior the cyanogen group is very similar to the halogens chlorine and bromine; with the metals it forms metallic cyanides ( $\text{KCN}$ ,  $\text{AgCN}$ ) very similar to the haloid salts. Hydrogen cyanide is evolved when the cyanides are warmed with sulphuric acid:—



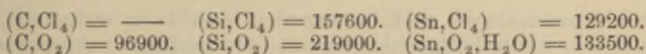
**Hydrogen Cyanide**,  $\text{HCN}$ , is a colorless, mobile liquid, of peculiar odor, and boiling at  $27^\circ$ . It is an acid, forming salts with metals and bases, and is known as *Hydrocyanic or Prussic acid*. Both it and its salts are very powerful poisons. If the CN group is separated from its salts it doubles itself, forming *dicyanogen* or *free cyanogen*,  $\text{C}_2\text{N}_2$  ( $\text{N} \equiv \text{C} - \text{C} \equiv \text{N}$ ), because, like the other monatomic groups (as  $\text{CH}_3$ , see p. 162), it cannot exist in a free condition.

The heat occurring in the formation of the above cited simplest carbon compounds corresponds with the symbols:—



If an element combine with another according to multiple proportions, there occurs, in the union of the first atom, generally, a greater disengagement of heat than with the following atom (compare nitrogen oxides, p. 204). On the contrary, it is seen that the union of the second atom of oxygen with carbon ( $\text{CO}, \text{O}$ ), sets free 68000 calories; that of the first atom ( $\text{C}, \text{O}$ ), however, only 28800 calories. This can only be explained by the fact that, for the vaporization and disaggregation of the solid carbon molecules, heat becomes latent (absorbed). If we assume that the direct union of the first atom also disengaged 68000 calories, it would follow from this that, in the dissociation of 12 weight parts carbon in gaseous free atoms, 39200 calories were absorbed. From this, the heat absorption, in the production of  $\text{CS}_2$ ,  $\text{CNH}$ ,  $\text{C}_2\text{H}_2$ , would be explained, while otherwise, in every direct chemical union, heat is invariably disengaged.

Comparing the elements of the carbon group with each other, we discover that the heat disengagement is greatest with the compounds of silicon:—

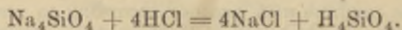


From these numbers we observe that tin dioxide, but not that of silicon can be reduced by carbon.

## 2. OXYGEN COMPOUNDS OF SILICON.

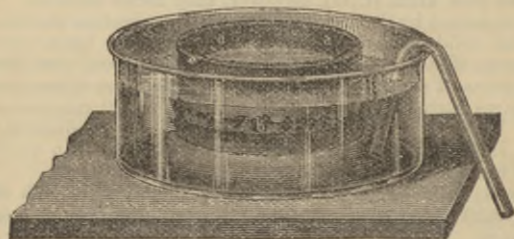
**Silicon Dioxide**,  $\text{SiO}_2$  (*Silica*), is widely distributed in nature as rock-crystal, quartz, sand, etc. It is artificially obtained as a white, amorphous powder, of specific gravity 2.2, by the combustion of amorphous silicon, or by the ignition of silicic acids. In crystalline form, it only occurs in nature in figures of the hexagonal system, with the specific gravity, 2.6; these crystals are colorless, or colored by impurities. In the oxy-hydrogen flame it fuses to a transparent glass.

Silicon dioxide is insoluble in water and all acids; only by hydrofluoric acid is it decomposed with the formation of silicon fluoride ( $\text{SiF}_4$ ) and water (p. 155). Strong ignition with carbon or potassium reduces it to metallic silicon. Boiled with potassium or sodium hydrate the artificially prepared dioxide dissolves; some of the naturally occurring amorphous varieties are also soluble, but not the crystallized dioxide. By fusion with the hydroxides or carbonates of the alkalis all varieties of silicic acid yield a glassy mass (water glass) soluble in water and containing silicates ( $\text{K}_4\text{SiO}_4$  or  $\text{K}_2\text{SiO}_3$ ). Upon the addition of hydrochloric acid to the aqueous solution of the potassium or sodium salt, a very voluminous gelatinous mass separates; this is probably *normal silicic acid*,  $\text{H}_4\text{SiO}_4$ :—



Washed with water and dried in the air it becomes a white amorphous powder having the composition  $\text{H}_2\text{SiO}_3$ . The

FIG. 88.

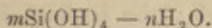


freshly precipitated acid is somewhat soluble in water, more readily in dilute hydrochloric acid. On adding to the excess of dilute hydrochloric acid a solution of sodium silicate, the separated silicic acid remains dissolved. From the hydro-

chloric acid and sodium chloride solution we can obtain by dialysis a perfectly pure aqueous solution of silicic acid. Proceed as directed in following lines. Pour the hydrochloric acid solution into a wide cylindrical vessel, whose lower opening is covered with animal bladder or parchment paper, and the vessel (dialyser) then suspended in another containing pure water, Fig. 88. Osmosis now sets in. The sodium chloride and hydrochloric acid particles pass through the parchment paper into the outer water, while on the other hand, water particles pass from the outer vessel into the dialyser; to silicic acid the parchment paper is not permeable. This alternate diffusion of the different particles occurs until the outer and inner liquid show the same quantity of diffusible substances. Upon introducing the dialyser into a fresh portion of water, the dialysis commences anew. After repeated renewal of the external water there is found, finally, in the dialyser a perfectly pure silicic acid solution, free from sodium chloride and hydrochloric acid. The solution may be concentrated by evaporation; then it readily passes into a gelatinous mass. The same occurs instantaneously in dilute solutions if a trace of sodium carbonate be added or carbon dioxide be led into it.

Like sodium chloride, all crystallizable soluble substances diffuse through parchment. These are known as *crystalloids*, to distinguish them from the non-diffusible colloids. To the latter belong gum, gelatine, albumen, starch, glue (colla, hence the name colloid), and especially the most substances which occur principally in vegetable and animal organisms. Like silicic acid these colloids exist in liquid soluble and solid gelatinous condition. By dialysis many other substances (like ferric and aluminum oxides) which ordinarily are insoluble, can be brought into aqueous solution.

We have already seen that acids like sulphuric, phosphoric, and arsenic, by the union of several molecules and the elimination of water, are capable of forming anhydro- or poly-acids. Silicic acid is particularly inclined to that kind of condensation. It forms a large number of *poly-silicic acids*, derived from the normal and ordinary acid, according to the common formula:—



These poly-acids are not known free; it appears, however, that many amorphous forms of silica occurring in nature, as agate, chalcedony, opal, which lose 5–15 %  $\text{H}_2\text{O}$  by ignition, represent such poly-acids. The natural *silicates* are the salts



of such acids. The majority are derived from the acids:  $H_2Si_2O_5$ ,  $H_4Si_3O_8$ ,  $H_2Si_3O_7$ ,  $H_4Si_4O_9$  and others. Only a few silicates are obtained from the normal acid, *e. g.*, chrysolite— $Mg_2SiO_4$ .

Corresponding to  $CS_2$  is

**Silicon Disulphide**,  $SiS_2$ , which may be made by heating amorphous silicon with sulphur, or by conducting sulphur vapors over an ignited mass of silica and carbon. It sublimes in shining, silky needles, which water changes to silicic acid and hydrogen sulphide.

To the group of carbon and silicon belongs also *Tin* (see p. 156), which forms perfectly analogous oxygen compounds. However, in them is plainly visible the metallic character of tin, and the basic of the oxides. The tin hydrates,  $Sn(OH)_4$  and  $SnO(OH)_2$ , are weak acids, which with the alkalis yield only feebly stable, basic reacting metallic salts. The basic character exhibits itself more in the lower stage of oxidation—stannous oxide,  $SnO$ , and hydrate  $Sn(OH)_2$ . Hence, we will consider tin with the metals.

#### Titanium.

Ti = 48.

#### Zirconium.

Zr = 90.

#### Thorium.

Th = 234.

Just as vanadium, niobium and tantalum attach themselves to the elements of the phosphorus group, so stand, in like relation to the silicon group, the three elements, titanium, zirconium and thorium:—

P = 31	V = 51	Si = 28	Ti = 48
As = 75	Nb = 94	.....	Zr = 90
Sb = 121	T = 182	Sn = 178	Th = 234

In all their department, they strongly resemble tin; they possess, however, in their derivatives, a more metallic character. They are tetratomic, forming compounds of the form  $MeX_4$ , in which X represents monatomic elements and groups; those of the form  $MeX_2$ , corresponding to the stannous derivatives, are unknown. The hydrates,  $Me(OH)_4$  and  $MeO(OH)_2$ , have a stronger basic nature than stannic acid and form stable salts with acids; the basicity increases successively with the atomic weights, in the order, Ti Zr Th. Corresponding to this, the acidity of the hydrates, *i. e.*, their capability of exchanging H for metals, gradually diminishes. Thorium hydroxide,  $Th(OH)_4$ , is not able to form metallic salts.

## TITANIUM.

Ti = 48.

By ignition the hydrates yield white amorphous

Occurs in nature as titanium dioxide (rutile, anatase, brookite) and in titanates (perovskite  $\text{TiO}_3 \text{Ca}$ , Menaccanite  $\text{FeTiO}_3$ ). Free titanium is a gray, metallic powder, obtained by heating potassium fluoride ( $\text{K}_2\text{TiF}_6$ ) with potassium. It burns when heated in the air, and decomposes water on boiling. Dissolves in dilute hydrochloric and sulphuric acids, with evolution of hydrogen.

**Titanium Chloride**— $\text{TiCl}_4$ —is formed, like silicon chloride, by conducting chlorine over a glowing mixture of the dioxide and carbon. A colorless liquid, of specific gravity 1.76, fuming strongly in the air, and boiling at  $136^\circ$ . The vapor density equals 95 ( $\text{H} = 1$ ), corresponding to the molecular formula  $\text{TiCl}_4 = 190$ . Not known in a free state. Behaves like tin tetrachloride with water. A compound  $\text{Ti}_2\text{Cl}_6$ , analogous to  $\text{C}_2\text{Cl}_6$ , is known.

**Titanium Fluoride**— $\text{TiF}_4$ —not known in a free condition; forms beautifully crystallized double salts *e. g.*,  $\text{TiF}_4 \cdot 2\text{KFl}$ , corresponding to the silico-fluorides ( $\text{K}_2\text{SiF}_6$ ).

**Titanic Acid**— $\text{H}_4\text{TiO}_4$ —separates as a white, amorphous powder, on adding ammonium hydrate to the hydrochloric acid solution of the titanates. Dried over sulphuric acid it loses 1 molecule  $\text{H}_2\text{O}$  and becomes  $\text{TiO} \cdot (\text{OH})_2$ . Titanic acid, like silicic and stannic, forms polyacids. The hydrates dissolve in alkalis and strong acids, to form salts.

**Titanium Dioxide**— $\text{TiO}_2$ , which may be procured crystallized as rutile, brookite and anatase. Glowed in a stream of hydrogen it changes to the oxide  $\text{Ti}_2\text{O}_3$ . Titanium dioxide is almost insoluble in the acids; only dissolved by hydrofluoric acid. It forms titanates upon fusion with the alkalis.

With strong acids the hydrates form salts, *e. g.*,  $\text{TiO} \cdot \text{SO}_4$ . Water decomposes this. The alkaline titanates ( $\text{K}_2\text{TiO}_3$ ) are very unstable. Other titanates occur in nature *e. g.*,  $\text{CaTiO}_3$ ,  $\text{MgTiO}_3$ , and the so-called Titanic Iron,  $\text{FeTiO}_3$ .

With nitrogen, titanium yields various compounds. When the dioxide is heated in ammonia gas, a dark violet powder of the composition  $\text{TiN}_2$  results. The compound  $\text{Ti}_3\text{CN}_4$ —the so-called cyan-titanium nitride, is sometimes found in copper red metallic cubes, in blast furnace slag, when iron ores containing titanium have been fused.

**ZIRCONIUM.**

Zr = 90.

Zirconium occurs only rarely in nature, generally in silicates, and especially as zircon  $ZrSiO_4$ . Zirconium is obtained free in the same way as titanium, and may be isolated as an amorphous black powder or in crystalline metallic leaflets of specific gravity, 4.15. Zirconium tetrachloride— $ZrCl_4$ , and fluoride,  $ZrF_4$ —are very similar to the corresponding titanium compounds.

**Zirconic Acid or Hydrate**— $Zr(OH)_4$ —is precipitated by ammonium hydrate, from acid solutions, as a white voluminous precipitate, which becomes  $ZrO_2$ , zirconium dioxide, upon ignition. Zirconic acid is insoluble in potassium and sodium hydrates; only on fusion with the alkalis and their carbonates does it yield zirconates— $Na_2ZrO_3$  and  $Na_4ZrO_6$ , which water decomposes.

The oxide and hydrate dissolve when warmed with sulphuric acid, forming  $Zr(SO_4)_2$ , which may be crystallized from water.

**THORIUM.**

Th = 234.

Occurs very rarely, mostly in silicates (Thorite). Free thorium, separated by sodium from the chloride, is a dark gray powder, of specific gravity 7.7, which in the air burns to the dioxide.

**Thorium Hydrate**— $Th(OH)_4$ —and **Thorium Dioxide**,  $ThO_2$ , do not form salts with the alkalis. In sulphuric acid they dissolve to the sulphate  $Th(SO_4)_2$ , which crystallizes from water with four molecules of water.

**BORON.**

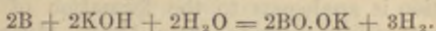
B = 11.

Generally classed with the metalloids, and stands isolated among them; it forms the transition from these to the metals, as appears plainly in its position in the periodic system. On the one side, especially when free, it resembles carbon and silicon, on the other, it approaches the metals—beryllium, aluminium and scandium (see the Periodic System of the Elements). Like the metals, it does not combine with hydrogen, and its oxide  $B_2O_3$ , although really of an acid



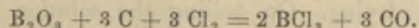
nature, approaches such undetermined metallic oxides as aluminium oxide,  $\text{Al}_2\text{O}_3$ . Boron is triatomic and forms compounds only of the form  $\text{BX}_3$ .

It is found in nature as boracic acid and in the form of borates, like borax (sodium salt), boracite (magnesium salt). It may be obtained free in an amorphous and crystallized state. The first results upon igniting boron trioxide with sodium, away from air contact; free boron and sodium borate are formed. On treating the fusion with water, the borate dissolves, leaving the metal as a greenish-brown powder, which, when heated in the air, burns with strong brilliancy to the trioxide. Nitric and sulphuric acids change it to boric acid. Fused with phosphoric acid, it liberates phosphorus. Upon boiling with aqueous alkalis it dissolves, like beryllium, silicon and aluminium, with formation of borates:—

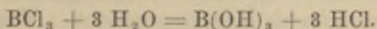


The *crystalline* variety may be obtained by igniting boron trioxide with aluminium. The boron, separated by the aluminium, dissolves in excess of the latter, and crystallizes from it on cooling; upon dissolving the aluminium in hydrochloric acid, the boron remains in shining, transparent, quadratic crystals, of specific gravity 2.63, which are more or less colored.\* Its lustre, refraction of light and hardness, resemble that of the diamond. Crystalline boron is more stable than the amorphous; it does not oxidize upon ignition, and is only slightly attacked by acids. Fused with potassium and sodium hydrate both modifications yield sodium borate.

**Boron Trichloride**,  $\text{BCl}_3$ , may be prepared by heating boron in chlorine or conducting a stream of the latter over a glowing mixture of the trioxide and carbon (see  $\text{SiCl}_4$  and  $\text{Al}_2\text{Cl}_6$ ):—

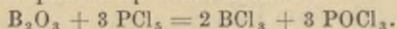


It is a colorless liquid of specific gravity 1.35, and boiling at  $18^\circ$ . Its vapor density equals 58.7 ( $\text{H} = 1$ ), corresponding to the molecular formula  $\text{BCl}_3 = 117.5$ . The liquid fumes strongly in the air and decomposes with water into boric and hydrochloric acids:—

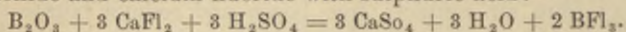


\* According to late investigations, the crystals are not pure boron, but contain aluminium and carbon (Hampe).

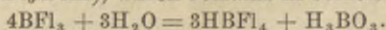
The trichloride also results from the action of the pentachloride of phosphorus upon the trioxide:—



**Boron Fluoride**,  $BF_3$ , similar to silicon fluoride, and produced according to the same methods, by the action of hydrofluoric acid upon the trioxide, or by warming a mixture of the trioxide and calcium fluoride with sulphuric acid:—



Is a colorless gas, burning strongly in the air, of specific gravity 34 ( $H = 1$ ) and may, under strong pressure, be condensed to a liquid. It dissolves extremely readily in water (700 volumes in 1 vol.) producing Hydrogen-Boro-fluoride,  $BF_4H$  ( $= BF_3 \cdot FH$ ), which remains in solution:—



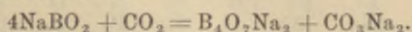
The reaction is analogous to the formation of hydrofluosilic acid from silicon fluoride (see p. 155). Hydrogen boro-fluoride is a monobasic acid, only known in solution and in its salts.

**Boric Acid**— $H_3BO_3 = B(OH)_3$ —occurs in salts and free in nature. In some volcanic districts, especially in Tuscany, steam escapes from the earth (fumaroles, etc.) containing small quantities of it. These vapors condense in small natural water pools, or are conducted into walled basins. By evaporation and concentration of the aqueous solution boric acid separates; the same occurs naturally as sassolite. To prepare pure boric acid precipitate a hot solution of borax with hydrochloric acid. The acid separates in colorless, shining scales; it dissolves in 25 parts,  $H_2O$  of  $14^\circ$ , or in 3 parts at  $100^\circ$ . The solution indicates a feeble acid reaction with litmus; turmeric paper moistened with it is colored red-brown, after drying. On boiling the solution boric acid escapes with the steam. An alcoholic solution of the acid burns with a green flame. By these reactions we are afforded a ready means for its detection.

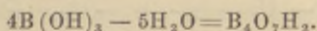
Heated to  $100^\circ$  the acid loses 1 molecule  $H_2O$  and passes into the anhydro or meta acid  $HBO_2$ , which at  $140^\circ$  is converted into Tetraboric acid— $B_4O_7H_2$ . When glowed boric anhydride or *Boron trioxide*  $B_2O_3$  is produced. This is a fusible, glassy mass, of specific gravity, 1.8, and is slightly volatile at a very high heat. Water dissolves the anhydride to boric acid.

Boric acid is a very weak acid ; it can be expelled from its salts by most other acids. When fused, in consequence of the difficult volatility of its anhydride, it removes the most acids from their salts.

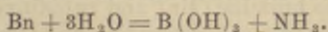
Salts of normal boric acid  $B(OH)_3$  are not known, while the ethers  $B(O.CH_3)_3$  are. The salts of metaboric acid  $BO$ .  $OK$  can be obtained crystallized, but they are very unstable. They are decomposed by carbon dioxide with production of salts of tetraboric acid :—



The latter, from which the ordinary borates are derived (see borax) may be viewed as an anhydro-acid, formed by the union of 4 molecules of trihydric boric acid (compare p. 186):—



On heating amorphous boron in a stream of  $N$  or ammonia, or by glowing a mixture of trioxide and carbon in nitrogen gas, there is formed *boron nitride*,  $BN$ . This is a white amorphous powder, which, heated in a flame, gives forth an extremely intense greenish-white light. On passing steam at  $200^\circ$  over this boric acid and ammonia are produced :—



## PERIODIC SYSTEM OF THE ELEMENTS.

In the preceding pages we have studied four groups of elements and their compounds with hydrogen, the halogens and oxygen. The remarkable relations of the elements of any one group, as, also, of the various groups to each other, to which we have repeatedly directed attention, appear more manifest if viewed in the same connection in which they present themselves in the *periodic system of elements*. The position which these elements occupy in the system determines, up to a marked degree, their entire physical and chemical character.

The system is based upon the grouping of the elements according to the magnitude of their atomic weights. For the longest time we have been cognizant of the remarkable relations existing between the atomic weights of analogous elements, but only recently has the *law of periodicity* underlying them been affirmed by Medelejeff and Lothar Meyer,



and, according to this, *the properties of the elements and their compounds present themselves as periodic functions of the atomic weights.*

Arranging the elements according to increasing atomic weight we observe that similar elements return after definite intervals. Thus they arrange themselves in several periods, consisting of the following horizontal series (for brevity the atomic weights are not attached to the symbols) :—

1.	Li	Be	B	C	N	O	F	Cl												
2.	Na	Mg	Al	Si	P	S	Cl													
3)	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	—	As	Se	Br			
4	Rb	Sr	Y	Zr	Nb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I			
{ 5)	Cs	Ba	(La	Ce	Di)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
{ 6)	—	—	Yb	—	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	—	—	—	—	—
7)	—	—	—	Th	—	Ur	—	—	—	—	—	—	—	—	—	—	—	—	—	—

The first series, lithium (Li) to fluorine (F), and sodium (Na) to chlorine (Cl), present two periods of seven members each, in which the corresponding (above and below) members exhibit a great but not complete analogy. Sodium resembles lithium, magnesium, beryllium, chlorine, fluorine, etc. Then follow two periods, consisting of 17 elements each: Potassium (K) to bromine (Br), and rubidium (Rb) to iodine (I). The series 5 and 6 are incomplete, and together constitute, as it appears, a period. In the 7th series there are as yet but two elements: thorium = 234 and uranium = 240. Thus result 3 *great periods*, whose corresponding members exhibit an almost complete analogy; the elements K Rb Cs, Ca Sr Ba, Ga In Tl, As Sb Bi, etc., are so similar that they remind us of the homologous series of the carbon compounds (compare p. 144), and, therefore, can be designated as *homologous elements*. Only in the third great period (series 5 and 6) do the middle members exhibit any variations.

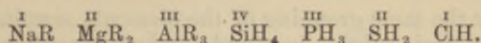
On now comparing the three great periods with the two small ones, we discover that the first members are analogous to each other: K Rb Cs resemble Na and Li; Ca Sr Ba resemble Mg and Be. Then the similarity gradually lessens, disappears apparently in the middle members, and only again appears toward the end of the periods: I and Br resemble chlorine and fluorine, Te and Se sulphur and oxygen, Bi Sb As phosphorus and nitrogen, etc. The character or the function of the three great periods is therefore

other than that of the two small periods. But in all five periods a gradual, regular alteration in the properties of the adjoining *heterologous* elements exhibits itself. Particularly distinct is this in the measurable physical properties, all of which, in the middle of the periods (both of the large and small), show a maximum or minimum, as is visible in the specific gravity of the elements in solid condition (compare further the atomic volumes p. 245).

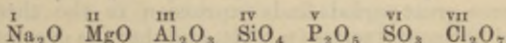
	Na	Mg	Al	Si	P	S	Cl												
Specific gravity,	0.97	1.7	2.5	2.5	2.0	1.9	1.3												
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	—	As	Se	Br			
0.86	1.6	—	—	5.5	6.8	7.2	7.9	8.5	8.8	8.8	7.1	5.9	—	5.6	4.6	2.9			

These relations show themselves very clearly in a graphic representation, by making the atomic weights the abscissæ, the value in numbers of the properties the ordinates; then the individual periods represent segments of curves, which blend to a curve with alternating maxima and minima.

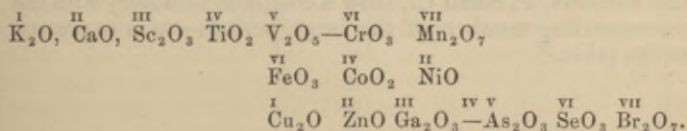
The same regularity exhibits itself with the 2 small periods, even in chemical properties, especially in the valence of the elements in their compounds with hydrogen or the hydrocarbon groups  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , etc., (compare p. 166 and p. 239). The hydrogen valence rises and falls periodically with the condensation of the substance (corresponding to the specific gravity) :—



On the other hand, the maximum valence of the elements in the salt-forming oxides increases successively :—



The chemical valence expresses itself somewhat differently in the three great periods. In them we have a *double periodicity*; thus, *e. g.*, with the salt-forming oxides :—



In consequence of this double periodicity, the first seven and the last seven members of the 3 great groups, as regards their valence (and consequently also their compounds), resemble the 7 members of the 2 small periods. To bring out this double periodicity and analogy, the 7 first and 7 last members of the great groups are divided into two series and arranged under the corresponding 7 members of the small periods.

In this way the three middle members of the great periods (which are found between the dotted lines of the table, p. 234), as they have no analogues, come to stand apart. In this manner arises the following table, in which the 7 (or 10) vertical columns include analogous elements:—

	Li	Be	B	C	N	O	F			
	Na	Mg	Al	Si	P	S	Cl			
K	Ca	Sc		Ti	V	Cr	Mn	Fe	Co	Ni
	Cu	Zn	Ga	—	As	Se	Br			
Rb	Sr	Y		Zr	Nb	Mo	—	Ru	Rh	Pd
	Ag	Cd	In	Sn	Sb	Te	I			
Cs	Ba	(LaCeDi)		—	—	—	—			
	—	Yb		—	Ta	W	—	Os	Ir	Pt
	Au	Hg	Tl	Pb	Bi	—	—			

Exactly the same grouping of the elements simultaneously with their atomic weights, in round numbers, is produced in the adjoining table (p. 237). In this arrangement we must always bring into consideration that the principal analogy (homology) of the three great periods finds expression in the three uninterrupted horizontal series (p. 234), and that the decomposition of the latter into every two series only corresponds to the secondary, double analogy with the small periods. It may be further remarked that in the second small period the three last numbers, P, S and Cl, show a complete homology with the corresponding numbers of the large periods—as is expressed in the table.



## ELEMENTS OF THE PERIODIC SYSTEM.

H-COMPOUNDS. Highest Salt- forming Oxides.	Periods. Series.							
	I	II	III	IV	V	VI	VII	VIII
—	Group.	Group.	Group.	Group.	Group.	Group.	Group.	Group.
M <sub>2</sub> O	—	MO	—	MH <sub>4</sub> MO <sub>2</sub>	MH <sub>3</sub> M <sub>2</sub> O <sub>5</sub>	MH <sub>2</sub> MO <sub>3</sub>	MH M <sub>2</sub> O <sub>7</sub>	MO <sub>3</sub>   MO <sub>2</sub>   (M <sub>2</sub> H) MO
H 1	Li 7	Be 9	B 11	C 12	N 14	O 16	Fl 19	
1st	1st							
2d	Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35	
3d	K 39 Cu 63	Ca 40 Zn 65	Sc 45 Ga 70	Ti 48 —73	V 51 As 75	Cr 52 Se 79	Mn 55 Br 80	Fe 56   Co 58   Ni 58
4th	Rb 85 Ag 108	Sr 87 Cd 112	Y 89 In 113	Zr 90 Sn 118	Nb 94 Sb 122	Mo 96 Te 126	—100 I 127	Ru 104   Rh 104   Pd 106
5th	Cs 132	Ba 137	(La139 Ce 140 Di144)	—	—	—	—	—
6th	—	—	—	—	—	—	—	—
7th	—	—	—	—	Ta 182 Bi 210	W 184	—	Os (198)   Ir 193   Pt 196
8th	—	—	—	—	—	—	—	—
9th	Au 197	Hg 200	Yb 173 Tl 204	Pb 206	—	—	—	—
10th	—	—	—	(Th 234)	—	Ur 240	—	—

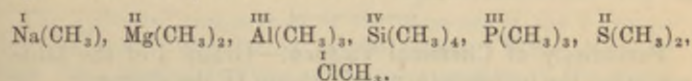
When the periodic grouping of the elements was first presented, some, at that time not sufficiently well established, atomic weights had to be more or less altered. Thus, the atomic weight of iridium, formerly 75.8, was made 113, and that of uranium 240 (before 120). All such alterations, through recent investigations, have been proven to be established. Further, the atomic weight of tellurium (formerly determined to be 128) had to be less than that of iodine (126.6); this also, has been established by recent researches, which place it at 126.8. There is, therefore, no doubt that the atomic weight of osmium (found 198) will also prove to be somewhat less,—only the more, because at present a smaller atomic weight (192.7) than formerly accepted (p. 197) has been discovered for iridium. Hence, the periodic system offers a control for the numbers of the atomic weight, while formerly they appeared to be irregular and, at the same time, accidental.

Further, upon the basis of the periodic system, the existence of new, not yet known, elements may be ascertained, which would correspond to yet unoccupied, free places, or vacancies in the table. In fact, two such formerly vacant places have been filled up by the discovery of gallium ( $\text{Ga} = 69.8$ ) and scandium ( $\text{Sc} = 45$ ); their properties have shown themselves to be perfectly accordant with those deduced from the periodic system. At present, of the elements of the first four periods only two are wanting (see p. 234): the first homologue of manganese (with atomic weight of about 100), and the lowest homologue of tin (atomic weight, about 73). The vacancies in the series 5 and 6 are partly explained from the somewhat varying function of the third great period (p. 234); partly also by the most recently discovered or characterized elements, erbium, terbium, wasium, and norwegium, whose atomic weights have not yet been determined with certainty. These would probably find a position here.

The entire character of a given element is determined to a very high degree by the law of periodicity; hence, all physical and chemical properties of the same are influenced by its position in the system. These relations we will examine more closely in the individual groups of the elements, and confine ourselves here to a notice of some general relations; further, the connection of atomic weight with the valence and the thermo-chemical phenomena.

Particularly distinct does the relation of metalloids to metals show itself in the periodic system. The first members of all periods (on the left side) consist of electro-positive metals, forming the strongest bases, the alkalis—Cs Rb K Na Li

and metals of the alkaline earths—Ba Sr Ca Mg and Be. The basic character diminishes successively, in the following heterologous members, and gradually passes over into the electro-negative, acid-forming character of the metalloids Fl Cl Br I. Here is observed that, in the periods following each other, with higher atomic weights, the basic metallic character constantly exceeds the metalloidal. The first period comprises 5 metalloids, (B C N O Fl), the second only four (Si P S Cl), the fourth and fifth periods each only 3 (or 2) metalloids (As Se Br and Sb Te I), which, at the same time, become less negative. With the metalloidal nature is combined the power of forming volatile hydrogen compounds. Similar volatile derivatives are also afforded by the metalloids with the monatomic hydrocarbon groups (as  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_3\text{H}_7$ , etc.), which, in many respects, resemble hydrogen. Such metallo-organic compounds, in which the elements show the same valence as in the hydrogen compounds, are also produced by the metals adjacent to the metalloids:—



Their stability gradually diminishes with the increasing basic nature of the metals; hence, in the three large periods, this power extends only to Zn, Cd and Hg (beginning with bromine, I and Bi).

In consequence of the opposite (metalloidal and metallic) character of the two ends of the periods, there are in the table representing the double periodicity of the great periods (p. 236 and 237) two sub-groups each, with the seven vertical groups; on the left with the more positive basic, and on the right the more negative metalloidal elements. Thus in group VI, in addition to O and S (belonging to the small periods) stands the more basic sub-group Cr Mo W and the metalloids Se and Te; in group II stand the strong basic metals Ca Sr Ba and the less basic heavy metals Zn Cd Hg. The elements of group VII form the gradual transition from the last to the first.

The fundamental deduction resulting necessarily from the law of periodicity is, that the various elementary atoms must be aggregates or condensations of one and the same original substance, a necessary correlative postulate of the recognized



unity of all forces. Only then will it be understood that the properties of the elements are functions of the atomic weight. That this original matter is not hydrogen, as supposed (hypothesis of Prout), follows from the fact that the atomic weights of the elements are not multiples of that of hydrogen; this is shown by the determinations, made with such accuracy by Stas, for some of the elements. These atomic weights referred to hydrogen = 1 are the following:—

Oxygen	O = 15.960	Silver	Ag = 107.660
Chlorine	Cl = 35.360	Potassium	K = 39.040
Bromine	Br = 79.750	Sodium	Na = 22.980
Iodine	I = 126.533		

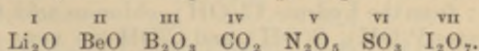
The ordinary atomic weights as they appear in this book are given in round numbers, which is sufficient for general purposes. If the atomic weights of all the elements had been fixed with equal accuracy, it would probably be possible to approach more closely the consideration of the nature of the periodic function.

**Periodicity of Chemical Valence.**—Group I of the table comprises the monatomic metals, group II the diatomic. In group III is the triatomic metalloid, boron (which does not furnish a hydrogen compound), and the triatomic metals Al Sc Y and Ga In Tl. In the tetratomic group of carbon the quantivalence arrives at its maximum; from here the valence gradually decreases with increasing atomic weight; the group of nitrogen is triatomic, the group of oxygen is diatomic, that of the halogens monatomic. This valence is derived from the compounds with hydrogen and hydrocarbons (compare p. 239), or where such do not exist, as in case of boron and many metals, from the halogen compounds:—

			<sup>IV</sup> CH <sub>4</sub>	<sup>III</sup> NH <sub>3</sub>	<sup>II</sup> OH <sub>2</sub>	<sup>I</sup> FlH
<sup>I</sup> LiCl	<sup>II</sup> BeCl <sub>2</sub>	<sup>III</sup> BCl <sub>3</sub>	<sup>IV</sup> CCl <sub>4</sub>	<sup>III</sup> NCl <sub>3</sub>	<sup>II</sup> OCl <sub>2</sub>	<sup>I</sup> Fl <sub>2</sub>
NaCl	MgCl <sub>2</sub>	AlCl <sub>3</sub>	SiCl <sub>4</sub>	PCl <sub>3</sub>	SCl <sub>2</sub>	Cl <sub>2</sub>

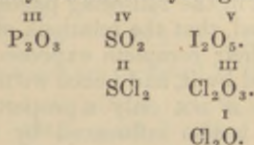
The elements of the 4 first groups are not capable of yielding higher compounds with the halogens. On the other hand, as we have seen, the higher analogues of nitrogen and other metalloids can unite with a larger number of halogen atoms (see p. 163). The higher valence of these elements shows itself yet plainer in the more stable oxygen compounds. On arrang-

ing together the *highest oxides* of the seven groups capable of forming salts (salt-building oxides), we get this series:—

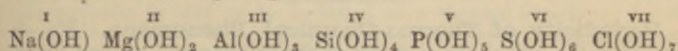


The elements of the four first groups in their oxygen compounds of course exhibit the same valence as in the compounds with hydrogen (or hydrocarbon radicals) and the halogens; in the three last series, however, there is noticed a constant increase of valence up to oxygen.

Besides the highest oxides, remarkable for their greater stability, the elements of the three last groups form lower oxides, as in this manner they return to hydrogen valence:—

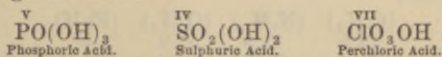


The hydroxyl compounds of the elements of the 7 groups are analogously constituted to the oxides. With them, we have the following limiting series, as expression of the maximum valence (compare p. 165):—

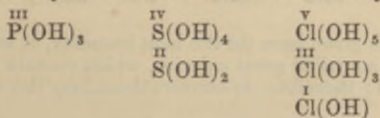


The hydroxyl compounds of the elements of the 4 first groups exist in free condition, excepting that of carbon, C(OH)<sub>4</sub>, which is only represented in its derivatives. The strong basic character of the hydrates of group I (NaOH) diminishes, step by step, down to the weak acid hydrate, Si(OH)<sub>4</sub>. The hydrates of the three last groups are of acid nature, and mostly unstable or not known.

By elimination of 1, 2 and 3 molecules H<sub>2</sub>O they yield the ordinary highest acids:—



In the same way behave the non-saturated hydrates:—



From the hydrate,  $S(OH)_4$  is derived sulphurous acid,  $SO(OH)_2$  (p. 179); from the hydrate,  $Cl(OH)_3$ , chloric acid,  $ClO_2, OH$ ; from the hydrate,  $Cl(OH)_2$ , chlorous acid,  $ClO, OH$ . The hydrates  $P(OH)_3$ ,  $S(OH)_2$  and  $ClOH$  are very unstable, and the two first appear to readily pass into  $H_2PO, OH$  and  $HSO, OH$  (compare p. 180).

It has already been shown, in the case of per-iodic, sulphuric and nitric acids, how the usually, so-called hydrates with water of crystallization (regarded as molecular compounds) find explanation by the acceptance of the existence of such hydroxyl compounds. The same may be carried out for many salts with water of crystallization.

Thus, we see, and in the following pages will find it more extensively developed, that the relations of quantivalence of the elements have their complete expression in the periodic system, are regulated by it, and hence we must conclude that, in fact, the valence is not only a property attaching to the elements *per se*, but is also influenced by the nature of the combining elements; the hydrogen valence is constant, the valence to oxygen and halogens, on the contrary, is variable, according to definite rules. Valence, therefore, is a relative function of the elements.

**Periodicity of Thermo-Chemical Phenomena.** We observed in the case of the elements of the chlorine and oxygen group, that, in their hydrogen compounds the heat liberation decreased successively with increasing atomic weight (p. 57), while, with the chlorine and oxygen derivatives (corresponding to the growing metallic character), generally an increase occurs. Similar relations exhibit themselves with the halogen, oxygen and sulphur compounds of the metals, as will later be more closely exemplified with the individual groups. Here it is sufficient to call attention to the relations in the heterologous series.

In the formation of the hydrogen compounds of the elements of the two first periods, according to present data, the following quantities of heat are set free:—

$(C, H_4)$	$(N, H_3)$	$(O, H_2)$	$(F, H)$
19.5	11.9	57.2	—
$(Si, H_4)$	$(P, H_3)$	$(S, H_2)$	$(Cl, H)$
33.2	36.5	4.5	22.0*

\* The numbers given here for the heat intensity, as well as those following, indicate so-called great calories, which contain 1000 ordinary or small calories; therefore, to convert them into the latter, multiply them by 1000.



In the halogen compounds the heat is more regular:—

Li, Cl	(Be, Cl <sub>2</sub> )	(B, Cl <sub>3</sub> )	(C, Cl <sub>4</sub> )	(N, Cl <sub>3</sub> )	(O, Cl <sub>2</sub> )	(F, Cl)
93.8	—	104	—	—38.1	—18	—
(Na, Cl)	(Mg, Cl <sub>2</sub> )	(Al, Cl <sub>3</sub> )	(Si, Cl <sub>4</sub> )	(P, Cl <sub>3</sub> )	(S, Cl <sub>2</sub> )	(Cl, Cl)
97.7	151.0	160.9	157.6	68.9	—	—

With the bromides, it is less throughout, and the least with the iodides. Consequently, a maximum appears to lie in the middle of the periods. On calculating, however, the heat intensity, which corresponds to 1 equivalent of the elements (united with 1 equivalent of chlorine) we obtain successively decreasing numbers, corresponding to the decrease of the basic-metallic character of the elements:—

(Na, Cl)	$\left(\frac{\text{Mg, Cl}_2}{2}\right)$	$\left(\frac{\text{Al, Cl}_3}{3}\right)$	$\left(\frac{\text{Si, Cl}_4}{4}\right)$	$\left(\frac{\text{P, Cl}_3}{3}\right)$	$\left(\frac{\text{S, Cl}_2}{2}\right)$	(Cl, Cl)
97.7	75.5	53.6	39.2	23	—	—

Perfectly similar relations are furnished by the oxides:—

(Na <sub>2</sub> O)	(Mg.O)	(Al <sub>2</sub> O <sub>3</sub> )	(Si <sub>2</sub> O <sub>2</sub> )	(P <sub>2</sub> O <sub>5</sub> )	(S <sub>2</sub> O <sub>3</sub> )	(Cl <sub>2</sub> O <sub>7</sub> ).
100.2	145.8	388.8	219	363	104	—

Calculated upon 1 equivalent, the heat intensity is:—

50.1	72.9	64.6	54.7	36.3	17.3
------	------	------	------	------	------

That the heat of combination is smaller with sodium oxide than with magnesium oxide, depends partly upon the solubility of the first, as this property is also to be included as a thermal function. A like diminution of heat intensity shows itself also with the heterologous elements in their compounds of similar form:—

(Mn, Cl <sub>2</sub> )	(Fe, Cl <sub>2</sub> )	(Co, Cl <sub>2</sub> )	(Ni, Cl <sub>2</sub> )	(Cu, Cl <sub>2</sub> )	(Zn, Cl <sub>2</sub> )
111.9	82	76.4	74.5	51.6	97.2
(Mn, O)	(Fe, O)	(Co, O)	(Ni, O)	(Cu, O)	(Zn, O)
94.7	68.2	63.4	60.8	40.8	85.4

Remarkable are also the following series:—

Ag, Cl,	Cd, Cl <sub>2</sub> ,	In, Cl <sub>3</sub> ,	Sn, Cl <sub>4</sub>	Sb, Cl <sub>3</sub>	Te, Cl <sub>2</sub>
29.3	93.2	—	127.2	87	—
(Ag <sub>2</sub> O)	(Cd, O)	(In <sub>2</sub> , O <sub>3</sub> )	(Sn, O <sub>2</sub> )	(Sb <sub>2</sub> , O <sub>3</sub> )	(Te, O)
5.9	65.6	—	133.5	—	—

## THE METALS.

Although there is no sharp line of demarkation between metals and non-metals, yet these two classes of bodies form, in their entire deportment, a distinct contradiction, as appears plainly in the periodic system of elements. In physical respects the character of metals determines itself by the external appearance and by the conductivity of heat and electricity; chemically, it shows itself chiefly in the basicity of the oxygen compounds; yet we see that with the increase of the number of the oxygen atoms, the basic character diminishes gradually and passes over into an acid-forming one.

### PHYSICAL PROPERTIES OF THE METALS.

At ordinary temperatures all the metals excepting mercury are solid, slightly volatile bodies. They are opaque, and only some, like gold, when beaten into thin leaflets, permit the passage of light to a limited extent. In compact mass they exhibit metallic lustre and possess mostly a whitish-gray color; only gold and copper are brilliantly colored. In powder form almost all the metals are black. The most crystallize in forms of the regular system; only a few, showing a metalloid character, are not regular. Thus, antimony and bismuth crystallize hexagonally, and tin is quadratic. The specific gravity of the metals is very different, and varies from 0.59 to 22.4 as seen from the following arrangement—

Lithium,	0.59	Antimony,	6.7	Lead,	11.3
Potassium,	0.86	Zinc,	7.1	Palladium,	11.8
Sodium,	0.97	Tin,	7.3	Thallium,	11.9
Rubidium,	1.52	Iron,	7.8	Mercury,	13.5
Calcium,	1.58	Cobalt,	8.5	Gold,	19.3
Magnesium,	1.75	Cadmium,	8.6	Platinum,	21.4
Aluminium,	2.56	Copper,	8.9	Iridium,	22.3
Chromium,	5.9	Bismuth,	9.8	Osmium,	22.4
Arsenic,	5.9	Silver,	10.5		

In general the specific gravity of the metals, as also of the metalloids, increases with the atomic weights; more especially do they stand in a sharp periodic dependence with reference to the latter. The first members of all periods possess low

specific gravities; the latter grow gradually until the middle of the period, where the maximum is attained, and then they again decrease (p. 235). These relations show themselves more fully if, instead of the specific gravity, we compare the specific volumes or atomic volumes; *i. e.*, the quotients from the atomic weights (A) and specific gravities (d):—

$$\frac{A}{d} = \text{specific volume.}$$

These quotients express the relative volumes of the atoms (in solid or liquid state). Thus the atomic volume of lithium  $\frac{7}{0.59} = 11.9$ , that of potassium  $\frac{39}{0.86} = 45.4$ ; *i. e.*, the potassium atom occupies a 3.8 times larger space than that of the lithium atom. The periodic alterations of the atomic volumes are set opposite to those of the specific gravities, as the former are obtained by the division of the atomic weights by the specific gravity. Therefore the atomic volumes decrease gradually, commencing from the first members of the periods (Li Na K Rb), attain a minimum in the middle of the periods and then increase again until to the last members (Cl Br I). On the other hand, with the homologous elements (the vertical series) with increase of atomic weight there is almost always seen an increase of the atomic volumes.

Since in the 3 large periods the alterations of the atomic volumes (as also of all other physical properties) indicate a simple periodicity (not double, like the valence), they are expressed in the following tables, by progressive series (page 234):—

ATOMIC VOLUMES OF THE ELEMENTS.

	Li	Be	B	C*	N	O†	F†												
	11.9	5.7	4.1	3.6	—	17	—												
	Na	Mg	Al	Si	P	S	Cl†)												
	23.7	13.8	10.7	11.2	13.5	15.7	25.6												
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	—	As	Se	Br			
45.4	25.4	—	—	9.3	7.7	6.9	7.2	7.0	6.7	7.2	9.7	11.6	—	13.2	16.9	26.9			
Rb	Sr	Y	Zr	Nb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te				
56.1	34.9	—	21.7	15.0	11.1	—	9.2	8.6	9.2	10.2	12.9	15.3	16.1	18.2	20.5				
I	Cs	Ba(La	Ce	Di)	—	—	—	—	—	—	—	—	—	—	—	—			
25.6	—	26.5	22	20	22														
	Yb	—	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	—	—				
	—	—	16.9	9.6	—	9.4	8.7	9.3	10.2	18.7	17.1	18.1	21.1						
	Th	—	—	Ur															
	30			13															

\* As diamond. † Liquid.



It is exceedingly noteworthy, that the elements standing at the beginning and end of the periods (one side the alkalis Li Na K Rb, and the alkaline earth metals Be Mg Ca Sr Ba—on the other, the halogens and the elements of the oxygen group), possess the greatest chemical energy, and there is scarcely a doubt that between chemical energy and atomic volume there exists a closer causal connection. We can suppose that the specifically light elements, with large atomic volumes, execute larger chemical oscillations, hence act together more readily and energetically. With this might be included, that, in energetic reactions, greater quantities of heat are eliminated. Further, might be deduced, that, between the elements of greater but opposite oscillations (the alkalis and halogens) the expressions of chemical valence are the simplest; that towards each other they deport themselves as monatomic.

The metals whose specific gravity is less than 5, are termed *light*, the rest *heavy*. The former have, in general, a greater chemical energy, therefore oxidize more easily and form strong basic oxides; their compounds are mostly readily soluble. The heavy metals possess, on the whole, a varying deportment. They are less energetic, less basic, and yield insoluble oxygen and sulphur derivatives; their naturally occurring compounds usually possess metallic lustre and are termed *ores*.

Most metals are very *malleable* and *tenacious*; hence can be beaten into thin plates and leaves and drawn out into wires; most malleable are gold and silver. Only a few, like antimony, bismuth and tin, which also possess a metalloidal character, are *brittle* and may be pulverized. Heat will fuse all metals, although some require the high temperature of the oxy-hydrogen flame.

The fusing points of the most important of them are the following:—

Mercury,	−39°	Aluminium,	750°
Rubidium,	+38°	Silver,	954°
Potassium,	62°	Gold,	1035°
Sodium,	95°	Copper,	1054°
Tin,	228°	Cast Iron,	1150°
Bismuth,	270°	Wrought Iron,	1500°
Cadmium,	315°	Palladium,	1500°
Lead,	334°	Platinum,	1779°
Zinc,	423°	Iridium,	1950°

A greater volatility also corresponds with the greater fusibility. Mercury boils at 360°; potassium and sodium about 440°; cadmium at 860°; zinc towards 1000°. The diffi-

cultly fusible metals may also be volatilized by the galvanic current.

All these physical properties bear a periodic dependence to the atomic weights, as will be more closely indicated in the individual groups.

### SPECIFIC HEAT—ATOMIC HEAT.

Of all physical properties of the elements, from a chemical standpoint, their heat capacity is the most important, and can serve for the determination of the atomic weights. To heat one and the same quantity, by weight, of the different metals or substances to one and the same temperature, a very varying amount of heat is required. This is evident from the following experiments:—

If we add to 1 kilogram of  $H_2O$  at  $0^\circ$  1 kilo. of  $H_2O$  at  $100^\circ$ , the temperature of the mixture of 2 kilograms is  $50^\circ$ . The quantity of heat necessary to raise 1 part by weight of  $H_2O$   $1^\circ$  is, for all temperatures from  $0$ – $100^\circ$  almost the same; this is designated the *heat unit* or calorie. On bringing to 1 kilogram  $H_2O$  at  $0^\circ$  1 kilogram Hg at  $100^\circ$ , the temperature of the water and of the mercury after their compensation will equal only  $3.2^\circ$ . Consequently the mercury has, as it cooled about  $96.8^\circ$  (from  $100$  to  $3.2^\circ$ ) given off 3.2 calories. The quantities of heat contained in equal parts by weight of water and mercury, therefore, deport themselves as  $96.8$  to  $3.2$ , *i. e.*, the specific heat of mercury (that of water being made = 1) is  $\frac{3.2}{96.8} = 0.0332$ .

On comparing the specific heats of solid elements found in this way with their atomic weights, we discover that these are inversely proportional to the latter, and hence the product of the specific heat and atomic weight for all solid elements (few excepted), is a constant quantity. This fact was first discovered by Dulong and Petit (1819) and formulated in the following law: *The solid elements possess the same atomic heat.*

In the subjoined table are presented the specific heats of the elements in solid condition (as far as they have yet been determined). *W* represents the specific heat, *A* the atomic weight, and the product,  $W \times A$ , the atomic heat:—

ELEMENTS.		W	A	W × A
Hydrogen*		5,880	1	5,6
Lithium	Li	0,941	7	6,6
Beryllium	Be	0,408	9,3	3,8
Boron (amorphous)	B	0,254	11	2,8
Graphite }	C	0,174	} 12	2,1
Diamond }		0,143		1,7
Sodium	Na	0,293	23	6,7
Magnesium	Mg	0,245	24	5,9
Aluminium	Al	0,202	27,3	5,5
Silicon (cryst)	Si	0,165	28	4,6
Phosphorus (yellow)	P	0,189	31	5,9
Sulphur (rhombic)	S	0,178	32	5,7
Potassium	K	0,166	39	6,5
Calcium	Ca	0,170	40	6,8
Chromium	Cr	0,100	52,4	5,2
Manganese	Mn	0,122	54,8	6,7
Iron	Fe	0,112	56	6,3
Cobalt	Co	0,107	58,6	6,3
Nickel	Ni	0,108	58,6	6,4
Copper	Cu	0,093	63,3	5,9
Zinc	Zn	0,093	65	6,1
Gallium	Ga	0,079	69,9	5,5
Arsenic (cryst)	As	0,082	75	6,2
Selenium (cryst)	Se	0,080	79	6,4
Bromine (solid)	Br	0,084	80	6,7
Zirconium	Zr	0,066	90	6,0
Molybdenum	Mo	0,072	96	6,9
Ruthenium	Ru	0,061	103,4	6,3
Rhodium	Rh	0,058	104	6,0
Palladium	Pd	0,059	106,3	6,3
Silver	Ag	0,056	107,6	6,0
Cadmium	Cd	0,054	111,6	6,0
Indium	In	0,057	113,4	6,5
Tin	Sn	0,054	117,8	6,5
Antimony	Sb	0,052	122	6,4
Tellurium	Te	0,047	126,8	6,0
Iodine	I	0,054	126,5	6,8
Lanthanum	La	0,045	139	6,2
Cerium	Ce	0,045	140	6,2
Didymium	Di	0,045	144	6,5
Tungsten	W	0,033	184	6,1
Osmium	Os	0,031	(198)	6,2
Iridium	Ir	0,032	192,7	6,3
Platinum	Pt	0,032	196,7	6,4
Gold	Au	0,032	196,2	6,4
Mercury (solid)	Hg	0,032	200	6,4
Thallium	Tl	0,033	204	6,8
Lead	Pb	0,031	206,4	6,5
Bismuth	Bi	0,030	210	6,5

\* As Palladium hydride.



From the table, it is evident that the atomic heats of the most elements lie between 5.9 and 6.8, and equal, upon an average, 6.4.

Only in the case of few elements is the atomic heat somewhat less (S, P, Si, Al) or considerably less (C, B, Be), than the mean. Such are those with low atomic weight, having a metalloidal character and occupying the middle of the two small periods. These variations bear distinct periodic dependence to the atomic weights:—

Na	Be	B	C	N	O	Fl
6.7	3.8	2.5	1.9	—	—	—
K	Mg	Al	Si	P	S	Cl
6.5	6.0	5.5	4.6	5.6	5.7	—

The variations in the middle are in part explained by the fact that most of the elements in their different modifications (crystalline, amorphous, malleable) possess a somewhat different heat capacity, as observed with carbon. More important, however, is the influence of temperature. The figures in the table indicate mostly the heat capacities at medium temperatures. It was known before that these show a slight increase with the temperature, but only recently, through H. E. Weber, has it been proven that, for the elements C, B and Ti, which, at medium temperatures, possess a remarkably low atomic heat, the increase is very considerable; that, beyond a definite temperature, the atomic heat becomes tolerably constant, and then almost agrees with the law of Dulong and Petit:—

	W.	A.	W × A.
Diamond, graphite, above 600°,	0.45	12	5.4
Boron, above 600°,	0.5	11	5.5
Silicon, above 200°,	0.2	28	5.6

It is probable that, for all elements, a definite temperature exists, at which their heat capacities become accurately comparable.

From this close agreement of the found atomic heat of the metals with the medium, follows, without doubt, the occurrence of a regularity, and we must conclude that the slight variations, apart from the inaccuracy of the observations, are influenced by secondary causes. Hence the specific heat may

serve for the derivation of the atomic weight of metals; *the atomic weight is equal to the constant quantity, 6.4 divided by the found specific heat* :—

$$A = \frac{6.4}{W}$$

The atomic weights derived from the specific heat—the so-called *thermal atomic weights*, agree almost in all instances with those obtained from the vapor density of the free elements or their volatile compounds.\* Where no volatile compounds of an element are known, the specific heat is the only certain means of fixing the actual atomic weight. By analysis the equivalent weight 37.8 (InCl) of indium is fixed with great accuracy; it is, however, unknown whether the atomic weight is double or triple that quantity. The specific heat of indium is 0.0569, from which the atomic weight would be  $\frac{6.4}{0.0569} = 112.5$ —a number closely approaching three times the equivalent weight of indium 113.4 ( $= 37.8 \times 3$ ). From this it follows that the true atomic weight of indium is 113.4 and that it is triatomic,  $\text{InCl}_3$ .

In their solid compounds the elements retain the specific heat attaching to them in their free, solid state; hence the molecular heat is equal to the sum of the atomic heats of the elements constituting the molecules—law of Neumann and H. Kopp. Hence the atomic heat of elements not known in solid condition may be derived from the molecular heat of their compounds. Thus are found the following atomic heats: for nitrogen, 6.4; for chlorine, 6.4; for oxygen, 4; for fluorine, 5; for hydrogen, 2.3.

In the free gaseous state the elements have mostly a slighter atomic heat, as seen from the following table:—

	A	W†	A × W
Oxygen....	16	0.156	2.5
Hydrogen..	6	2.405	2.4
Nitrogen...	14	0.172	2.4
Chlorine...	35.4	0.093	3.3

\* It is only for iron that the atomic weight derived from its few volatile compounds is twice as large (112) as that resulting from the heat capacity—of free iron, hence we must conclude that in these compounds two iron atoms are present.

† By constant volume.

The law, that the atoms in solid condition possess the same heat capacity ( $A. W = A'. W'$ ), finds an interesting analogy and exemplification in the result coming from the mechanical gas theory, and in the proposition of Avogadro, that the molecules in gas condition, at like temperatures, have similar degree of motion ( $M. v. = M'. v'$ ) and experience like increases. As in the gas condition the molecules, so for the solid the atoms, are the smallest mass particles, which have the same heat energy. The velocity of their heat motion, both for the molecules and for the atoms, is so much the greater, the smaller their masses.

### ISOMORPHISM.

As indicated in the preceding pages, the atomic weights of the elements may be directly derived from the heat capacity of solids, while from the gas density of the volatile compounds the molecular weights, and from the latter, then, indirectly, are ascertained the atomic weights (compare p. 100). A third, if, although less general and certain, means of determining the atomic and molecular weights is afforded by *isomorphism*. By this is understood the phenomenon observed by Mitscherlich (1819), that chemically similar bodies possess the same or almost the same crystal form; as an essential mark of isomorphous bodies is added their ability of crystallizing together—to form so-called isomorphous mixtures. Conversely, therefore, from the isomorphism of two compounds may be concluded an analogous chemical composition, a similar number of atoms in the molecule. From this, such quantities of the elements which can replace each other in isomorphous compounds, are accepted as the relative atomic weights. Thus, for example, for the metals calcium, strontium and barium, not yielding any volatile compounds, the atomic weights were not derived from the heat capacity; the isomorphism, however, of many of their derivatives with those of magnesium determined the same; the quantities of these elements, replacing 24 weight parts of magnesium (1 atom), were accepted as the true atomic weights.

In the present state of chemistry, but merely secondary importance attaches to isomorphism as a method of determining atomic weights. The phenomena of pleomorphism, according to which one and the same substance frequently possesses several crystalline forms, teach us that the latter are not only



dependent upon the chemical molecules, but that the latter (according to as yet unknown laws) may unite to more complicated crystal molecules. Hence, isomorphism affords a means for determining the molecular size of solid substances.

Upon the other hand, many cases are known where chemically dissimilar compounds possess similar isomorphous crystalline form. Thus, dimorphous calcium carbonate ( $\text{CaCO}_3$ ), as calcite is isomorphous with soda saltpetre ( $\text{NO}_3\text{Na}$ ), while as aragonite it is isomorphous with potassium saltpetre ( $\text{KNO}_3$ ). Consequently, isomorphism is only to be applied with care, in chemical conclusions. Yet, generally, it is seen that chemically similar bodies have like crystalline form, especially if the similarity of the elements according to groups be taken into consideration, as expressed in the periodic system. Thus, the isomorphism of the sodium compounds with the silver and cuprous derivatives, of the permanganates with the perchlorates ( $\text{ClO}_4\text{K}$ ), of the chromates with the sulphates ( $\text{SO}_4\text{Na}_2$ ), confirms the relations presented in the periodic system. Details upon this will be noticed in the consideration of the individual groups.

#### CHEMICAL PROPERTIES OF THE METALS.

The metals combine, generally without difficulty, with the metalloids, and form with them well characterized compounds the properties of which are essentially different from the elements composing them. The greater the chemical difference of two bodies (metals and non-metals, bases and acid) the more energetic, in general, is their effort to unite, and the more different and more stable the resulting products. As we have seen, the analogous metalloids (the group of chlorine, of sulphur) form but slightly characteristic derivatives with each other. Similarly also the metals, by fusion with each other, form indefinite metal-like compounds, known as alloys.

**Alloys**, for the solid condition, are essentially the same as solutions for the liquid. Solutions and alloys constitute the change from the mechanical mixtures to the real chemical compounds. In both instances the constituents possess only a slight affinity for each other, and, therefore, unite in almost all proportions to the so-called *undetermined compounds* (see p. ). We, however, know that in solutions *definite* compounds frequently preëxist; thus in an aqueous solution of sulphuric

acid the hydrate  $H_2SO_4 \cdot 2H_2O$ ; in aqueous nitric acid the hydrate  $HNO_3 \cdot H_2O$ . Also in the solutions of the salts crystallizing with water of crystallization at definite temperatures, definite compounds with water (*e. g.*,  $Na_2SO_4 \cdot 10H_2O$ ,  $CoCl_2 \cdot 6H_2O$ ) preëxist. Similarly constituted combinations also appear to be present in the alloys, which represent compounds according to atomic relations. Antimony and tin form a crystalline compound of the composition  $Sb_2Zn_3$ . The crystalline form is always influenced by definite chemical compounds. This double character of the alloys manifests itself in their properties. In many respects they show the average deportment of the metals from which they arise. By combining the various metals we can procure alloys of the desired properties; on this is founded the technical application of the same. Thus, to gold and silver, which are very soft in pure condition, can be imparted a greater hardness if they are alloyed with copper; and the latter, again, may be rendered harder by fusion with zinc. In other properties of alloys, however, is exhibited the character of a chemical compound. Their temperature of fusion generally is not the average of the metals constituting them, but always lies lower. An alloy of 8 parts lead, 15 Bi, 4 Sn and three of Ca melts at  $65^\circ$ , although each of the single metals fuses above  $200^\circ$ .

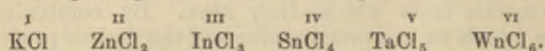
Mercury is able to dissolve almost all metals forming alloys known as *amalgams*, which can crystallize. With hydrogen, which, in a chemical respect, possesses complete metallic character, the most metals do not combine, probably owing to its volatility. Only palladium, potassium and sodium furnish the compounds  $Pd_2$ ,  $K_2H$  and  $Na_2H$ , which deport themselves as alloys, while copper forms a pulverulent compound ( $CuH$ ). That antimony yields a gaseous product ( $SbH_3$ ), depends upon its pronounced metalloidal character. The ability of individual metals of the platinum and iron group to permit the passage of hydrogen at a red heat depends, probably, upon a chemical attraction; hydrogen first dissolves and is then evaporated again.

---

**Halogen Compounds.** The metals unite directly with the halogens to salt-like compounds, which are not decomposed by water at ordinary temperatures, and, in general, are very stable; on the opposite hand, the halogen compounds of the

metalloids (excepting those of carbon) are easily broken up by water. These compounds are also produced by the action of the haloid acids upon the free metals, their oxides, hydrates and carbonates, whereby they plainly characterize themselves as salts of the haloid acids. A third procedure for the formation of chlorides and bromides, essentially analogous to the first, rests upon the simultaneous action of carbon and chlorine, or bromine upon the oxides (see Chloride of aluminium and silicon).

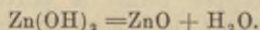
Corresponding to the various valences of the metals exist the following compound forms of halogen derivatives:—



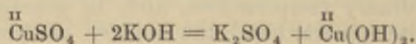
The higher valence of the elements pronounces itself more emphatically in their more stable oxygen compounds.

### OXIDES AND HYDROXIDES—HYDRATES.

The affinity of the metals for oxygen varies. Some of them oxidize in moist air and decompose water, even at ordinary temperatures. Such are the so-called alkalis and alkaline earths (the potassium and calcium groups). Their oxides dissolve readily in water and form strong basic hydroxides or hydrates (KOH, Ca(OH)<sub>2</sub>), which, mostly, are not decomposed by glowing. Other metals (the so-called heavy metals) oxidize and decompose water only at higher temperatures; their oxides are insoluble in water, generally afford no hydrates, as the latter, upon heating, readily decompose into oxides (anhydrides) and water:—

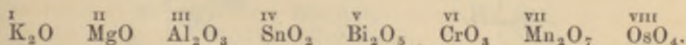


They are of a less basic nature, and their soluble salts usually exhibit acid reaction. Some metals, finally, as gold and platinum (the noble metals), are incapable of combining directly with oxygen. Their oxides, obtained in another way, decompose readily under the influence of heat into metal and oxygen. The universal method for the preparation of insoluble oxides and hydroxides of the heavy metals depends upon the precipitation of the solutions of their salts by alkaline bases:—

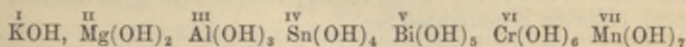




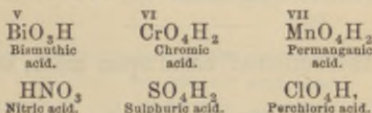
The different valence of the metals exhibits itself most distinctly in their salt-forming oxygen derivatives. Corresponding to the eight groups of the periodic system of the elements we have the following eight forms or types of the highest salt-producing oxides (see p. 241):—



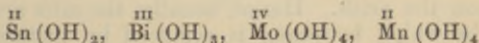
From these are derived the hydroxides or hydrates:—



The oxides and hydrates of the two first forms possess a strong basic character and furnish salts with acids. In the oxides and hydrates of the succeeding forms there is shown an acid-like character together with the predominating basic character. Hence they dissolve in alkalis and form salt-like derivatives with bases, in which hydrogen is replaced by metals, *e. g.*  $\text{Al(ONa)}_3$ . These higher (normal) hydrates are not very stable, give up water and pass into *metahydrates*, which retain the acid character. Thus, from  $\text{Al(OH)}_3$  is derived  $\text{AlO.OH}$ , which yields salt-like compounds, *e. g.*,  $\text{AlO.OK}$ ; from  $\text{Sn(OH)}_4$  is derived the stannic acid  $\text{SnO(OH)}_2$  and its salts, as  $\text{SnO}_3\text{K}_2$ . The oxides of the three last groups, finally, are only of an acid nature, and afford salts with bases. Their corresponding highest hydrates are very unstable or do not exist; inasmuch as, giving up 1, 2 and 3 molecules of water, they yield the ordinary acids (p. 241):—

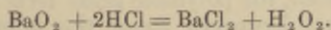


Like the metalloids, the metals of the four last series form lower oxides and hydrates (p. 241) in which they exhibit a lower atomicity:—

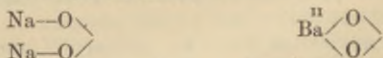


These lower oxides have a basic character, and it is the more pronounced the further removed they are from the limiting form. Throughout they resemble, in department, the corresponding combination forms of the metals of the three first groups.

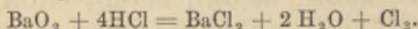
The metals of the two first groups have higher oxygen compounds, called *peroxides*, *e. g.*,  $\text{Na}_2\text{O}_2$ ,  $\text{BaO}_2$ . These do not form corresponding salts, and readily lose an atom of oxygen. By the action of dilute acids hydrogen peroxide is produced:—



Based on this reaction, it is very probable that in the peroxides, as in that of hydrogen, the oxygen atoms are arranged in a chain-like manner:—



When concentrated acid acts upon them, oxygen is evolved, and salts of the lower oxides result; heated with hydrochloric acid, chlorine is generated:—

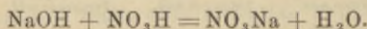


Ordinarily, all higher oxides which are not able to form salts and which evolve chlorine with hydrochloric acid are termed peroxides, *e. g.*,  $\text{PbO}_2$ , lead peroxide, and  $\text{MnO}_2$ , manganese peroxide. However, the compounds do not, indeed, possess the structure of true peroxides.

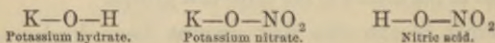
Lead dioxide,  $\text{PbO}_2$ , is throughout analogous to tin dioxide,  $\text{SnO}_2$ , and is capable of combining with bases; therefore, we must grant in it a direct union of the two oxygen atoms with tetra-tomic lead. So, too, is manganese probably tetratomic in manganese peroxide. The difference of these oxygen compounds from the true peroxides shows itself in that they are not able to form hydrogen peroxide.

Finally, some monatomic metals are capable of forming oxides containing 4 atoms of metal, *e. g.*,  $\text{K}_4\text{O}$ ,  $\text{Ag}_4\text{O}$ ; these compounds are termed *quadrant oxides* or *suboxides*.

**Salts.** By the action of bases upon acids, salts and water are formed:—



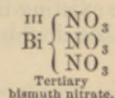
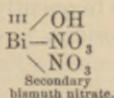
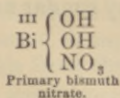
These are also produced by the direct union of basic with acid oxides:  $\text{Na}_2\text{O} + \text{SO}_3 = \text{Na}_2\text{SO}_4$ , and by the action of metals upon the acids. Hence, usually, the salts are viewed as acids in which hydrogen is replaced by metals. Upon inquiring, however, into the composition of salts we discover them so constituted that a diatomic oxygen atom connects the metal with the acid radical (p.     ).



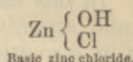
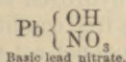
The salts, therefore, according as it is more practicable, can be regarded as acid derivatives, and also as derived from the basic hydrates by replacement of hydrogen.

As we have seen, the polybasic acids form by replacement of one or several hydrogen atoms the *primary*, *secondary*,

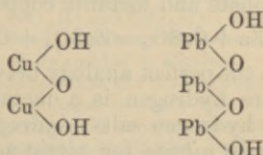
*tertiary, etc., salts.* Similarly are derived from polyatomic metals (or the polyacid, polyhydric bases) primary, secondary, etc., salts:—



Such salts in which not all the hydroxyl groups of the polyacid hydroxide are replaced by acid residues are called *basic*:—

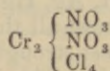
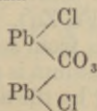
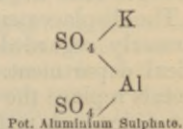
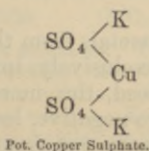
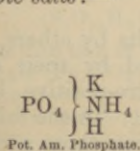


Besides these basic salts there exist some of another form. We saw that the polybasic acids can combine to poly or anhydro acids; similarly, also, can polyhydric bases form polyhydrates:—

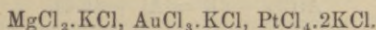


from which, by replacement of hydroxides by acid residues basic salts are obtained (see copper and lead).

By replacement of the hydrogen atoms in the polyhydric acids or bases by various radicals arise the so-called mixed or *double salts*:—



The halogen double salts are usually viewed as molecular compounds:—

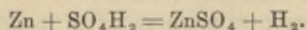




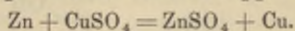
If, however, the fluorides of boron and silicon  $\text{BF}_3$ ,  $\text{KFl}$ ,  $\text{SiFl}_4$ ,  $2\text{KFl}$  be derived from peculiar, atomic constituted acids,  $\text{HBF}_4$ ,  $\text{H}_2\text{SiFl}_6$ , then a peculiar union of atoms may be regarded as existing in the frequently very similar and isomorphous metallic double chlorides.

#### ACTION OF METALS UPON SALTS AND ACIDS.

We have seen that the metals by solution in acids are able to form salts. In this case the hydrogen is directly replaced by the metal and separated in a free condition (providing in the moment of its formation it does not act upon the acid):—

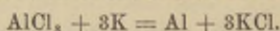


In the same manner do the metals deport themselves with the salts. Zinc introduced into a solution of copper sulphate is dissolved to sulphate and metallic copper deposits:—



Herein is shown the perfect analogy between acids and salts. In chemical nature hydrogen is a metal. Hence the acids may be viewed as hydrogen salts; *hydrogen sulphate* for sulphuric acid, *hydrogen nitrate* for nitric acid, etc. The similarity of salts and acids shows itself, too, in their acidity. All soluble salts of the metals, whose hydrates are weak bases, exhibit acid reaction, and color blue litmus paper red. Only the salts of the strong basic metals, like potassium and calcium, show a neutral or basic reaction—providing the base is stronger than the acid.

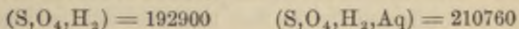
The displacement of metals from their salts by others, was formerly regarded as exclusively influenced by their electrical deportment. Indeed, the more electro-positive basic metals replace the electro-negative, less basic. In the following series each metal throws out from solution those preceding it: Au, Pt, Ag, Hg, Cu, Pb, Sn (Fe, Zn). Iron and zinc precipitate almost all the heavy metals from solutions of their salts. The most strongly positive potassium is able to displace all other metals. This is most evident by the action of molten potassium upon the haloid salts—a reaction which frequently serves for the separation of the metals in free condition:—



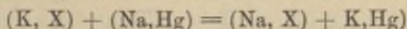
In its electrical deportment, hydrogen stands near zinc; like the latter it must, therefore, displace all more negative metals. If this does not happen, the cause must be sought in the volatility of the hydrogen; in fact, we know that hydrogen, under pressure, is capable of separating gold, silver, and some other metals from their salt solutions.

Formerly great importance was attributed to the electrical behavior of the elements, and all were arranged in an electro-chemical series, in which oxygen figured as the negative and potassium the positive pole,  $O \dots + K$ . The opinion prevailed that the chemical affinity of the elements depended upon their electrical differences, and that chemical union occurred because the opposite electricities united—*electro-chemical theory* of Berzelius. Now, however, we know that in the expression of chemical affinity only secondary importance is attached to the electrical deportment of bodies. Although in general the affinity corresponds to the electrical difference, yet this does not always occur. Thus the strongly negative chlorine expels bromine or iodine from their hydrogen, and nearly all their metallic compounds; conversely, chlorine and bromine are displaced by iodine from their oxygen compounds as  $(ClO_2, H)$  and  $(ClO_4, H)$ . Similarly, lead separates tin from its chloride,  $SnCl_4$ , while on the other hand, tin throws out lead from the solution of its oxides in alkalies.

At present it is established that the mutual deportment of the metals is dependent upon and regulated by their thermo-chemical relations. A metal displaces another from its oxygen salts, as also from its oxides, sulphides or halogen compounds, if the heat of formation of the resulting bodies is greater than the ones acting; this agrees with the principle of greatest heat development. Thus copper displaces silver from its sulphate, because the heat of formation of the copper sulphate (in aqueous solution) is about 33570 calories greater than that of silver sulphate. Sulphuric acid dissolves most metals with heat liberation, because their heat of formation—



is less than that of the most sulphates. The heat of formation of lead sulphate  $(Pb, S, O_4)$  equals 213500; therefore lead is not dissolved by concentrated but by dilute sulphuric acid, because in the latter the produced lead sulphate is not soluble. For the same reason potassium displaces almost all the other metals; on the opposite hand, potassium is separated by sodium amalgam, with formation of potassium amalgam, as the heat of formation of the latter is much greater than that of sodium amalgam, and therefore, in the equation—



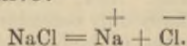
the heat upon the right side overbalances. (Berthelot).

Although the affinity relations dependent upon the quantity of heat frequently also correspond with the electrical differences of the free elements, this is so influenced that the electro-motive energy is induced by the heat, and proportional to the same (see p. 262). The latter

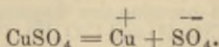
constitutes the primary cause; it varies in the different compounds and explains the opposing deportment of the elements. Chlorine displaces iodine in iodides, not because it is more strongly electro-negative, but because the heat of formation of the chlorides is greater. Conversely, from chloric acid chlorine is eliminated by iodine.

### ELECTROLYSIS OF SALTS.

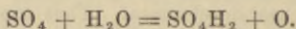
On subjecting a salt in a fused or dissolved condition to the action of a galvanic current, it is decomposed, so that the metal separates upon the negative pole and the acid group or halogen upon the positive:—



The oxygen salts behave in the same way; the metal upon the negative pole, the acid residue upon the positive:—

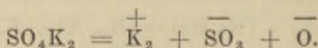


As the liberated acid residue cannot exist in a free condition, a secondary reaction occurs, by which it generally, especially in the electrolysis of aqueous solutions, breaks up into oxygen and an acid oxide, which with the water of the solution forms the acid anew:—

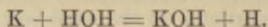


Thus, in the electrolysis of salts, the metal and oxygen separate out—the first at the negative, the latter at the positive pole. That indeed the decomposition occurs in the manner indicated is confirmed by the fact that free acid arises at the positive pole.

All neutral salts are decomposed in like manner. If, however, the metal contained in the salt acts upon water when free, manifestly a secondary reaction occurs at the negative pole. The real electrolytic decomposition of potassium sulphate would then take place according to the following equation:—



The separated potassium decomposes water with formation of potassium hydrate and the disengagement of hydrogen:—

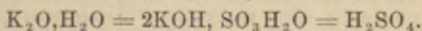




Therefore, hydrogen and potassium hydrate occur as definite decomposition products, at the negative pole; at the positive, however, oxygen and sulphuric acid. On coloring the liquid exposed to the electrolysis with a little violet syrup that part at the + pole will be reduced by the acid formed, while that at the - pole will have a green color from the base.

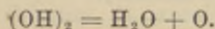
That, in fact, the electrolytic decomposition of potassium sulphate and similar salts proceeds in the manner given, may be experimentally proven by using mercury as negative electrode; then the separated potassium unites to an amalgam with the mercury, which acts only gradually upon the water.

Formerly it was supposed that the alkali salts, upon electrolysis, were directly decomposed into metallic and acid oxides, which with water, yielded the hydrates ( $\text{KOH}$  and  $\text{SO}_4\text{H}_2$ ); the appearance of H and O was attributed to the simultaneous electrolytic decomposition of water (a view which was set aside by the behavior of the other salts). Based on this erroneous idea all salts were held to be binary compounds of the metallic oxides (bases) with acid oxides (acids), e. g.,  $\text{K}_2\text{O}$ ,  $\text{SO}_3 = \text{K}_2\text{SO}_4$ ,  $\text{K}_2\text{O}$ ,  $\text{N}_2\text{O}_5 = 2\text{KNO}_3$ —dualistic theory of Berzelius. The acids and bases were also thought to be binary compounds of a metallic oxide or acid anhydride with water:—

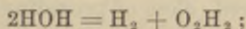


The acid oxides or anhydrides were termed acids and the true acids hydrates.

Other compounds are decomposed in the same way as the salts. Thus molten caustic potash  $\text{KOH}$ , breaks up into K and OH; the first separates in metallic form upon the negative pole (and gradually acts upon  $\text{KOH}$  with hydrogen disengagement), while at the positive pole water and oxygen appear—produced by decomposition of the at first formed hydrogen peroxide:—



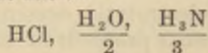
It is, therefore, probable that also water is decomposed in analogous manner:—



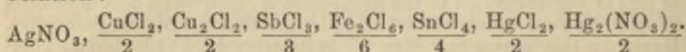
the peroxide produced at first breaks up, however, mostly into water and oxygen.

Considering the quantity relations which are deposited from various compounds, by the same electric current, we will discover that *invariably a like number of valences is dissolved in like time, i. e., equivalent quantities in the idea of the valence theory are separated* (p. 162). Thus in the simultaneous de-

composition of hydrochloric acid, water and ammonia (pp. 64, 88, 119) equal volumes of hydrogen (= 1 part) are liberated, while at the positive pole 1 volume chlorine (= 35.5 parts),  $\frac{1}{2}$  volume oxygen (= 8 parts), and  $\frac{1}{3}$  volume nitrogen (= 4.66 parts) appear. The electrolytically decomposed quantities stand, therefore, in the ratio:—



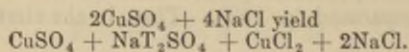
In the same way, from all metallic chlorides (and other salts) equal quantities of chlorine are set free (as the chlorine atoms in all are alike), whilst the quantity of the precipitated metals agrees with their chemical activity. The electrolytically decomposed quantities of different salts stand in the following relation:—



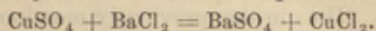
As the quantity of heat liberated in the formation of equivalent quantities of the compounds, consequently, too, that necessary for the decomposition, is very different; equivalent quantities, however, being separated by the galvanic current, the energy of the latter must distribute itself unequally upon the various electrolytes and, indeed, in proportion to the heat of decomposition. Joule has experimentally proven that the electro-motive energy disengaged by a galvanic element is proportional to (if no secondary actions occur) or equal to the amount of heat of the reaction producing it. Thus the electro-motive energy of a Daniell's element (combination of zinc in dilute sulphuric with copper in copper sulphate) depends on the chemical replacement of copper in its sulphate by zinc, a reaction setting free 50100 calories. As, however, 69000 calories are requisite for the decomposition of one molecule of water, it is obvious that the electrolysis of water cannot be effected by one Daniell's element, but that the combination of at least two of these is necessary.

A chemical action will frequently occur when two salts in solution or fusion come together. The resulting phenomena Berthollet endeavored (close of preceding century) to explain in the following manner, in that he referred them to pure physical causes and excluded every special chemical affinity.

In the opinion of Berthollet, in the solution of two salts four always arise. For example, on mixing solutions of copper sulphate and sodium chloride, there exist in solution copper sulphate, sodium sulphate, copper chloride and sodium chloride:—

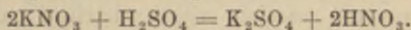


That copper chloride is really present in the solution together with the sulphate, follows, from the fact that the blue color of the latter, by the addition of sodium chloride, acquires a greenish color, peculiar to the copper chloride. Suppose one of the four salts formed in the solution is insoluble or volatile, the reaction will occur somewhat differently. Upon adding barium chloride to the copper sulphate solution, at the beginning, as in the first case, four salts will be formed. The barium sulphate produced separates, however, in consequence of its insolubility, the equilibrium of the four salts will be disturbed, and new quantities of  $\text{CuSO}_4$  and  $\text{BaCl}_2$  act upon each other to complete transposition:—



And the same may therefore be explained by the insolubility of the barium sulphate. On adding  $\text{HCl}$ , or soluble chlorides to the solution of a silver salt all the silver is precipitated as chloride, as the latter is insoluble.

Take another example. On adding sulphuric acid to a solution of potassium nitrate there is apparently no perceptible alteration. We may suppose that the four compounds,  $\text{KNO}_3$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ , are present in the solution. Upon warming the latter volatile nitric acid will evaporate, and, in proportion to its separation, new quantities of potassium nitrate and hydrogen sulphate will act upon each other until the transposition is complete:—

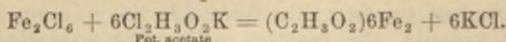


The decomposition of potassium nitrate by sulphuric acid, therefore, is the consequent of the volatility of the nitric acid. Sulphuric acid decomposes sodium chloride in the cold, because hydrogen chloride is volatile. Carbonates are decomposed even by very weak acids, because the carbonic acid,  $\text{H}_2\text{CO}_3$ , at once separates gaseous carbon dioxide,  $\text{CO}_2$ .

By such physical causes, in many instances, the chemical transpositions may be explained, and there is no doubt that to them attaches an important role. It is, however, not justifiable to ignore any special chemical affinity between the various substances, as happened with Berthollet. Independent of all physical causes, chemical affinity is a self-active cause. This is obvious in the solutions of salts. Mix, *e. g.*, ferric chloride with potassium acetate, and there is obtained a dark red solution, in consequence of the formation of

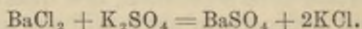


iron acetate. Although an insoluble salt is not produced here, yet the rearrangement of the two salts, evident from the optical properties of the solution, is a perfect one; in solution are only iron acetate and potassium chloride:—

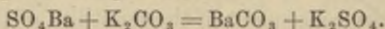


The transposition is determined by the strong affinity of potassium for chlorine and by the weak basic nature of ferric oxide. If the difference between the affinities of the bases and salts is not so great, then four salts will exist in solution; their quantity, however, will be proportional to the different affinities and determined by the equilibrium of all the forces of attraction. Thus in the previously mentioned solution of copper sulphate and sodium chloride are contained four salts, the quantities of copper chloride and sodium sulphate are, however, much greater than those of copper sulphate and sodium chloride (proven by the optical properties of the solution), because the affinity of sulphuric acid for sodium is greater than the same for copper.

To make this plainer, let us examine the following example: barium sulphate is almost perfectly insoluble in water and acids, hence always results in the action of sulphates upon barium salts:—



If barium sulphate, however, be boiled with potassium carbonate, the reverse reaction occurs; barium carbonate and potassium sulphate are produced:—



Although the carbonate is somewhat less insoluble than the sulphate, the transposition is yet a complete one, because the affinity of  $\text{SO}_4$  for potassium is greater than for barium.

The relative affinity of various compounds for each other is, as yet, but little investigated. A criterion for the magnitude of the same is afforded by the quantity of heat disengaged in chemical unions. Investigations in this direction have recently been taken up and executed with much zeal.

The thermo-chemical investigations of recent date have shown that mutual transpositions of the salts, or the action of the acids upon bases and salts—just as all other chemical affinity relations, are dependent upon and regulated by the law of the greatest heat development. The relations are here, however, sometimes more complicated,

as the production of acid salts or double salts, further, the decomposition (dissociation) of many salts by water, into their component bases and acids, must be taken into consideration. By regarding these secondary reactions all chemical transpositions, according to Berthelot, find their explanation in the heat regulating them, without making it necessary to accept a particular affinity function of the acids and bases, which is termed their *avidity*. Even the physical properties of the resulting compounds, their volatility and insolubility, are, contrary to the supposition of Berthelot, only of secondary and slight influence.

---

### GROUP OF THE ALKALI METALS.

Potassium,	39		Lithium,	7
Rubidium,	85.2		Sodium,	23
Cæsium,	132.5		(Ammonium),	

The metals of this group are decidedly the most pronounced in metallo-basic character, and this constitutes a visible contrast with the elements of the chlorine group, the most energetic among the metalloids. This contradictory character of both groups is seen, too, in their monovalence; in their combinations with each other, their affinities saturate by single atoms. The more distinct the chemical character of two elements and the more unlike they are, so much the simpler and the more definite in general are the expressions of equivalence between them.

The alkali metals in physical and chemical properties exhibit great similarity. They oxidize readily in the air, decompose water violently, even in the cold, with the formation of strong basic hydrates, readily soluble in water, called *alkalies* (caustic potash, caustic soda), hence the name alkali metal. They are not decomposed by ignition. Their chemical energy increases with increasing atomic weight (more correctly atomic volume, p. 245); sodium is more energetic than lithium, potassium more than sodium, and rubidium more than potassium. Cæsium is not known in free condition, but, to conclude, from its compounds, it possesses a more basic character than rubidium. We see that in other analogous groups (of chlorine, oxygen, phosphorus, carbon), with the increasing atomic weight the metalloidal, negative character diminishes and the basic increases.

At the same time with the atomic weights the specific gravities increase; as, however, the increase of the first is greater than that of the latter, so are the atomic volumes (the quo-

tients  $\frac{A}{\text{sp. gr.}}$ ) always greater. The increasing fusibility and volatility correspond to the increase of the atomic volumes; rubidium distills already at a red heat, while lithium only volatilizes with difficulty:—

	Li	Na	K	Rb	Cs
Atomic Weight,	7	23	39	85	132
Specific Gravity,	0.59	0.97	0.86	1.52	(2,4)
Atomic Volume,	11.9	23.7	45.4	56.1	—
Fusion Temperature,	180°	95.6°	62.5°	38.5°	—

If, consequently, the alkali metals exhibit in their chemical deportment a great similarity, we will discover yet more marked relations between potassium, rubidium and calcium upon the one hand, and lithium and sodium on the other, as appears in the periodic system of the elements. Especially is this noticed in the salts. The first three metals form difficultly soluble tartrates and chlorplatينات (see platinum). Their carbonates deliquesce in the air, while those of sodium and lithium are stable under similar circumstances; the latter is, indeed, tolerably insoluble in water. The phosphates deport themselves similarly; lithium phosphate is very difficultly soluble. It must be remarked that the normal carbonates and phosphates of all other metals are insoluble. In lithium, then, which possesses the lowest atomic weight, it would seem the alkaline character has not yet reached expression, and approaches, in many respects, the elements of the second group, especially magnesium, just as beryllium approaches aluminium. This is indicated in the table, p. 237, by the position of the elements. The elements of the two small periods are, indeed, similar, but not completely analogous, while, in K Rb Cs the homology of the three great periods finds expression.

The affinity relations of the alkalis are expressed and explained by their thermo-chemical relations. Generally, with increase of atomic weights, the heat liberation is greater; thus, *e. g.*, in the formation of the chlorides and hydrates (the numbers represent large calories, p. 243).

(Li, Cl) = 93.8	(Li, Cl, Aq) = 102.2	(Li, O, H, Aq) = 117.4
(Na, Cl) = 97.7	(Na, Cl, Aq) = 91.5	(Na, O, H, Aq) = 111.8
(K, Cl) = 105.6	(K, Cl, Aq) = 101.1	(K, O, H, Aq) = 116.4
(Na <sub>2</sub> O) = 100.2	(Na, O, H) = 102.0	(K, O, H) = 103.9



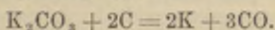
The varying deportment of the lithium compounds, which frequently show a greater heat disengagement than the compounds of sodium, finds expression in the position of lithium in the periodic system. On the contrary, it is very probable that, with the true homologues of potassium—rubidium and caesium, a constant increase of heat occurs.

From the above numbers is explained, upon the basis of the principle of the greatest heat liberation, how that sodium and lithium are displaced from their chlorides, etc., by potassium. In like manner, also, are the most other metals separated by potassium, because the heat of formation of the potassium compounds, generally, is much greater (see p. 259). From the comparison with the heat of formation of water ( $H_2O = 69000$  calories) is explained further its ready decomposition by the alkali metals. All metals which, in the production of their oxides,  $Me_2O$ , or hydrates,  $MeOH$ , disengage more than 69000 calories, decompose water, and with so much more energy, the greater the difference of heat. The insolubility of the oxides constitutes an obstacle to the action; this, however, by addition of neutral solvent acids, may be removed (see Aluminium). Conversely, all oxides with a less heat of formation are reduced by hydrogen.

### POTASSIUM.

K — 39.1.

In nature potassium is found principally in silicates, viz.: feldspar and mica. By disintegration of these silicates occurring in many rocks potassium passes into the soil and is absorbed by plants; the ashes of the latter consist chiefly of different potassium salts. The chloride and sulphate are also found in sea water, and in large deposits at Stassfurt, at Magdeburg, and in Galicia, where they were left by the evaporation of the water of enclosed seas. Metallic potassium was first obtained by Davy, in the year 1807, by the decomposition of the hydrate, by means of a strong galvanic current. At present it is prepared by igniting an intimate mixture of carbon and potassium carbonate:—



Such a mixture may be made by the carbonization of organic potassium salts, like crude tartar. It is then ignited to white heat, in an iron retort, and the escaping potassium vapors collected in receivers of peculiar construction, filled with rock-oil. The latter, an hydrocarbon, serves as the best means of preserving potassium, which would otherwise oxidize in the air and decompose other liquids.

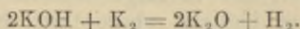
In a fresh section, potassium shows a silver white color and brilliant metallic lustre. At ordinary temperatures it is soft,

like wax, and may be easily cut. It melts at 62.5 and is converted, at a red heat into a greenish vapor. In the air it becomes dead in color at once, by oxidation; heated, it burns with a violet flame. Decomposes water energetically, with formation of potassium hydrate and the liberation of water. If a piece be thrown upon water, it will swim on the surface with a rotatory motion; by the reaction so much warmth is disengaged that the generated hydrogen and the potassium inflame. Finally, there usually results a slight explosion, by which pieces of potassium are tossed here and there; it is advisable, therefore, to execute the experiment in a tall beaker glass, covered with a glass plate. Potassium combines directly and very energetically with the halogens.

On conducting hydrogen over metallic potassium heated to 300–400°, there results potassium hydride,  $K_2H$ , a metallic, shining, brittle compound, which upon stronger heating, readily in vacuo, is again decomposed. Exposed to air it ignites spontaneously. The similarly obtained sodium hydride,  $Na_2H$  does not possess this latter property.

Potassium forms three oxygen compounds, of which only the following oxide yields corresponding salts.

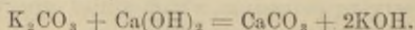
**Potassium Oxide**— $K_2O$ —results from the oxidation of thin pieces of metallic potassium in dry air, and by heating potassium hydrate with metallic potassium in a current of hydrogen:—



It is a white powder, fusing at a high temperature, and evaporating somewhat. With water it gives potassium hydrate, with evolution of much heat.

Potassium peroxide,  $KO_2$  or  $K_2O_4$ , and potassium suboxide,  $K_4O$ , are very unstable, and pass readily into potassium oxide. The first is formed, together with potassium oxide, by the combustion of potassium in dry air or oxygen, and is a yellow mass. The suboxide has a violet color, due to the oxidation of potassium vapors.

**Potassium Hydrate**, or *Caustic Potash*— $KOH$ —is obtained by the action of potassium or its oxide upon water. For its preparation potassium carbonate is decomposed by calcium hydrate (slacked lime):—



The solution of 1 part potassium carbonate in 10–12 parts water is boiled with 1 part slaked lime in an iron pot, until a

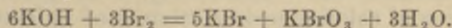
filtered portion causes no effervescence, when hydrochloric acid is added; *i. e.*, there is no longer any carbonic acid present. The turbid liquid becomes clear upon standing, as the insoluble calcium carbonate subsides. The clear solution of potassium hydrate is poured off, evaporated, the residue melted in a silver dish (which it does not attack) and poured into moulds. The thus prepared caustic potash is not entirely pure, but contains potassium chloride and other salts. To get chemically pure hydrate potassium nitrate is fused with copper filings and the fusion lixiviated with water.

Potassium hydrate forms a white, crystalline, tolerably easily fusible mass, which volatilizes undecomposed at a very high temperature. Exposed to the air it deliquesces, as it absorbs water and carbon dioxide and changes into carbonate. In alcohol, and especially water, it is very soluble. The solution reacts strongly alkaline, saponifies the fats, and has a corrosive action upon the skin and organic tissues; hence it cannot be filtered through paper. From concentrated solutions at low temperature the hydrate  $\text{KOH} + 2\text{H}_2\text{O}$  crystallizes out.

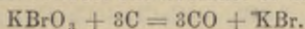
The haloid salts of potassium are formed by the direct union of the halogens with potassium, and by saturation of the hydrate or carbonate with haloid acids. They are readily soluble in water, have a salty taste, and crystallize in cubes. When heated they melt and are somewhat volatile.

**Potassium Chloride**— $\text{KCl}$ —occurs in Stassfurt in large deposits, as *sylvite*, and combined with magnesium chloride as *carnallite* ( $\text{MgCl}_2, \text{KCl} + 6\text{H}_2\text{O}$ ). The latter salt serves as the chief source for the preparation of potassium chloride, which meets with varied application in the arts, and also for the preparation of potassium carbonate. The chloride crystallizes in vitreous cubes, of specific gravity 1.84. 100 parts water dissolve at  $0^\circ \text{C}$ ., 30 parts, at  $100^\circ$ , 59 parts of the salt.

**Potassium Bromide**— $\text{KBr}$ —is generally obtained by warming a solution of potassium hydrate with bromine, when the bromate also is produced:—



The solution is evaporated to dryness, mixed with charcoal and ignited, which reduces the bromate to bromide:—





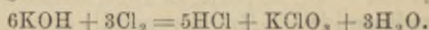
It is readily soluble in water and alcohol, and is employed in photography and medicine.

**Potassium Iodide**—KI—may be prepared like the preceding. Usually it is obtained according to the following method: Iodine and iron filings are rubbed together under water, and potassium carbonate added to the solution of iron oxide; this will precipitate ferrous-ferric oxide; carbon dioxide escapes and potassium iodide will be found in solution. It forms large white crystals, is easily fusible and tolerably volatile. Its specific gravity equals 2.9. At medium temperature it dissolves in 0.7 parts water. The aqueous solution dissolves iodine in large quantity. Many metallic, insoluble iodides dissolve without difficulty in it, forming double iodides, *e. g.*,  $\text{HgI}_2, 2\text{KI}$ . The iodide is employed in medicine and photography.

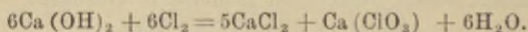
**Potassium Fluoride**—KFl. Obtained by dissolving the carbonate in aqueous hydrofluoric acid, forms easily soluble cubes. The aqueous solution attacks glass. It is greatly inclined to combine with other fluorides; KFl, HFl,  $\text{BFl}_3$ , KFl. On adding hydrofluosilicic acid to the solution of potassium salts, a gelatinous precipitate of potassium silicofluoride is thrown down; this is very difficultly soluble in water.

**Potassium Cyanide**—KCN. By saturating potassium hydrate with hydrocyanic acid, and by heating yellow potassium prussiate (see Iron) we can produce this salt. It forms a white, easily fusible mass, which deliquesces in the air. The solution may be easily decomposed. It crystallizes in cubes, has an alkaline reaction, smells like prussic acid, as this is set free by the carbon dioxide of the air. By fusion potassium cyanide reduces many oxides, and hence is employed in reduction processes. It is just as poisonous as prussic acid. It is applied in many ways, especially in photography and for galvanic silvering and gilding.

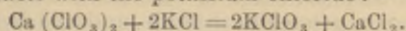
**Potassium Chlorate**— $\text{KClO}_3$ . Upon conducting chlorine gas through a hot concentrated potassium hydrate solution, the following reaction occurs:—



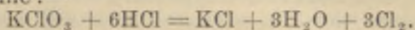
When the solution cools, the difficultly soluble potassium chlorate separates out. Technically it is generally made by the action of chlorine upon a mixture of calcium hydrate and potassium chloride. The reaction occurs in two phases: first calcium chlorate is formed:—



This then reacts with the potassium chloride:—

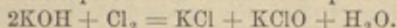


From the hot solution potassium chlorate crystallizes in shining tables of the monoclinic system, which are difficultly soluble in water (100 parts at ordinary temperature dissolve 6 parts of the salt). Its taste is cooling and astringent. When heated it melts (at  $330^\circ$ ), giving up a portion of its oxygen and changing to the **Perchlorate**— $\text{KClO}_4$ —which on further heating decomposes into oxygen and potassium chloride (see p. 172). As it gives up oxygen readily, it serves as a strong oxidizing agent. With hydrochloric acid it liberates chlorine:—

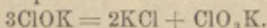


Mixed with sulphur or some sulphides it explodes on heating and when struck a sharp blow. The igniting material upon the so-called Swedish (parlor) matches consists of antimony sulphide and potassium chlorate; rubbed upon the friction surface coated with red phosphorus they ignite.

**Potassium Hypochlorite**— $\text{KClO}$ —is formed when chlorine is permitted to act upon a cold solution of potassium hydrate:



It only exists in aqueous solution; when the latter is evaporated the salt is decomposed into chloride and chlorate:—



The solution has a chlorine odor and bleaches strongly, especially upon the addition of acids. The bleaching solutions occurring in trade (Eau de Javelle) are prepared by the action of chlorine upon solutions of soda and potassium carbonate; they also contain free hypochlorous acid.

The oxy-salts of bromine and iodine are perfectly analogous to those of chlorine. Potassium Bromate— $\text{KBrO}_3$ —and Potassium Iodate— $\text{KIO}_3$ —are prepared by the action of bromine or iodine upon potassium chlorate; in these there is a direct substitution of chlorine (p. 176). If the latter be passed through a hot solution of potassium iodate in potassium hydrate—the periodate of potassium,  $\text{KIO}_4$ , arises; it is difficultly soluble, and upon heating decomposes into  $\text{O}$  and  $\text{KI.O}_3$ , which then breaks up into potassium iodide and oxygen.

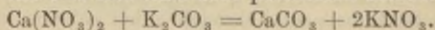
Together with the normal periodates,  $\text{KIO}_3$ ,  $\text{NaIO}_3$ , exist other salts which are derived from the highest hydroxyl compound  $\text{I}(\text{OH})_7$  and its anhydro-derivatives (p. 174). These salts are very numerous and partly monoperiodates,  $\text{IO}(\text{OH})_5$  and  $\text{IO}_2(\text{OH})_3$ ; partly poly-periodates, produced by the condensation of several molecules of the highest hydrates, like  $\text{I}_2\text{O}_3(\text{OH})_8$  and  $\text{I}_2\text{O}_5(\text{OH})_4$ .

**Potassium Sulphate**— $K_2SO_4$ —is formed in the action of sulphuric acid upon potassium chloride, and as a bye-product in many technical operations. Crystallizes without water, in small rhombic prisms of a bitter, salty taste, and dissolves in 10 parts  $H_2O$  of ordinary temperature. It is employed principally for the preparation of potassium carbonate, according to the method of Le Blanc (see Soda).

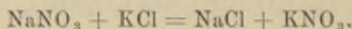
The *acid* or *primary* salt— $HKSO_4$ —crystallizes in large rhombic tables, very readily soluble in water. It fuses about  $200^\circ$ , loses water and is converted into Potassium pyrosulphate— $K_2S_2O_7$  (p. 187)—which at  $600^\circ$  yields  $K_2SO_4$  and  $SO_3$ .

The salts of sulphurous acid—the *primary*  $SO_3KH$  and the *secondary*  $SO_3K_2$ —form when  $SO_3$  comes in contact with a potassium carbonate solution; they are very soluble and crystallize with difficulty. The first salt shows an acid, the second an alkaline reaction. If sulphur dioxide be passed into a solution of potassium carbonate until effervescence ceases and then cooled, pyrosulphite— $K_2S_2O_5$ —corresponding to the pyrosulphate, will crystallize out.

**Potassium Nitrate**, Saltpetre,  $KNO_3$ , does not occur anywhere in large quantity, but is widely distributed in the upper strata of the earth and in some regions of the hot zone (in Egypt and East India) it is exposed by disintegration. It is produced whenever nitrogenous organic substances decay in the presence of potassium carbonate—conditions, which are present in almost every soil. Upon the intentional introduction of the same depends the artificial nitre production in the so-called saltpetre plantations. Manures and various animal offals are mixed with wood ashes (potassium carbonate) and lime, arranged in porous layers, and submitted to 2–3 years' action of the air, whereby, from the slow oxidation of the nitrogen, nitrates are produced. The heaps are then treated with water and potassium carbonate added to the solution, which contains potassium, calcium and magnesium nitrates, to convert the two last salts into potassium nitrate:—



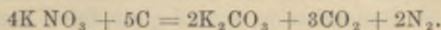
The precipitate of calcium and magnesium carbonate is filtered off and the solution evaporated. This procedure was formerly universally employed in the manufacture of potassium nitrate. At present, however, almost all of it is obtained by the decomposition of the sodium salt, occurring in large deposits in Chili, by means of potassium carbonate or chloride:—



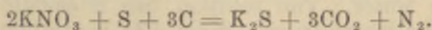


Warm saturated solutions of sodium nitrate and potassium chloride are mixed and boiled. Then four salts are formed, of which sodium chloride, the least soluble in hot water, separates. On cooling the solution, potassium nitrate, the least soluble in cold water, crystallizes; sodium chloride is nearly equally soluble in the warm and cold water, for which reason the portion not separated by boiling remains in solution.

Potassium saltpetre crystallizes without water in large six-sided prisms. It is far more soluble in hot than in cold water; 100 parts of water dissolve 244 parts at 100°, but at 0° only 13 parts. It possesses a cooling taste, fuses about 340°, and decomposes by further heating into oxygen and potassium nitrite,  $\text{KNO}_2$ . Heated with carbon it yields potassium carbonate:—



Its principal use is in the manufacture of gunpowder. This is a granular mixture of potassium nitrate, sulphur and charcoal. The relative quantities of these constituents are somewhat different in the various kinds of powder (sporting, blasting and cannon). Upon an average, the powder consists of 75 per cent.  $\text{KNO}_3$ , 12 per cent. sulphur and 13 per cent. carbon, which closely corresponds to the atomic composition  $2\text{KNO}_3 + \text{S} + 3\text{C}$ . The decomposition of the powder by burning may be approximately expressed by the following equation:—



The effectiveness of the powder, therefore, depends upon the disengagement of carbon dioxide and nitrogen gas, the volume of which is almost 100 times as great as that of the decomposed powder.

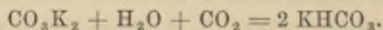
**Potassium Nitrite**,  $\text{KNO}_2$ , is obtained by the fusing of saltpetre with lead, which withdraws one atom of oxygen from the former. A white, fusible mass results; this deliquesces in the air.

The potassium salts of *phosphoric acid*:  $\text{K}_3\text{PO}_4$ ,  $\text{K}_2\text{HPO}_4$ , and  $\text{KH}_2\text{PO}_4$ , meet with no practical application, as they are easily soluble in water and crystallize poorly; therefore, the sodium salts are generally used. The borates, too,  $\text{BO}_2\text{K}$  and  $\text{B}_4\text{O}_7\text{K}_2 + 5\text{H}_2\text{O}$  (See Borax), crystallize with difficulty.

**Potassium Carbonate**— $\text{K}_2\text{CO}_3$ —ordinarily known as **pot-ashes**, is a principal ingredient of plant ashes. The field plants absorb potassium salts from the earth; these are then transformed, in them, into salts of organic acids. By the combustion of the plants the organic acids are destroyed and potassium carbonate produced. The ashes are lixiviated with

water, the filtrate evaporated and the residue ignited. The *crude potashes* thus obtained contain, besides the carbonate, also chloride, sulphate and other salts. To purify them, treat with a little water, which will dissolve the easily soluble carbonate, leaving the other ingredients, for the most part, behind. Thus purified potashes are obtained. This method for the production of the potash from plant ashes was formerly extensively pursued in America, Hungary and Russia; it is not much used at present, because, upon the one hand, potassium carbonate is, in practice, replaced by the cheaper sodium carbonate; on the other hand, the immense deposits in Stassfurt and Galicia afford an inexhaustible source of supply for potassium salts. Considerable quantities of potassium carbonate, which, at present, are almost entirely limited to the production of Bohemian or crystal glass, have been recently obtained from Stassfurt, according to the methods for preparing sodium carbonate from the chloride (see Soda). Chemically pure potassium carbonate is obtained most conveniently by the ignition of cream of tartar.

The commercial carbonate is a white, deliquescent powder. From concentrated aqueous solution it crystallizes, with  $1\frac{1}{2}$  molecules of water, in monoclinic prisms; at  $100^\circ$  it loses  $\frac{1}{2}$  molecule water. The solution has a caustic taste and shows an alkaline reaction. When  $\text{CO}_2$  is conducted through the liquid it is absorbed and *primary potassium carbonate* produced:—

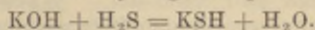


This salt, ordinarily called *bi-carbonate*, crystallizes in monoclinic prisms, free from water. It dissolves in 3–4 parts water and exhibits neutral reaction. Heated to  $80^\circ$ , it decomposes into  $\text{K}_2\text{CO}_3\text{CO}_2$  and water.

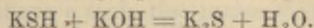
**Potassium Silicate**, water-glass, does not possess a constant composition and cannot be obtained crystallized. It forms by the solution of silicic acid or amorphous silicon dioxide in potassium hydrate, or by the fusion of silica with potassium hydrate or carbonate. It constitutes a transparent, glassy mass, soluble in water. The concentrated solution dries when exposed, to a glassy, afterwards opaque, mass. Potassium (and also sodium) water-glass has an extended application, especially in cotton printing, for the fixing of colors (stereochromy), in rendering combustible material fireproof, in soap boiling, etc.

## SULPHUR COMPOUNDS.

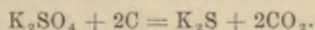
**Potassium Sulphhydrate**, KSH, is obtained when potassium hydrate is saturated with hydrogen sulphide:—



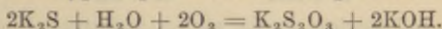
Evaporated in vacuo it crystallizes in colorless rhombohedra, of the formula,  $2\text{KSH} + \text{H}_2\text{O}$ , which deliquesce in the air. At  $200^\circ$ , it loses its water of crystallization, and at a higher temperature fuses to a yellowish liquid, which solidifies to a reddish mass. Like the hydrate, it has an alkaline reaction. On adding an equivalent quantity of the hydrate to the sulphhydrate solution, we get potassium sulphide:—



**Potassium Sulphide**,  $\text{K}_2\text{S}$ , also obtained by fusing potassium sulphate with carbon:—



Fused, it solidifies to a red crystalline mass. From concentrated aqueous solution it crystallizes with 5 molecules of  $\text{H}_2\text{O}$ , in colorless prisms, which deliquesce in the air. The solution absorbs oxygen from the latter, and is decomposed into potassium hyposulphite and caustic potash:—



Potassium sulphhydrate and sulphide precipitate insoluble sulphides from the solutions of many metallic salts. By acids they are decomposed with liberation of hydrogen sulphide.

When the aqueous solution of the sulphide is boiled with sulphur the *polysulphides*  $\text{K}_2\text{S}_3$ ,  $\text{K}_2\text{S}_4$  and  $\text{K}_2\text{S}_5$  are formed, which after fusion solidify to yellowish-brown masses. The aqueous solutions of the polysulphides are decomposed by acids, with disengagement of  $\text{H}_2\text{S}$  and separation of sulphur (milk of sulphur). The so-called *liver of sulphur* (*Hepar sulfuris*), a liver-brown mass, which is used in medicine, is obtained by the fusion of potassium carbonate with sulphur, and consists of a mixture of potassium polysulphides with potassium sulphate.

The aqueous solution of the potassium, as of the sodium sulphide, dissolves some metallic sulphides and forms sulphosalts with them (p. 214).



When dry ammonia is conducted over heated potassium, potassamide ( $\text{NH}_2\text{K}$ ), a dark blue liquid which solidifies to a yellowish-brown mass, results. Water decomposes it into potassium hydrate and ammonia. When potassamide is ignited away from the air ammonia escapes and leaves behind potassium nitride, a blackish compound which is spontaneously inflammable.

**Recognition of the Potassium Compounds.**—Almost all the potassium compounds are easily soluble in water, with the exception of a few, which, therefore, serve for the characterization and separation of potassium. Tartaric acid added to the solution of a potassium salt gives a crystalline precipitate of acid potassium tartrate. Platinic chloride ( $\text{PtCl}_4$ ) produces in solutions a yellow, crystalline precipitate of  $\text{PtCl}_4 \cdot 2\text{KCl}$ . Potassium compounds introduced into the flame of an alcohol or gas lamp impart to the same a *violet* coloration. The spectrum of the flame is characterized by bright lines, a red and violet (see Spectrum Analysis).

### RUBIDIUM and CÆSIUM.

Rb = 85.4.

Cs = 132.

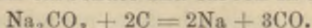
Rubidium and Cæsium are the perfect analogues of potassium (p. 265). They were discovered by means of the spectroscope, by Bunsen and Kirchhoff, in 1860. Although only occurring in small quantities they are yet very widely distributed, and frequently accompany potassium in mineral springs, salt, and plant ashes. The mineral lepidolite contains 0.5 per cent. of rubidium; in the very rare pollucite, a silicate of aluminium and cæsium, upwards of 30 per cent. of cæsium oxide is present. The spectrum of rubidium is marked by two red and two violet lines; cæsium, by two distinct blue lines; hence, the names of these elements.

With platinum chloride rubidium and cæsium form double chlorides ( $\text{PtCl}_4 \cdot 2\text{RbCl}$ ), which are more insoluble than the double platinum salt of potassium, and, hence, may answer for the separation of these elements from potassium. In a free state they may be separated by decomposition of the molten chlorides, by means of the galvanic current. Rubidium is also obtained by the ignition of its carbonate with charcoal. Metallic rubidium is of a silver white color, with a somewhat yellowish tinge; its vapor is greenish blue. Cæsium has only been obtained alloyed with mercury.

**SODIUM.**

Na — 23.

Sodium is widely distributed in nature, especially as chloride in sea water and as rock salt; also in silicates. The metal was obtained in 1807, by Davy, by the action of the galvanic current upon fused sodium hydrate. At present, like potassium, it is obtained upon a large scale by glowing a mixture of sodium carbonate and carbon in an iron retort:—

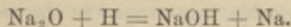


The liberated sodium vapors are condensed on flat iron receivers of peculiar construction, and the liquefied sodium collected under rock-oil.

Sodium, in external properties, is very similar to potassium. It melts at 95.6°, distills at a red heat, and is converted into a colorless vapor, which burns with a bright yellow flame in the air. It oxidizes readily on exposure, and decomposes water even in the cold, although less energetically than potassium. A piece of sodium thrown upon water swims about upon the surface with a rotatory movement, the disengaged hydrogen, however, not igniting. If we prevent the motion, by confining the metal to one place, the heat liberated by the reaction attains the ignition temperature of hydrogen, and a flame follows.

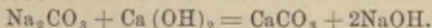
**Sodium Oxide**— $\text{Na}_2\text{O}$ , and suboxide,  $\text{Na}_4\text{O}$ , are very similar to the corresponding potassium compounds; the peroxide is somewhat different. It is obtained by burning sodium in an oxygen current. Its formula is  $\text{Na}_2\text{O}_2$ . When heated it absorbs iodine vapors, forming the compound  $\text{Na}_2\text{OI}_2$  ( $\text{Na}_2\text{O}_2 + \text{I}_2 = \text{Na}_2\text{OI}_2 + \text{O}$ ), soluble in water, but decomposed by acids into free iodine and sodium salt. This compound, as also some others, seems to indicate that sodium has several equivalences.

It is very remarkable that upon heating sodium oxide it is decomposed by hydrogen, with separation of metallic sodium and formation of sodium hydrate:—



This is explained by the fact that the heat of formation of  $\text{NaOH}$  (102° C.) is greater than that of  $\text{Na}_2\text{O}$  (100.2° C.) and hence the reaction occurs, according to the above equation, accompanied by heat disengagement. Conversely, therefore,  $\text{NaOH}$  cannot be decomposed by sodium (Beketoff).

**Sodium Hydrate**— $\text{NaOH}$ —like potassium hydrate, is formed by boiling a solution of sodium carbonate with calcium hydrate:—



At present it is directly produced in the soda manufacture by adding a little more carbon to the fusion (see Soda).

The sodium hydrate which solidifies after the fusion is a white, radiating, crystalline mass, and resembles caustic potash very much. It attracts water from the air, becomes moist, and coats itself by carbon dioxide absorption with a white layer of sodium carbonate (caustic potash deliquesces perfectly, as the resulting carbonate is also deliquescent). The aqueous solution of sodium hydrate resembles that of potassium. From the concentrated solution separate at  $0^{\circ}$  crystals of  $\text{NaOH} + 3\frac{1}{2}\text{H}_2\text{O}$ .

**Sodium Chloride**— $\text{NaCl}$ —is abundant in nature. It is found almost everywhere in the earth and in natural waters; in sea water it averages 2.7–3.2 %. Rock salt forms large deposits in many districts—at Stassfurt and Wielicza in Galicia.

In warm climates, on the coasts of the Mediterranean sea, sodium chloride is gotten from the sea, according to the following procedure. At high tide, sea water is allowed to flow into wide, flat basins (salt gardens), in which it evaporates under the sun's heat; the working is limited, therefore, to summer time. After sufficient concentration, pure sodium chloride first separates, and this is collected by itself. Later, there crystallizes a mixture of the sodium chloride and magnesium sulphate; finally potassium chloride, magnesium chloride and some other salts appear (among them potassium iodide and bromide), the separation of which constitutes a particular industrial branch in some regions. In cold climates, as in Norway and at the White Sea, the cold of winter is employed for the production of salt. In the freezing of sea water, as also of other solutions, at first almost pure ice separates; the enriched sodium chloride solution is then concentrated in the usual way.

The *rock salt* is either mined in shafts or where the strata are not so large and are admixed with other varieties of rock, a lixiviation process is employed. Borings are made in the earth and water run into them, or into any already formed openings. When the water has saturated itself with sodium chloride, it is pumped to the surface and the brine then further worked up. In many regions, especially in Reichenhall, in Bavaria, more or less saturated, natural salt or brine springs flow from the earth. The concentration of the non-saturated brine occurs at first in the so-called "graduation" houses. These are long wooden frames filled with fagots, and on letting the salt water run upon these it will be distributed and evaporated by the fall; the concentrated brine collects in the basin below, and is then evaporated over a free fire.

Sodium chloride crystallizes from water in transparent cubes, which by slow cooling arrange themselves in hollow,



four-sided pyramids. It is only slightly more soluble in hot than in cold water; 100 parts at  $0^{\circ}$  dissolve 36 parts salt; at  $100^{\circ}$  39 parts. The saturated solution, therefore, contains 26 % sodium chloride. The specific gravity of the crystals equals 2.13. If the saturated solution be cooled below  $10^{\circ}$ , large monoclinic tables ( $\text{NaCl} + 2\text{H}_2\text{O}$ ) separate; these lose water at  $0^{\circ}$  and become cubes.

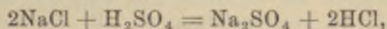
The ordinary sodium chloride contains, usually, a slight admixture of magnesium salts, in consequence of which it gradually deliquesces in the air; the perfectly pure salt is not hygroscopic. When heated the crystals crackle, as mechanically enclosed water escapes. At red heat the chloride fuses and vaporizes at higher temperatures.

Sodium bromide and iodide at ordinary temperatures crystallize with 2 molecules of  $\text{H}_2\text{O}$ , which they lose again at  $30^{\circ}$ .

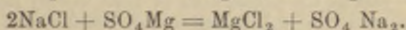
Sodium chlorate ( $\text{NaClO}_3$ ) and perchlorate ( $\text{NaClO}_4$ ) are considerably more soluble in water than the corresponding potassium salts.

**Sodium Iodate**— $\text{NaIO}_3$ —obtained same as the potassium salt, and at ordinary temperatures crystallizes with 3 molecules of  $\text{H}_2\text{O}$  in silky needles. If chlorine gas be conducted through the warmed solution of sodium iodate in sodium hydrate, on cooling the periodate  $\text{IO} \begin{cases} (\text{ONa})_2 \\ (\text{OH})_3 \end{cases}$  (see p. 175) crystallizes out. This, when dissolved in nitric acid, becomes the normal salt ( $\text{NaIO}_4 + 3\text{H}_2\text{O}$ ).

**Sodium Sulphate**— $\text{Na}_2\text{SO}_4$ —crystallizes at ordinary temperatures with 10 molecules of water of crystallization, and is then known as Glauber's salt (*Sal mirabile Glauberi*). It occurs in many mineral waters, and in large deposits, with or without water, in Spain. It is a bye-product in the manufacture of sodium chloride from sea water and brine. It is produced in large quantities by heating salt with sulphuric acid—



and is used in making soda (sodium carbonate). In modern times the sulphate has been obtained by a transposition of sodium chloride with magnesium sulphate at winter temperature—a procedure which is prosecuted chiefly in Stassfurt, where immense quantities of magnesium sulphate exist:—



Sodium sulphate crystallizes at ordinary temperatures with 10 molecules of  $\text{H}_2\text{O}$ , in large, colorless, monoclinic prisms, which in the air weather and fall into a white powder. When the

salt is heated to  $33^{\circ}$ , it fuses in its own water of crystallization; by further increase of temperature it gradually loses this, becomes solid, and again fuses at a red heat. The solubility of Glauber's salt ( $\text{Na}_2\text{SO}_4 + 10 \text{H}_2\text{O}$ ) shows the following interesting deportment: 100 parts of water dissolve, at  $0^{\circ}$ , 12 parts; at  $18^{\circ}$ , 48 parts; at  $25^{\circ}$  100 parts; at  $30^{\circ}$ , 200 parts; at  $33^{\circ}$ , 237 parts of the hydrous salt. At the last temperature the solubility is greatest; by further increase of heat, it gradually diminishes; at  $50^{\circ}$ , 100 parts water dissolve only 263 parts; at  $100^{\circ}$ , 238 parts of the salt. While, ordinarily, the solubility increases with temperature, Glauber's salt exhibits a varying deportment. This is explained in that the hydrate,  $\text{Na}_2\text{SO}_4 + 10 \text{H}_2\text{O}$ , in aqueous solution, above the temperature of  $33^{\circ}$ , decomposes into water and the salt,  $\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$ , which is less soluble in water. The decomposition does not occur at once, but only gradually, with increasing temperature, for which reason the quantity of the salt dissolved gradually grows less. Here we have an example of dissociation taking place in aqueous solution. The solution, saturated at  $33^{\circ}$ , becomes turbid upon cooling, and a portion of the dissolved salt separates in anhydrous, small, rhombic octahedra.

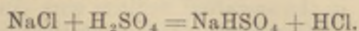
The following interesting deportment in the solution of Glauber's salt may also be noticed. When the solution, saturated at  $33^{\circ}$ , is cooled down to the ordinary temperature, and even lower, not the slightest separation of crystals occurs, although the salt is vastly more insoluble at lower temperatures than at  $33^{\circ}$ . Many other salts form similar *supersaturated solutions*, although they are less striking than that of Glauber's salt. The supersaturated solution of the latter may be agitated and twirled about without consequent crystallization. If, however, a glass rod, or some other solid body, be introduced into the solution, it will solidify, suddenly, to a crystalline mass. The particles of dust floating about in the air will have a like effect; therefore, to preserve the supersaturated solution, the vessel containing it should be kept well corked. By accurately made investigations, it has been determined that the crystallization of the supersaturated Glauber salt solution is only induced by contact with already formed crystals. These must then be present everywhere in the atmosphere, because only solids exposed to the air, and not purified bring about the crystallization. Hence the formation of a crystal of Glauber's salt is always dependent upon the previous existence of a similar crystal—just as the production of cells is only caused by cells.

In the crystallization of a supersaturated Glauber salt solution considerable heat is disengaged, and the mass increases in temperature. This is because the latent heat of all substances in the liquid condition is greater than in the solid. At  $10^{\circ}$ , occasionally, and of their own accord, transparent crystals,  $\text{Na}_2\text{SO}_4 + 7 \text{H}_2\text{O}$ , separate from the

supersaturated solution. Exposed to the air and in contact with solid bodies, these crystals are changed to anhydrous sodium sulphate and Glauber's salt.

This salt is employed in medicine as a purgative. Finds extended application technically for the fabrication of glass and the preparation of soda.

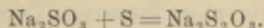
The **primary** or **acid sodium sulphate**— $\text{NaHSO}_4$ —is obtained by the action of sulphuric acid upon the neutral salt or upon sodium chloride:—



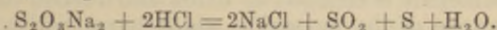
At ordinary temperatures it crystallizes with one molecule of water, and is perfectly analogous to the potassium salt.

The sodium salts of sulphurous acid are obtained by conducting sulphur dioxide into solutions of sodium hydrate or carbonate. The secondary sulphite,  $\text{Na}_2\text{SO}_3$ , crystallizes at ordinary temperatures with 7 molecules of  $\text{H}_2\text{O}$ ; in the presence of sodium hydrate or by warming the solution, it separates in the anhydrous state. The primary *sulphite*— $\text{NaHSO}_3$ —gives up sulphur dioxide in the air, and is oxidized to sodium sulphate.

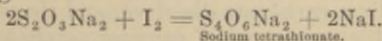
**Sodium Hyposulphite**— $\text{Na}_2\text{S}_2\text{O}_3$ —is prepared by boiling the aqueous solution of neutral sulphite with flowers of sulphur:—



It crystallizes with 5 molecules of  $\text{H}_2\text{O}$ , in large monoclinic prisms, dissolves very readily in water, and in the air is somewhat deliquescent. At  $56^\circ$  it melts in its water of crystallization; loses all water at  $100^\circ$  and decomposes by further heating into  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{S}_3$ . When the dry salt is heated in the air the polysulphide burns with a blue flame. Acids decompose the aqueous solution with separation of sulphur and evolution of sulphur dioxide:—



Like the sulphate it readily affords supersaturated solutions. The hyposulphite is used as a reducing agent; chlorine, bromine and iodine are converted by it into the corresponding halogen salts:—



Sodium tetrathionate.

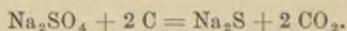
An iodine solution is instantaneously decolorized by sodium hyposulphite; sulphuric acid and sodium chloride are produced. Upon this reaction rests the application of sodium



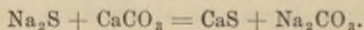
hyposulphite as an antichlor in chlorine bleaching, to remove the excess of the chlorine, which has a destructive effect upon the tissue. In consequence of its property of dissolving the halogen silver derivatives, it is employed in photography.

**Sodium Carbonate (Soda)**— $\text{Na}_2\text{CO}_3$ .—This technically very important salt occurs frequently in nature. In some districts, like in Hungary and in Africa, it disintegrates from the soil, and occurs also in the so-called sodium seas (in Egypt, upon the coast of the Caspian Sea). It is contained in the ashes of many sea plants, chiefly the algæ, etc. These assimilate the sodium salts of the earth, while the land plants absorb the potassium salts, and for this reason contain potashes in their ash. The ash of the sea plants (in Normandy called *varec*, in England *kelp*) formerly served as the principal source of the soda manufacture. At present it is, however, almost exclusively made in large quantities from sodium chloride, according to a method devised in 1808 by Leblanc.

According to this method the sodium chloride is converted, by warming with sulphuric acid, into sodium sulphate (p. 279). When the latter is dry, it is mixed with charcoal and chalk and glowed in a reverberatory furnace. Two principal phases may be distinguished in this reaction. First, the carbon reduces the sodium sulphate:—

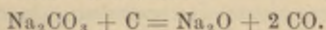


The sodium sulphide then acts upon the calcium carbonate to form the calcium sulphide and sodium carbonate:—



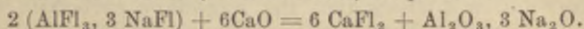
At the same time, by the high temperature, a portion of the calcium carbonate is changed to oxide and carbon dioxide; the appearance of the monoxide, which burns with a bluish flame, indicates the end of the action. The chief products in the soda fusion are, then, sodium carbonate, calcium sulphide and oxide; in addition, different other sulphur salts are formed in smaller quantity. The fusion is lixiviated with hot water; the sodium carbonate dissolves, and there remains behind an insoluble compound of calcium sulphide with oxide,  $\text{CaO}$ ,  $2\text{CaS}$ , the *soda residue*. By evaporation of the solution and ignition of the residue, we get the commercial or *crude calcined soda*, containing different admixtures, among them

sodium hydrate. The latter is formed by the action of excess of carbon upon sodium carbonate:—

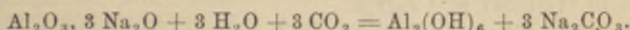


By purposely adding more carbon to the fusion, sodium hydrate is obtained, together with the carbonate. To purify the crude soda it is recrystallized from water; large, transparent crystals,  $\text{Na}_2\text{CO}_3 + 10 \text{H}_2\text{O}$ , *crystallized soda*, separate out; in solution remains sodium hydrate.

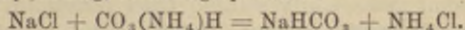
Considerable quantities of soda are, at present, obtained from cryolite, a compound of aluminium fluoride with sodium fluoride ( $\text{AlF}_3, 3 \text{NaF}$ ), which occurs in great deposits in Iceland. The pulverized mineral is ignited with burned lime; insoluble calcium fluoride and a very soluble compound of aluminium oxide with sodium oxide, called sodium aluminate (see Aluminium) are produced:—



The mass is treated with water and carbon dioxide conducted into the liquid, which causes the precipitation of aluminium oxide, and sodium carbonate dissolves:—



Latterly, a third procedure has appeared. It depends upon the double decomposition of a solution of sodium chloride with primary ammonium carbonate, by heating, under high pressure:—

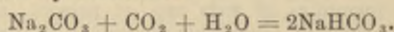


The difficultly soluble primary sodium carbonate separates from solution, leaving ammonium chloride dissolved, which can afterwards be converted again into carbonate by aid of calcium carbonate. In this way, one and the same quantity of ammonium carbonate will suffice for the conversion of an indefinite quantity of sodium chloride into soda. The technical difficulties which at first opposed the extension of this, in chemical respects, so simple a process, are now mostly removed, and we can expect that the so-called *ammonia process* for the soda manufacture will replace, at least partially, that of Leblanc.

At ordinary temperatures sodium carbonate crystallizes with 10 molecules of  $\text{H}_2\text{O}$  ( $\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$ ) in large monoclinic crystals, which disintegrate upon exposure and become a white powder. It melts at  $50^\circ$  in its water of crystallization, and upon additional application of heat a pulverulent hydrate— $\text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O}$ —separates, which in dry air has 1 molecule of  $\text{H}_2\text{O}$ , and at  $100^\circ$  loses all of this. At  $30^\circ$ – $50^\circ$  rhombic prisms of the composition  $\text{CO}_3\text{Na}_2 + 7\text{H}_2\text{O}$ , crystallize from the aqueous solution. The anhydrous salt absorbs water from the air but does not deliquesce. It melts at a red heat

and volatilizes somewhat at a very high temperature. 100 parts  $H_2O$  dissolve 10 parts at  $0^\circ$ , and at  $38^\circ$  138 parts of the dry salt. At more elevated temperatures the solubility is less, owing, as in the case of the sulphate, to the formation of less soluble lower hydrates. Sodium carbonate has a strong alkaline reaction; acids liberate carbon dioxide from it.

**Primary Sodium Carbonate**—*Natrium bicarbonicum*— $NaHCO_3$ —is produced by the action of carbon dioxide upon hydrous secondary carbonate:—



It crystallizes without water, in small monoclinic tables; dissolves, however, at ordinary temperatures in 10–11 parts water, and possesses feeble alkaline reaction. By heating and boiling the solution it passes into the secondary carbonate with disengagement of carbon dioxide. By rapid evaporation small monoclinic prisms of the so-called sodium sesquicarbonate— $C_3O_8Na_4 + 3H_2O$ , separate; this also deposits in the sodium seas of Hungary and Egypt.

**Sodium Nitrate**— $NaNO_3$ —Chili saltpetre, is found in immense deposits in Peru. It crystallizes in rhombohedra very similar to cubes, hence designated *cubic saltpetre*. In water it is somewhat more easily soluble than potassium saltpetre. In the air it attracts moisture, hence is not adapted to the manufacture of gunpowder. In other respects it is perfectly similar to potassium nitrate. It is largely used in the manufacture of nitric acid, as it is much cheaper than the potassium salt.

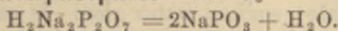
**Sodium Phosphates.** The sodium salts of phosphoric acid are less soluble and crystallize better than those of potassium. The *tri-sodium phosphate*— $Na_3PO_4$ —is made by saturating 1 molecule of phosphoric acid with 3 molecules  $NaOH$ , and crystallizes in six-sided prisms with 12 molecules of  $H_2O$ . It reacts strongly alkaline, absorbs carbon dioxide from the air, and is converted into the secondary salt.

**Di-sodium Phosphate**— $Na_2HPO_4$ —is the most stable of the sodium phosphates, and hence, generally employed in laboratories (*Natrium phosphoricum*). It may be obtained by saturating phosphoric acid with sodium hydrate to feeble alkaline reaction. It crystallizes at ordinary temperatures with  $12H_2O$  in large monoclinic prisms which disintegrate rapidly

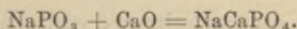


upon exposure. It is soluble in 4 parts water, and shows a feeble alkaline reaction. The solution absorbs carbon dioxide abundantly, without suffering any alteration. When heated the salt loses water, melts about  $300^{\circ}$ , becoming *Sodium Pyrophosphate*— $\text{Na}_4\text{P}_2\text{O}_7$ —which crystallizes with 10 molecules of  $\text{H}_2\text{O}$ , and upon boiling with nitric acid passes into primary sodium phosphate.

The **primary or monosodium phosphate**— $\text{Na H}_2\text{PO}_4$ —crystallizes with 1 molecule of  $\text{H}_2\text{O}$  and exhibits an acid reaction. At  $100^{\circ}$  it loses its water of crystallization, and at  $200^{\circ}$  becomes  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ , disodium pyrophosphate, which at  $240^{\circ}$  forms **sodium metaphosphate**— $\text{NaPO}_3$ —



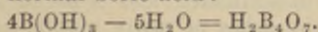
We get various modifications of the metaphosphate according to the conditions of fusion and cooling; they are probably polymerides corresponding to the formulas  $\text{Na}_2\text{P}_2\text{O}_6$ ,  $\text{Na}_3\text{P}_3\text{O}_9$ , etc. Upon heating sodium metaphosphate with metallic oxides the latter dissolve, and salts of orthophosphoric acid are formed, *e. g.* :—



In this manner, with various metals characteristic colored glasses (phosphorus beads) are obtained, which in blow-pipe analysis serve for the detection of the respective metals.

The salts of arsenic acid are perfectly analogous to those of phosphoric acid. Of the antimonates may be mentioned the disodium-pyroantimonate  $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7 + 6\text{H}_2\text{O}$ , which is insoluble in cold water.

**Sodium Borate.** The normal salts of boric acid  $\text{B}(\text{OH})_3$  and metaboric acid  $\text{BO.OH}$ , (see p. 233) are not very stable. The ordinary alkaline borates are derived from tetraboric acid ( $\text{H}_2\text{B}_4\text{O}_7$ ), which results from the condensation of 4 molecules of the normal boric acid :—



The most important of the salts is *borax*, which at ordinary temperatures crystallizes with 10 molecules of  $\text{H}_2\text{O}$ , in large monoclinic prisms,  $\text{Na}_2\text{B}_4\text{O}_7 + 10\text{H}_2\text{O}$ . Borax occurs naturally in some lakes of Thibet, whence it was formerly imported under the name of *tinkal*. At present it is artificially prepared by boiling or fusing boric acid with sodium carbonate. At ordinary temperatures the crystals dissolve in 14 parts water; at  $100^{\circ}$  in one-half part; the solution is feebly alkaline.

When warmed to  $70^{\circ}$  octahedra crystallize from the solution and have the composition  $\text{Na}_2\text{B}_4\text{O}_7 + 5\text{H}_2\text{O}$ , *octahedral borax*. Upon heating, both salts puff up, lose water and yield a white, porous mass (*burned borax*), which at a red heat fuses to a transparent, vitreous mass ( $\text{Na}_2\text{B}_4\text{O}_7$ ). In fusion this dissolves many metallic oxides, forming transparent glasses (borax beads), which frequently possess characteristic colors; thus copper salts give a blue, chromic oxide, a green glass. Therefore borax may be employed in blow-pipe tests for the detection of certain metals. Upon this property of dissolving metallic oxides depends the application of borax for fusion and soldering of metals.

**Sodium Silicate**—sodium water glass—is analogous to the potassium salt, and is most readily made by fusing quartz with sodium sulphate and charcoal.

The sulphur compounds of sodium are also analogous to those of potassium.

---

#### RECOGNITION OF SODIUM COMPOUNDS.

Almost all the sodium salts are easily soluble in water, sodium pyroantimoniate— $\text{H}_2\text{Na}_2\text{Sb}_2\text{O}_7$ —excepted; therefore, this may be used in precipitating sodium from its salts. Sodium compounds, exposed in a colorless flame, impart to the latter an intense yellow. The spectrum of the sodium flame is characterized by a very bright yellow line, which, when more strongly magnified, splits into two lines.

---

#### LITHIUM.

Li = 7.

Lithium only occurs in nature in small quantities, but is tolerably widely disseminated, and is found in some mineral springs and in the ashes of many plants, notably in that of tobacco and the beet. As compound silicate, it occurs in lepidolite or lithia mica; as phosphate (with iron and manganese) in triphylite.

The metal is separated from the chloride by means of the galvanic current, and is silver white in color, decomposing water at ordinary temperatures. Its specific gravity is 0.59. It is the lightest of all the metals, and swims upon naphtha. It melts at  $180^{\circ}$ , and burns with an intense white light.

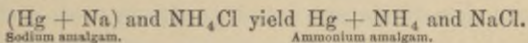
The lithium salts are very similar to those of sodium, closely approach, however, those of magnesium (p. 266).

**Lithium Chloride**— $\text{LiCl}$ —crystallizes, at ordinary temperatures, in anhydrous, regular octahedra; below  $10^\circ$ , however, with two molecules of  $\text{H}_2\text{O}$ , it deliquesces in the air.

**Lithium Phosphate**— $\text{Li}_3\text{PO}_4 + \frac{1}{2}\text{H}_2\text{O}$ —and *Lithium Carbonate*— $\text{Li}_2\text{CO}_3$ —are with difficulty soluble in water; therefore, precipitated from solutions of lithium salts by sodium phosphate or carbonate. By strong ignition the carbonate loses carbon dioxide. As regards these two salts, lithium approaches the metals of the calcium group (p. 266). Its compounds color the flame a beautiful red; the spectrum shows an intense red line.

### AMMONIUM COMPOUNDS.

Upon page 119 we observed that ammonia combines directly with acids to form salt-like compounds, which are analogous to metallic salts, especially those of potassium. The monatomic group,  $\text{NH}_4$ , playing the rôle of metal in these derivatives, is called *ammonium*, and its compounds ammonium compounds. The metallic character of the group  $\text{NH}_4$  is confirmed by the existence of *ammonium amalgam*, which, as regards its external appearance, is very similar to the sodium and potassium amalgams. Ammonium amalgam may be prepared by letting the galvanic current act upon ammonium chloride,  $\text{NH}_4\text{Cl}$ , viz., by immersing the negative platinum electrode into a depression in the ammonium chloride, which is filled with mercury. There then separates, just as in the decomposition of potassium or sodium chloride—a metal at the negative pole—ammonium which forms the amalgam with mercury. The amalgam may also be obtained if sodium amalgam be covered with a concentrated solution of ammonium chloride:—



Sodium amalgam.

Ammonium amalgam.

Ammonium amalgam forms a very voluminous mass with a metallic appearance. It is very unstable, and decomposes rapidly into mercury, ammonia and hydrogen.

On dissolving in water, ammonia yields a strong alkaline solution; however, no proofs are present to lead us to



accept the existence of ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) in solution. On the opposite hand, there exist organic derivatives of ammonium hydrate, in which the hydrogen of the ammonium is replaced by hydrocarbon residues; *e. g.*, tetramethyl ammonium hydrate— $\text{N}(\text{CH}_3)_4\text{OH}$ . These are thick liquids, of strong basic reaction, which, throughout, are very similar to potassium and sodium hydrate.

**Ammonium Chloride**— $\text{NH}_4\text{Cl}$ —is sometimes found in volcanic districts, and formerly was obtained by the dry distillation of camel's dung (*Sal ammoniacum*). At present it is prepared, almost exclusively, by saturating the ammonia water from gas works with hydrochloric acid. The solution is evaporated to dryness and the residue heated in iron vessels, when the ammonium chloride sublimes as a compact, fibrous mass. It dissolves in 2.7 parts of cold and one part of boiling water, and crystallizes from the solution in small, mostly feather-like, grouped octahedra or cubes, of sharp, salty taste. When heated, ammonium chloride sublimes without melting; at the same time a dissociation into  $\text{NH}_3$  and  $\text{HCl}$  is sustained, but these products recombine again to ammonium chloride, on cooling. The dissociation is complete at  $350^\circ$ , and the vapor density then equals 13 ( $\text{H} = 1$ ) corresponding to that of a mixture of similar molecules, of  $\text{NH}_3$  (8.5) and  $\text{HCl}$  (18.2). A like decomposition is sustained by the ammonium chloride when its solution is boiled; ammonia escapes and the solution contains some free hydrochloric acid.

**Ammonium Sulphate**— $(\text{NH}_4)_2\text{SO}_4$ —is obtained by saturating the ammonia water from gas works with sulphuric acid. It crystallizes without water in rhombic prisms, soluble in two parts of cold and one part of hot water. It fuses at  $140^\circ$ , and by further heating decomposes into ammonia, nitrogen, water and ammonium sulphite.

**Ammonium Nitrate**— $\text{NH}_4\text{NO}_3$ —is isomorphous with potassium nitrate and deliquesces in the air. When heated it melts, and then decomposes into hyponitrous oxide and water (p. 203).

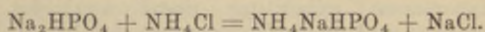
**Ammonium Nitrite**— $\text{NH}_4\text{NO}_2$ —is present in minute quantities in the air, and results from the action of the electric spark upon the latter when moist, and also in the oxidation of phosphorus. It may be obtained by the saturation of aqueous ammonia with nitrous acid—in a perfectly pure condition, by

the decomposition of silver or lead nitrite by ammonium chloride. Heat decomposes it into nitrogen and water (p. 107).

**Ammonium Carbonate.** The *neutral* or *secondary* salt,  $(\text{NH}_4)_2\text{CO}_3$ , separates as a crystalline powder, when ammonia gas is conducted through a concentrated solution of the so-called sesquicarbonate. In the air it yields up ammonia and becomes the *primary* or *acid* salt,  $\text{NH}_4\text{HCO}_3$ , which when heated to  $58^\circ$ , decomposes into carbon dioxide, ammonia and water.

The ordinarily occurring, commercial, so-called sesquicarbonate of ammonium  $(\text{CO}_2)_2$ ,  $(\text{NH}_3)_3$ ,  $\text{H}_2\text{O}$ , which can be regarded as a compound of primary ammonium carbonate with ammonium carbamate,  $\text{CO}_3(\text{NH}_4)\text{H} + \text{NH}_2$ ,  $\text{CO}_2$ ,  $\text{NH}_4$  (see organic chemistry), arises in the decay of many nitrogenous hydrocarbons, *e. g.*, the urine, and was formerly prepared by the dry distillation of bones, horn, and other animal substances. At present it is obtained by heating a mixture of ammonium chloride, or sulphate, with calcium carbonate. Then it sublimes as a white, transparent, hard mass, which gives off ammonia and carbon dioxide in the air, falling into a white powder of primary ammonium carbonate. The latter, obtained by the weathering of the two first salts, or by saturating ammonium hydrate with carbon dioxide, is a white, odorless powder, more insoluble in water. In aqueous solution it gradually loses carbon dioxide and is changed to secondary carbonate.

**Ammonium Phosphates.** The most important of these is the secondary ammonium-sodium phosphate,  $\text{PO}_4(\text{NH}_4)\text{NaH} + 4\text{H}_2\text{O}$ , ordinarily termed salt of phosphorus. It is found in guano and decaying urine. It can be obtained by crystallization of di-sodium phosphate and ammonium chloride:—



It consists of large, transparent, monoclinic crystals. When heated it fuses, giving up water and ammonia and forming a transparent glass of sodium metaphosphate  $\text{NaPO}_3$  (p. 285). It will serve in blowpipe tests for the detection of various metals.

The **tertiary ammonium phosphate**— $(\text{NH}_4)_3\text{PO}_4$ —separates upon mixing concentrated solutions of phosphoric acid and ammonia. Upon drying, it loses ammonia and passes into

the *secondary salt*  $(\text{NH}_4)_2\text{HPO}_4$ , which, upon boiling its solution changes to the *primary salt*,  $\text{PO}_4(\text{NH}_4)\text{H}_2$ .

**Ammonium Sulphide**— $(\text{NH}_4)_2\text{S}$ —results upon mixing 1 vol.  $\text{H}_2\text{S}$  with 2 vols.  $\text{NH}_3$  at  $-18^\circ$ . It is a white crystalline mass, decomposing, at ordinary temperatures, into  $\text{NH}_4\text{HS}$  and  $\text{NH}_3$ . In aqueous solution it is obtained by saturation of ammonium hydrosulphide solution with ammonia.

**Ammonium Hydrosulphide**.— $\text{NH}_4\text{SH}$ —is produced upon conducting hydrogen sulphide into an alcoholic ammonia solution. In aqueous solution it is obtained by saturating *aqua ammonia* with hydrogen sulphide. At first, the solution is colorless, but assumes a yellow color on standing in contact with the air, owing to the formation of ammonium polysulphides— $(\text{NH}_4)_2\text{S}_n$ . The so-called yellow ammonium sulphide is more simply obtained by the solution of sulphur in the colorless hydrosulphide. Both solutions are often employed in laboratories for analytical purposes.

**Recognition of Ammonium Compounds.** All ammonium salts are volatile and decompose upon heating. The alkalis and other bases liberate ammonia from them, which is recognized by its odor and the blue color imparted to red litmus paper. Platinum chloride produces in solutions of ammonium chloride a yellow crystalline precipitate of ammonio-platinum chloride  $\text{PtCl}_4 \cdot 2\text{NH}_4\text{Cl}$ . Tartaric acid precipitates *primary ammonium tartrate*.

---

## METALS OF THE SECOND GROUP.

The second group of the periodic system (see table p. 237) comprises chiefly the diatomic metals, forming compounds only according to the diatomic type,  $\text{MeX}_2$ , and in their entire deportment exhibiting many analogies. Their special relations and analogies are more closely regulated by the law of periodicity. Beryllium and magnesium belong to the two small periods whose members are similar but do not show complete analogy. Beryllium exhibits many variations from magnesium, and in many properties approaches aluminium; just like lithium, attaches itself to magnesium. (p. 266). The metals, calcium, strontium and barium, constitute the second members of the three great periods, are among themselves perfectly homologous (p. 234), and according to



their strong basic character attach themselves to the alkali metals K Rb and Cs. The members of the second sub-group corresponding to them, zinc, cadmium and mercury, belong really to the right negative sides of the three great periods. They fall in with the heavy metals, are much less basic, and resemble the alkaline earth metals only in their combination forms. In consequence of the double periodicity of the three great periods both sub-groups (Ca Sr Ba and Zn Cd Hg) exhibit many analogies with magnesium and beryllium.

#### GROUP OF THE ALKALINE EARTHS.

##### Calcium.

Ca = 40.

##### Strontium.

Sr = 87.2.

##### Barium.

Ba = 136.8.

The metals of this group are termed alkaline earth metals, because their oxides in their properties attach themselves on the one side to the oxides of the alkalis, upon the other to the real earths (alumina, etc.) In properties they show the same gradation as the elements of the potassium group, and as regards their atomic weight bear the same relation to each other. With increase in atomic weight their chemical energy and basicity become greater. Barium decomposes water energetically, and oxidizes more readily than strontium and calcium. In accord with this we find barium hydrate a stronger base; it dissolves tolerably easily in water, does not decompose upon ignition and rapidly absorbs carbon dioxide from the air. Barium carbonate is also very stable, fuses at a white heat, and only disengages a little carbon dioxide. Calcium hydrate is much more difficultly soluble in water, and upon ignition breaks up into water and calcium oxide; the carbonate also yields up carbon dioxide upon similar treatment. In its entire character strontium stands between barium and calcium. All these affinity relations find full expression in the heat of formation of the corresponding compounds.

While thus the alkaline earth metals, in free condition and in their hydrates, are similar to the alkalis, they essentially distinguish themselves from them by the insolubility of their carbonates and phosphates, and still more by their sulphates. In water and acids barium sulphate is almost insoluble, while that of calcium dissolves in 400 parts water; strontium sulphate occupies a medium position.

The metals of this group do not form any volatile compounds and their specific heats have not yet been determined. As the determination of the vapor densities of the elements or their volatile compounds, further the ascertainment of the specific heat of the metals, afford the only two direct means for the derivation of the true atomic weights, it was allowable to place the atomic weights of the calcium group equal to their equivalent weights ( $\text{Ca} = 20, \text{CaCl}$ ). But the great analogy of their compounds with those of the metals of the magnesium group, for instance, their isomorphism, argues with great probability that the metals of the group are diatomic, and that the present accepted double atomic weights are the true ones (compare p. 251). This conclusion at present for calcium is confirmed by the experimental determination of its heat capacity.

---

### CALCIUM.

Ca — 40.

Calcium belongs to the class of elements most widely distributed upon the earth's surface. As calcium carbonate (limestone, marble, chalk) and the sulphate (gypsum, alabaster), it represents immense deposits in all stratified formations. As phosphate it constitutes *phosphorite*, as fluoride, *fluorite*, both of which are abundant. As silicate it is found in most of the oldest crystalline rocks.

The metal is obtained by the electrolysis of the fused chloride; further, by heating calcium iodide with sodium, or calcium chloride with sodium and zinc. Although the affinity of calcium for oxygen is less than that of the alkalis, yet the oxide (also  $\text{BaO}$  and  $\text{SrO}$ ) cannot be reduced to metal by ignition with carbon, iron or sodium—due, probably, to the non-fusibility of the oxide.

Calcium is a yellow, shining metal, of specific gravity 1.55–1.6. In dry air it is tolerably stable, in moist it covers itself with a layer of hydrate. It decomposes water with considerable energy. It fuses at a red heat, and in the air burns with a brilliant yellow light.

**Calcium Oxide**—Lime— $\text{CaO}$ —may be obtained pure by igniting the nitrate or carbonate. On a large scale it is prepared by burning the ordinary limestone or marble ( $\text{CaCO}_3$ ) in lime-kilns. It is a grayish-white mass, which does not fuse even at the highest temperatures. The oxy-hydrogen flame thrown upon a piece of lime causes it to emit an extremely intense white light (Drummond's Lime Light). In

the air lime attracts moisture and  $\text{CO}_2$ , becoming calcium carbonate. Burned lime unites with water with evolution of much heat, breaking up into a white voluminous powder of calcium hydrate  $\text{Ca}(\text{OH})_2$ —*slaked lime*.

When limestone contains large quantities of aluminium, magnesium, carbon, or other constituents, the lime from it slakes with difficulty, and is known as *poor* lime, to distinguish it from pure, *fat* or *rich* lime, which readily becomes a powder with water.

**Calcium Hydrate**— $\text{Ca}(\text{OH})_2$ —slaked lime—is a white, porous powder, forming a thick paste, milk of lime, with water. It dissolves with difficulty in cold water (1 part in 160 parts), but still more difficultly in warm water; the solution saturated in the cold (lime water) becomes cloudy upon warming. It reacts strongly alkaline. In the air it attracts carbon dioxide, and forms calcium carbonate. At a red heat it decomposes into oxide and water.

Slaked lime is employed in the preparation of ordinary mortar, a mixture of calcium hydrate, water and quartz sand. The hardening of the mortar in the air depends principally upon the fact that the calcium hydrate combines with the  $\text{CO}_2$  of the air to form the carbonate; at the same time, by the action of the hydrate upon the silicic acid of the sand calcium silicate is produced, whereby the durability of the mortar increases with time.

Hydraulic mortar, or cement, is produced by a gentle burning of a mixture of limestone or chalk with aluminium silicate (clay) and quartz powder. On stirring the powdered burnt mass with water it soon hardens, and is not dissolved by water. Some naturally occurring limestones, containing upwards of 20 per cent. clay, yield hydraulic cements, without any admixtures after burning. The composition of these latter is variable, also the process of their hardening; it depends principally, however, upon the formation of calcium and aluminium silicates.

**Calcium Peroxide**— $\text{CaO}_2$ —is precipitated as a hydrate in crystalline leaflets, if lime water be added to a solution of barium peroxide in dilute hydrochloric acid; it is very unstable.

---

The halogen derivatives of calcium, like those of other metals, are prepared by the solution of the oxide or carbonate in the haloid acids. Also formed by the direct union of cal-



cium with the halogens; calcium burns in the vapors of chlorine, bromine and iodine. Technically, calcium chloride is often obtained as a bye-product, as in the preparation of ammonia.

**Calcium Chloride**— $\text{CaCl}_2$ —crystallizes from aqueous solution with 6 molecules of  $\text{H}_2\text{O}$ , in large, six-sided prisms, which deliquesce in the air. In vacuo it loses 4 molecules  $\text{H}_2\text{O}$ . When heated it melts in its water of crystallization, loses water, but only after it is exposed above  $200^\circ$  does it become anhydrous, when it becomes a white, porous mass. The dry salt fuses at a red heat and solidifies to a crystalline mass, which attracts water energetically, and may be employed in the drying of gases and liquids. The dry calcium chloride also absorbs ammonia, forming the compound  $\text{CaCl}_2 \cdot 8\text{NH}_3$ . The crystallized hydrous salt dissolves in water with reduction of temperature; by mixing with snow or ice the temperature is lowered to  $-48^\circ$ . Upon fusing the dry chloride in the air, it will partially decompose into the oxide and hydrogen chloride.

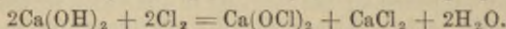
Calcium bromide and iodide are very similar to the chloride.

**Calcium Fluoride**— $\text{CaF}_2$ —occurs in nature as **fluorite**, in large cubes or octahedra, also massive. Often discolored by impurities. It is found, in sparing quantities, in ashes of plants, bones, and the enamel of the teeth. A soluble fluoride added to the solution of calcium chloride throws down insoluble calcium fluoride as a white voluminous precipitate.

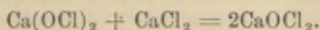
The fluoride is perfectly insoluble in water and is only decomposed by strong acids. It easily fuses at a red heat, serving, therefore, as a flux in the smelting of ores. When heated it shows phosphorescence.

**Calcium Hypochlorite**— $\text{Ca}(\text{ClO})_2$ —is not known in a pure condition. The so-called *bleaching lime*, or *chloride of lime*, obtained by conducting chlorine, at ordinary temperatures, over slaked lime, contains calcium hypochlorite as active principle.

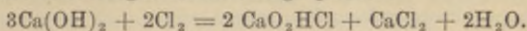
According to the analogy with the action of chlorine upon potassium, or sodium hydrate, the reaction, in the case of calcium hydrate may be expressed by the following equation:—



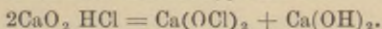
From this, chloride of lime would have to be looked upon as a mixture of calcium hypochlorite and water. In accordance with the equation of the reaction, the completely chlorinated chloride of lime must contain 48.9 % chlorine, which is never the case, as invariably a portion of the calcium hydrate appears to remain unaltered. When chloride of lime is treated with water, calcium hypochlorite and calcium chloride dissolve, the hydrate, for the most part, remaining. It was thought the atomic constitution,  $\text{Ca} \begin{matrix} \text{OCl} \\ \text{Cl} \end{matrix}$ , must be ascribed to the mixture of calcium hypochlorite and calcium chloride, according to similar molecules:—



According to the more recent investigations of Stahlschmidt, the active constituent of chloride of lime consists of a basic calcium hypochlorite,  $\text{Ca} \begin{matrix} \text{OCl} \\ \text{OH} \end{matrix}$ , and the action of chlorine upon calcium hydrate takes place according to the following equation:—

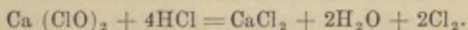


From this the completely saturated chloride of lime does not contain more than 39 per cent. Cl, which agrees with actual observation. The formation of calcium hydrate by the action of water is explained by the decomposition of the basic calcium hypochlorite:—

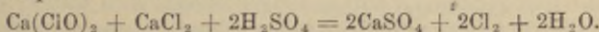


Chloride of lime is a white, porous powder, of a chlorine-like odor. The aqueous solution reacts strongly alkaline and bleaches. In the air it decomposes, as the carbon dioxide of the former liberates hypochlorous acid. Even in closed vessels it gradually breaks up, with elimination of oxygen; the decomposition is hastened by sunlight and heat, and may occur with explosion. Hence chloride of lime should be preserved in loosely closed vessels, in a cool, dark place.

Dilute hydrochloric or sulphuric acid expel chlorine from chloride of lime, and in just twice the quantity that the hypochlorite in the chloride contains:—



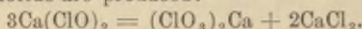
When sulphuric acid acts, the calcium chloride present participates in the reaction:—



Upon this is founded the application of chloride of lime for the production of chlorine in chlorine bleaching and disinfection.

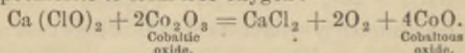
The quantity of chlorine set free by acids from the chloride of lime represents its quantity of so-called *active chlorine*; good chloride of lime should contain at least 25%.

Upon boiling the aqueous solution of chloride of lime calcium chlorate and chloride are produced:—



On this is based the application of chloride of lime for the production of potassium chlorate ( $\text{KClO}_3$ ) by a transposition of calcium chlorate with potassium chloride.

When to the solution of bleaching lime a small quantity of cobaltic oxide is added, upon warming, a regular stream of oxygen is disengaged; this is an advantageous method of preparing oxygen. Other oxides, like those of manganese, copper and iron, behave similarly. In this reaction there occurs apparently a contact action of the oxides. The reaction is explained, doubtless, in the same way as the action of hydrogen peroxide upon certain oxides (see p. 92). The feebly combined oxygen atom in cobaltic oxide unites with the oxygen of the calcium hypochlorite to form free oxygen:—



The resulting cobaltous oxide is then again converted by the chloride of lime into cobaltic oxide, which acts upon a fresh quantity of bleaching lime.

**Calcium Sulphate**— $\text{CaSO}_4$ —is very abundant in nature. In anhydrous condition it forms the mineral *anhydrite*, crystallizing in forms of the rhombic system. With two molecules of water it occurs as gypsum, in large monoclinic crystals or in granular, crystalline masses (Alabaster, etc.). Also upon precipitating the soluble calcium salts with sulphuric acid,  $\text{CaSO}_4 + 2\text{H}_2\text{O}$  separates as a fine crystalline powder. Calcium sulphate is only difficultly soluble in water; 1 part at average temperatures dissolves in 400 parts  $\text{H}_2\text{O}$ . When heated to  $200^\circ$  gypsum loses all its water and becomes *burnt gypsum*, which pulverized and mixed with water forms a paste, that in a short time hardens to a solid mass. The hardening is dependent upon the reunion of anhydrous calcium sulphate with 2 molecules of  $\text{H}_2\text{O}$ . On this depends the use of burned gypsum for the production of moulds, figures, etc. In case gypsum has been too intensely heated, (dead-burnt gypsum) it will no longer harden with water; the naturally occurring anhydrite behaves in the same manner.

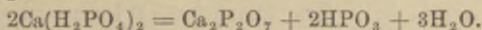


**Calcium Nitrate**— $\text{Ca}(\text{NO}_3)_2$ —is produced by the decay of nitrogenous organic substances in the presence of lime, therefore it frequently is found disintegrated upon walls (in cattle stables). From water it crystallizes in monoclinic prisms having four molecules of water; the anhydrous salt deliquesces in the air. By the action of potassium carbonate or chloride calcium nitrate may be transposed into potassium nitre (p. 272).

**Calcium Phosphate.** The *tertiary* phosphate— $\text{Ca}_3(\text{PO}_4)_2$ —is found in slight quantities in the most of the mountain rocks. In combination with calcium fluoride it crystallizes as *apatite*. In compact masses, more or less intimately mixed with other constituents, it constitutes, as *phosphorite*, immense deposits in Spain, France, Germany and Russia. When these minerals disintegrate the calcium phosphate passes into the soil and is absorbed by the plants. In the latter it accumulates chiefly in the seeds and grains. In the animal kingdom it is principally found in the bones, the ashes of which contain upwards of 85% calcium phosphate. The tertiary calcium phosphate is entirely insoluble in water. If disodium phosphate be added to the aqueous solution of a calcium salt and then ammonium hydrate, it will separate as a gelatinous precipitate, which, after drying, forms a white amorphous powder. In acids, even acetic, it is very readily soluble.

The *secondary* calcium phosphate— $\text{PO}_4\text{CaH} + 2\text{H}_2\text{O}$ —is sometimes present in guano, in the form of small, shining prisms, and separates as an amorphous precipitate if disodium phosphate be added to a solution of calcium chloride mixed with some acetic acid.

The *primary* phosphate— $\text{Ca}(\text{H}_2\text{PO}_4)_2$ —is produced by the action of sulphuric or hydrochloric acid upon the two first phosphates. It is readily soluble in water and deliquesces in the air. Heated to  $200^\circ$  it decomposes into pyrophosphate, metaphosphoric acid and water:—



On igniting the mixture with charcoal the metaphosphoric acid is reduced to phosphorus. In this manner the latter is extracted from calcium phosphate.

Calcium phosphate is present in all plants. Its presence in the soil is, therefore, an indispensable condition for its fertility. When there is a scarcity of phosphoric acid it must be added. To this end

bone meal and pulverized phosphorite were formerly employed. As, however, the phosphoric acid is contained in these substances as tricalcium phosphate, which is not easily absorbed by the plants, at present the primary phosphate is extensively employed as a fertilizer, or, better, the mixture resulting from the action of sulphuric acid upon the tertiary salt. Superphosphate is the name applied to the resulting mass.

**Calcium Carbonate**— $\text{CaCO}_3$ —is very widely distributed in nature. It crystallizes in two crystallographic systems, hence dimorphous. In rhombic crystals with the specific gravity 3.0 it forms aragonite. In hexagonal rhombohedra with specific gravity 2.7 it occurs as calcite. Iceland spar, employed for optical purposes, is perfectly pure, transparent calcite. The common calcite, which constitutes immense mountain chains, is an amorphous, or indistinct crystalline stratum, and usually is mixed with other constituents, like clay. When the limestone is granular and crystalline it is termed marble. Dolomite, which also constitutes large layers, is a compound of calcium and magnesium carbonate, containing generally excess of the former. *Chalk* is very pure amorphous calcium carbonate, consisting of the microscopic shells of sea animals. Further, calcium carbonate is a regular constituent of all plants and animals; the shells of eggs, of mussels, also corals and pearls, consist chiefly of it.

A soluble carbonate added to the aqueous solution of a calcium salt precipitates calcium carbonate as a white, amorphous powder, which soon becomes crystalline. In the cold it assumes the form of calcite; upon boiling the liquid it changes generally into aragonite crystals.

In pure water the carbonate is almost insoluble; dissolves somewhat in water containing carbon dioxide, as it very probably is changed to *primary* carbonate— $\text{Ca}(\text{HCO}_3)_2$ . For this reason we find calcium carbonate dissolved in all natural waters. When the solution stands exposed, more rapidly, on warming, carbon dioxide escapes and secondary carbonate again separates out. The formation of lime scales, thermal tufts, stalactites, boiler scales and similar deposits, are due to this. Calcium carbonate, like all carbonates, is decomposed by acids with evolution of carbon dioxide. At a red heat it decomposes into  $\text{CaO}$  and  $\text{CO}_2$ .

**Calcium Silicate**— $\text{CaSiO}_3$ —occurs as white, crystalline wollastonite. It is also a constituent of most natural silicates and of the artificial silicate fusions—of glass.

**Glass.**—The silicates of potassium and sodium are readily fusible and soluble in water. The silicates of calcium and the other alkaline earths are insoluble, very difficultly fusible, and generally crystallize when they cool. If, however, the two silicates be fused together, an amorphous, transparent mass, of average fusibility, results; it is only slightly attacked by water and acids—it is glass. To prepare the latter, a mixture of sand, lime and soda, or potash, is heated to fusion in a muffle furnace. Instead of the carbonates of potassium and sodium a mixture of sulphates with charcoal can be employed; the carbon reduces the sulphates to sulphides, which form silicates when fused with silicon dioxide.

The following are varieties of glass:—

**Soda glass**—a mixture of sodium and calcium silicates—is easily fusible, and is employed for window panes and ordinary glass vessels. Potash, or Bohemian Glass, also Crown Glass, consists of calcium and potassium silicates, is not so easily fused, is harder, and withstands the action of water and acids better than soda glass; therefore employed in the manufacture of chemical glass ware.

**Glass Crystal, or Flint Glass**, is composed of potassium and lead silicate. It is not as hard, tolerably readily fused, refracts light strongly, and when polished, acquires a clear lustre. On this account it is employed for optical purposes (for lenses, prisms) and used in ornamental glassware. **Strass**—a lead glass containing boron trioxide is used to imitate precious stones. The opaque varieties of enamel consist of lead glass and contain insoluble admixtures, as tin dioxide and calcium phosphate in the fused glass.

Ordinary window glass is obtained by the fusion of rather impure materials; in consequence of the presence of ferrous oxide it is ordinarily colored green. To remove this coloration, manganese peroxide is added to the fusion. It oxidizes a portion of the ferrous to ferric oxide, the silicate of which is colored slightly yellow, while manganese forms a violet silicate. Both colors, violet and green, almost neutralize each other as complementaries. The colored glasses contain silicates of colored metallic oxides; chromium and copper color green; cobalt, blue; cuprous oxide, a ruby red, etc., etc.

The sulphur compounds of calcium are very much like those of the alkalis. **Calcium Sulphide**— $\text{CaS}$ —is most readily obtained by heating the sulphate with carbon, and is a whitish-yellow mass. By solution in water is obtained **Calcium Hydrosulphide**— $\text{Ca}(\text{SH})_2$ —which decomposes on boiling the aqueous solution. When calcium oxide is ignited with sulphur in a closed crucible a yellowish-gray mass, consisting of calcium polysulphides and sulphate, is obtained. Milk of lime boiled with sulphur yields a deep yellow solution



of calcium polysulphides. By acids, very finely divided sulphur—milk of sulphur—together with evolution of  $H_2S$ , is precipitated from solutions of the polysulphides. If the reverse, the addition of a solution of polysulphides to excess of dilute acids, be made, hydrogen persulphide will separate.

---

## STRONTIUM.

Sr = 87.2.

This element is rather rare in nature, and is principally found in strontianite (strontium carbonate) and celestite (strontium sulphate). Its compounds are very similar to those of calcium.

The metal is obtained by the electrolysis of fused strontium chloride. It is a brass-yellow metal, of specific gravity, 2.5. In the air it oxidizes and burns, when heated, with a bright light. Water decomposes it at ordinary temperatures.

Of the compounds of strontium we may mention the following:—

**Strontium Oxide**— $SrO$ —is most readily obtained by glowing the nitrate. With water it unites, with strong evolution of heat, to **Strontium Hydrate**— $Sr(OH)_2$ —which is more readily soluble in water than calcium hydrate. From aqueous solution it crystallizes with 8 molecules of  $H_2O$ . When ignited it decomposes into  $SrO$  and  $H_2O$ , but with more difficulty than calcium hydrate.

**Strontium Chloride**— $SrCl_2 + 6H_2O$ —crystallizes from water in hexagonal tables, which deliquesce in the air; it is somewhat soluble in alcohol.

**Strontium Sulphate**— $SrSO_4$ —is much more difficultly soluble in water than calcium sulphate, but not so much so as barium sulphate.

**Strontium Nitrate**— $Sr(NO_3)_2$ —is obtained by dissolving the carbonate in nitric acid, and is readily soluble in water. From warm solutions it crystallizes in anhydrous octahedra, but from cold with 4 molecules  $H_2O$ , in monoclinic prisms. Mixed with combustible substances it colors the flame a beautiful carmine red, and for this reason is employed in pyrotechny.

**Strontium Carbonate**— $\text{SrCO}_3$ —is precipitated from aqueous solutions of strontium salts, as an amorphous, insoluble powder, by soluble carbonates. By ignition it breaks up into  $\text{SrO}$  and  $\text{CO}_2$ , however, more difficultly than calcium carbonate.

---

### BARIUM.

Ba — 136.8.

Barium occurs in nature in large masses, as heavy spar or barium sulphate, and as witherite (barium carbonate). All its compounds are distinguished by their high specific gravity, hence the name barium, from  $\beta\alpha\rho\upsilon\varsigma$ , heavy. In accordance with its general character barium is a stronger basic metal than strontium and calcium (p. 291).

The barium salts are either prepared from the natural witherite, by dissolving it in acids, or from heavy spar. The latter is almost insoluble in all acids; to obtain the other compounds from it, it must first be converted into sulphide. For this purpose a mixture of barium sulphate with carbon is heated to redness, whereby the sulphate is reduced to sulphide, which is soluble in water and readily transposed by acids.

Metallic barium was first obtained by the electrolysis of the fused chloride. The following method is more convenient: Sodium amalgam is added to a hot saturated barium chloride solution; the sodium displaces the barium, which forms an alloy with the mercury. The resulting liquid barium amalgam is kneaded with water, to remove all the sodium, and then heated in an hydrogen stream, to volatilize the mercury.

Barium is a bright yellow metal, of specific gravity 3.6. It fuses at a red heat, but does not vaporize. It is rapidly oxidized in the air; it decomposes water very energetically, even at ordinary temperatures, like sodium.

**Barium Oxide**— $\text{BaO}$ —is obtained by the ignition of barium nitrate. It is a gray, amorphous mass, of specific gravity 4.0, and fusible in the oxy-hydrogen flame. With water it yields the hydrate, with evolution of much heat.

**Barium Hydrate**— $\text{Ba}(\text{OH})_2$ —is precipitated from concentrated solutions of barium salts by potassium or sodium hydrate, not, however, by ammonium hydrate. At ordinary temperatures it dissolves in 20 parts, upon boiling, in 3 parts water. From aqueous solution it crystallizes with 8 mole-

cules of  $H_2O$  in four-sided prisms or leaflets. The solution—called *Baryta water*—is strongly alkaline and is very similar to the alkalis. When exposed to the air it absorbs carbon dioxide and becomes turbid, with separation of barium carbonate. At a red heat it fuses without decomposition and solidifies to a crystalline mass.

**Barium Peroxide**— $BaO_2$ —is produced when barium oxide is heated in a stream of air or oxygen, and always contains oxide. To purify it, the commercial peroxide is rubbed together with water and added to very dilute hydrochloric acid, until the latter is almost saturated. To the solution containing barium chloride and hydrogen peroxide, is added excess of baryta water. *Hydrated barium peroxide*— $BaO_2 + H_2O$ —separates in shining scales, which, upon warming, lose water readily and break up into a white powder of barium peroxide. The latter, obtained directly from the oxide, is a compact, gray mass.

The peroxide dissolves in dilute acids, with production of hydrogen peroxide. Concentrated sulphuric acid sets free ozonized oxygen from it. When strongly ignited (above  $400^\circ$ ) it decomposes into barium oxide and oxygen.

**Barium Chloride**— $BaCl_2$ —crystallizes from aqueous solution, with two molecules of  $H_2O$ , in large, rhombic tables, which are stable in the air. It dissolves readily in water, and is poisonous, like all soluble barium salts.

**Barium Nitrate**— $Ba(NO_3)_2$ —crystallizes in anhydrous, shining octahedra, of the regular system, soluble in 12 parts of cold and 3 parts of hot water. It is employed for green flames in pyrotechny.

**Barium Sulphate**— $BaSO_4$ —found in nature as heavy spar, in rhombic prisms, with a specific gravity of 4.6. Artificially, it is obtained by the precipitation of barium salts with sulphuric acid as a white, amorphous powder, almost insoluble in water and acids. Under the name of *permanent white*, it is used as a paint, as a substitute for poisonous *white lead*, from which it is also distinguished by its unalterability.

**Barium Carbonate**— $BaCO_3$ —as witherite, occurs in shining, rhombic crystals, and is precipitated from barium solutions by soluble carbonates, as a white, amorphous powder. It fuses at a white heat, and loses some carbon dioxide.



**Barium Sulphide**— $BaS$ —is obtained by igniting the sulphate with carbon. It dissolves in water, with decomposition into hydrate and hydrosulphide.

#### Recognition of the Compounds of the Alkaline Earths.

The carbonates and phosphates of this group are insoluble in water; hence precipitated from aqueous solution of the salts upon addition of soluble carbonates and phosphates (of the alkalies). The sulphates are also insoluble in acids (only calcium sulphate is somewhat soluble); for this reason they are thrown down from acid solutions by soluble sulphates or free sulphuric acid; the precipitation is complete, even with calcium, if alcohol be added to the solution. The hydrates of the alkaline earths, which are more or less soluble in water, are only precipitated by sodium or potassium hydrate from concentrated solutions. Hydrofluosilicic acid produces, in solutions of barium salts, a crystalline precipitate of barium silico-fluoride,  $BaSiF_6$ .

Very characteristic are the flame colorations produced by the volatile compounds; calcium salts impart a reddish yellow color; strontium, an intense crimson; barium, a yellowish green. The spectra correspond to these flame colors. The spectrum of calcium exhibits several yellow and orange lines, and in addition, a green and a violet line (see the spectrum table); that of strontium contains, besides several red lines, two less distinct, but very characteristic lines, an orange and a blue. Finally, the barium spectrum consists of several orange, yellow and green lines, among which a bright green is particularly prominent.

#### METALS OF THE MAGNESIUM GROUP.

In this group are usually included beryllium, magnesium, zinc and cadmium. However, these metals do not exhibit complete analogy, as clearly seen in the periodic system (p. 290). Generally, beryllium, which approaches aluminium, differs, while magnesium is not only similar to zinc and cadmium, but also to the alkaline earths, calcium, strontium and barium. The similarity with the latter shows itself in the basic nature of magnesium, while with zinc and cadmium it chiefly consists in isomorphism of compounds.

Beryllium and magnesium bear the same relation to Ca Sr Ba as lithium and sodium to the metals of the potassium group.

The alkaline character of the alkaline earths, which gradually diminishes from barium to calcium, becomes almost nothing in magnesium and beryllium, which possess the lowest atomic weights (see p. 291). Magnesium and beryllium are scarcely capable, even at boiling temperature, of decomposing water. Their oxides and hydrates are almost insoluble in it; the hydrates decompose, on gentle ignition, into oxides and water. Their carbonates are very unstable; their chlorides, too, suffer, even on drying, a partial decomposition into oxide and hydrogen chloride. More decidedly do magnesium and beryllium distinguish themselves from the alkaline earths by the solubility of their sulphates. The specific properties of beryllium and magnesium are maintained in zinc and cadmium, which, with the former, constitute a natural group. Zinc and cadmium do not decompose water at boiling heat; their hydrates are insoluble in it, and little stable; their carbonates and chlorides easily undergo decomposition; their sulphates are readily soluble in water. The similarity expresses itself further in the isomorphism of most of their compounds. Thus, magnesium and zinc sulphates crystallize with 7 molecules of  $H_2O$ , in perfectly similar forms. If the solution of a mixture of both salts be allowed to crystallize, we get crystals with variable quantities of zinc and magnesium; the formation of such *isomorphous mixtures* in *ad libitum* proportions, is a characteristic indication of the isomorphism of chemically similar compounds.

The difference between beryllium and magnesium upon the one side, and zinc and cadmium on the other, is shown distinctly in their specific gravity. While the two first possess a low specific gravity (Be — 2.1 Mg — 1.75), zinc and cadmium (with specific gravities 7.2 and 8.6) belong to the so-called heavy metals (see p. 246).

The difference in specific gravity determines, also, many differences in chemical character. The light metals (especially the alkalis and alkaline earths) form rather unstable sulphides, readily soluble in water, while the sulphides of zinc and cadmium, like those of all heavy metals, are insoluble in water, and, usually, in acids; in these respects, magnesium and beryllium behave like the alkalis, while zinc and cad-

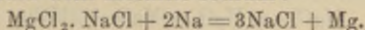
mium are precipitated by hydrogen sulphide or alkaline sulphides, from solutions of their salts, as sulphides. Further, the oxides of the light metals are very stable, and are only reduced by carbon, if they are readily fusible (like potassium and sodium oxides); the heavy metals, on the other hand, are easily separated from their oxides by carbon. Zinc and cadmium oxides are reduced by carbon, while those of magnesium and beryllium are not altered. All these affinity relations find closer expression and explanation in the thermochemical departments.

### MAGNESIUM.

Mg — 24.

Magnesium is abundant in nature, and almost always accompanies calcium in its compounds. As carbonate, it occurs in compact masses, as magnesite, etc. Dolomite, which forms entire mountains, is an isomorphous mixture of calcium and magnesium carbonates. Further, it is present in most of the natural silicates; its soluble salts are contained in almost all natural waters.

Metallic magnesium may be obtained by the electrolysis of the chloride or by heating the same with sodium. On a large scale it is prepared by heating the double chloride of magnesium and sodium with metallic sodium:—



The fusion is treated with water and the residual magnesium purified by distillation.

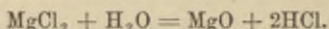
Magnesium is a brightly shining, almost silver-white metal, of specific gravity 1.75; its atomic volume equals 13.7. It is tenacious and ductile, and when heated may be converted into wire and rolled out into thin ribbons. It fuses at a dark red and distills at bright glowing heat. At ordinary temperature it scarcely oxidizes in the air; when heated it burns with an extremely intense white light, owing to the glowing non-volatile magnesium oxide. Magnesium is rich in chemically active rays, and for this reason is employed for photographing in dark chambers. Instead of pure magnesium, ordinarily its alloy with zinc is employed; this burns with an almost equally bright light. Boiling water is very slowly decomposed by magnesium. In dilute acids it dissolves easily to form salts; the alkalis do not attack it.



**Magnesium Oxide**— $MgO$ —or magnesia, formed by the combustion of magnesium, is ordinarily obtained by ignition of the hydrate or the carbonate (magnesia usta). It is a white, very voluminous, amorphous powder, which finds application in medicine. The feebly ignited magnesia combines with water, with slight generation of heat, to produce magnesium hydrate.

**Magnesium Hydrate**— $Mg(HO)_2$ —is precipitated from solutions of magnesium salts, as a gelatinous mass, by potassium or sodium hydrate. Dried at  $100^\circ$  it is a white, amorphous powder. In water and alkalis it is almost insoluble; moist litmus paper is, however, colored blue. Ammonium salts dissolve it tolerably easily, forming soluble double salts. Magnesium hydrate attracts carbon dioxide from the air and forms magnesium carbonate. By gentle ignition it yields the oxide and water.

**Magnesium Chloride**— $MgCl_2$ —is present in traces in many mineral springs. It may be obtained by solution of the carbonate or oxide in hydrochloric acid. By evaporation of its solution the salt crystallizes out with six molecules of  $H_2O$  in deliquescent crystals isomorphous with calcium chloride. When heated these give up water; at the same time a partial decomposition of the chloride into oxide and hydrogen chloride takes place:—



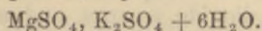
The chlorides of beryllium and zinc, as also those of several other metals, behave similarly. To get anhydrous magnesium chloride ammonium chloride is added to the solution. The double salt  $MgCl_2, NH_4Cl + 6H_2O$  is formed. When heated this at first loses water, and at  $460^\circ$  throws off ammonium chloride; anhydrous magnesium chloride remains. This is a leafy, crystalline mass, which fuses easily, and at a red heat distills undecomposed; in the air it is very deliquescent.

Double salts similar to the above are also formed with potassium and calcium chloride. The potassium double salt— $MgCl_2, KCl + 6H_2O$ —occurs as carnallite, in considerable deposits, at Stassfurt.

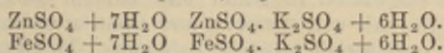
**Magnesium Sulphate**— $MgSO_4$ —is found in sea water and in many mineral springs. With more or less water it is *kieserite*, which abounds extensively at Stassfurt. At ordinary temperatures it crystallizes with 7 molecules  $H_2O$  —

$\text{MgSO}_4 + 7\text{H}_2\text{O}$ —in four-sided rhombic prisms readily soluble in water (at  $0^\circ$  in 2 parts water). It has a bitter, salt-like taste, and serves as an aperient. From solutions heated to  $70^\circ$  it crystallizes with 6 molecules of  $\text{H}_2\text{O}$ ; at  $0^\circ$ , however, with 12 molecules. Heated to  $150^\circ$  these hydrates lose all their water of crystallization, excepting *one molecule*, which escapes above  $200^\circ$ .<sup>5</sup> *One* molecule of water, therefore, in magnesium sulphate, is more closely combined than the rest. Many other salts containing water deport themselves similarly. The more intimately combined water is termed *Water of Constitution*.

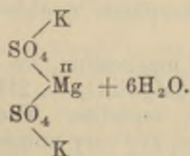
Magnesium sulphate forms double salts with potassium and ammonium sulphates, which crystallize with 6 molecules of  $\text{H}_2\text{O}$  in monoclinic prisms, *e. g.* :—



The sulphates of zinc and several other metals, as iron, cobalt, and nickel, in their diatomic forms, are very similar to magnesium sulphate. Their sulphates crystallize with 7 molecules of  $\text{H}_2\text{O}$ , are isomorphous, and contain 1 molecule of intimately combined water. With potassium and ammonium sulphates they form double salts, crystallizing with  $6\text{H}_2\text{O}$ , and also isomorphous; *e. g.* :—



The constitution of these double salts may be viewed in the same way as that of potassium—sodium sulphate, or of mixed salts of polybasic acids. We may suppose that in the given instance the diatomic metal unites two molecules of sulphuric acid :—



**Magnesium Phosphates.** The tertiary phosphate  $(\text{PO}_4)_2\text{Mg}_3$ , in small quantities accompanies the *tertiary* calcium phosphate in bones and in plant ashes. The *secondary* phosphate,  $\text{MgHPO}_4 + 7\text{H}_2\text{O}$ , is precipitated from the soluble magnesium salts, by disodium phosphate  $(\text{Na}_2\text{HPO}_4)$  as a salt difficultly soluble in water. In presence of ammonium salts in the same case *magnesium-ammonium phosphate*,  $\text{MgNH}_4\text{PO}_4 + 6\text{H}_2\text{O}$ , insoluble in water, is precipitated as a double salt. The latter is found in guano, forms in the decay

of urine, and sometimes is the cause of the formation of calculi. The *primary* salt,  $H_4Mg(PO_4)_2$ , has not been obtained.

The magnesium salts of arsenic acid,  $H_3AsO_4$ , are very similar to those of phosphoric acid. Magnesium-ammonium arseniate ( $MgNH_4AsO_4 + 6H_2O$ ) is also almost insoluble in water.

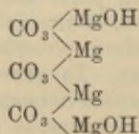
**Magnesium Carbonate**,  $MgCO_3$ , occurs crystallized in rhombohedra in nature (isomorphous with calcite), as magnesium spar; in compact masses, as magnesite. Combined with calcium carbonate, it forms dolomite, to which, when pure, the formula,  $CaCO_3, MgCO_3$ , is ascribed; ordinarily, however, it contains excess of calcium carbonate. On adding sodium or potassium carbonate to the aqueous solution of a magnesium salt, some carbon dioxide escapes, and a white precipitate forms, which consists of a mixture of magnesium carbonate and hydrate. If the precipitate be dried at low temperature, a white, voluminous powder, the composition of which generally corresponds\* to the formula,  $Mg(OH)_2, 3CO_3Mg + 4H_2O$  is obtained.

If it be suspended in water and carbon dioxide passed through it, the salt will dissolve, and upon standing exposed to the air, crystals of *neutral carbonate*,  $MgCO_3 + 3H_2O$ , separate. These, boiled with water, give up carbon dioxide and are again converted into basic carbonate. The naturally occurring magnesite sustains no change when boiled.

With potassium and ammonium carbonate, magnesium carbonate yields isomorphous double salts, *e. g.*,  $MgCO_3, K_2CO_3 + 4H_2O$ .

Of the *silicates* of magnesium, we may mention olivine ( $Mg_2SiO_4$ ), serpentine ( $Mg_3Si_2O_7 + 2H_2O$ ), talc ( $Si_5O_{14}Mg_4$ ), ( $Si_3O_8Mg_2 + 2H_2O$ ), sepiolite. The mixed silicates of magnesium and calcium are very numerous; to these belongs asbestos.

\* This compound is viewed as a basic carbonate, with the following formula:—



It is the salt employed in medicine under the name *magnesia alba*.



### Recognition of Magnesium Compounds.

The fixed alkaline hydrates precipitate magnesium hydrate from magnesium salts; the carbonates throw down basic magnesium carbonate. The precipitates are insoluble in pure water and the alkalis, but readily dissolve in solutions of ammonium salts. In presence of the latter, neither the alkaline hydrates nor carbonates cause precipitation. Disodium phosphate precipitates, in presence of ammonium salts, magnesium-ammonium phosphate,  $MgNH_4PO_4 + 6H_2O$ , insoluble in water.

### BERYLLIUM.

Be = 9.3.

Among the metals of the second group beryllium occupies a position similar to that of lithium in the first group; in both elements, which have the lowest atomic weight in their group, the specific group character is considerably diminished, or does not find expression. As lithium in many respects attaches itself to magnesium, so does beryllium approach aluminium. Like the latter, it is scarcely at all attacked by nitric acid, but dissolves easily in sodium or potassium hydrate, with elimination of hydrogen. Like aluminium oxide, that of beryllium dissolves in the alkalis, and is almost invariably accompanied by the former in its natural compounds. Beryllium sulphate, like that of aluminium, forms a difficultly soluble double salt with potassium sulphate. However, beryllium, in most of its compounds, stands nearer to magnesium than to aluminium.

Beryllium occurs but rarely in nature, principally in beryl, a double silicate of aluminium and beryllium— $Al_2Be_3(SiO_3)_6$ . Emerald has the same composition, and is only colored green by a slight amount of chromium oxide.

Metallic beryllium is obtained by the ignition of the chloride with sodium, and is a white ductile metal, of specific gravity 2.1. Its specific heat equals 0.4084, the atomic heat is, therefore, 3.8 (p. 248). It does not decompose water, even upon boiling. At ordinary temperature it does not oxidize in the air. Heated, it burns in the air with a very bright light, but only if it be finely divided, not, however (as magnesium), in a compact mass. It is readily dissolved by dilute hydrochloric and sulphuric acids; also by potassium and sodium hydrates.

**Beryllium Chloride**— $BeCl_2$ —is obtained, like aluminium chloride, by ignition of a mixture of beryllium oxide and carbon in a stream of chlorine. It sublimes in shining needles, which deliquesce in the air. From aqueous solution it crystallizes with four molecules of  $H_2O$ ; upon drying it suffers a decomposition, like magnesium chloride.

The salts of beryllium have a sweet taste, therefore it has, also, been called *glucinum*. From the soluble salts, ammonium hydrate

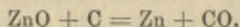
precipitates a white, gelatinous beryllium hydrate,  $\text{Be}(\text{OH})_2$ . This dissolves readily in sodium and potassium hydrate, but on boiling, is again separated from solution. When heated, the hydrate breaks up into water and beryllium oxide,  $\text{BeO}$ , which is a white, amorphous powder, of specific gravity 3.08. Its specific heat equals 0.2471.

**Beryllium Sulphate**— $\text{BeSO}_4$ —crystallizes from water at various temperatures, with four or seven molecules of  $\text{H}_2\text{O}$ , of which one is more closely combined. With magnesium sulphate it crystallizes in an isomorphous mixture. The double salt,  $\text{SO}_4\text{Be}, \text{SO}_4\text{K}_2, + 3\text{H}_2\text{O}$ ; is, like the alums, with difficulty soluble in water.

## ZINC.

Zn — 65.

The natural compounds of the heavy metals have generally a high specific gravity, frequently possess metallic lustre, occur usually in the older crystalline rocks in veins, and are termed *ores*. The most important zinc ores are the carbonate— $\text{ZnCO}_3$ —the silicate and sphalerite or blende  $\text{ZnS}$ . The principal sources of these ores are in Silesia, England, Belgium, Poland and the United States. To get the metal the carbonate or sulphide is converted into oxide by roasting in the air, this, then mixed with carbon, is ignited in earthen ware cylindrical tubes. In this manner the oxide is reduced:—



and the liberated zinc distilled off. In the receivers, together with the fused compact zinc is a gray, pulverulent mass, called *zinc dust*, which consists of a mixture of zinc oxide with finely divided metal. This material is used in laboratories as a strong reducing agent.

Metallic zinc has a bluish-white color, and exhibits rough, crystalline fracture; its specific gravity equals 7-7.2. At ordinary temperatures it is brittle and can be pulverized; at 100-150° it is malleable and can be rolled into thin leaves and drawn out into wire. At 200° it becomes brittle again and may be easily broken. It fuses at 412° and distills about 1000°.

In moist air it coats itself with a thin layer of basic carbonate. Heated in the air it burns, with a very intense, bluish-white light, to zinc oxide. Compact zinc decomposes water only at a red heat; zinc dust, however, acts at ordinary temperatures. In dilute acids zinc is readily soluble; in

potassium or sodium hydrate, as also in ammonia, upon boiling, it dissolves with liberation of hydrogen.

Owing to its slight alteration in the air zinc meets with extensive application as sheet-zinc for coating statues and in architectural adornment, and galvanizing sheet iron. It also forms an important constituent of many important alloys, like brass and argentan (see these).

**Zinc Hydrate**— $\text{Zn}(\text{OH})_2$ —is precipitated as a white amorphous powder, from aqueous solution, by alkalis, and is soluble in excess of the reagent. When heated it decomposes into water and zinc oxide.

**Zinc Oxide**— $\text{ZnO}$ —is usually prepared by igniting the precipitated basic carbonate, and as *zinc white*, is employed as a stable white paint. The oxide obtained by burning the metal is a white, voluminous, flocculent mass, called *flores Zinci* or *Lana philosophica*. When zinc oxide is heated it acquires a yellow color, which disappears on cooling.

In nature zinc oxide occurs as *zincite*, colored by other admixtures.

**Zinc Chloride**— $\text{ZnCl}_2$ —anhydrous, is obtained by heating zinc in a stream of chlorine, by the evaporation of the solution of zinc in hydrochloric acid, and by distillation of zinc sulphate with calcium chloride. It forms a white, deliquescent mass, fusing when heated and subliming without decomposition. In pure aqueous solution the zinc chloride upon evaporation partially decomposes (like magnesium chloride) into zinc oxide and hydrochloric acid. When the concentrated zinc chloride is mixed with zinc oxide, a plastic mass is obtained, which hardens rapidly; a mixture of magnesium chloride and oxide does the same. In both instances the hardening depends upon the formation of basic oxy-chlorides, *e. g.*,  $\text{ZnClOH}$ . Zinc chloride forms deliquescent double salts with the alkaline chlorides *e. g.*,  $\text{ZnCl}_2 \cdot 2\text{KCl}$ . With ammonia it yields various compounds, of which  $\text{ZnCl}_2 \cdot \text{NH}_3$ , is characterized by great stability.

**Zinc Sulphate**— $\text{ZnSO}_4$ —is formed by dissolving zinc in sulphuric acid. It is prepared upon a large scale by a gentle roasting of zinc blende ( $\text{ZnS}$ ); the zinc sulphate is extracted by water. At ordinary temperatures it crystallizes from aqueous solution with 7 molecules of  $\text{H}_2\text{O}$  (zinc or white vitriol)



in rhombic crystals, resembling those of magnesium sulphate very much. It forms double salts with the alkaline sulphates; these contain six molecules of water (p. 307).

**Zinc Carbonate**— $ZnCO_3$ —occurs native as smithsonite in hexagonal crystals. Sodium carbonate precipitates basic carbonates of varying composition, from solutions of zinc salts.

**Zinc Sulphide**— $ZnS$ —is zinc blende, usually colored brown by ferric oxide or other admixtures. Ammonium sulphide precipitates it as a white compound, from zinc solutions. Insoluble in water, but readily dissolved by dilute acids, excepting acetic; therefore, precipitated by hydrogen sulphide from zinc acetate solutions. This reaction serves to separate zinc from other metals.

**Zinc Silicate**— $Zn_2SiO_4 + H_2O$ —occurs native as calamine.

---

### CADMIUM.

Ca — 111.6

Cadmium very often accompanies zinc in its ores. In the Silesian zinc ores as much as  $\frac{5}{100}$  per cent. are present, and in these it was discovered in 1819. Being more volatile than zinc, in obtaining the latter it first distills off, and may be easily separated from the first portions of the distillate. It is a white, tenacious and tolerably soft metal, of specific gravity 8.6. It fuses at  $315^\circ$ , and boils at  $860^\circ$ . In the air it does not alter much. Heated, it burns with the separation of a brown smoke of cadmium oxide. It is difficultly soluble in dilute hydrochloric and sulphuric acids, but dissolves readily in nitric. Zinc throws out the metal from the soluble cadmium salt solutions.

St. Claire Deville found the specific gravity of cadmium vapors (at  $1040^\circ$ ) to be 3.9 (air = 1) or 56 (H = 1). Therefore, the molecular weight of cadmium is 112. Now, as the atomic weight of cadmium (determined from its specific heat and the vapor density of the volatile compounds) is also 112, it follows that the gas molecule of cadmium consists of but *one* atom. We saw that the molecules of other elements in the gaseous state were composed of two or more atoms ( $O_2, N_2, O_4, S_8$ ). Cadmium forms an exception to this rule. Mercury, and probably also other diatomic metals, like zinc, deport themselves similarly. These relations remind us of the behavior of the hydrocarbon residues (radicals); while the diatomic or tetratomic groups, *e. g.*, ethylene  $C_2H_4$  and acetylene  $C_2H_2$ , exist in free condition, the monatomic groups (as  $CH_3, CN$ ) cannot appear free, but double themselves, if separated from their compounds.

Of the cadmium compounds may be mentioned:—

**Cadmium Hydrate**— $\text{Cd}(\text{OH})_2$ —which is precipitated as a white powder, from the soluble cadmium salts, by the alkalis; it is insoluble in sodium and potassium hydrates, but easily soluble in ammonium hydrate.

**Cadmium Oxide**— $\text{CdO}$ —is prepared by igniting the nitrate. A brownish-black powder, consisting of microscopic octahedra.

**Cadmium Chloride**— $\text{CdCl}_2$ —crystallizes from aqueous solution, with two molecules of  $\text{H}_2\text{O}$ , and may be dried without decomposition. The dry salt is fusible and volatile.

**Cadmium Iodide**— $\text{CdI}_2$ —is obtained by the direct action of iodine upon metallic cadmium in presence of water. Crystallizes from the latter in hexagonal tables. Used in photography.

**Cadmium Sulphate**— $\text{CdSO}_4$ —crystallizes from water, not like the sulphates of zinc and magnesium, with 7 molecules of  $\text{H}_2\text{O}$ , but with  $3\text{H}_2\text{O}$ ; the crystals weather in the air. Yet, with the sulphates of the alkali metals it forms double salts, *e. g.*,  $\text{CdSO}_4 \cdot \text{K}_2\text{SO}_4 + 6\text{H}_2\text{O}$ , which are perfectly analogous to those of zinc and magnesium, and isomorphous with them.

**Cadmium Sulphide**— $\text{CdS}$ —occurs native as greenockite, in yellow hexagonal prisms. From cadmium salt solutions hydrogen sulphide precipitates it as a yellow powder, insoluble in dilute acids. It is employed as a pigment.

Almost all the alloys of cadmium have a low fusion temperature. Cadmium amalgam forms, freshly prepared, a white plastic mass, which speedily becomes hard. It is used in filling teeth.

---

The chemical energy of cadmium is less than that of zinc; this shows itself, among other things, in that cadmium may be displaced from its salts by zinc. We saw that, with the elements of the group of potassium and calcium, the chemical energy was inversely proportional to the increasing atomic weight; caesium is more energetic than rubidium, barium more than calcium. It is worthy of remark that almost throughout, the elements belonging to the second sub-groups of the seven main groups of the periodic system exhibit a similar diminution in chemical energy with rising atomic weight. Copper displaces silver; phosphorus is more energetic than arsenic and antimony; sulphur more energetic than selenium and silver; chlorine sets free or displaces bromine and iodine.

The relations of affinity find full expression in the thermo-chemical phenomena whereby the double periodicity of the great periods and the relations of the two sub-groups, Ca Sr Ba and Zn Cd Hg to magnesium distinctly appear; with the basic character increasing from magnesium to barium corresponds the increase of the heat liberation in the formation of their compounds; thus, for example, of the chlorides, hydrates and sulphhydrates:—

(Mg, Cl <sub>2</sub> ) = 151.0.	(Mg, O, H <sub>2</sub> O) = 148.9.	(Mg, S, Aq) = —
(Ca, Cl <sub>2</sub> ) = 170.2.	(Ca, O, Aq) = 149.4.	(Ca, S, Aq) = 98.3.
(Sr, Cl <sub>2</sub> ) = 184.5.	(Sr, O, Aq) = 157.7.	(Sr, S, Aq) = 106.6.
(Ba, Cl <sub>2</sub> ) = 194.2.	(Ba, O, Aq) = 158.2.	(Ba, S, Aq) = 107.1.

That the increase is so slight with the hydrates is explained, probably by the decreasing solubility of the same from Ba to Mg, which would correspond with an absorption of heat (heat of precipitation).

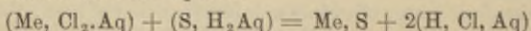
The series Mg, Zn, Cd, Hg departs itself differently. In this, corresponding with the diminution of basicity, the heat disengagement becomes successively less:—

(Mg, Cl <sub>2</sub> ) = 151.0.	(Mg, O) = 145.0.	(Mg, S) = —
(Zn, Cl <sub>2</sub> ) = 97.2.	(Zn, O) = 86.4.	(Zn, S) = 41.5.
(Cd, Cl <sub>2</sub> ) = 93.2.	(Cd, O) = 66.4.	(Cd, S) = 33.9.
(Hg, Cl <sub>2</sub> ) = 63.1.	(Hg, O) = 30.6.	(Hg, S) = 16.8.

Comparing these numbers with the quantity of heat which is disengaged in the formation of aqueous hydrochloric acid (H, Cl, Aq = 39.3), we find explained the behavior of the metals toward this acid. All metals liberating a greater quantity of heat than 39.3 C., in the formation of their chlorides (calculated for 1 equivalent of metal) are in condition to decompose the acid. To this class belong the majority of the metals; only mercury, copper, silver, gold, lead, thallium, and some others, set free a less amount of heat, and hence are incapable of decomposing dilute hydrochloric acid (see p. 259).

The slight quantity of heat developed in the formation of hydrogen sulphide (S, H<sub>2</sub> = 4.5) indicates that the same is readily decomposed by all the metals. In the same way, by adding the heat of solution (S, H<sub>2</sub>, Aq = 9.2), we can easily ascertain which metals are precipitated by hydrogen sulphide from their chlorides, etc.

If in thermo-chemical equation



the sum of the heat developed upon the right side is greater than that upon the left, the reaction will occur (precipitation of metallic sulphides); in the opposite case the sulphide is decomposed by the dilute hydrochloric acid.

To the group of zinc and cadmium belongs, also, *Mercury*, according to the magnitude of its atomic weight. The relation-ship of these three heavy metals exhibits itself in the many similarities of the free elements, and also in their compounds.



Occupying a similar position in the three great periods (234) they are distinguished in a physical point of view by their ready fusibility and volatility, which, like the specific gravities, increase with rising atomic weight (just as with the metals of the potassium group, p. 265).

	Zn	Cd	Hg
Atomic weight,	65	111.6	200
Fusing point,	412°	315°	- 40°
Boiling point,	towards 1000°	860°	360°
Specific gravity,	7.1	8.6	13.6

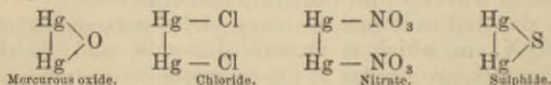
Also the gradation in the heat of formation of their compounds (p. 314) clearly indicates that mercury must be arranged in a group with cadmium and zinc.

Like zinc and cadmium, mercury yields compounds of the form  $HgX_2$ , in which it appears diatomic, and which, in many respects, are similar to the corresponding compounds of zinc and cadmium. Thus mercuric sulphate affords double salts with the alkaline sulphates, which crystallize with six molecules of  $H_2O$  ( $SO_4Hg, SO_4K_2 + 6H_2O$ ) and are isomorphous with the double sulphates of the metals of the magnesium group (p. 307). The similarity, however, limits itself only to a few compounds. As in each group the properties of it experience, with increasing atomic weight, a gradual alteration, so with mercury (with high atomic weight of 200) does this become the more evident, as the middle member (p. 234), belonging to the third great period, is not known. Mercury differs essentially from zinc and cadmium in that, in addition to the compounds of the form  $\overset{II}{Hg}X_2$  (mercuric compounds), it is also capable of yielding such of the form  $\overset{I}{Hg}X$  (mercurous compounds), in which it seems to be monatomic. Here we meet an instance, frequently to be observed, that one and the same metal (as with the most metalloids) is capable of forming compounds of two or more forms, which are to be referred to a different valence of the metal; and it is seen that the compounds of one and the same metal, according to different forms or types, frequently are more essentially distinguished from one another than the compounds of different elements according to the same type. Thus, the mercuric compounds ( $HgX_2$ ) are similar to those of zinc and cad-

mium, after the same form, while the mercurous compounds  $\overset{I}{\text{Hg}}\text{X}$  exhibit great resemblance to the cuprous ( $\overset{I}{\text{Cu}}\text{X}$ ) and silver ( $\overset{I}{\text{Ag}}\text{X}$ ) compounds, constituted according to a similar type.

It shows that the similarity of the compounds is not only influenced by the nature of the metals, but frequently, in high degree, by the forms or types according to which they are constituted (p. 324).

As above viewed, mercury in its *ic* compounds is a dyad, in the *ous* a monad. According to the theory of constant valence, the mercury atom in the *ous* compounds is, however, also diatomic. We suppose that the molecules of the same are twice as large, and that in them every two Hg atoms form a diatomic group, as seen from the following:—



An experimental decision upon the above has not yet been given (p. 318).

## MERCURY.

Hg = 200.

Mercury (*Hydrargyrum*) occurs in nature principally as *Cinnabar*, more rarely native in form of little drops scattered through rocks. Its most important localities are Almaden in Spain, New Almaden in California, Idria in Illyria, Mexico, Peru, China and Japan.

The metallurgical separation of mercury is very simple. *Cinnabar* is roasted in reverberatory furnaces, whereby the sulphur burns to dioxide; the mercury vapors are condensed in large chambers. Or, it is distilled with lime or iron from iron retorts. Commercial mercury usually contains, dissolved, a slight quantity of other metals. To purify it, it is poured in a thin stream into a deep layer of sulphuric or dilute nitric acid, by which the accompanying tin and lead are more easily dissolved than the mercury. Finally the metal is distilled out of a small glass retort and passed through chamois skin.

Mercury is the only metal which is liquid at ordinary temperatures. At 0° its specific gravity equals 13.59; it

solidifies at  $40^{\circ}$  and crystallizes in regular octahedra; it evaporates somewhat at medium temperatures and boils at  $360^{\circ}$ . Its vapors are very poisonous. The specific gravity of mercury vapors is 100 ( $H = 1$ ) or 6.97 ( $air = 1$ ). Therefore its molecular weight is 200; as its atomic weight is also 200 the molecule is composed, like that of cadmium, of only *one* atom. At ordinary temperatures mercury is not altered in the air; near the boiling point, however, it gradually oxidizes to red mercuric oxide. Hydrochloric and cold sulphuric acids do not act upon mercury; by hot sulphuric acid it is changed, with evolution of sulphur dioxide, into mercury sulphate. Even dilute nitric acid will readily dissolve it. It combines at ordinary temperatures with the halogens and sulphur.

Mercury dissolves almost all metals (not iron) forming amalgams. With potassium and sodium it unites upon gentle warming, with production of heat and light. When the quantity of potassium and sodium exceeds 3% the alloy is solid and crystalline; by less amount it remains liquid. Tin amalgam is employed for coating mirrors.

---

Mercury forms two series of compounds, *mercurous* and *mercuric*. The first are analogous to the cuprous, and have the form  $HgX$ . In them mercury appears to be monatomic; we, however, do not know, whether their molecules are not to be expressed by the double formula  $Hg_2X_2$  (p. 315). In many respects the *ous* compounds are similar to the cuprous and silver derivatives. The halogen compounds are insoluble, and darken on exposure to light.

In the *ic* derivatives— $HgX_2$ —mercury is diatomic and is very much like zinc and cadmium. Thus mercuric sulphate forms double salts with the alkaline sulphates, which crystallize with  $6H_2O$ , and are isomorphous with the double sulphates of the metals of the magnesium group. The *ic* compounds almost always form, if the substance reacting with the mercury is in excess; when the opposite is the case, mercurous salts result. The *ic* derivatives, by the addition of mercury pass into the *ous*, *e. g.*,  $Hg(NO_3)_2 + Hg = Hg_2(NO_3)_2$ . Oxidizing agents convert the *ous* into the *ic* compounds; the latter are, on the opposite hand, converted by reducing substances to the first.



The heat of formation of some mercuric compounds corresponds to the symbols:—

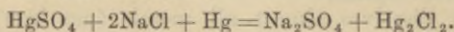
$$(\text{Hg}, \text{O}) = 30.6 \quad (\text{Hg}, \text{Cl}_2) = 63.1 \quad (\text{Hg}, \text{I}_2) = 34.3 \quad (\text{Hg}, \text{S}) = 16.8.$$

That of the corresponding mercurous salts:—

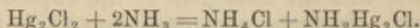
$$(\text{Hg}_2, \text{O}) = 42.2 \quad (\text{Hg}_2, \text{Cl}_2) = 82.5 \quad (\text{Hg}_2, \text{I}_2) = 48.3 \quad (\text{Hg}_2, \text{S}) = -$$

### MERCUROUS COMPOUNDS.

**Mercurous Chloride**— $\text{HgCl}$  or  $\text{Hg}_2\text{Cl}_2$ —calomel, is an amorphous, white precipitate, produced by the addition of hydrochloric acid or soluble chlorides to the solution of mercurous salts. Generally it is formed by the sublimation of  $\text{HgCl}_2$  with mercury or a mixture of  $\text{HgSO}_4$ , mercury and sodium chloride is sublimed:—

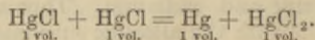


It then sublimes as a radiating, crystalline mass, quadratic prisms, of specific gravity 7.2. Calomel is insoluble in water and dilute acids; it gradually decomposes when exposed to the light, with separation of mercury. Heated, it sublimes without fusing. By the action of strong acids it is converted into mercuric salts and free mercury. When ammonium hydrate is poured over calomel, it blackens and reacts according to the equation—



The latter compound is viewed as ammonium chloride, in which 2H are replaced by  $\text{Hg}_2$ .

The vapor density of calomel vapors is 117.7 ( $H=1$ ), the molecular weight, therefore, 235.4, and corresponds to the formula  $\text{HgCl}$  (235.4). It appears, however, that its vapors consist of a mixture of mercury and mercuric chloride. Such a mixture must have the same density as  $\text{HgCl}$ :—



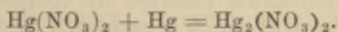
The question, whether the mercurous compounds contain one or two atoms of mercury, whether, for example, the formula  $\text{Hg}_2\text{Cl}_2$  or  $\text{HgCl}$  properly belongs to calomel, is, therefore, not decided by the determination of its vapor density.

**Mercurous iodide**— $\text{HgI}$  or  $\text{Hg}_2\text{I}_2$ —is prepared by rubbing together 8 parts of mercury with 5 parts I, or by precipitating mercurous nitrate with potassium iodide. It is a greenish powder, insoluble in water and alcohol. Light changes it to  $\text{HgI}_2$  and  $\text{Hg}$ .

**Mercurous Oxide**— $\text{Hg}_2\text{O}$ —is black in color and formed by the action of potassium or sodium hydrate upon mercurous salts. In the light it decomposes into  $\text{HgO}$  and  $\text{Hg}$ .

**Mercurous Nitrate**— $\text{HgNO}_3$  or  $\text{Hg}_2(\text{NO}_3)_2$ —is produced by allowing somewhat dilute nitric acid to act upon excess of mercury. It crystallizes in large monoclinic tables. It dissolves readily in water acidulated with nitric acid; by pure water it is decomposed into the *acid* salt which passes into solution and becomes the *basic* salt— $\text{Hg}_2\left\langle \begin{array}{l} \text{OH} \\ \text{NO}_3 \end{array} \right.$ , which separates as a yellow powder.

The nitric acid solution of mercurous nitrate oxidizes when exposed to the air, and gradually becomes mercuric nitrate; this may be prevented by adding metallic mercury to the solution, whereby the resultant *ic* salt is again changed to the *ous* state—

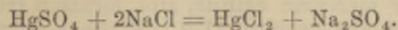


**Mercurous Sulphate**— $\text{Hg}(\text{SO}_4)$ —results upon gentle warming of excess of mercury with sulphuric acid; it separates as a crystalline precipitate, difficultly soluble in water, if sulphuric acid be added to a mercurous nitrate solution. It fuses upon application of heat, and decomposes into  $\text{SO}_2$ ,  $\text{O}_2$  and  $\text{Hg}$ .

**Mercurous Sulphide**— $\text{Hg}_2\text{S}$ —is precipitated by potassium hydrosulphide, as a black compound, from the dilute solution of mercurous nitrate. When gently warmed it decomposes into  $\text{HgS}$  and mercury.

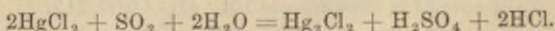
#### MERCURIC COMPOUNDS.

**Mercuric Chloride**— $\text{HgCl}_2$ —Corrosive sublimate—is produced when mercuric oxide is dissolved in  $\text{HCl}$ , or metallic mercury in aqua regia. On a large scale it is obtained by the sublimation of a mixture of mercuric sulphate with sodium chloride:—



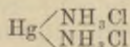
It crystallizes from water in fine rhombic prisms, and dissolves at medium temperatures in 15 parts, at  $100^\circ$ , in 3 parts water; in alcohol it is still more soluble. Its specific gravity is 5.4. It fuses at  $260$ – $270^\circ$ , and boils about  $300^\circ$ . The vapor density is 135.5 ( $\text{H} = 1$ ), corresponding to the molecular formula  $\text{HgCl}_2 = 271$ .

By reducing substances, like  $\text{SO}_2$  and  $\text{SnCl}_2$ , it is changed to insoluble mercurous chloride:—



By stannous chloride, mercurous chloride is at first precipitated:  $2\text{HgCl}_2 + \text{SnCl}_2 = \text{Hg}_2\text{Cl}_2 + 2\text{SnCl}_4$ , which afterwards, by excess of the first, is reduced to metallic quicksilver:  $\text{Hg}_2\text{Cl}_2 + \text{SnCl}_2 = 2\text{Hg} + \text{SnCl}_4$ .

Mercuric chloride is greatly inclined to form double salts with metallic chlorides, *e. g.*,  $\text{HgCl}_2 \cdot \text{KCl} + \text{H}_2\text{O}$ . When ammonium hydrate is added to its solution, a white, heavy precipitate, called *white precipitate*,  $\text{NH}_2\text{HgCl}$ , is thrown down. This compound is regarded as a derivative of ammonium chloride, in which two atoms of H are replaced by diatomic mercury, and it has been called **Mercur-ammonium Chloride**. It forms with ammonium chloride the compound  $\text{NH}_2\text{HgCl} \cdot \text{NH}_4\text{Cl}$ , the structure of which is expressed by the formula:—



Similar mercur-ammonium derivatives are numerous.

**Mercuric Iodide**— $\text{HgI}_2$ —is formed by the direct union of mercury with iodine. When potassium iodide is added to a solution of mercuric chloride,  $\text{HgI}_2$  separates as a yellow precipitate, which immediately becomes red. In  $\text{HgCl}_2$  and KI solution  $\text{HgI}_2$  is readily soluble; from alcohol it crystallizes in bright red quadratic rhombohedra. Upon warming  $\text{HgI}_2$  to  $150^\circ$  it suddenly becomes yellow, fuses and sublimes in yellow, shining, rhombic needles. On touching these with some solid they become red with separation of heat, and are changed into an aggregate of quadratic octahedra. Therefore, mercuric iodide is dimorphous.

**Mercuric Oxide**— $\text{HgO}$ —is obtained by continued heating of metallic mercury near the boiling point, or by ignition of mercurous or mercuric nitrate, and forms a red crystalline powder, of specific gravity 11.2. When sodium hydrate is added to a mercuric chloride solution, mercuric oxide separates as a yellow, amorphous precipitate. Both modifications become black when heated, yellowish-red, however, on cooling. At about  $400^\circ$  mercuric oxide breaks up into mercury and oxygen.

Mercuric oxide combines directly with ammonia, to the



compound  $2\text{HgO}\cdot\text{NH}_3$ , which on being heated explodes with violence.

**Mercuric Nitrate**— $\text{Hg}(\text{NO}_3)_2$ —is with difficulty obtained pure, as it is inclined to form basic salts. A solution of it may be made by dissolving mercury or mercuric oxide in excess of hot nitric acid. On diluting the solution with water the basic salt,  $\text{Hg}(\text{NO}_3)_2\cdot 2\text{HgO}$ , separates. Boiling with water changes this to pure  $\text{HgO}$ .

**Mercuric Sulphate**— $\text{HgSO}_4$ —is produced by warming mercury or its oxide with excess of concentrated sulphuric acid, and is an insoluble white crystalline mass, which becomes yellow on heating. With a little water it forms the hydrate  $\text{HgSO}_4 + \text{H}_2\text{O}$ , which with more water is decomposed into sulphuric acid and into the yellow insoluble *basic* salt  $\text{HgSO}_4\cdot 2\text{HgO}$  (*Turpetum minerale*).

With the alkaline sulphates mercuric sulphate forms double salts, *e. g.*,  $\text{HgSO}_4, \text{K}_2\text{SO}_4 + 6\text{H}_2\text{O}$ , which are isomorphous with the corresponding double salts of the magnesium group (p. 307).

**Mercuric Sulphide**— $\text{HgS}$ —occurs in nature as *cinnabar*, in radiating crystalline masses, or in hexagonal prisms of red color. It is obtained by rubbing together mercury and flowers of sulphur with water, or by precipitation of a solution of a mercuric salt with hydrogen sulphide it is got as a black amorphous mass. If the black sulphide be heated with exclusion of air it sublimes as a dark red mass of radiating crystalline structure, which is perfectly similar to natural *cinnabar*. A similar conversion of the black modification into the red is attained by continued heating of the same to  $50^\circ$  with a solution of potassium or ammonium sulphide. The thus obtained red mercury sulphide is employed as *artificial cinnabar* in painting.

The mercury compounds can readily be recognized by the following reactions. On fusion with dry sodium carbonate, mercury escapes, which (if the operation be executed in a small tube) condenses upon the wall in metallic drops. Tin, copper and zinc throw out metallic mercury from its solutions. If a pure piece of sheet copper be dipped into the same, mercury is deposited as a gray coating, which on being rubbed acquires a metallic lustre. The mercurous compounds are distinguished from the mercuric by their precipitation with hydrochloric acid.

**COPPER, SILVER AND GOLD.**

As regards their atomic weights, copper, silver and gold bear the same relation to the alkali group, especially to sodium, as zinc, cadmium and mercury to magnesium :—

Na = 23	Mg = 24
Cu = 63.3	Zn = 65
Ag = 107.6	Cd = 111.6
Au = 197	Hg = 200

They occupy an entirely analogous position in the three great periods of the periodic system of the elements (p. 234), and constitute the transition from the elements of group VIII, especially from nickel, palladium and platinum, to the less basic elements of group II—zinc, cadmium and mercury :—

Ni = 58.6	Cu = 63.3	Zn = 65
Pd = 106	Ag = 107.6	Cd = 111.6
Pt = 196.7	Au = 197	Hg = 200

This medium position of the three elements to be treated distinctly shows itself in their entire physical department. While the elements of group VIII, with the last members, Ni, Pd and Pt, are with difficulty fusible, and not volatile, Cu, Ag and Au, as regards their fusibility and volatility, form the transition to the readily fusible and volatile elements, Zn, Cd and Hg. They take a medium position, also, with reference to their coefficients of expansion, their atomic volumes, and other physical properties. It is noteworthy that the ability to conduct heat and electricity attains its maximum in Cu, Ag and Au.

As the physical properties of the free elements, so, also, those of their compounds, and, especially, those depending upon the valence of the elements, are determined, in great degree, by the position of the latter in the periodic system. In accordance with the double periodicity of the system of the elements, Cu, Ag and Au, although really belonging to the three great groups, attach themselves to group I, and especially sodium, just as the immediately following elements, Zn, Cd and Hg, arrange themselves with group II and magnesium. Corresponding with this, Cu, Ag and

Au, like Na, yield compounds of the form  $\text{MeX}$ , in which they appear monatomic. Some of these are isomorphous; thus NaCl, CuCl and AgCl crystallize in forms of the regular system. So, also, is silver sulphate,  $\text{Ag}_2\text{SO}_4$ , isomorphous with

sodium sulphate,  $\text{SO}_4\text{Na}_2$ ; likewise some of the other salts of these two metals, Cu and Ag, like the alkalis, form so-called sub- or quadrant oxides,  $\text{Na}_2\text{O}$ ,  $\text{Cu}_2\text{O}$ ,  $\text{Ag}_2\text{O}$ .

But to these few, so to say, external properties is almost limited the similarity of Cu, Ag and Au with sodium. Just as the heavy metals, Zn, Cd and Hg, as regards many properties, differ from the light metal magnesium, so do the high specific gravity metals, Cu, Ag and Au, and in a marked degree, distinguish themselves from the light metal sodium. They show all the properties belonging to the heavy metals, which, chiefly, are marked by the insolubility of the oxides, sulphides and many salts. Their differing from sodium is explained by the fact that they really belong to the three great periods, and only in a slight degree arrange themselves with the alkalis. Particularly irregular is the department of gold, with the high atomic weight, 197, which, in this respect, agrees with mercury (p. 314).

In the compounds constituted according to the form,  $\text{MeX}$ , in which they appear monatomic, Cu, Ag and Au exhibit, as regards their physical and chemical properties, great resemblance. The chlorides  $\text{CuCl}$ ,  $\text{AgCl}$  and  $\text{AuCl}$ , are colorless and insoluble in water, soluble, however, in hydrochloric acid, ammonia, the alkaline hyposulphites, etc., and furnish perfectly similar double compounds. While silver only enters compounds of the form  $\text{AgX}$ , copper and gold are capable of yielding another form; indeed, copper forms, besides cuprous,  $\text{CuX}$ , also cupric,  $\text{CuX}_2$ , derivatives, in which it appears diatomic. The latter are much more stable than the former, and embrace the most usual copper salts. Gold, however, besides furnishing *ous*,  $\text{AuX}$ , compounds, has *ic* derivatives,  $\text{AuX}_3$ , in which it appears triatomic.

While in their *ous* forms, Cu and Au are analogous to silver (and in less degree, Na) the cupric derivatives show a great resemblance to those of the metals of the magnesium group and other metals, in their diatomic combinations. Thus, the sulphates of zinc, magnesium, cupric oxide ( $\text{CuO}$ ), ferrous oxide ( $\text{FeO}$ ), nickelous oxide ( $\text{NiO}$ ), cobaltous oxide ( $\text{CoO}$ ), manganous oxide ( $\text{MnO}$ ), are similarly constituted, resemble each other, are isomorphous, and form, with the alka-



line sulphates, entirely analogous double salts (p. 307). In the same way the carbonates ( $\overset{\text{II}}{\text{MeCO}_3}$ ), the chlorates and bromates ( $\overset{\text{II}}{\text{MeCl}_2\text{O}_6 + 6\text{H}_2\text{O}}$ ) and others, are exactly similarly constituted and isomorphous. In its *ic* derivatives, gold exhibits some similarity to the aluminium compounds ( $\overset{\text{III}}{\text{AlX}_3}$ ), to those of indium ( $\overset{\text{III}}{\text{InX}_3}$ ) and other metals, in their triatomic combinations. Here we see, as already with mercury (p. 316), that *the similarity of the compounds of the metals is influenced by the similarity of forms or types*, according to which they are composed, *i. e.*, by the valence of the metals. If a metal form several series of compounds according to different types, each series is usually more or less similar to the compounds of other metals of like type. In this manner, the resemblance of the compounds of the following types shows itself:—

$\text{Na}_2\text{O}$	$\text{Ag}_2\text{O}$	$\text{Cu}_2\text{O}$	$\text{Au}_2\text{O}$	$\text{Tl}_2\text{O}$
Sodium oxide.	Silver oxide.	Cuprous oxide.	Aurous oxide.	Thalious oxide.
$\text{MgO}$	$\text{ZnO}$	$\text{CuO}$	$\text{FeO}$	$\text{HgO}$
Magnesium oxide.	Zinc oxide.	Cupric oxide.	Ferrous oxide.	Mercuric oxide.
$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{Au}_2\text{O}_3$	$\text{Tl}_2\text{O}_3$	
Aluminium oxide.	Ferric oxide.	Auric oxide.	Thallic oxide.	

The character of their derivatives varying with the degree of combination or valence, shows itself distinctly, as we have seen, with chromium, manganese and iron. In the monatomic combinations the heavy metals also exhibit a strong, positive basic character. Thus silver oxide ( $\text{Ag}_2\text{O}$ ) and thalious oxide ( $\text{Tl}_2\text{O}$ ) are strong bases, forming neutral reacting salts with acids, and even cuprous and aurous oxides are more strongly basic than their higher forms of oxidation. In the triatomic combination appears the metalloidal character of the metals, the acidic of their oxides. In the hydroxyl derivatives of aluminium, indium and gold,  $\text{Al}(\text{OH})_3$ ,  $\text{In}(\text{OH})_3$ ,  $\text{Au}(\text{OH})_3$ , hydrogen may be replaced by the alkalis. Their higher forms of oxidation show, like those of the metalloids, a pronounced acid-like character, (as  $\text{PbO}_2$ ,  $\text{PtO}_2$ ,  $\text{CrO}_3$ ,  $\text{FeO}_3$ ) which is only lessened by a high atomic weight of the metal (as in  $\text{PbO}_2$  and  $\text{PtO}_2$ ). In a less, if not an unimportant degree, is the character of the compound influenced by the position of the elements in the periodic system. According to this the properties of the metallic compounds are not only influ-

enced by the nature of the metals, but to a high degree by the combination forms. These forms of the elements, and particularly those of the metals, are, however, if not entirely, yet to a considerable degree, regulated by the periodic system, as has already been declared (see p. 240).

This connection of Cu, Ag and Au in an analogous group expresses itself also in the heat resulting from the formation of their compounds of the form MeX:—

(Na, Cl) = 97.6	(Na <sub>2</sub> , O) = 100.2	(Na <sub>2</sub> , S) = 88.0.
(Cu, Cl) = 32.8	(Cu <sub>2</sub> , O) = 40.8	(Cu <sub>2</sub> , S) = 20.2.
(Ag, Cl) = 29.8	(Ag <sub>2</sub> , O) = 5.9	(Ag <sub>2</sub> , S) = 5.3.
(Au, Cl) = 5.8	(Au <sub>2</sub> , O) = —	(Au <sub>2</sub> , S) = —.

Here occur relations exactly the same as in the elements of the zinc group (p. 314), and from the thermal data perfectly analogous conclusions as regards affinity relations may be deduced. Thus, for example, copper is able to decompose concentrated but not dilute hydrochloric acid. The heat of formation of some cupric compounds equals:—

$$\begin{aligned} (\text{Cu, O}) &= 37.1 & (\text{Cu, Cl}_2) &= 51.6 & (\text{Cu, Cl}_2, \text{Aq}) &= 62.7 \\ & & (\text{Cu, S, O}_4) &= 182. \end{aligned}$$

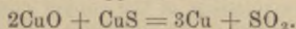
---

## COPPER.

Cu = 63.3.

In native condition, copper is found frequently crystallized in cubes and octahedra, in large quantities, in America, China, Japan, also in Sweden and in the Urals. The most important and most widely distributed of its ores are: cuprite (Cu<sub>2</sub>O), malachite and azurite (basic carbonates), chalcocite (Cu<sub>2</sub>S), and especially chalcopyrite or speckled copper ore (CuFeS<sub>2</sub>).

*Metallurgy of Copper.*—The extraction of copper from its oxygen ores is very simple; by ignition of the same with charcoal, metallic copper is melted out. The divided ores are first roasted in the air, by which means copper sulphide is partly converted into oxide. The mass is afterward roasted with sand, silica fluxes and carbon, whereby iron sulphide is converted into oxide and passes into the slag. By several repetitions of this process the so-called *copper stone*—a mixture of copper sulphide with oxide—is obtained. This is repeatedly roasted and heated, whereby, by the action of copper oxide upon the sulphide, metallic copper is obtained:—



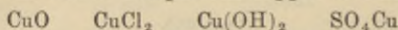
The molten copper is again fused with charcoal, to free it from the oxide.

To obtain chemically pure copper the pure oxide is heated in a stream of hydrogen or the solution of copper sulphate is decomposed by electrolysis.

Metallic copper possesses a characteristic red color; in thin leaflets it transmits a green light. It is rather soft and ductile, and possesses a specific gravity 8.9. It fuses about  $1054^{\circ}$  and vaporizes in the oxy-hydrogen flame. In dry air it remains unaltered, in moist it is gradually coated with a green layer of copper carbonate. On heating it oxidizes to black cupric oxide.

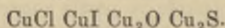
Copper is not changed by dilute hydrochloric or sulphuric acids; if, moistened with these, it be exposed to the air, it absorbs oxygen and gradually dissolves. It is similarly dissolved by ammonium hydrate. By hot concentrated sulphuric acid it is changed to copper sulphate, with evolution of sulphur dioxide. In dilute nitric acid it dissolves in the cold, with evolution of nitrogen oxide. From the aqueous solutions of copper salts, zinc, iron and also phosphorus precipitate metallic copper.

Copper forms two series of compounds, known as *cuprous* and *cupric*. In the *ic* compounds copper is diatomic:—



These are more stable than the *ous* derivatives; to them belong the ordinary copper salts. In many respects they resemble the other dyad metals, namely, those of the magnesium group and *ous* compounds of iron (FeO), manganese (MnO), cobalt and nickel (see p. 323).

The cuprous compounds are the reverse, very unstable, and pass rapidly in the air, with absorption of oxygen, into cupric compounds. They show some similarity to the mercurous derivatives (p. 318), and possess an analogous composition:—

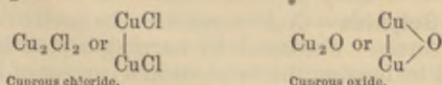


Oxygen compounds of the same are, however, not known.

Corresponding to the above formula, copper in the *ous* compounds, like silver, appears to be monatomic. However, it has not been determined whether really these formulas express the true molecular size, as, owing to the non-volatility of the copper compound, we possess no means of fixing the size of the molecules. It is generally supposed that the molecules of cuprous compounds correspond to the double formula, that also, in them the copper atom is diatomic and that they



contain a diatomic group, formed of two copper atoms, as seen from the following formulas:—



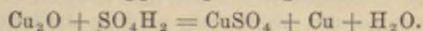
Cuprous chloride.

Cuprous oxide.

Owing to the isomorphism with the compounds of silver we use exclusively the simpler formulas.

### CUPROUS COMPOUNDS.

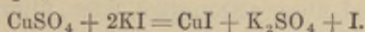
**Cuprous Oxide**— $\text{Cu}_2\text{O}$ —occurs as cuprite crystallized in regular octahedra. Artificially it is obtained by boiling a solution of copper sulphate and grape sugar with potassium hydrate, when it separates as a crystalline, bright red powder. In the air it does not change. In ammonium hydrate it is readily soluble. The solution absorbs oxygen, and while forming cupric oxide acquires a blue color. By the action of sulphuric and other oxygen acids, it forms cupric salts, the half of the copper separating as metal:—



The hydrate  $\text{Cu}_2(\text{OH})_2$  is precipitated by the alkalis as a yellow powder from hydrochloric acid solutions of  $\text{Cu}_2\text{Cl}_2$ . In the air it oxidizes to cupric hydrate.

**Cuprous Chloride**— $\text{CuCl}$  or  $\text{Cu}_2\text{Cl}_2$ —is produced by the combustion of metallic copper in chlorine gas (together with  $\text{CuCl}_2$ ), upon conducting  $\text{HCl}$  over copper at a moderate glowing heat, by boiling the solution of cupric chloride with copper ( $\text{CuCl}_2 + \text{Cu} = \text{Cu}_2\text{Cl}_2$ ) and by the action of many reducing substances upon cupric chloride. It is most conveniently made if through the concentrated copper sulphate solution and sodium chloride, sulphur dioxide be passed, when it separates as a white, shining powder, consisting of small tetrahedra. In the air it rapidly becomes green, owing to oxygen absorption, basic cupric chloride being formed  $\text{Cu} \begin{smallmatrix} \text{Cl} \\ \text{OH} \end{smallmatrix}$ . Cuprous chloride is readily soluble in concentrated hydrochloric acid and in ammonium hydrate; both solutions possess the characteristic property of absorbing carbon monoxide.

**Cuprous Iodide**— $\text{CuI}$  or  $\text{Cu}_2\text{I}_2$ —is precipitated from soluble cupric salts by potassium iodide:—

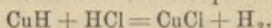


By extracting the co-precipitated iodine by means of ether it is obtained as a gray powder insoluble in acids.

**Cuprous Sulphide**— $\text{Cu}_2\text{S}$ —occurs as chalcocite crystallized in rhombic forms. Produced by burning copper in vapor of sulphur and by heating the sulphide in a current of hydrogen; after fusion it solidifies in crystals of the regular system. Combined with silver sulphide, it constitutes the mineral stromeyerite  $\left. \begin{matrix} \text{Cu} \\ \text{Ag} \end{matrix} \right\} \text{S}$  or  $\text{Cu}_2\text{S} \cdot \text{Ag}_2\text{S}$ , isomorphous with chalcocite.

**Copper Hydride**— $\text{CuH}$  or  $\text{Cu}_2\text{H}_2$ —belongs to the derivatives of monatomic copper. It separates as a yellow amorphous precipitate, rapidly becoming brown, if a solution of copper sulphate be warmed with hypophosphorous acid. At  $60^\circ$  it decomposes into copper and hydrogen.

With hydrochloric acid it forms cuprous chloride:—



Copper suboxide  $\text{Cu}_2\text{O}$  or tetrantoxide, corresponds to potassium suboxide. On adding an alkaline stannous chloride solution to one of copper sulphate, there separates at first cupric hydrate, which is further reduced to cuprous hydrate and then to suboxide. The latter is an olive-green powder, which easily oxidizes and is decomposed by  $\text{H}_2\text{SO}_4$  in  $\text{CuSO}_4$  and  $3\text{Cu}$ .

### CUPRIC COMPOUNDS.

The cupric salts when hydrous are generally colored blue or green; when dry they are colorless.

**Cupric Hydrate**— $\text{Cu}(\text{OH})_2$ —separates as a voluminous bluish precipitate when sodium or potassium hydrate is added to soluble copper salts. When heated, even under water, it loses water and is changed to black cupric oxide.

**Cupric Oxide**— $\text{CuO}$ —is usually obtained by the ignition of copper turnings in the air, or by heating cupric nitrate. It forms a black amorphous powder, which at higher temperature settles together and acquires a metallic lustre. By heating with organic substances their carbon is converted into carbon dioxide, and the hydrogen into water, the cupric salt being reduced to metal; upon this rests the application of cupric oxide in the analysis of such compounds.

Copper oxide and hydrate dissolve in ammonium hydrate, with dark blue color. The solution possesses the power of dissolving wood fibre (cotton-wool, linen, filter paper, etc.)—*Schweizer's reagent*.

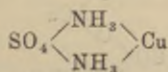
**Cupric Chloride**— $\text{CuCl}_2$ —is formed by the solution of cupric oxide or carbonate in hydrochloric acid. From aqueous solution it crystallizes with 2 molecules of water, in bright green rhombic needles, and is readily soluble in water and alcohol. When heated it parts with its water, becoming anhydrous chloride, which at a red heat is decomposed into chlorine and cuprous chloride. With potassium and ammonium chlorides it yields beautifully crystallized double salts. Cupric bromide is like the chloride; the iodide is not known, as in its formation it at once breaks up into cuprous iodide and iodine.

**Copper Sulphate**— $\text{CuSO}_4 + 5\text{H}_2\text{O}$ —cupric sulphate, copper vitriol—may be obtained by the solution of copper in concentrated sulphuric acid. On a large scale it is produced by roasting chalcocite. It forms large blue crystals of the triclinic system, which on exposure become somewhat weathered. At  $100^\circ$  the salt loses 4 molecules of water; the fifth separates above  $200^\circ$ . The anhydrous sulphate is colorless, absorbs water very energetically, and again becomes the blue hydrous compound.

Although copper sulphate only crystallizes with 5 molecules of  $\text{H}_2\text{O}$ , it is capable, like the sulphates of the magnesium group, of forming double salts with potassium and ammonium sulphates, which crystallize with  $6\text{H}_2\text{O}$ , and are isomorphous with double salts of the metals of the magnesium group.

Copper sulphate is employed in electro-plating. When its solution is decomposed by the galvanic current copper separates at the negative pole and deposits in a regular layer upon the conducting objects connected with the electrode.

Ammonium hydrate added to a copper sulphate solution in sufficient quantity to dissolve the cupric hydrate at first produced, changes the color of the liquid to a dark blue, from which alcohol precipitates a dark blue crystalline mass with the composition  $\text{CuSO}_4, 4\text{NH}_3 + \text{H}_2\text{O}$ . Heated to  $150^\circ$  this compound loses water and 2 molecules of  $\text{NH}_3$  and becomes  $\text{CuSO}_4, 2\text{NH}_3$ . It is supposed that these compounds are ammonium salts in which a part of the hydrogen is replaced by copper; they have been designated *cuprammonium compounds*, e. g. :—





The other soluble copper salts give similar compounds with ammonium hydrate.

**Cupric Nitrate**— $\text{Cu}(\text{NO}_3)_2$ —crystallizes with three or six molecules of water, has a dark blue color and is readily soluble in water and alcohol. When heated it leaves behind cupric oxide.

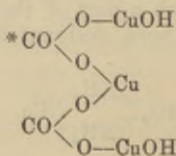
**Copper Carbonates.** The neutral salt ( $\text{CuCO}_3$ ) is not known. When sodium carbonate is added to a warm solution of a copper salt the basic carbonate separates as a green precipitate,  $\text{CuCO}_3$ ,  $\text{Cu}(\text{OH})_2$ , or  $\text{CO} \begin{matrix} \text{O.Cu.OH.} \\ \text{O.Cu.OH.} \end{matrix}$ . It occurs in nature as *malachite*, which is especially abundant in Siberia. Another basic salt— $2\text{CO}_3\text{Cu.Cu}(\text{OH})_2^*$  is the beautiful blue *azurite*.

**Copper Arsenite**— $(\text{AsO}_3)_2\text{Cu}$ —separates as a beautiful, bright green precipitate, upon the addition of sodium arsenite to a copper solution. Formerly, under the name of Scheele's green, it was extensively employed as a color, but at present, owing to its poisonous character, it has been replaced by other green colors (Guignet's green and aniline green).

**Cupric Sulphide**— $\text{CuS}$ —is a black compound, produced by hydrogen sulphide in copper solutions. It is insoluble in dilute acids. When moist, it slowly oxidizes in the air to cupric sulphate. Heated in a stream of hydrogen, it forms cuprous sulphide,  $\text{Cu}_2\text{S}$ .

**Alloys of Copper.** Pure copper is very ductile, and may be readily rolled and drawn out into a fine wire. It cannot be well poured into moulds, because, upon cooling, it contracts unequally and does not fill out the moulds. For such purposes, alloys of copper are employed, which, in addition, possess other technically valuable properties. The most important of these are:—

*Brass*, consisting of two to three parts copper and one part zinc. It has a yellow color, and is considerably harder than pure copper. Ordinarily, one to two per cent. of lead are



added to the brass, which facilitates its working upon the turning-lathe. *Tombac* contains 15% zinc, and has a gold-like color. The alloy of 1 part zinc and 5.5 parts copper answers for the manufacture of spurious gold leaf. The alloys of copper with tin are called *bronze*. Most of the modern bronzes also contain zinc and lead; those from Japan, gold and silver. The *cannon bronze* contains 90% copper and 10% tin; bell metal has 20%-25% of tin.

Argentan is an alloy of copper, zinc and nickel (see latter.) The so-called Talmi gold consists of 90-95% Cu and 5-10% aluminium. The German copper coins consist of 95% Cu 4% Sn and 1% Zn.

---

### Recognition of Copper Compounds.

Most copper compounds containing water have a blue or green color. With the exception of copper sulphide they all dissolve in ammonium hydrate, with a blue color. When a pure piece of iron is introduced into a copper solution, it becomes covered with a red layer of metallic copper. Volatile copper compounds tinge the flame blue or green. The spectrum of such a flame is characterized by several blue and green lines.

---

### SILVER.

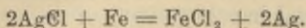
Ag = 107.6.

Silver frequently occurs native. Its most important ores are  $Ag_2S$  and various compounds with sulphur, arsenic, antimony, copper and other metals. Of rarer occurrence are combinations with chlorine (hornsilver  $AgCl$ ), bromine and iodine. Slight quantities of silver sulphide are present in almost every galenite ( $PbS$ ). The principal localities for silver ores are America (Chili, Mexico, California), Saxony (Freiberg), Hungary, the Altai and Nertschinsk.

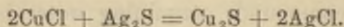
*Metallurgy of Silver.*—The separation of the metal from its ores is tolerably complicated and variously effected; its elaborate description belongs to the province of metallurgy. At present, the ores containing silver and copper are, in Saxony and the Hartz, roasted in a divided state and fused with slags rich in silicic acid. In this way, as with copper, a copper stone consisting of iron, copper and silver sulphides is obtained. This is then oxidized in a furnace; from the resulting mixture of ferric and cupric oxides and silver sulphate ( $SO_4Ag_2$ ), the

latter is extracted by water. From the aqueous solution the silver is precipitated by copper.

Formerly, in Saxony, the separation of the silver was executed according to the so-called amalgamation process. According to this the mixture of sulphides is roasted with sodium chloride, whereby silver chloride is produced. The divided material is then mixed in rotating vessels with iron scraps and water. The iron causes the precipitation of the metallic silver from its chloride:—

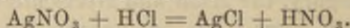


To free the metal from various impurities it is dissolved in mercury and the liquid amalgam glowed; mercury distills off and silver remains. Owing to scarcity of combustible material, the conversion of silver ores into silver chloride is executed, in Mexico and Peru, by mixing the ores with sodium chloride and copper sulphate in the presence of water. In this way cuprous chloride is produced, which, with silver sulphide, is transposed into silver chloride and cuprous sulphide:—

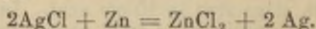


To get silver from galenite, proceed as follows:—First, metallic lead is obtained. In this way all the silver in the ore passes into the lead and may be obtained with profit from the latter, even if it does not constitute more than  $\frac{1}{300}$  per cent of it. To this end, the metallic lead is fused and allowed to cool slowly; pure lead first crystallizes out, which can be removed by sieves, while a readily fusible alloy of lead with more silver remains behind. This method of Pattison's is repeated until the residual liquid lead contains 1 per cent. of silver. The lead, rich in silver, is subjected to cupellation: it is fused in a reverberatory furnace with air access. The bottom of the oven consists of some porous substance. In this process the lead is changed to readily fusible oxide, which partly flows out of side openings from the hearth, or is, in part, absorbed by the porous bed; the unoxidized silver remains in the cupel in metallic condition.

The ordinarily occurring silver (work silver) is not pure, but invariably contains, in greater or less quantity, copper and traces of other metals. To prepare chemically pure metal, the work silver is dissolved in nitric acid, and from the solution of the nitrates thus obtained, hydrochloric acid precipitates the silver as chloride:—



The latter is reduced by various methods; either by fusion with sodium carbonate, or by the action of zinc or iron in the presence of water:—

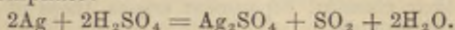


Silver is a pure white, brilliant metal, of specific gravity 10.5. It is tolerably soft and very ductile, and can be drawn



out to a thin wire. It crystallizes in regular octahedra. It fuses about  $954^{\circ}$ , and in the oxy-hydrogen flame is converted into a greenish vapor. Silver is not oxidized by oxygen; by the action of ozone it is covered with a very thin layer of silver peroxide. When in molten condition, silver absorbs 22 volumes of oxygen without combining chemically with it; the absorbed oxygen escapes again when the metal cools.

Silver unites directly with the halogens; by the action of hydrochloric acid it becomes coated with an insoluble layer of silver chloride. Boiled with strong sulphuric acid, it dissolves to sulphate:—



Nitric acid is the best solvent for silver; cold and in dilute state it converts it into nitrate.

As silver is rather soft, it is usually employed in the arts alloyed with copper, whereby it acquires a greater hardness. Most silver coins consist of 90% silver and 10% copper; the English shillings contain 95% silver.

Oxygen forms three compounds with silver, but only the oxide affords corresponding salts.

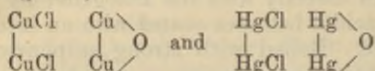
**Silver Oxide**— $\text{Ag}_2\text{O}$ —is thrown out of silver nitrate solutions as a dark-brown amorphous precipitate, by sodium or potassium hydrate. It is somewhat soluble in water, and blues red litmus paper. In this, and by the neutral reaction of the nitrate, the strong, basic, alkaline nature of silver and its oxide exhibits itself; the soluble salts of all other heavy metals show an acid reaction. When heated, the oxide decomposes into metal and oxygen; at  $100^{\circ}$  it is reduced by hydrogen. The hydrated oxide is not known; the moist oxide reacts, however, mostly like the hydrate.

On dissolving precipitated silver oxide in ammonium hydrate, there separates, on evaporation, black crystals ( $\text{Ag}_2\text{O} \cdot 2\text{NH}_3$ ), which, in a dry condition, explode by the slightest disturbance. (Fulminating silver.)

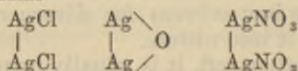
**Silver Suboxide**— $\text{Ag}_4\text{O}$ —corresponding to potassium suboxide, is produced by the heating of silver citrate in an hydrogen stream, and forms a black, very unstable powder, which decomposes readily into silver oxide and silver.

**Silver Superoxide**— $\text{AgO}$  or  $\text{Ag}_2\text{O}_2$ —is formed by passing ozone over silver or its oxide, and by the decomposition of the nitrate by the galvanic current. It consists of black, shining octahedra, and at  $100^{\circ}$  decomposes into  $\text{Ag}_2\text{O}$  and oxygen.

The salt-like compounds of silver are, corresponding to the oxide  $\text{Ag}_2\text{O}$ , exclusively constructed after the form  $\text{AgX}$  and termed argentic. They are analogously constructed to the cuprous and mercurous derivatives, and show, especially as regards physical and chemical properties, a great resemblance to the former. It would, therefore, be more correct to designate them *argentous*. Compounds of the diatomic form  $\text{AgX}_2$ , as of copper and mercury, are not known for silver. If, however, the mercurous and cuprous compounds are expressed by double formulas (p. 327)—



for which their chemical department argues, those of silver must have analogous formulas—



ascribed them. Then the silver atom will appear diatomic and a complete parallelism with copper would be re-established. The non-existence of the silver compounds  $\text{AgX}_2$  is explained by their slight stability, just as lead, the perfect analogue of tin ( $\text{SnX}_2$  and  $\text{SnX}_4$ ), yields almost exclusively only compounds of the form  $\text{PbX}_2$ .

**Silver Chloride**— $\text{AgCl}$ —exists in nature as hornsilver. When hydrochloric acid is added to solutions of silver salts, a white, curdy precipitate separates; the same fuses at  $260^\circ$  to a liquid, which solidifies to a horn-like mass. The chloride is insoluble in acids; it dissolves somewhat in sodium chloride, readily in ammonium hydrate, potassium cyanide and sodium hyposulphite. From ammoniacal solutions it crystallizes in large, regular octahedra. Dry silver chloride absorbs 10% of ammonia gas, forming a white compound— $2\text{AgCl} \cdot 3\text{NH}_3$ —with it, which at  $38^\circ$  gives up its ammonia.

**Silver Bromide**— $\text{AgBr}$ —is precipitated from silver salts by hydrobromic acid or soluble bromides. It has a bright yellow color, and dissolves with more difficulty than the chloride in ammonium hydrate; in other respects it is perfectly similar to the latter. Heated in chlorine gas it is converted into chloride.

**Silver Iodide**— $\text{AgI}$ —is distinguished from the chloride and bromide by its yellow color and its insolubility in ammonia. In hydriodic acid it dissolves readily to  $\text{AgI} \cdot \text{HI}$ , which upon evaporation of the solution separates in shining scales. Heated in chlorine or bromine gas, it is converted into chlo-

ride or bromide; conversely are, however, chloride and bromide of silver, by action of hydriodic acid, converted into silver iodide.

Sunlight, and also other chemically active rays (magnesium light, phosphorus) color silver chloride, bromide and iodide, at first violet, then dark black, whereby they are probably converted into compounds of the form  $Ag_2X$ . In such an altered condition, they are capable of fixing finely divided silver; on this depends their application in photography.

In photographic work a *negative* is first prepared. A glass plate is covered with collodion (a solution of pyroxylin in an ethereal solution of alcohol) holding in solution halogen salts of potassium or cadmium. After the evaporation of ether the glass plate is covered with a dry collodion layer containing the haloid salts. Now the plate is immersed in a solution of silver nitrate, whereby haloids of silver are precipitated upon the surface. The plate thus prepared is exposed to light in the camera obscura, and then, after the action, dipped into a solution of pyrogallie acid or ferrous sulphate. These reducing substances separate metallic silver in a finely divided state, which is precipitated upon the places where the light has acted. Now the plate is introduced into a solution of potassium cyanide, which dissolves the silver salts not affected by the light, while the metallic, unaltered silver remains. The negative thus formed is covered at the places upon which the light shone, with a dark silver layer, while the places corresponding to the shadows of the received image are transparent. The copying of the glass negative on paper is executed in a perfectly similar manner.

**Silver Cyanide**— $AgCN$ —is precipitated from silver solutions by potassium cyanide, as a white, curdy mass, not affected by light. It readily dissolves in ammonium hydrate and potassium cyanide, forming with the latter the crystalline compound  $AgCN.KCN$ . The solution of potassium cyanide is employed in the *galvanic silvering* of metals.

**Silver Nitrate**— $AgNO_3$ —is obtained by dissolving pure silver in somewhat dilute nitric acid, and crystallizes from its aqueous solution in large rhombic tables, isomorphous with potassium saltpetre. At ordinary temperatures it is soluble in one part water or in four parts alcohol. It fuses about  $200^\circ$ , and on further heating decomposes into oxygen and silver nitrite  $AgNO_2$ , which at higher temperatures decomposes into nitrogen, oxygen and silver. In sunlight it turns black, with separation of metallic silver. Organic substances also



reduce it to metal. Silver nitrate is employed in the cauterization of wounds (Lunar caustic).

By dissolving work silver in nitric acid a mixture of silver and copper nitrates is obtained. To separate the silver salt from such a mixture it is heated to redness, the copper thus converted into oxide and the unaltered nitrate extracted with water.

**Silver Nitrite**— $\text{AgNO}_2$ —is precipitated from silver solutions by potassium nitrite. It crystallizes in needles, difficultly soluble in water.

**Silver Sulphate**— $\text{Ag}_2\text{SO}_4$ —is obtained by the solution of silver in hot sulphuric acid, and crystallizes in small rhombic prisms that are difficultly soluble in water. It is isomorphous with anhydrous sodium sulphate.

**Silver Sulphite**,  $\text{Ag}_2\text{SO}_3$ , is precipitated as a white, curdy mass, if sulphurous acid be added to the solution of the nitrate. It blackens in the air and decomposes at  $100^\circ$ .

**Silver Sulphide**,  $\text{Ag}_2\text{S}$ , occurs in regular octahedra, as argentite. Hydrogen sulphide precipitates black amorphous sulphide from silver solutions. By careful ignition in the air it is oxidized to silver sulphate. In water and ammonium hydrate it is insoluble and dissolves with difficulty in boiling nitric acid.

**Silvering.**—When silver contains more than 15 per cent. copper it has a yellowish color. To impart a pure white color to objects made of such silver they are heated, by air access, to redness. The copper is thus superficially oxidized, and may be removed by dilute sulphuric acid. The surface of pure silver is then polished.

The silvering of metals and alloys (new silver, argentan) is executed in a dry or wet way. In the first, the objects to be silvered are coated with liquid silver amalgam, with a brush, and then heated in an oven; the mercury is volatilized, and the silver surface then polished.

At present, the galvanic process has almost completely superseded the other processes. It depends on the electrolysis of the solution of the double cyanide of silver and potassium, whereby the silver is thrown out upon the electro-negative pole and deposits upon the metallic surface, in connection with that electrode.

To silver glass, cover it with a mixture of an ammoniacal silver solution with reducing organic substances like aldehyde, lactic and tartaric acids. Under definite conditions, the reduced silver deposits upon the glass as a regular metallic mirror.

### Recognition of Silver Compounds.

Hydrochloric acid throws down a white, curdy precipitate from acid silver solutions. Ammonium hydrate dissolves the compound readily. Zinc, iron, copper and mercury throw out metallic silver from solutions of silver salts, and from insoluble compounds, like the chloride.

---

### GOLD.

Au — 196.2.\*

Gold (*aurum*) occurs usually in the native state, and is found disseminated in veins in some of the oldest rocks. By the breaking and disintegration of these, gold sands are formed. In slight quantity it is found in the sand of almost every river. Combined with tellurium it forms sylvanite, found in Transylvania and California. Contained in minute quantity in the most varieties of pyrites and in many lead ores. For the separation of the gold grains, the sand or pulverized rocks are washed with running water, which removes the lighter particles and the specifically very heavy gold remains.

Native gold almost invariably has accompanying it silver, copper and various other metals. To free it from these it is boiled with nitric or concentrated sulphuric acid. The removal of the silver by the latter acid is only complete if that metal predominates; in the reverse case a portion of it will remain with the gold. Therefore, to separate pure gold from alloys poor in silver they must first be fused with about three-fourths their weight of the latter. Gold may be separated from copper and lead by cupellation (p. 332).

Pure gold is tolerably soft (almost like lead), and has a specific gravity 19.32. It is the most ductile of all metals and may be drawn out into extremely fine wire and beaten into thin leaves, which transmit green light. About 1100° it melts to a greenish liquid. Not altered by oxygen even upon glowing, and is not attacked by acids. Only in a mixture of nitric and hydrochloric acids (aqua regia) which yields free

---

\* The atomic weight of gold was last (1850) found, by Levol, to be 196.2. In accordance with its position in the periodic system it is, however, very probable that its atomic weight is somewhat greater than that of platinum (196.7).

chlorine, is it dissolved to gold chloride  $\text{AuCl}_3$ . Free chlorine behaves similarly. Most metals and many reducing agents (ferrous sulphate, oxalic acid) precipitate gold from its solutions as a dark brown powder.

Gold being very soft and readily extracted, is, for use, generally alloyed with silver or copper, which have greater hardness. The alloys with copper, have a reddish color, those with silver are paler than pure gold. The German, French, and English gold coins contain 90% gold and 10% copper. For ornamental objects a 14-karat gold is generally employed. This contains about 58% pure gold.

Gold, according to its atomic weight, belongs to the group of copper and silver, and, upon the other hand, forms the transition from platinum to mercury, by which double relation its character is, in an important measure, determined (p. 322). Having the high atomic weight 196-197, it exhibits, like the other elements of high atomic weight belonging to the 10th horizontal series of the periodic system—mercury, thallium, lead and bismuth—a deportment more varying from the lower analogues;—like the elements of the 1st horizontal series (lithium to fluorine) which have the lowest atomic weights, and also differ somewhat from the other members of their groups.

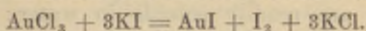
Like silver and copper, gold yields compounds of the form  $\text{AuX}$ —aurous, analogous to the cuprous and argentous. In addition, it has those of the form  $\text{AuX}_3$ , auric derivatives, in which it is triatomic. These show the typical character of the triatomic combination form, which expresses itself in the acidity of the hydrates (p. 324); auric hydrate,  $\text{Au}(\text{OH})_3$ , unites almost solely with bases. On the other hand, they show many similarities to the highest combination forms of the metals with high atomic weight; platinum ( $\text{PtX}_4$ ), mercury ( $\text{HgX}_2$ ), thallium ( $\text{TlX}_3$ ), and lead ( $\text{PbX}_4$ ).

#### AUROUS COMPOUNDS.

**Aurous Chloride**— $\text{AuCl}$ —is produced by heating auric chloride,  $\text{AuCl}_3$ , to  $150^\circ$ , and forms a white powder insoluble in water. When ignited, it decomposes into gold and chlorine: boiled with water it decomposes into the trichloride and gold.



**Aurous Iodide**— $\text{AuI}$ —separates as a yellow powder, if potassium iodide be added to a solution of auric chloride.



When warmed it breaks up into gold and iodine.

When auric oxide or sulphide is dissolved in potassium cyanide, upon evaporation, large colorless prisms of the double cyanide,  $\text{AuCN} \cdot \text{KCN}$ , crystallize out. The galvanic current and many metals precipitate gold from this compound; hence it serves for electrolytic gilding, which, at present, has almost entirely superseded the gilding in the dry way (see p. 336).

**Aurous Oxide**— $\text{Au}_2\text{O}$ —is formed by the action of potassium hydrate upon aurous chloride. It forms a dark violet powder which at  $100^\circ$  decomposes into gold and oxygen. By the action of hydrochloric acid it is changed to  $\text{AuCl}_3$  and gold.

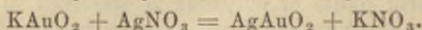
Of the oxygen derivatives of monatomic gold but a few double salts are known.

#### AURIC COMPOUNDS.

**Auric Chloride**— $\text{AuCl}_3$ —results by the solution of gold in aqua regia, and by the action of chlorine upon the metal. By evaporation of the solution it is obtained as a reddish-brown, crystalline mass, which rapidly deliquesces in the air. It is readily soluble in alcohol and ether.

With many metallic chlorides gold chloride forms beautifully crystallized double salts, *e. g.*,  $\text{AuCl}_3 \cdot \text{KCl} + 2\frac{1}{2}\text{H}_2\text{O}$  and  $\text{AuCl}_3 \cdot \text{NH}_4\text{Cl} + \text{H}_2\text{O}$ . When auric chloride is heated with magnesium oxide a brown precipitate is obtained, from which all the magnesia is removed by concentrated nitric acid, leaving **Auric Oxide** ( $\text{Au}_2\text{O}_3$ ). This is a brown powder which, near  $250^\circ$ , decomposes partly into gold and oxygen. If the precipitate containing the magnesia be treated, not with concentrated, but with dilute nitric acid, **Auric Hydrate**— $\text{Au}(\text{OH})_3$ —remains as a yellowish-red powder. Both the oxide and hydrate are insoluble in water and acids; they possess, however, acid properties, and dissolve in alkalis. Therefore the hydrate is also called *auric acid*. Its salts, the aurates, are constituted according to the formula  $\text{MeAuO}_3$ , and are derived from the meta-acid  $\text{HAuO}_2 = \text{HO} \cdot \text{AuO}$ .

**Potassium Aurate**— $\text{KAuO}_2 + 3\text{H}_2\text{O}$ —crystallizes in bright yellow needles, from a potassium hydrate solution of auric oxide. These are readily soluble in water; the solution reacts alkaline. From this solution the corresponding aurates are precipitated by many metallic salts. *e. g.*—



The precipitate produced by magnesia in a solution of auric chloride (see above) consists of magnesium aurate  $(\text{AuO}_2)_2\text{Mg}$ . Oxygen salts of auric oxide are not known.

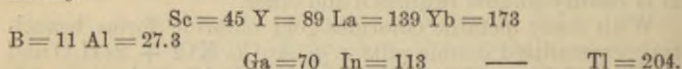
**Auric Sulphide**— $\text{Au}_2\text{S}_3$ —is precipitated as a blackish-brown compound, from gold solutions, by hydrogen sulphide. It dissolves in alkaline sulphides with formation of sulphosalts.

Stannous chloride ( $\text{SnCl}_2$ ) added to an auric chloride solution causes, under definite conditions, a purple-brown precipitate, purple of Cassius, which is employed in glass and porcelain painting. It probably consists of a mixture of aurous stannate and stannous oxide.

On pouring ammonium hydrate over auric oxide a brown compound is produced—*fulminating gold*.

### METALS OF GROUP III.

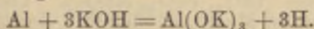
To group III of the periodic system (p. 237) belong the triatomic elements affording derivatives chiefly of the forms  $\text{MeX}_3$ :—



Among themselves, these show perfectly similar relations, as do the elements of group II (p. 290). In boron, with the lowest atomic weight, the metallic basic character is very much diminished or does not appear. According to its exclusively acidic hydroxide  $\text{B}(\text{OH})_3$ , it approaches the metalloids, hence treated with them, although it does not afford a volatile hydride (p. 231).

Aluminium is a perfect metal; its hydrate  $\text{Al}(\text{OH})_3$  exhibits a predominating basic character, and with acids yields salts. Its relations to boron are like those of silicon to carbon, or of magnesium to beryllium. The connection of aluminium and boron with one group plainly shows itself in the entire character of the free elements, as also of their compounds. Thus

aluminium and boron are not dissolved by nitric acid, but, indeed, upon boiling with alkalis:—

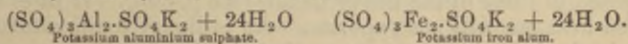


The difference between the hydrates is only a gradual one. As boron hydrate  $\text{B}(\text{OH})_3$  represents a feeble acid, so does aluminium hydrate present an acidic-like character, as it is capable (p. 324) of forming metallic salts with strong bases (chiefly the alkalis); owing to its higher atomic weight the basic character with aluminium exceeds the acidic. The similarity is also shown by the existence of perfectly analogous compounds; thus, *e. g.*, the chlorides  $\text{BCl}_3$  and  $\text{AlCl}_3$  can unite with  $\text{PCl}_5$  and  $\text{POCl}_3$ .

To aluminium attach themselves, as *first sub-group*: scandium, yttrium, lanthanum and ytterbium. These constitute the third members of the great periods, and hence, exhibit a pronounced basic character. As light metals, they are, in their compounds, very similar to aluminium, so that they all are embraced in one group, which (corresponding to the earthy nature of their oxides) is designated the *Group of Earth Metals*. In peculiar relation to lanthanum stand cerium and didymium, with closely agreeing atomic weights and very similar properties. The apparent abnormal existence of the same is explained by the fact that the 5th but very imperfect period (series 7 and 8) in its middle members possesses a somewhat varying function (p. 238). Here too may be classed, very probably, the but recently discovered, and as yet little characterized metals—erbium, terbium, phillipium, thulium and decipium.

More distinctly characterized and accurately investigated is the *second sub-group*, consisting of the heavy metals, gallium, indium and thallium. These belong to the right side of the great period, possess, therefore, a less basic character, and bear the same relation to each other as  $\text{Zn}$ ,  $^{\text{C}}\text{Cd}$  and  $\text{Hg}$ .

Formerly, aluminium was classed together with chromium, iron, manganese, cobalt and nickel, in one group, as they all afford sesquioxides,  $\text{Me}_2\text{O}_3$ , whose salts are very much alike. Particularly proof bearing for this classification was thought to be the existence of the perfectly similarly constituted alums:—



Yet in its entire behavior, aluminium is distinguished very essentially from the other here mentioned metals—by the acid nature of its



hydrate,  $\text{Al}(\text{OH})_3$ —and by its inability to form higher or lower combination forms, while the others yield basic monoxides,  $\text{MeO}$ , and acid-forming trioxides ( $\text{CrO}_3$ ,  $\text{FeO}_3$ ,  $\text{MnO}_3$ ). The similarity of the sesquioxide compounds,  $\text{Me}_2\text{O}_3$  is, therefore, here, like those of the monoxide compounds,  $\text{MeO}$ , to be regarded as chiefly influenced by the similarity of the combination forms.

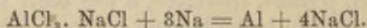
The, at present, accepted triatomic nature of aluminium apparently contradicts the circumstance that not the simple formulas,  $\text{AlCl}_3$ ,  $\text{AlBr}_3$ , but the double ones,  $\text{Al}_2\text{Cl}_6$ ,  $\text{Al}_2\text{Br}_6$ , fall to its halogen derivatives (the result of vapor density determinations). On the other hand, however, exist the so-called metallo-organic compounds of aluminium, whose molecules are constituted according to the formulas  $\text{Al}(\text{CH}_3)_3$ ,  $\text{Al}(\text{C}_2\text{H}_5)_3$ ; from them, undoubtedly, follows the trivalence of aluminium, as the compounds with hydro-carbons (like those with hydrogen) afford the surest guide for the deduction of the valence (p. 239). The existence of the molecules  $\text{Al}_2\text{Cl}_6$ ,  $\text{Br}_2\text{Cl}_6$ , etc., does not prove anything against its being a triad, but must be explained by a polymerization of the simple chemical molecules  $\text{AlCl}_3$ ,  $\text{BrCl}_3$ —as with arsenious oxide,  $\text{As}_2\text{O}_3$ , and antimony trioxide,  $\text{Sb}_2\text{O}_3$ , the molecules in vapor form correspond with the doubled formulas  $\text{As}_4\text{O}_6 = (\text{As}_2\text{O}_3)_2$  and  $\text{Sb}_4\text{O}_6$ .

## ALUMINIUM.

Al — 27.3.

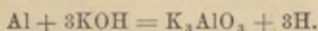
This is one of the most widely distributed elements. As oxide, it crystallizes as ruby, sapphire and corundum; less pure as emery. It is commonly found as aluminium silicate (clay, kaolin), and in combination with other silicates, as feldspar, mica, and also in most crystalline rocks. It occurs, too, united with fluorine and sodium, as cryolite, in large deposits, in Iceland.

Metallic aluminium is obtained by igniting the chloride, or better, the double chloride of sodium and aluminium with metallic sodium:—



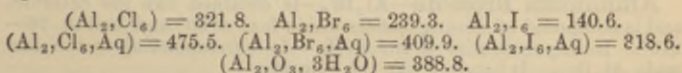
It is a silver white metal of strong lustre, is very ductile, and may be drawn out into thin wire and beaten into thin leaflets. Its specific gravity is 2.56; it belongs, consequently, to the light metals and possesses, therefore, all the properties opposed to those of the heavy metals (see p. 305). It fuses at a red heat but will not vaporize. At ordinary temperatures, as also by heat, it changes very little in the air; if, however, thin leaves be heated in a stream of oxygen they burn with a

bright light. Nitric acid does not affect aluminium; sulphuric acid only dissolves it on boiling, while in hydrochloric acid it is readily soluble, even in the cold. It dissolves in potassium and sodium hydrate, with evolution of H, to form aluminates:—



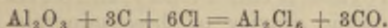
Owing to its stability in air and beautiful lustre, aluminium is sometimes employed for vessels and ornaments. The alloy of copper with 10–12 per cent. aluminium is distinguished by its great hardness and durability. It may be poured into moulds, and possesses a gold-like color and lustre. Under the name of aluminium bronze, it is used for the composition of various articles, like pocket watches, spoons, etc. It forms only compounds of the form  $\text{AlX}_3$  or  $\text{Al}_2\text{X}_6$  (p. 340). Its salts soluble in water have an acid reaction, and sweet, astringent taste.

The heat of formation of some of the aluminium compounds equals:—



The heat evolved in the formation of a quantity of aluminium hydrate, corresponding to one atom of oxygen, is 129.6; as that of water is far less ( $\text{H}_2, \text{O} = 69.0$ ), it must be decomposed by aluminium, with liberation of hydrogen (p. 267). If this does not transpire under ordinary conditions, the reason is to be sought for in the insolubility of aluminium hydrate. Indeed, the reaction occurs if there be added to water aluminium chloride, or another salt, in which the aluminium oxide is soluble. Conversely, from the high heat of formation is explained why aluminium oxide is not reduced by carbon.

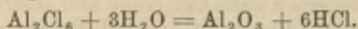
**Aluminium Chloride**,  $\text{AlCl}_3$ , or  $\text{Al}_2\text{Cl}_6$ , is produced by the action of chlorine upon warmed or heated aluminium; also by heating a mixture of aluminium oxide and carbon in a current of chlorine:—



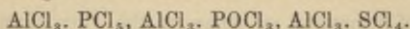
Chlorine and carbon alone do not act upon the oxide; by their mutual action, however, the reaction occurs in consequence of the affinity of carbon to oxygen, and of chlorine for aluminium. Similar deportment is shown by the oxides of boron and silicon.

By sublimation aluminium chloride may be got in white, hexagonal leaflets. It readily sublimes, but under elevated pressure fuses. Its vapor density is 133.9 ( $H = 1$ ), from which the molecular formula,  $Al_2Cl_6 = 367.8$ , is derived. From the specific heat of free aluminium it follows that its atomic weight is 27.3.

Aluminium chloride absorbs moisture from the air and deliquesces. From concentrated hydrochloric acid solution it crystallizes with 6 molecules of water. On evaporating the aqueous solution, the chloride decomposes into aluminium oxide and hydrogen chloride:—



It forms double chlorides with many metallic chlorides, viz.:  $AlCl_3 \cdot NaCl$ ,  $AlCl_3 \cdot KCl$ . The solutions of these may be evaporated to dryness without decomposition. Further, it unites with many halogen derivatives of the metalloids:—



**Aluminium Bromide**— $Al_2Br_6$ —is obtained like the chloride, and is composed of shining leaflets which fuse at  $90^\circ$  and boil at  $265-270^\circ$ . Its vapor density is 267.4 ( $H = 1$ ), corresponding to the formula  $Al_2Br_6$ . It behaves like the chloride.

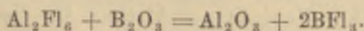
**Aluminium Iodide**— $Al_2I_6$ —is formed by the direct union of aluminium filings with iodine, with gentle application of heat. It is a white, crystalline mass, fusing at  $185^\circ$ , and boiling about  $400^\circ$ .

**Aluminium Fluoride**— $AlF_3$  or  $Al_2F_6$ —obtained by conducting hydrogen fluoride over heated aluminium oxide or hydrate, sublimes at a red heat, in colorless rhombohedra. It is insoluble in water, unaltered by acids, and is very stable. With alkaline fluorides it yields insoluble double fluorides. The compound— $AlF_3 \cdot 3NaF$ —occurs in Greenland, in large deposits, as Cryolite, and is employed in the soda manufacture (p. 283).

**Aluminium Oxide**— $Al_2O_3$ —is found crystallized in hexagonal prisms in nature, colored by other admixtures, as ruby, sapphire and corundum. Impure corundum, containing aluminium and iron oxides, is called emery, and serves for polishing glass. The specific gravity of these minerals is 3.9; their hardness is only a little below that of the diamond. Artificially, aluminium oxide may be obtained by igniting the hydrate, as a white amorphous powder, which, in the oxy-hydrogen flame, fuses to a transparent glass. A mixture of aluminium fluoride and boron trioxide heated to white heat has the boron



fluoride volatilized, and crystallized aluminium oxide remains:—



The crystallized or strongly ignited aluminium oxide is almost insoluble in acids; to decompose it, it is fused with caustic alkalies or with primary potassium sulphate— $\text{HKSO}_4$ .

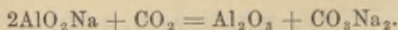
**Aluminium Hydrates**—The *normal hydrate*,  $\text{Al}(\text{OH})_3$  or  $\text{Al}_2(\text{OH})_6$ , occurs in nature as Hydrargillite. The hydrate  $\text{Al}_2\text{O}_2(\text{OH})_2$  is diaspore. Bauxite is a mixture of the hydrate  $\text{Al}_2\text{O}(\text{OH})_3$ , with ferric oxide. The normal hydrate is artificially obtained as a white voluminous precipitate, by adding ammonium hydrate or carbonate (in latter case carbon dioxide escapes, p. 347) to a soluble aluminium salt. Freshly precipitated, it dissolves in acids and in potassium and sodium hydrates. By long standing under water, or after drying, it is, without any alteration in composition, difficultly soluble in acids. Carefully heated, the normal hydrate first passes into  $\text{AlO.OH}$ .

The freshly precipitated hydrate dissolves readily in a solution of aluminium chloride or acetate. On dialysing this solution the aluminium salt or crystalloid diffuses, and in the dialyser remains the pure aqueous solution of the hydrate. This has a faint alkaline reaction and is coagulated by slight quantities of acid, alkalies and many salts; the soluble hydrate is converted into the insoluble gelatinous modification.

Gelatinous aluminium hydrate possesses the property of precipitating many dyestuffs from their solutions, forming with them colored insoluble compounds (lakes). On this is based the application of aluminium hydrate as a mordant in dyeing. Generally the acetate is used for this purpose. The fibre of goods saturated with this salt is heated with steam, which causes the decomposition of the weak acetate; acetic acid escapes, while the separated aluminium hydrate sets itself upon the fibre of the material. If the latter now be introduced into the solution of coloring matter it is fixed by the aluminium hydrate upon the fibre. At present, sodium aluminate is employed instead of the acetate.

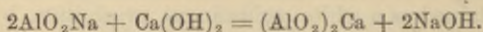
Aluminium hydrate has a feeble acid character, and can form salt-like compounds with strong bases. On carefully evaporating its solution in sodium and potassium hydrate, or upon addition of alcohol, white amorphous compounds of  $\text{KAlO}_2$ ,  $\text{NaAlO}_2$  and  $(\text{NaO})_3\text{Al}$  are obtained. The potassium compound can be obtained in crystalline form. These derivatives, known as *aluminates*, are not very stable, and are even

decomposed by carbon dioxide, with elimination of aluminium hydrate:—



The thus produced aluminium hydrate, in distinction to that precipitated from acid aluminium solutions by the alkalis, is not gelatinous, and is more difficultly soluble in acids, especially acetic. It comprises the ordinary alumina of commerce.

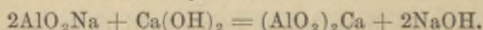
On adding calcium hydrate to the solution of potassium or sodium aluminate, insoluble calcium aluminate is precipitated:—



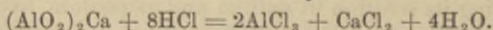
Barium and strontium aluminates are, however, readily soluble in water. Similar aluminates frequently occur as crystallized minerals, in nature. Thus the spinels consist chiefly of magnesium aluminate,  $\begin{matrix} \text{AlO.O} \\ \text{AlO.O} \end{matrix} \rangle \text{Mg}$ ; chrysoberyl is beryllium aluminate,  $\begin{matrix} \text{AlO.O} \\ \text{AlO.O} \end{matrix} \rangle \text{Be}$ ; gahnite is zinc aluminate,  $\begin{matrix} \text{AlO.O} \\ \text{AlO.O} \end{matrix} \rangle \text{Zn}$ .

Technically, alumina is obtained from cryolite, bauxite and other alumina-containing minerals. The pulverized bauxite is heated with dry sodium carbonate, in furnaces, and the formed sodium aluminate extracted with water. From the clear solution carbon dioxide precipitates the hydrate, while sodium carbonate remains dissolved, and is afterward recovered. The dried aluminium hydrate comes as a white powder in trade.

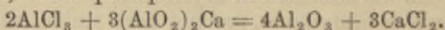
The gelatinous, readily soluble (colloidal) aluminium hydrate (see above) precipitated from acid solutions by alkalis, has lately been prepared upon a large scale, according to the method of Löwig, by treating the sodium aluminate solution with milk of lime; calcium aluminate precipitates, while in solution remains sodium hydrate:—



Calcium aluminate is dissolved in hydrochloric acid:—

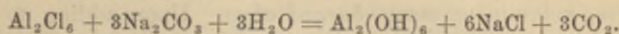


and to the solution the necessary quantity of calcium aluminate added, which precipitates aluminium oxide:—

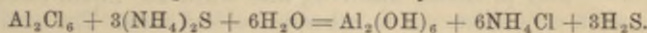


According to this procedure, the sodium hydrate formed in the first reaction is obtained together with the alumina.

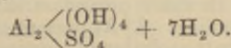
The basic character of aluminium hydrate exceeds the acid; it is, however, so feeble, that it is not capable of forming salts with weak acids, like carbon dioxide, sulphurous acid and hydrogen sulphide. When sodium carbonate is added to aluminium salt solutions, aluminium hydrate is precipitated, while  $\text{CO}_2$  is set free:—



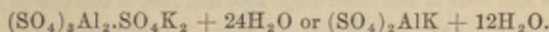
The alkaline sulphides behave similarly:—



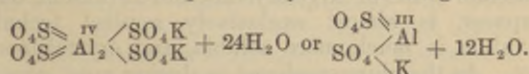
**Aluminium Sulphate**— $\text{Al}_2(\text{SO}_4)_3$ —crystallizes from aqueous solution with 18 molecules of  $\text{H}_2\text{O}$  in thin leaflets with pearly lustre. These dissolve readily in water; when heated, they melt and lose all their water of crystallization. The sulphate is obtained by dissolving the hydrate in sulphuric acid, or by the decomposition of pure clay with the same acid; the residual silicic acid is removed by filtration, and the solution of the sulphate evaporated. When a quantity of ammonium, insufficient for complete precipitation, is added to the sulphate, *basic* sulphates separate out. Salts similar to the latter are also found in nature; thus, aluminite, used to prepare alum, has the composition:—



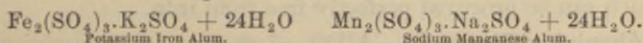
Aluminium sulphate can combine with the alkaline sulphates to form double salts, termed *alums*:—



Their constitution is expressed by the following formula:—



In this compound the potassium may be replaced by sodium, ammonium, rubidium, caesium, and also by thallium. Iron, chromium and manganese form like derivatives:—



All these alums crystallize in regular octahedra or cubes, and can form isomorphous mixtures.



The most important of them is *Potassium Aluminium Sulphate*, or *ordinary alum*,  $\text{AlK}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ . From water it crystallizes in large, transparent octahedra, soluble in 8 parts water of ordinary temperature, or in  $\frac{1}{3}$  part boiling water. The solution has an acid reaction and a sweetish, astringent taste. When placed over sulphuric acid, alum loses 9 (or 18) molecules of  $\text{H}_2\text{O}$ . It melts, when heated in its water of crystallization, loses all the latter and becomes a white, voluminous mass—*burned alum*. Upon adding to a hot alum solution a little sodium or potassium carbonate, the hydrate first produced dissolves, and when the liquid cools, the alum crystallizes out in cubes, as *cubical alum*. The addition of more sodium carbonate causes the precipitation of the basic salt— $\text{AlK}(\text{SO}_4)_2 \cdot \text{Al}(\text{OH})_3$ . Alunite, found in large quantities near Rome and in Hungary, has a similar composition.

Commercially, alum is obtained according to various methods: 1. From alunite, in which it exists already, by heating and extracting with water. In this way alum dissolves, while the hydrate remains; from such solutions the former crystallizes in combinations of the octahedron with cube faces—Roman alum. 2. The most common source of alum was formerly *alum shale*, a clay containing pyrite and peat. This is roasted and moistened with water exposed for a long time to the action of the air. By this means  $\text{FeS}_2$  is converted into  $\text{FeSO}_4$  and free sulphuric acid, which, acting upon the clay, forms aluminium sulphate. The mass is extracted with water, potassium sulphate added, and the whole permitted to crystallize. 3. At present clay is directly treated with sulphuric acid, and to the solution of aluminium sulphate potassium or ammonium sulphate are added. Bauxite and cryolite are admirable material for the preparation of alum. The working of cryolite for alumina and soda is described on p. 283, and that of bauxite p. 345.

**Ammonium Alum**— $(\text{SO}_4)_2 \text{Al NH}_4 + 12\text{H}_2\text{O}$ —crystallizes like potassium alum, in large crystals, and at present, owing to its cheapness, is almost exclusively applied technically. Sodium alum is much more soluble, and crystallizes with difficulty. As the alum employed in dyeing must contain no iron, we understand why this salt is not applicable. Furthermore, at present, in practice we find alum more and more supplanted by aluminium sulphate and sodium aluminate, which can be procured perfectly free from iron.

**Aluminium Phosphate**— $\text{AlPO}_4$ —is thrown out of aluminium solutions by sodium phosphate, as a white gelatinous precipitate; this is readily soluble in acids, excepting acetic.

**Aluminium Silicates.** The most important of the aluminium double silicates, so widely distributed in nature, is ordinary feldspar—Orthoclase— $\text{AlKSi}_3\text{O}_8$ —and the various micas, which, with quartz, compose granite. By disintegration of these, under the influence of water and  $\text{CO}_2$  of the air, alkaline silicates are dissolved and carried away by water, while the insoluble aluminium silicate, clay, remains. Perfectly pure clay is white, and is called kaolin, or porcelain clay; its composition mostly corresponds to the formula,  $\text{Al}_2(\text{SiO}_2)_3, \text{Al}_2\text{O}_3\text{H}_4$ . When clay is mixed with water a tough, kneadable mass is obtained. By drying and burning it becomes compact and hard, and is the more fire-proof, the purer the clay. On this depends the use of clay for the manufacture of earthen ware, from the red brick to porcelain.

To produce porcelain a very fine mixture of kaolin, feldspar and quartz is employed. On strong ignition, feldspar fuses, fills the pores of the clay and thus furnishes a fused transparent mass—porcelain. When it is not so strongly glowed, it remains porous—faience—serving for finer clay vessels. To render these impervious to water, they are covered with glazing. This consists of various readily fusible silicates. Rough earthenware vessels are constructed from impure clay, and they are ordinarily glazed by throwing salt, at the time of burning, into the ovens. The hot steam decomposes this into hydrochloric acid and sodium hydrate, which forms with the clay, on its surface, an easily fusible silicate.

**Ultramarine.** The rare mineral *Lapis lazuli*, which formerly, under the name of *Ultramarine*, was employed as a very valuable blue color, is a compound of aluminium sodium silicate with sodium polysulphides. At present ultramarine is prepared artificially, in large quantities, by heating a mixture of clay, dry soda (or sodium sulphate), sulphur and wood ashes, away from air. *Green* ultramarine is the product. This is then washed with water, dried, mixed with powdered sulphur and gently heated with air contact until the desired blue color has appeared—*blue* ultramarine. The cause of the blue coloration is generally assumed to be due to the existence of a complicated sulphur compound, whose nature is not yet explained. On pouring hydrochloric acid over the blue product, the color disappears with liberation of sulphur and hydrogen sulphide—which would point to the existence of a polysulphide. At present violet and red ultramarines are prepared.

## RARE METALS.

In some very rare minerals, like cerite, gadolinite, euxenite, orthite, occurring principally in Sweden and Greenland, is found a series of metals which in their entire deportment closely resemble aluminium (p. 341). These are yttrium, cerium, lanthanum, didymium, and the more recent scandium, ytterbium, erbium, terbium, thulium (phillipium, decipium). These mostly form difficultly soluble oxalates; they are precipitated from solution by oxalic acid. They also afford difficultly soluble sulphates and double sulphates, of which all the potassium double salts are constituted, according to the formula  $\text{Me}_2(\text{SO}_4)_3, 3\text{K}_2\text{SO}_4$ . The different decomposability of their nitrates upon application of heat affords an excellent means for their isolation and separation.

Most accurately investigated are lanthanum, cerium and didymium, whose atomic weights, by the determination of the specific heat of the free metals are at least very approximately established. That of yttrium (89) appears, from the isomorphism of its sulphate with that of didymium to be positively established. Erbium, formerly regarded as an elementary substance, consists, according to Nilson and Cleve, of six different earths: scandium, ytterbium, thulium, erbium, terbium, and a metal designated X. Only the first two are as yet accurately characterized, and especially does scandia offer particular interest, as the metal scandium contained in it, with the atomic weight 44, fills out an until now vacant place in the first large period. All its properties have essentially shown themselves the same as those of the element *ekaboron*, theoretically deduced from the periodic system.

**Scandium**— $\text{Sc}=44$ —chiefly contained in euxenite and gadolinite, has not yet been obtained in a free condition. Its oxide,  $\text{Sc}_2\text{O}_3$ , is obtained by igniting the hydrate or nitrate, and is a white, infusible powder (like magnesia and oxide of beryllium). Its specific gravity equals 3.86; the specific heat 0.1530. The hydrate  $\text{Sc}(\text{OH})_3$  is precipitated as a gelatinous mass from its salts by the alkalis, and insoluble in an excess of the latter. The nitrate crystallizes in little prisms, and is decomposed with difficulty upon heating. The potassium double sulphate  $\text{Sc}_2(\text{SO}_4)_3, 3\text{K}_2\text{SO}_4$ , is soluble in warm water, but not in a solution of potassium sulphate. The chloride affords a characteristic spark spectrum.

**Yttrium**— $\text{Y}=89$ , has long been known in its compounds, but has never been investigated in pure condition. Occurs chiefly in gadolinite (upwards of 35 per cent.) Its potassium double sulphate is soluble in a potassium sulphate solution, whereby it can readily be separated from cerium, lanthanum, and didymium. Its nitrate is much more difficult to decompose than that of scandium and ytterbium. The chloride  $\text{YCl}_3 + 7\text{H}_2\text{O}$  forms large prisms and gives a spark spectrum.

**Lanthanum**— $\text{La}=139$ —separated from its chloride by electrolysis, resembles iron as regards color and lustre, oxidizes in the air, and burns in a flame with a bright light. Its specific gravity equals 6.16,



the specific heat 0.0448. The hydrate  $\text{La}(\text{OH})_3$  is precipitated as a gelatinous mass, and reacts alkaline.

**Cerium**— $\text{Ce} = 140$ —occurs in cerite (60 per cent.), and is also obtained by the electrolysis of the chloride. Very similar to lanthanum, but at ordinary temperatures is more stable than the latter; burns much more readily, so that broken off particles of it inflame of their own accord. The specific gravity of the fused metal is 6.72, the specific heat 0.0448. Besides the salts of the sesquioxide  $\text{Ce}_2\text{O}_3$ , it forms some from the dioxide  $\text{CeO}_2$ . The first are colorless, while the latter are colored yellow or brown; from the first, on addition of hypochlorites, red ceric hydrate  $\text{Ce}(\text{OH})_4$  is precipitated.

**Didymium**— $\text{Di} = 142$  or  $146.5$ —in free condition very closely resembles lanthanum, but shows a somewhat yellowish color; it oxidizes in the air and burns in the flame with a brilliant light. Its specific gravity is 6.54, the specific heat 0.0456. Its hydrate  $\text{Di}(\text{OH})_3$  and salts are rose red or violet in color.

All three metals, didymium, cerium and lanthanum, as chlorides, yield spark spectra. Didymium is distinguished by the ability of its salts, in solid or dissolved form, of absorbing definite light rays and yielding a very characteristic absorption spectrum.

**Ytterbium**— $\text{Yb} = 173$ .—Its oxide,  $\text{Yb}_2\text{O}_3$ , is obtained from the so-called erbium earth (from euxenite and gadolinite) by repeated partial heating of the mixed nitrates, whereby the scandium nitrate first decomposes. It is a white infusible powder, of specific gravity 9.17; its specific heat is 0.0646. The salts of ytterbium are colorless, and show no absorption spectrum.

**Erbium Oxide**— $\text{Er}_2\text{O}_3$  ( $\text{Er} = 166$ )—is red in color. Its salts, like those of didymium yield an absorption spectrum.

### GALLIUM GROUP.

The same relation that  $\text{Cu}$ ,  $\text{Ag}$  and  $\text{Au}$  bear to  $\text{Na}$ , and  $\text{Zn}$ ,  $\text{Cd}$  and  $\text{Hg}$  to Magnesium, do the three heavy metals, gallium, indium, and thallium, bear to aluminium:

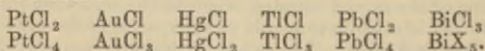
$\text{Cu}$	63.3	$\text{Zn}$	65.0	$\text{Ga}$	69.8	—————	$\text{As}$	75.0	
$\text{Ag}$	107.6	$\text{Cd}$	111.6	$\text{In}$	113.4	$\text{Sn}$	118.0	$\text{Sb}$	122.0
$\text{Au}$	197.0	$\text{Hg}$	200.0	$\text{Tl}$	203.6	$\text{Pb}$	206.0	$\text{Bi}$	210.0

They constitute the corresponding members of the three great periods, and as second sub-group attach themselves to aluminium, while the first more basic group is formed by some cerite metals (p. 341). The entire character of the three elements under consideration is influenced by their position in the periodic system, as in all respects, regular relations appear, *e. g.*, seen in the specific gravities, fusing points and other physical properties of the free metals.

	Ga	In	Tl
Atomic Weight,	69.8	113.4	203.6
Specific Gravity,	5.9	7.4	11.8
Fusing Point,	29.5°	176°	290°

Belonging to Group III of the periodic system, Ga, In and Tl yield compounds of the triatomic form, which in many respects are analogous to those of aluminium.

Like other elements with high atomic weight (Au, Hg, Pb), thallium exhibits great variations from the group properties (p. 315) which are seen in the fact that in addition to the compounds of the form  $TlX_3$ , the metal is also capable of affording those of the form  $TlX$ . Regarding thallium as a member of the last great period (Pb, Au, Hg, Tl, Pb, Bi) we discover that its combination forms, like those of other elements of this series, are constructed upon a remarkable regularity, and as well according, indeed, with reference to the highest as to the lowest forms:—



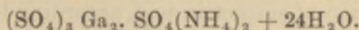
### 1. GALLIUM.

Ga — 69.8.

Gallium was discovered in 1875, by Lecoq de Boisbaudran, by means of the spectroscope, in zinc blende from Pierrefitte. Already, in the year 1870, Mendelejeff, upon the basis of the table of the periodic system devised by him, predicted the existence of an element (standing between aluminium and indium, with an atomic weight of nearly 64), which he named Eka-aluminium, the properties of which were, to an important degree, determined by its position in the periodic system. The agreement of the most at that time known properties of gallium with those of the theoretical eka-aluminium, made it exceedingly probable that gallium represented this theoretically established element. At present the complete confirmation is afforded by the fact that the experimentally determined atomic weight has shown itself like the theoretical.

As yet gallium has only been found in very small quantity, and is but imperfectly investigated. It is characterized by a spectrum consisting of two violet lines. Separated by the electrolysis from an ammoniacal solution of its sulphate, it is a white, hard metal, of specific gravity 5.9, with a fusing point 29.5°. It is only superficially oxidized in the air, not altered by water, and up to a red heat is not volatile. Like aluminium, it is scarcely attacked by nitric acid, but dissolves readily in hydrochloric acid.

The oxide  $Ga_2O_3$  is thrown out of its solutions as a white precipitate, readily soluble in potassium hydrate, but little soluble in hydrate of ammonium. The chloride  $GaCl_3$  is very deliquescent, and is decomposed by much water. The nitrate and sulphate are readily crystallized; the latter forms a double salt with ammonium sulphate—similar to the alums:—



Hydrogen sulphide only precipitates gallium from acetate solutions.

## INDIUM.

In — 113.

Owing to its resembling zinc, indium was regarded as a dyad metal, and its compounds composed according to the formula,  $InX_2$ ; from this its atomic weight was found to be 75.4. From the specific heat, however, it follows that the atomic weight is one and a half times as large. (p. 250). Therefore it is triatomic and its derivatives are constituted according to the form,  $InX_3$ . It belongs to the group of aluminium, to which, in its derivatives, it manifests some similarity.

It was discovered in 1863, by Reich and Richter, by the aid of spectrum analysis. Its spectrum is characterized by a very bright indigo blue line, hence its name. It only occurs in very minute quantities in some zinc blendes from Freiberg and the Hartz.

It is a silver white, soft and tenacious metal, of specific gravity, 7.42. It fuses at  $176^\circ$  and distills at a white heat. At ordinary temperatures it is not altered in the air; heated, it burns with a blue flame to indium oxide. In hydrochloric and sulphuric acids it is difficultly soluble, but readily dissolved by nitric acid.

**Indium Chloride**— $InCl_3$ —results from the action of chlorine on metallic indium, or upon a glowing mixture of indium oxide and carbon. It sublimes in white, shining leaflets, which deliquesce in the air.

**Indium Oxide**— $In_2O_3$ —is a yellow powder resulting from the ignition of the hydrate.

**Indium Hydrate**— $In(OH)_3$ —is precipitated as a gelatinous mass, by alkalies, from indium solutions. It is soluble in sodium and potassium hydrates.

**Indium Nitrate**— $In(NO_3)_3$ —crystallizes with three molecules of water, in white deliquescent needles.

**Indium Sulphate**— $In_2(SO_4)_3$ —is a gelatinous mass, with three molecules of water, remaining after the evaporation of a solution of indium in sulphuric acid. With ammonium sulphate it forms an alum.

**Indium Sulphide**— $In_2S_3$ —is precipitated as a yellow colored compound, from indium solutions by hydrogen sulphide.



## THALLIUM.

Tl — 204.

Is rather widely distributed in nature, but in very small quantity. It is present in some pyrites. On roasting these, for the production of sulphuric acid, according to the chamber process, it deposits as soot in the chimney and in the chamber sludge, and was discovered in the latter, in 1861, almost simultaneously, by Crookes and Lamy, by means of the spectroscope.

To get the thallium the chimney dust is boiled with water or sulphuric acid, and from the solution thallic chloride is precipitated by hydrochloric acid. Then the chloride is converted into sulphate, and from the latter, by means of zinc or the galvanic current, the metal is separated. Thallium is a white metal as soft as sodium, of specific gravity 11.9. It fuses at  $285^{\circ}$  and distills at a white heat. In moist air it oxidizes very rapidly. It does not decompose water at ordinary temperatures. It is best preserved under water, in a closed vessel. By air access it gradually dissolves in water to hydrate and carbonate. Heated in the air it burns with a beautiful green flame whose spectrum shows a very intense green line, hence the name thallium, from *θαλλός*, green. Thallium is readily soluble in sulphuric and nitric acids, little attacked by hydrochloric acid, owing to the insolubility of thallic chloride.

Thallium forms two series of compounds: **Thallic**— $TlX$  and **thalic**— $TlX_3$ . The first are very similar to the compounds of the alkalis (and also those of silver). This is especially seen in the solubility of the hydrate and carbonate in water; their solutions have an alkaline reaction. Further, many thallic salts are isomorphous with those of potassium, and form perfectly similar double salts. The insolubility of its sulphur and halogen compounds would make monatomic thallium approach silver and lead.

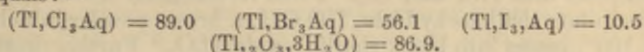
In the compounds constituted according to the form  $TlX_3$ , thallium, like aluminium, is triatomic; otherwise it scarcely shows any similarity to it.

The heat of union of some of the thallic compounds is:—

$(Tl_2O) = 42.2$	$(Tl,Cl) = 48.5$	$(Tl,Br) = 41.2$	$(Tl,I) = 30.$
$(Tl,O,H) = 56.9$	$(Tl_2,S,O_4) = 210.9$	$(Tl,N,O_3) = 58.1.$	

The heat of solution of all these compounds is negative. From the cited numbers is explained the deportment of thallium to water and the acids.

The heat of formation of the *ic* compounds in aqueous solution equals:—



### THALLOUS COMPOUNDS.

**Thalious Oxide**— $\text{Tl}_2\text{O}$ —is formed by the oxidation of thallium in the air, or by heating the hydrate to  $100^\circ$ . It forms a black powder which dissolves in water to yield the hydrate.

**Thalious Hydrate**— $\text{Tl}(\text{OH})$ —may be prepared by decomposing thallium sulphate with an equivalent amount of barium hydrate, and crystallizes with one molecule of water in yellowish prisms. It dissolves readily in water and alcohol to strong alkaline solutions.

**Thalious Chloride**— $\text{TlCl}$ —is thrown down from solutions of thalious salts by hydrochloric acid as a white, curdy precipitate, which is very difficultly soluble in water. Like potassium chloride it forms an insoluble double salt— $\text{PtCl}_4, 2\text{TlCl}$ —with platinic chloride. In the same manner thalious bromide is obtained as a white and thalious iodide as a yellow precipitate.

**Thalious Sulphate**— $\text{Tl}_2\text{SO}_4$ —crystallizes in rhombic prisms, isomorphous with potassium sulphate. At ordinary temperatures it dissolves in 20 parts of water. With the sulphates of the metals of the magnesium group, of ferrous oxide, of cupric oxide, etc. (p. 307), it affords double salts, *e. g.*,  $\text{MgSO}_4, \text{Tl}_2\text{SO}_4 + 6\text{H}_2\text{O}$ , which are perfectly similar and analogous to the corresponding double salts of potassium and ammonium. Further, with the sulphates of the sesquioxides of the iron group it forms **Thallium Alums**, *e. g.*,  $\text{AlTl}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ , similar to potassium alum— $\text{AlK}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ .

**Thalious Carbonate**— $\text{Tl}_2\text{CO}_3$ —is formed from the oxide by absorption of  $\text{CO}_2$ , crystallizes in needles, which dissolve at ordinary temperatures, in 20 parts of water, and has an alkaline reaction.

**Thalious Sulphide**.— $\text{Tl}_2\text{S}$ —is precipitated from thalious salts by hydrogen sulphide, as a black compound, insoluble in water.

## THALLIC COMPOUNDS.

**Thallic Chloride**— $TlCl_3$ —is formed by the action of chlorine upon  $TlCl$ , and is very soluble in water. At  $100^\circ$  it decomposes into  $TlCl$  and  $Cl_2$ . From its solutions the alkalis precipitate thallos hydrate,  $TlO.OH$ , a brown powder, which, at  $100^\circ$ , passes into black thallic oxide  $Tl_2O_3$ . Further heating decomposes the latter into thallos oxide and oxygen.

The oxide and hydrate are soluble in hydrochloric, nitric, and sulphuric acids, forming  $Tl(NO_3)_3$ ,  $Tl_2(SO_4)_3$ ,  $TlCl_3$ .

On conducting chlorine through a solution of thallic hydrate in potassium hydrate, the same assumes an intense violet color, due probably to the formation of the potassium salt of thallic acid, the composition of which is yet unknown.

The thallium compounds are poisonous. They are employed in making thallium glass, which refracts light more strongly than lead glass. The spectrum of the thallium flame shows a very bright green line.

## TIN AND LEAD.

Tin and lead, with silicon and carbon, belong to one group in which the transition, corresponding with the increasing atomic weight, from metalloidal to metallic character, finds distinct expression:  $C = 12$ ,  $Si = 28$ ,  $— = 73$ ,  $Sn = 117.8$ ,  $Pb = 206.4$ . The differences between these elements are purely gradual; the apparent greater difference between metalloidal silicon and metallic tin is explained by the fact that a member corresponding to arsenic of the nitrogen group, with atomic weight 73, is not known (p. 156).

Tin, like carbon and silicon, is tetratomic, and yields perfectly analogous compounds,  $SnCl_4$ ,  $SnO_2$ . Corresponding to the latter are the hydrates  $Sn(OH)_4$ , and  $SnO(OH)_2$ , of which only the latter forms salts (p. 218). Yet stannic acid is but a weak acid, the alkali salts of which react alkaline and are not very stable. At the same time these hydrates have a basic character, hence form salts with acids. Therefore stannic acid anhydride is called stannic oxide, and stannic acid stannic hydrated oxide. The metallic salts of stannic acid (like  $SnO_3.Na_2$ ), are called *stannates*; those, with acids, are *stannic salts*.

Thus, too, tin affords compounds of the form  $SnX_2$  (corresponding to  $CO$ ), in which it figures as a dyad. The mon-



oxide, also called *stannous oxide*, possesses a decided basic character, and only yields salts with acids—*stannous* or *stanno*-salts.

A further advance in metallic basic character is exhibited by lead, which, like tin, forms two series of compounds of the forms  $PbX_4$  and  $PbX_2$ . While, however, with tin the compounds  $SnX_4$  are more stable than those of the form  $SnX_2$ , lead affords almost exclusively compounds of the form  $PbX_2$  in which it figures as a dyad.

The tetravalence of lead shows itself almost entire in its metallo-organic compounds: as  $(Pb(CH_3)_4, Pb(C_2H_5)_4)$ —p. 239); further in lead dioxide  $PbO_2$ . The latter does not form corresponding salts with the acids, but yields up one atom of oxygen with formation of salts of the monoxide  $PbO$ . Warmed with hydrochloric acid, it liberates chlorine; hence behaves like the peroxides, and is commonly called lead peroxide (p. 256).

A distinct gradation shows itself in the series  $SiO_2, SnO_2, PbO_2$ . The stability and acidity grow less successively, yet lead dioxide preserves the acidic character and forms salts with the alkalis (as  $PbO_2K_2$ ) which are very similar to the salts of stannic acid; therefore lead dioxide  $PbO_2$  is to be regarded as the oxide of a plumbic acid  $H_2PbO_3$ .

The connection of tin and lead in one group results from the heat of formation of their compounds:—

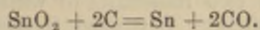
$(Sn.Cl_2) = 80.8$	$(Sn.O) = 68.0$	$(Sn.Cl_4) = 127.0$	$(Sn.O_2) = 136.0$
$Pb.Cl_2 = 82.7$	$(Pb.O) = 50.3$	$(Pb.Cl_4) = \text{—}$	$(Pb.O_2) = 74.0$

From these numbers is seen that from tin chloride (as from other acid salts), the metal is separated by lead, while conversely, from lead oxide in alkaline solution, lead is precipitated by tin (p. 259).

### 1. TIN.

Sn — 118.

In nature tin occurs principally as dioxide (Cassiterite-tin stone) in England (Cornwall), Saxony and India. To prepare the metal the oxide is roasted, lixiviated and heated in a furnace with charcoal:—



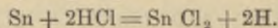
Thus obtained, it usually contains iron, arsenic and other metals; to purify it the metal is fused at a low temperature,

when the pure tin flows away, leaving the other metals. The tin obtained in the Indian isles (Malacca) is almost chemically pure, while that of England contains traces of arsenic and copper.

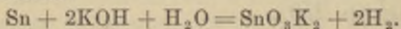
Tin is an almost silver white, strongly lustrous metal, with a specific gravity of 7.3. It possesses a crystalline structure; on bending a rod of it, a peculiar noise (tin cry) is heard, due to the friction of the crystals. Upon etching a smooth tin surface with hydrochloric acid its crystalline structure is recognized by the appearance of remarkable striations. Perfectly pure compact tin, at low temperature, passes into an aggregate of small quadratic crystals. The metal is tolerably soft and very ductile, and may be rolled out into thin leaves. At  $200^{\circ}$  it becomes brittle, and may then be fractured. It fuses at  $228^{\circ}$ , and distills at a white heat; heated in the air, it burns with an intense white light, forming tin dioxide. It does not oxidize in the air at low temperatures, and withstands the action of many bodies, hence employed in tinning copper and iron vessels for household use.

Of the alloys of tin, besides bronze and soft solder, britannia metal is remarkable. It contains 9 parts tin and 1 part antimony, and frequently, also, 2-3% tin and 1% copper.

In hot hydrochloric acid, tin dissolves to stannous chloride, with evolution of hydrogen gas:—



By somewhat dilute nitric acid, it is oxidized to metastannic acid; anhydrous nitric acid  $\text{HNO}_3$  does not change it. When boiled with potassium or sodium hydrates, it dissolves, forming stannates:—



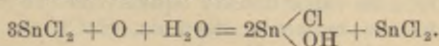
Tin forms two series of compounds; the stannous and stannic, or compounds of stannic acid (p. 356).

### 1. STANNOUS COMPOUNDS.

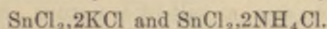
**Tin Dichloride**—*Stannous chloride*,  $\text{SnCl}_2$ —results when tin dissolves in concentrated hydrochloric acid. Upon evaporation it crystallizes with two molecules of water ( $\text{SnCl}_2 + 2\text{H}_2\text{O}$ ) which it loses at  $100^{\circ}$  C. It is used in dyeing, as a mordant, under the name of **Tin Salt**. The anhydrous chloride, obtained by heating the metal in dry hydrochloric acid gas,

fuses at  $250^{\circ}$  and distills without decomposition at a red heat. Its vapor density at  $600\text{--}700^{\circ}$  agrees with the formula  $\text{Sn}_2\text{Cl}_4$ ; at  $900^{\circ}$  with  $\text{SnCl}_2$ .

Water in part decomposes stannous chloride. Its solution is strongly reducing, and from air it absorbs oxygen with the separation of basic tin chloride:—

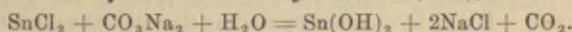


In presence of hydrochloric acid only stannic chloride is produced. From mercuric chloride solution stannous chloride precipitates mercurous chloride and metallic mercury (p. 320). It unites with chlorine to form stannic chloride, and with many chlorides to yield double salts, *e. g.*,



**Tin Monoxide**,  $\text{SnO}$ , or *Stannous Oxide*, is obtained by heating its hydrates,  $\text{SnO}_2\text{H}_2$ , in an atmosphere of carbon dioxide, and is a blackish-brown powder which burns when heated in the air, becoming stannic oxide. Sodium carbonate added to a solution of stannous chloride precipitates white

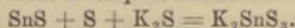
**Stannous Hydrate**—*stanno-hydrate*— $\text{Sn}(\text{OH})_2$ :—



It is insoluble in ammonium hydrate, but is readily dissolved by potassium hydrate. Upon slow evaporation of the alkaline solution dark crystals of  $\text{SnO}$  separate; on boiling the solution the hydrate decomposes into potassium stannate,  $\text{K}_2\text{SnO}_3$ , which remains dissolved, and metallic tin. By solution in acids the hydrate forms salts.

**Tin Dichloride**—*Stannous chloride*— $\text{SnCl}_2$ —and **stanno-sulphate**— $\text{SnSO}_4$ —are formed when tin is warmed with concentrated hydrochloric or sulphuric acids. The sulphate separates by the evaporation of the solution, in small, granular crystals.

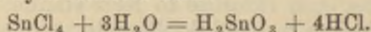
**Tin Monosulphide**—*Stannous sulphide*— $\text{SnS}$ —is precipitated from stannous solutions by hydrogen sulphide, as a dark brown amorphous precipitate. Obtained by fusing together tin and sulphur; it is a lead-gray crystalline mass. Dissolves in concentrated hydrochloric acid, with liberation of  $\text{H}_2\text{S}$  to form stannous chloride; if boiled at same time with sulphur it dissolves as a sulpho-stannate:—





## 2. STANNIC COMPOUNDS.

**Tin Tetrachloride**—*Stannic Chloride*— $\text{SnCl}_4$ —is produced by the action of chlorine upon heated tin or stannous chloride— $\text{SnCl}_2$ . It is a colorless liquid (*Spiritus fumans Libavii*), fuming strongly in moist air, of specific gravity 2.27, and boiling at  $150^\circ$ ; its vapor density equals 130 ( $H = 1$ ), corresponding to the molecular formula,  $\text{SnCl}_4 = 260$ . It attracts moisture from the air and is converted into a crystalline mass (Butter of Tin),  $\text{SnCl}_4 + 3\text{H}_2\text{O}$ , readily soluble in water. Boiling decomposes the solution into metastannic acid ( $\text{H}_2\text{SnO}_3$ ) and hydrochloric acid:—



Tin chloride possesses a salt-like nature, combining with metallic chlorides to the so-called double salts, *e. g.*,  $\text{SnCl}_4 \cdot 2\text{KCl}$  and  $\text{SnCl}_4 \cdot 2\text{NH}_4\text{Cl}$ ; the latter compound is known as *pink salt* in calico printing. With chlorides of the metalloids it also yields crystalline double salts, *e. g.*,  $\text{SnCl}_4 \cdot \text{PCl}_3$  and  $\text{SnCl}_4 \cdot 2\text{SbCl}_3$ .

**Tin Bromide**— $\text{SnBr}_4$ —forms a white, crystalline mass.

**Tin Iodide**— $\text{SnI}_4$ —orange red octahedra, fusing at  $146^\circ$  and boiling at  $295^\circ$ . It may be obtained by heating tin with iodine to  $50^\circ$ .

**Tin Fluoride**— $\text{SnF}_4$ —only known in combination with metallic fluorides (*e. g.*,  $\text{K}_2\text{SnF}_6$ ), very similar and generally isomorphous with the salts of hydrofluosilicic acid ( $\text{SiF}_6\text{K}_2$ ).

**Tin Dioxide**—*Stannic oxide*— $\text{SnO}_2$ —is found in nature, as tin stone, in quadratic crystals or thick brown masses, of specific gravity 6.8. It is prepared, artificially, by heating tin in the air, and forms then a white, amorphous powder. It may be obtained, crystallized, by conducting vapors of the tetrachloride and water through a glowing tube. The dioxide is infusible, and not soluble in acids or alkalis. Fused with sodium and potassium hydrate it yields stannates soluble in water.

On adding ammonium hydrate to the aqueous solution of tin tetrachloride or hydrochloric acid to the solution of potassium stannate ( $\text{SnO}_3\text{K}_2$ ), a white precipitate of stannic acid will separate. This dissolves readily in concentrated nitric acid, hydrochloric acid and the alkalis. Preserved under water, or in vacuo, it becomes insoluble in acids and sodium hydrate. Both modifications appear to have the same composition,  $\text{H}_2\text{SnO}_3$ , and the cause of the isomerism is not yet

explained. The insoluble modification is commonly called *metastannic acid*. It is also obtained as a white powder by warming tin with dilute nitric acid. On adding sodium hydrate to the insoluble stannic acid it is converted into sodium metastannate, insoluble in sodium hydrate, but readily dissolved by pure water. The salts of stannic oxide with acids, *e. g.*, the sulphate, are not very stable, and washing with warm water decomposes them. More stable are the metal salts of stannic acid. The most important of these is *sodium stannate*— $\text{Na}_2\text{SnO}_3$ —which is employed in calico printing, under the name of *preparing salts*. Prepared upon a large scale by fusing tin stone with sodium hydrate. On evaporating the solution, it crystallizes in large, transparent, hexagonal crystals, containing three molecules of water.

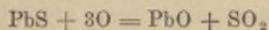
**Tin Disulphide**—*Stannic Sulphide*— $\text{SnS}_2$ —precipitated as an amorphous, yellow powder by  $\text{H}_2\text{S}$  from stannic solutions. If a mixture of tin filings, sulphur and ammonium chloride be heated, it is obtained in form of a brilliant crystalline mass, consisting of gold yellow scales. It is then called *mosaic gold*, and is applied in bronzing. The precipitated tin disulphide is dissolved by concentrated hydrochloric acid, converting it into stannic chloride; nitric acid converts it into metastannic acid. The sulphides and hydrosulphides of the alkalies dissolve tin disulphide as sulphostannates (see p. 214). Sodium sulphostannate  $\text{SnS}_2\text{Na}_2 + 2\text{H}_2\text{O}$  crystallizes in colorless octahedra. Acids decompose the sulphostannates, with the separation of tin disulphide.

---

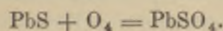
### LEAD.

Pb — 206.4.

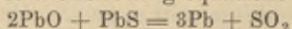
Lead (*Plumbum*) is found in nature principally as *Galenite*— $\text{PbS}$ . Of the other more widely distributed lead ores may be mentioned, *Cerussite*— $\text{PbCO}_3$ —*Crocoisite* ( $\text{PbCrO}_4$ ) and *Wulfenite* ( $\text{MoO}_4\text{Pb}$ ). For the preparation of lead, galenite is almost exclusively employed; the process of its separation is very simple. The galenite is first roasted in the air and then strongly ignited away from it. In the roasting a portion of the lead sulphide is oxidized to oxide and sulphate:—



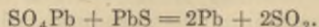
and



Upon ignition these two substances react with the lead sulphide, according to the following equations:—



and



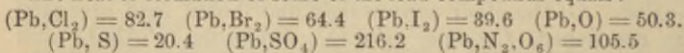
Metallic lead has a bluish white color, is very soft and tolerably ductile. Upon a freshly cut face it shows a bright lustre, but on exposure to air becomes dull by oxidation. Its specific gravity is 11.37. It fuses at  $325^\circ$  and volatilizes somewhat at a white heat. Heated in the air it burns to lead oxide.

In contact with air and water, lead oxidizes to lead hydrate,  $\text{Pb}(\text{OH})_2$ , which is somewhat soluble in water. If the water contain carbonic acid and mineral salts, if only in slight quantity, as in mineral waters, no lead goes into solution, but it is covered with an insoluble layer of lead carbonate and sulphate. (When much carbon dioxide is present the carbonate is somewhat soluble in the water.) This behavior is very important for practical purposes, as lead pipes are frequently employed in conducting water for various objects.

Sulphuric and hydrochloric acid have little effect on the metal, owing to the insolubility of its sulphate and chloride; it dissolves readily in nitric acid to nitrate. Zinc, tin and iron precipitate it, as metal, from solution; a strip of zinc immersed in a dilute lead acetate solution is covered with an arborescent mass, consisting of shining crystalline leaflets (lead tree).

**Alloys.**—An alloy of equal parts lead and tin fuses at  $186^\circ$  and is used for soldering (soft solder). An alloy of 4–5 parts of lead and 1 part of antimony is very hard and answers for the manufacture of type (hard lead or type metal).

The heat of formation of some of the lead compounds equals:—



From these numbers, calculating in the heat of solution, is explained the conduct of lead toward acids, as also the various other transpositions of its compounds (p. 259).

**Lead Oxide**— $\text{PbO}$ —is produced when lead is heated in air. After fusion it solidifies to a reddish-yellow mass, of rhombic scales (litharge). By careful roasting of lead, or by heating the hydrate or nitrate, a yellow amorphous powder,

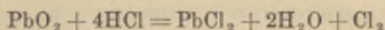


called massicot, is obtained. Lead oxide has strong basic properties; in the air it absorbs carbon dioxide and imparts an alkaline reaction to water as it dissolves as hydrate. Like other strong bases it saponifies fats. In hot potassium hydrate it dissolves, and on cooling crystallizes from solution in rhombic prisms.

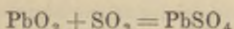
**Lead Hydrate**— $\text{Pb}(\text{OH})_2$ —is thrown down as a white, voluminous precipitate by alkalis from solutions of lead salts.

It imparts an alkaline reaction to water, as it is somewhat soluble, and absorbs carbon dioxide with formation of lead carbonate. When heated, it decomposes into lead oxide and water.

Lead, or the amorphous oxide heated to  $300\text{--}400^\circ$ , for some time, in the air, absorbs oxygen and is converted into a bright red powder, called *red lead*, or minium. Its composition most probably is expressed by the formula,  $\text{Pb}_3\text{O}_4$ ; it is considered a compound of  $\text{PbO}$  with lead peroxide, ( $\text{Pb}_3\text{O}_4 = 2\text{PbO} + \text{PbO}_2$ ). When treated with somewhat dilute nitric acid, lead nitrate is formed in solution, while a dark brown amorphous powder—*lead peroxide*  $\text{PbO}_2$ —remains. The latter warmed with hydrochloric acid yields lead chloride, and chlorine:—

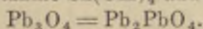


Oxygen is disengaged when sulphuric acid acts upon it, and lead sulphate ( $\text{PbSO}_4$ ) formed. When dry sulphur dioxide is conducted over it, lead sulphate, accompanied by glowing, is the result:—



When ignited  $\text{PbO}_2$  breaks up into  $\text{PbO}$  and oxygen.

As previously mentioned, lead dioxide, like that of tin, has an acid nature. When warmed with potassium hydrate, it dissolves, and on cooling, large crystals of *potassium plumbate*— $\text{K}_2\text{PbO}_3 + 3\text{H}_2\text{O}$ —separate out; these are perfectly analogous to potassium stannate— $\text{K}_2\text{SnO}_3 + 3\text{H}_2\text{O}$ . An alkaline lead oxide solution added to that of this salt produces a yellow precipitate ( $\text{Pb}_3\text{O}_4 + \text{H}_2\text{O}$ ), which loses water upon gentle warming, and is converted into *red lead*. Therefore, the latter must be considered as the lead salt of a normal plumbic acid  $\text{Pb}(\text{OH})_4$  which corresponds to stannic  $\text{Sn}(\text{OH})_4$  and silicic  $\text{Si}(\text{OH})_4$  acids:—



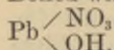
Another oxide— $\text{Pb}_2\text{O}_3$ —which is precipitated as a reddish-yellow powder, on the addition of sodium hypochlorite to an alkaline lead solution, is very probably the lead salt of metaplumbic acid:  $\text{Pb}_2\text{O}_3 =$

$\text{PbPbO}_3$ . Nitric acid decomposes it into lead nitrate and peroxide. It dissolves in hydrochloric acid without liberation of chlorine; when the solution is heated this gas escapes.

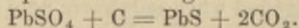
**Lead Chloride**— $\text{PbCl}_2$ —separates as a white precipitate, when hydrochloric acid is added to the solution of a lead salt. In cold water it is almost insoluble; from hot water, of which it requires 30 parts for solution, it crystallizes in white, shining needles. At a red heat it fuses to a horn-like mass.

**Lead Iodide**— $\text{PbI}_2$ —is thrown down as a yellow precipitate from lead solutions by potassium iodide; from a hot solution it crystallizes in shining, yellow hexagonal leaflets.

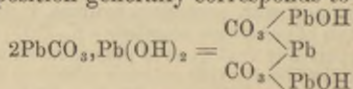
**Lead Nitrate**— $\text{Pb}(\text{NO}_3)_2$ , obtained by solution of lead in nitric acid, crystallizes in regular octahedra (isomorphous with barium nitrate) and dissolves in 8 parts water. It melts at a red heat, and is decomposed into  $\text{PbO}$ ,  $\text{NO}_2$  and oxygen. Boiled with lead oxide and water, it forms the basic nitrate



**Lead Sulphate**— $\text{PbSO}_4$ , occurs in nature as *Anglesite*, in rhombic crystals, isomorphous with barium sulphate. It is precipitated as a white, crystalline mass by sulphuric acid from lead solutions. It dissolves with difficulty in water, more readily in concentrated sulphuric acid. Ignited with carbon, it is decomposed according to the following equation:



**Lead Carbonate**— $\text{PbCO}_3$ , occurs as *Cerussite* in nature. Is precipitated by ammonium carbonate from lead nitrate solutions. Potassium and sodium carbonates precipitate basic carbonates, the composition of which varies with the temperature and concentration of the solution. A similar basic salt, which in composition generally corresponds to the formula:—



is prepared on a large scale by the action of carbon dioxide upon lead acetate. It bears the name of *white lead*.

Formerly white lead was manufactured by what is termed the Dutch process. Rolled lead sheets were moistened in earthenware pots, with acetic acid, and these covered with manure and permitted to stand undisturbed for some time. In this way, by the action of acetic acid and air upon the lead

a basic acetate is formed, which by the  $\text{CO}_2$  evolved from the decaying manure is converted into basic lead carbonate. At present it is more rationally prepared, that is, by dissolving litharge in acetic acid the basic acetate is produced, and into this carbon dioxide is passed, for the formation of the carbonate.

White lead is employed for the manufacture of white oil colors. As it is poisonous, and further blackened in air by hydrogen sulphide (formation of lead sulphide), it is at present being more and more replaced by zinc white and permanent white ( $\text{BaSO}_4$ ).

**Lead Sulphide**— $\text{PbS}$ —occurs crystallized in metallic, shining cubes and octahedra. Hydrogen sulphide precipitates it as an amorphous black powder. In dilute acids it is insoluble.

The lead compounds are very poisonous. The soluble salts have a sweetish, astringent taste. They are readily recognized by the following reactions: sulphuric acid precipitates white lead sulphate, which is blackened by hydrogen sulphide; potassium iodide precipitates yellow lead iodide.

---

## BISMUTH.

Bi = 210.

Bismuth constitutes a natural group with antimony, arsenic, phosphorus and nitrogen, and like these affords compounds of the forms  $\text{BiX}_3$  and  $\text{BiX}_5$ . We observed that with increase of atomic weight the metalloidal character of the lower members becomes more metallic (see p. 139); the acid nature of the oxides passes into a basic. Antimony oxide ( $\text{Sb}_2\text{O}_3$ ) is a base, while the higher oxide  $\text{Sb}_2\text{O}_5$  represents an acid anhydride. In bismuth the metallic nature attains its full value. This is manifest in its inability to unite with hydrogen. Bismuth trioxide is a base, and the pentoxide also possesses a but very feeble acid character, yielding with alkalies only indefinite compounds; it behaves more like a metallic peroxide, and in its properties exhibits great similarity to lead peroxide.

---

Bismuth usually occurs native and in combination with sulphur, as bismuthinite. To obtain the metal the sulphide is roasted in the air and the resulting oxide reduced with charcoal.

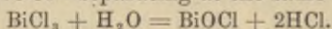
Bismuth is a reddish-white metal, of specific gravity 9.9.



It is brittle and may be easily pulverized. It crystallizes in rhombohedra. It fuses at  $267^{\circ}$  and distills at a white heat. At ordinary temperatures it does not change in the air; heated it burns to bismuth oxide— $\text{Bi}_2\text{O}_3$ . In hydrochloric acid it is insoluble; by boiling sulphuric acid it is dissolved to sulphate with evolution of sulphur dioxide. Nitric acid readily dissolves it in the cold.

Water decomposes bismuth solutions in the same manner as those of antimony; insoluble basic salts are precipitated while acid salts pass into solution.

**Bismuthous Chloride**— $\text{BiCl}_3$ —arises from the action of chlorine upon heated bismuth, and by the solution of the metal in aqua regia. It is a soft, white mass which readily fuses, sublimes and deliquesces in the air. Water renders its solution turbid, a white, crystalline precipitate of *Bismuth Oxychloride*— $\text{BiOCl}$ —separating at the same time:—



The metalloidal character of bismuth is indicated by this reaction.

The compounds  $\text{BiBr}_3$  and  $\text{BiI}_3$  are very similar to bismuth chloride. All three combine with many metallic chlorides to form double chlorides.

Halogen derivatives of pentatomic bismuth are unknown.

**Bismuth Oxide**— $\text{Bi}_2\text{O}_3$ —prepared by burning bismuth or heating the nitrate, is a yellow powder insoluble in water and the alkalis.

Normal **bismuth hydrate**— $\text{Bi}(\text{OH})_3$ —is not known in a free state. Potassium hydrate added to a bismuth solution precipitates a white, amorphous *metahydrate*— $\text{BiO.OH}$ .

Chlorine conducted through a concentrated potassium hydrate solution in which there is suspended bismuth oxide, precipitates red **bismuthic acid** ( $\text{BiO}_3\text{H}$  or  $\text{Bi}_2\text{H}_4\text{O}_7$ ), which when gently heated becomes  $\text{Bi}_2\text{O}_5$ , bismuthic oxide. Strong ignition converts the latter into  $\text{Bi}_2\text{O}_3$  and  $\text{O}_2$ ; by hydrochloric acid it is dissolved to bismuthic chloride, with liberation of chlorine.

**Bismuth Nitrate**— $\text{Bi}(\text{NO}_3)_3$ —is obtained by the solution of bismuth in nitric acid, and crystallizes with 5 molecules of  $\text{H}_2\text{O}$  in large, transparent tables. In a little water it dissolves without any change; much water renders it turbid, owing to the

precipitation of white, curdy basic salts:  $\text{Bi} \begin{Bmatrix} \text{NO}_3 \\ \text{NO}_3 \\ \text{OH} \end{Bmatrix}$  and  $\text{Bi} \begin{Bmatrix} \text{NO}_3 \\ \text{OH} \\ \text{OH} \end{Bmatrix}$ .

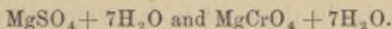
The precipitate is employed in medicine under the name of *Magisterium bismuthi*.

**Bismuth Sulphate**— $\text{Bi}_2(\text{SO}_4)_3$ —is formed when bismuth dissolves in sulphuric acid. It crystallizes in delicate needles. *Bismuth Sulphide*— $\text{Bi}_2\text{S}_3$ —occurring as bismuthinite, is thrown down as a black precipitate from bismuth solutions by hydrogen sulphide. Unlike antimony and arsenic sulphides, it does not form sulpho-salts.

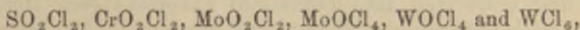
The alloys of bismuth are for the most part readily fusible. An alloy of 4 parts Bi, 1 part Cd, 1 part tin and 2 parts Pb, fuses at  $65^\circ$ . The alloy of 2 parts bismuth, 1 part lead and 1 part tin (Rose's metal) fuses at  $94^\circ$ .

### CHROMIUM GROUP.

We observed that to the metalloidal elements, carbon, silicon and tin, a group of more metallic analogous elements, titanium, zirconium and thorium, attaches itself; further, that an analogous group of metallic elements—vanadium, niobium and tantalum—corresponds to the metalloidal group of phosphorus (p. 137). In a perfectly similar relation to the elements of the sulphur group stand the metals chromium, molybdenum, tungsten, and somewhat removed, uranium (see Periodic System of the Elements). The resemblance of these elements to sulphur and its analogues is plainly manifest in their highest oxygen derivatives (see also Manganese). As the elements of the sulphur group in their highest oxygen compounds are hexatomic, so chromium, molybdenum, tungsten and uranium form acid oxides— $\text{CrO}_3$ ,  $\text{MoO}_3$ ,  $\text{WO}_3$ ,  $\text{UO}_3$ . Many of the salts corresponding to these are very similar to and isomorphous with the salts of sulphuric acid. The sodium chromate, like sodium sulphate, crystallizes with 10 molecules of water; the potassium salts of both groups form isomorphous mixtures; the magnesium salts, as also, that of tungstic acid, have the same constitution:—

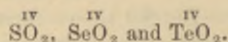


Corresponding to the acid oxides are the chlorine derivatives:—



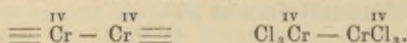
which, as regards chemical deportment, are perfectly analogous.

Besides these highest oxides the elements of the sulphur group form yet feeble acid oxides—



Of these the last approaches the bases. Their analogues in the chromium group:  $\text{CrO}_2$ ,  $\text{MoO}_2$ ,  $\text{WO}_2$  in which the elements appear tetratomic, possess an undetermined, neither acid nor basic, character.

The tetratomic nature of chromium also shows itself in the basic oxide  $\text{Cr}_2\text{O}_3$  and its corresponding salts  $\text{Cr}_2\text{X}_6$ . These contain an hexatomic group, composed of two chromium atoms:



The oxide derivatives of chromium, in their properties, are very similar to the compounds of aluminium, iron and manganese, constituted according to the same type. (See p. 341.)

Finally, for chromium we have yet compounds of the form  $\overset{\text{II}}{\text{CrX}}_2$ , in which it figures as a dyad. These so-called **Chromous** compounds are very much like the compounds of the metals of the magnesium group, especially the ferrous salts, ( $\text{FeX}_2$ ). They are very unstable, and by oxidation in the air readily pass into chromic compounds.

The salts corresponding to the lowest grades of oxidation for molybdenum and tungsten are not known, as they mostly occur as hexads. Uranium, which has the highest atomic weight of the group, shows some variations from its analogues, which, as in similar cases, are explained by its high atomic weight.

## CHROMIUM.

Cr = 52.4.

Chromium is found principally as chromite in nature. This is a combination of chromic oxide with ferrous oxide— $\text{Cr}_2\text{O}_3\text{FeO}$ —and occurs in North America, Sweden, Hungary, and particularly in the Ural in large quantities. Rarer is Crocoisite— $\text{PbCrO}_4$ . Chromic iron is almost exclusively used for the preparation of all other chromium derivatives, in that it is first converted into potassium chromate (see this) by fusion with potassium carbonate and nitrate.

Metallic chromium may be isolated by very strong ignition



of the oxide with charcoal. It is more conveniently obtained by igniting a mixture of chromium chloride, potassium chloride and sodium chloride with zinc, in a closed crucible. The separated chromium dissolves in the molten zinc, and when the latter is dissolved in nitric acid it remains behind as a gray, metallic, crystalline powder, of specific gravity 6.8. It is very hard (cuts glass), and extremely difficultly fusible. Heated in the air it slowly oxidizes to chromic oxide; ignited in oxygen it burns with a bright light. In hydrochloric and warm dilute sulphuric acid it dissolves readily, with elimination of hydrogen; it is not altered by nitric acid.

Chromium forms three series of compounds: chromous— $\text{CrX}_2$ , chromic— $\text{Cr}_2\text{X}_6$ , and the derivatives of chromic acid called *chromates*. All chromium compounds are brightly colored, hence, too, the name chromium (from  $\chi\rho\omega\mu\alpha$ , color).

#### CHROMOUS COMPOUNDS.

These are very unstable, and by oxidation readily pass into *ic* compounds. Like ferrous salts they are produced by the reduction of the higher oxides. The following may be mentioned:—Chromous Chloride  $\text{CrCl}_2$ . This is obtained by heating chromic chloride  $\text{Cr}_2\text{Cl}_6$  in a stream of hydrogen. It is a white crystalline powder, dissolving in water with a blue color; the solution attracts oxygen with avidity and becomes green colored. The alkalis precipitate brown chromous hydrate,  $\text{Cr}(\text{OH})_2$ , from it. This is oxidized by the oxygen of the water to  $\text{Cr}_3\text{O}_4$  ( $\text{Cr}_2\text{O}_3\text{CrO}$ ), corresponding to magnetic iron  $\text{Fe}_3\text{O}_4$ .

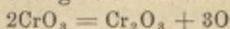
#### CHROMIC COMPOUNDS.

**Chromic Chloride.**— $\text{Cr}_2\text{Cl}_6$ , like  $\text{Al}_2\text{Cl}_6$  is obtained by ignition of the oxide and charcoal in a chlorine stream. At a red heat, in the latter it sublimes in shining violet leaflets, which, heated in the air, are transformed into chromic oxide. Pure chromic chloride only dissolves in water after very long continued boiling; if, however, it contains traces of  $\text{CrCl}_2$ , it dissolves readily at ordinary temperatures. From the green solution on evaporation—green crystals of  $\text{Cr}_2\text{Cl}_6 + 12\text{H}_2\text{O}$  separate—which deliquesce in the air. These crystals are obtained from solutions of chromic hydrate  $\text{Cr}_2(\text{OH})_6$  in hydrochloric acid. When they are dried intermediate oxychlorides  $\text{Cr}_2\text{Cl}_4(\text{OH})_2$  and  $\text{Cr}_2\text{Cl}_2(\text{OH})_4$ , and at last  $\text{Cr}_2(\text{OH})_6$  result.

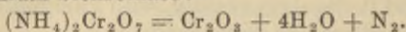
**Chromic Hydrate**— $\text{Cr}_2(\text{OH})_6$ . The alkalis throw it down from chromic solutions as a voluminous, grayish blue, hygroscopic

precipitate. It dissolves readily in potassium and sodium hydrates, with an emerald green color. In an excess of ammonium hydrate in the cold, it dissolves with a beautiful purple color. When the solution is boiled, chromic hydrate is again precipitated. Upon ignition it becomes chromic oxide.

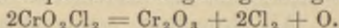
**Chromic Oxide**— $\text{Cr}_2\text{O}_3$ —is a green, amorphous powder. It is formed also by the ignition of chromium trioxide:—



or of ammonium bichromate:—

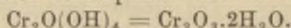


It is obtained in black, hexagonal crystals, if the vapors of the oxychloride be passed through a glowing tube:—



Ignited chromic oxide is insoluble in acids. Fused with silicates, it colors them emerald green, and serves, therefore, to color glass and porcelain.

A particularly beautiful green-colored hydrate, finding use as a color, under the name of *Guignet's Green* is obtained by glowing a mixture of one part potassium bichromate with three parts boric acid; extracting the mass with water, whereby potassium borate dissolves, there remains a green powder, the composition of which corresponds with the formula:—



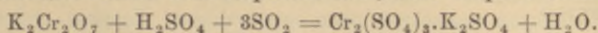
**Chromium Sulphate**— $\text{Cr}_2(\text{SO}_4)_3$ —is obtained by dissolving the oxide in sulphuric acid, and upon slow evaporation it crystallizes with 12 molecules of  $\text{H}_2\text{O}$ , in violet blue octahedra, which dissolve in water with a beautiful violet color. On warming the liquid its color changes to green, and upon evaporation an amorphous green mass is obtained, the green solution of which, upon protracted standing, becomes violet, and violet blue crystals of sulphate again separate. From the violet solution alcohol precipitates the violet salt crystalline, while in the green liquid no precipitation occurs. Therefore chromium sulphate exists in two modifications, the *violet crystalline* and the *green amorphous*.

Similarly, the other chromium compounds,  $\text{Cr}_2\text{Cl}_6$ ,  $\text{Cr}_2(\text{NO}_3)_6$ , soluble in water, exist in two different modifications.

With the alkaline sulphates, chromium sulphate forms double salts—the chromium alums (p. 342).

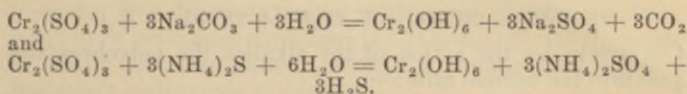
**Potassium Chromium Alum**— $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 + 24\text{H}_2\text{O}$ —crystallizes in large, dark violet octahedra. It may be most

conveniently made by acting upon a solution of potassium bichromate mixed with sulphuric acid, with sulphur dioxide:



At  $80^\circ$  the violet solution of the salt becomes green, and on evaporation affords an amorphous green mass.

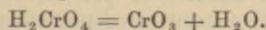
As chromium hydrate has only a feeble basic nature salts with weak acids, like  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$  (see Aluminium, p. 347) do not exist. Therefore the alkaline carbonates and sulphides precipitate chromium hydrate from solutions of chromium salts:—



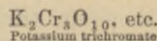
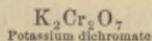
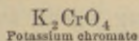
Ammonium sulphide produces a black precipitate— $\text{CrS}$ —in solutions of chromous salts.

#### DERIVATIVES OF CHROMIC ACID.

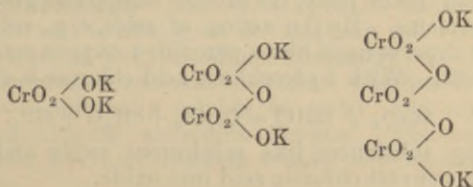
In its highest oxygen derivative,  $\text{CrO}_3$ , chromium possesses a complete metalloidal, acid-forming character. Chromic acid  $\text{H}_2\text{CrO}_4$  is perfectly analogous to sulphuric acid  $\text{H}_2\text{SO}_4$ , but has not been obtained free, as upon liberation from its salts it at once breaks up into the oxide and water:—



The chromates are often isomorphous with the sulphates (p. 367). Polychromates also exist, and are derived from polychromic acids, formed by the condensation of several molecules of the normal acid (see disulphuric acid, p. 186):—

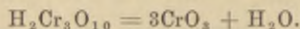


The constitution of these salts is expressed by the following formulas:—



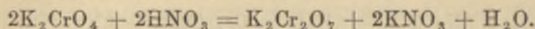


The free polychromic acids are not known as separated from their salts, they immediately break up into the acid oxide and water:—

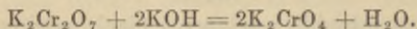


Frequently, but incorrectly, the polychromates are called acid salts; true acid or primary salts, in which only one H atom is replaced by metal, are unknown for chromic acid.

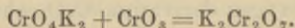
The salts of normal chromic acid are mostly yellow colored, while the polychromates are red. The latter are formed from the former by the action of acids:—



Conversely, by the action of the alkalies, the polychromates pass into the normal salts:—

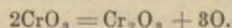


Their formation may also be as follows: The chromic acid liberated from its salts by stronger acids breaks up into water and the acid oxide, which combines with the excess of the normal chromate:—

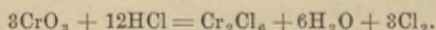


When there is an excess of acid free oxide is formed.

**Chromium Trioxide**—*Chromic acid*— $\text{CrO}_3$ . It consists of long, red, rhombic needles or prisms, obtained by adding sulphuric acid to the concentrated potassium dichromate solution. The crystals deliquesce in the air and are readily soluble in water. When heated, they blacken, and at about  $250^\circ$  decompose into chromic oxide and oxygen:—



Chromium trioxide is a powerful oxidizing agent, and destroys organic matter; hence its solution cannot be filtered through paper. When alcohol is poured on the crystals, detonation takes place, the alcohol burns, and green chromic oxide remains. By the action of acids, *e. g.*, sulphuric, the trioxide deports itself like a peroxide; oxygen escapes and a salt results. With hydrochloric acid chlorine is evolved:—



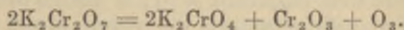
Reducing substances, like sulphurous oxide and hydrogen sulphide, convert chromic acid into oxide.

**Chromate of Potassium**— $K_2CrO_4$ —is obtained by adding potassium hydrate to potassium dichromate. It forms yellow, rhombic crystals, isomorphous with potassium sulphate ( $K_2SO_4$ ); from the solution of both salts isomorphous mixtures crystallize out.

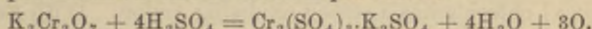
**Bichromate of Potassium**— $K_2Cr_2O_7$ —called acid potassium chromate, is manufactured on a large scale, and in commerce bears the name *red chromate of potash*. It is obtained by igniting pulverized chromite,  $Cr_2O_3FeO$ , with potashes and nitre, whereby potassium chromate and ferric oxide are formed. The fusion is treated with water, and the resulting solution of potassium chromate,  $K_2CrO_4$ , mixed with the acetic or nitric acid (see above); from the concentrated solution potassium bichromate crystallizes.

This method in practice is advantageously replaced by the following: the pulverized chromite is ignited, together with lime, in furnaces allowing air access. Calcium chromate ( $CaCrO_4$ ) (together with ferric oxide) is produced. This dissolves in sulphuric acid to dichromate  $CaCr_2O_7$ ; the latter is converted by potassium carbonate into potassium bichromate.

Bichromate of potassium crystallizes in large, red, triclinic prisms, soluble at ordinary temperatures in 10 parts of water. When heated the salt fuses without change; at higher heat it decomposes into potassium chromate, chromic oxide and oxygen:—



When the salt is warmed with sulphuric acid, oxygen escapes and potassium chromium alum is produced:—



This reaction answers for the preparation of perfectly pure oxygen. Further, the mixture is made use of in laboratories, as an oxidizing agent.

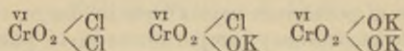
**Chromate of Sodium**— $Na_2CrO_4 + 10H_2O$ —forms deliquescent crystals, and is analogous to Glauber's salt ( $Na_2SO_4 + 10H_2O$ ). **Barium** and **Strontium Chromates**— $BaCrO_4$  and  $SrCrO_4$ —are almost insoluble in water. **Calcium Chromate**— $CaCrO_4$ —is difficultly soluble in water, and crystallizes like gypsum, with two molecules of water. The magnesium salt,  $MgCrO_4 + 7H_2O$ , dissolves readily and corresponds to Epsom salt.

The chromates of the heavy metals are insoluble in water, and are obtained by transposition.

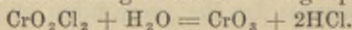
**Chromate of Lead**— $\text{PbCrO}_4$ —is obtained by the precipitation of soluble lead salts with potassium chromate. It is a yellow, amorphous powder, which serves as a yellow paint. When heated it fuses and decomposes, with liberation of oxygen. It is employed in the analysis of carbon compounds. In nature lead chromate exists as crocoisite.

The oxide  $\text{CrO}_2$ , called peroxide, which, among others, is obtained by the careful ignition of chromium trioxide, is, most likely, a salt-like compound:  $\text{Cr}_2\text{O}_3\text{CrO}_3$  or  $\text{CrO}\cdot\text{CrO}_3$ . Its hydrate is precipitated from chromium solutions upon the addition of potassium chromate. On warming the peroxide with hydrochloric acid, chlorine is evolved.

**Chromic Acid Chloranhydrides.** This acid forms chloranhydrides similar to those of sulphuric acid (p. 187). Corresponding to  $\text{SO}_2\text{Cl}_2$ , we have chromyl chloride  $\text{CrO}_2\text{Cl}_2$ ; and for the first sulphuric acid chloranhydride,  $\text{SO}_2 \left\{ \begin{array}{l} \text{Cl} \\ \text{OH} \end{array} \right.$  is the salt  $\text{CrO}_2 \left\{ \begin{array}{l} \text{Cl} \\ \text{OK} \end{array} \right.$ :



**Chromyl Chloride**— $\text{CrO}_2\text{Cl}_2$ —Chromium oxychloride is produced by heating a mixture of potassium bichromate and sodium chloride with sulphuric acid; it distills over as a dark red liquid, of specific gravity 1.92, which fumes strongly in the air. Boils at  $118^\circ$ ; the vapor density equals 77.7 ( $\text{H} = 1$ ), corresponding to the molecular formula  $\text{CrO}_2\text{Cl}_2 = 155$ . Chromyl chloride has a strong oxidizing action. With water it is decomposed according to the following equation:—



If potassium dichromate be heated with concentrated hydrochloric acid, there crystallizes from the cold solution the salt  $\text{CrO}_2 \left\langle \begin{array}{l} \text{Cl} \\ \text{OK} \end{array} \right.$  called *potassium chlorochromate*. Heated to  $100^\circ$ , it gives up chlorine. By water it is decomposed into potassium chloride and chromium trioxide.

The chromium compounds can readily be recognized by their color. The following reaction is very characteristic for chromic acid. On adding to a solution of chromium trioxide



or the acidified solution of a chromate, some hydrogen peroxide, the red liquid is colored blue. The nature of the compound causing this coloration is not known; usually it is assumed to be a higher oxide of chromium. On shaking the blue solution with ether, the latter withdraws the blue compound, and is, in consequence, beautifully colored. The ethereal solution is somewhat more stable than the aqueous. Both, gradually, are decolorized, with liberation of oxygen.

### MOLYBDENUM.

Mo — 95.8.

Molybdenum occurs rather rarely in nature; usually as molybdenite ( $\text{MoS}_2$ ) and wulfenite ( $\text{MoO}_4\text{Pb}$ ). Free molybdenum is obtained as a silver white metal, of specific gravity 8.6, by igniting the chlorides or oxides in a stream of hydrogen. It is very hard, and fuses at a higher temperature than platinum. Heated in the air it oxidizes to molybdenum trioxide. It is soluble in concentrated sulphuric and nitric acids. By the latter it is also converted into insoluble  $\text{MoO}_3$ .

Like chromium, molybdenum forms compounds of the forms  $\text{MoX}_2$ ,  $\text{MoX}_4$  and  $\text{MoX}_6$ ; besides which, also, are known derivatives in which it appears to act as a *pentad* and also a *triad*.

**Molybdenum Dichloride**— $\text{MoCl}_2$ —resulting from the trichloride  $\text{MoCl}_3$ , when heated in a stream of carbon dioxide (together with  $\text{MoCl}_4$ ) is a bright yellow, non-volatile powder. By potassium hydrate it is converted into the hydrate  $\text{Mo}(\text{OH})_2$ , a black powder.

**Molybdenum Trichloride**— $\text{MoCl}_3$  or  $\text{Mo}_2\text{Cl}_6$ —produced by gentle heating (at  $250^\circ$ ) of  $\text{MoCl}_5$  in a current of H or  $\text{CO}_2$ . A reddish-brown powder which, upon strong ignition, yields a dark blue vapor. Soluble in concentrated sulphuric acid, with beautiful blue color. By potassium hydrate it is converted into the hydrate  $\text{Mo}(\text{OH})_3$  or  $\text{Mo}_2(\text{OH})_6$ , which forms salts with acids. Upon glowing the hydrate there results the black oxide  $\text{Mo}_2\text{O}_3$ . Strong heating of the trichloride in a current of  $\text{CO}_2$  leaves  $\text{MoCl}_2$  and it sublimes.

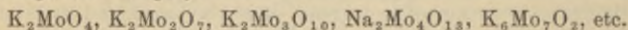
**Molybdenum Tetrachloride**— $\text{MoCl}_4$ —a brown, crystalline powder, which appears by evaporation to break up into  $\text{MoCl}_5$  and  $\text{MoCl}_3$ . With ammonium hydrate it yields a hydrate, forming salts with acids. The brown solution of the salts readily assumes a blue color by oxidation in the air. The ignition of the hydrate leaves the dioxide  $\text{MoO}_2$ , which is converted by nitric acid into the trioxide  $\text{MoO}_3$ . Molybdenum disulphide,  $\text{MoS}_2$ , is got by ignition of the trisulphide  $\text{MoS}_3$  away from air as a shining black powder, which occurs native as *molybdenite*, in hexagonal crystals, with a specific gravity of 4.5.

**Molybdenum Pentachloride**— $\text{MoCl}_5$ —is prepared by heating  $\text{MoS}_2$ , or molybdenum in chlorine gas. It is a metallic, shining, black, crystalline mass, fusing at  $194^\circ$  and distilling at  $268^\circ$ ; the vapor density

equals 136.5, corresponding to the molecular formula  $\text{MoCl}_5 = 273$ . It fumes and deliquesces in the air, and dissolves with brown color in water, with hissing. Soluble in alcohol and ether with a dark green color.

The hexachloride  $\text{MoCl}_6$  is not known, but the oxychlorides  $\text{MoOCl}_4$  and  $\text{MoO}_2\text{Cl}_2$  are. The first results from the ignition of  $\text{MoO}_2$  and carbon in a stream of chlorine, and is a green crystalline mass subliming under  $100^\circ$  and yielding a dark red vapor. Bromine forms perfectly analogous compounds with molybdenum.

**Molybdenum Trioxide**— $\text{MoO}_3$ —results by roasting metallic molybdenum or the sulphide in the air. It is a white, amorphous mass, which turns yellow on heating; it fuses at a red heat and then sublimes. It is insoluble in water and acids; but dissolves readily in the alkalis and ammonium hydrate. When fused with the alkaline hydrates or carbonates salts are produced which are partly derived from the normal acid,  $\text{H}_2\text{MoO}_4$ , and partly from the polyacids, and correspond to the polychromates:—



The ammonium salt— $(\text{NH}_4)_2\text{MoO}_4$ —is obtained by dissolving the trioxide in concentrated ammonium hydrate. In the laboratory it serves as a reagent for phosphoric acid. Alcohol causes it to separate out of its solution in crystals; upon evaporation, however, the salt  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} + 4\text{H}_2\text{O}$  crystallizes out. Both salts are decomposed by heat, leaving molybdenum trioxide.

Hydrochloric acid added to a concentrated solution of a molybdate causes the precipitation of molybdic acid— $\text{H}_2\text{MoO}_4$ . It is a white, crystalline compound, readily dissolved by an excess of acid. Zinc added to this solution causes it to become blue and then green, in consequence of the formation of lower oxides (like  $\text{Mo}_3\text{O}_8 = 2\text{MoO}_3, \text{MoO}_2$ ).

Molybdic acid can also form polyacids with phosphoric and arsenic acids, *e. g.*,  $\text{H}_3\text{PO}_4, 10\text{MoO}_3$ . These complex phosphomolybdic acids are distinguished by the fact that they form insoluble salts with the metals of the potassium group, with ammonia and with organic bases in dilute acids. On adding to the nitric acid solution of ammonium molybdate a solution containing phosphoric (or arsenic) acid, there is produced a yellow crystalline precipitate of ammonium phospho-molybdate— $(\text{NH}_4)_3\text{PO}_4, 10\text{MoO}_3 + 1\frac{1}{2}\text{H}_2\text{O}$ . This reaction serves for the detection and separation of phosphoric acid.

**Molybdenum Trisulphide**— $\text{MoS}_3$ —is thrown down as a brown precipitate from acidulated molybdenum solutions by hydrogen sulphide. It dissolves in alkaline sulphides forming sulpho-salts. Ignited away from air it is converted into molybdenum disulphide,  $\text{MoS}_2$ , which occurs native as molybdenite.

## 3. TUNGSTEN.

W = 184.

Tungsten is found in nature in the tungstates: as wolframite,  $\text{FeWO}_4$ , as scheelite,  $\text{CaWO}_4$ , and as stolzite,  $\text{PbWO}_4$ .

The metal is obtained, like molybdenum, by the ignition of the oxides in a stream of hydrogen. It has a grayish-yellow color, is very hard and difficultly fusible; specific gravity 16.6. It becomes trioxide when ignited in the air.

Wolfram forms the following chlorides  $\text{WCl}_2$ ,  $\text{WCl}_4$ ,  $\text{WCl}_5$  and  $\text{WCl}_6$ .

The **Dichloride**— $\text{WCl}_2$ —arises by strong ignition of  $\text{WCl}_6$  and  $\text{WCl}_4$  in a  $\text{CO}_2$  stream, and forms a bright gray, non-volatile mass, that yields the brown oxide,  $\text{WO}_2$ , with water.

The **Tetrachloride**— $\text{WCl}_4$ —obtained by gentle ignition of  $\text{WCl}_6$  and  $\text{WCl}_5$ , in an H or  $\text{CO}_2$  stream, is grayish-brown and upon sublimation decomposes into  $\text{WCl}_2$  and volatile  $\text{WCl}_5$ . With water it forms a brown oxide.

The **Pentachloride**— $\text{WCl}_5$ —is formed by the distillation of  $\text{WCl}_6$  in an H or  $\text{CO}_2$  stream, and forms shining, black, needle-like crystals. It fuses at  $248^\circ$  and boils at  $275^\circ$ , forming a dark brown vapor, with the vapor density 180.4 ( $\text{WCl}_5 = 360.8$ ). With water it gives an olive green solution and a blue oxide,  $\text{W}_2\text{O}_5$ ; in carbon disulphide it dissolves with a deep blue color.

**Tungsten Hexachloride**— $\text{WCl}_6$ —arises when heating the metal or a mixture of wolframite with carbon in a current of chlorine. It forms a dark violet, crystalline mass, fusing at  $245^\circ$  and boiling at  $346^\circ$ . The vapor density equals 198 ( $\text{WCl}_6 = 396.4$ ). In  $\text{CS}_2$  it dissolves with a reddish-brown color; with water it forms  $\text{WO}_3$ .

The **Oxychloride**— $\text{WCl}_4\text{O}$ —consists of red crystals, fusing at  $210^\circ$  and boiling at  $227^\circ$ ; its vapor density equals 170 ( $\text{WCl}_4\text{O} = 341.6$ ). The **Dioxychloride**— $\text{WCl}_2\text{O}_2$ —sublimes in bright yellow, shining leaflets.

**Tungsten Trioxide**— $\text{WO}_3$ —is thrown out of the hot solution of tungstates by nitric acid, as a yellow precipitate, insoluble in acids, but dissolving readily in potassium and sodium hydrates. From the cold solution, however, tungstic acid,  $\text{WO}(\text{OH})_2$ , is precipitated, which on standing over sulphuric acid becomes,  $\text{WO}_2(\text{OH})_2$  and at  $100^\circ$  passes into di-tungstic acid,  $\text{W}_2\text{O}_7\text{H}_2 = \text{W}_2\text{O}_5(\text{OH})_2$ .

The salts of tungstic acid are perfectly analogous to the molybdates and are derived from the normal acid or the polyacids. The normal sodium salt,  $\text{Na}_2\text{WO}_4 + 2\text{H}_2\text{O}$ , and the so-called meta-tungstate of sodium,  $\text{Na}_2\text{W}_4\text{O}_{13} + 10\text{H}_2\text{O}$ , are practically applied. Materials saturated with their solutions do not fall into a flame, but smoulder away slowly.

Like molybdic acid, it combines with phosphoric and arsenic acids.

The metal is used in the manufacture of tungsten steel; a slight quantity of it increases the hardness of the latter very considerably.



## 4. URANIUM.

U = 240.

In nature it occurs chiefly as uraninite, a compound of uranic and uranous oxides— $\text{UO}_2$ ,  $2\text{UO}_3 = \text{U}_3\text{O}_8$ .

The metal is obtained by heating uranous chloride with sodium. It has a steel-gray color and a specific gravity of 18.3. When heated in the air it burns to uranous-uranic oxide. There are two series of uranium compounds. In the one, the metal is a tetrad.  $\text{UX}_4$ ; these uranous or urano compounds are very unstable, and readily pass into the uranic or derivatives of hexatomic uranium. Uranous oxide is of a basic nature, and only forms salts with acids.

The compounds of hexatomic uranium are called the uranic compounds.  $\text{UO}_3$  and  $\text{UO}_2(\text{OH})_2$  have a predominant basic character, and are called *uranates*, but are also capable of forming salts with bases. In the salts formed from acids like  $\text{UO}_2(\text{NO}_3)_2$  and  $\text{UO}_2\text{SO}_4$  the group  $\text{UO}_2$  plays the rôle of a metal; it is called *uranyl*, and its salts are termed *uranyl salts*. They may also be regarded as basic salts.

## URANOUS COMPOUNDS.

**Uranous Chloride**— $\text{UCl}_4$ —is obtained by heating metallic uranium in a stream of chlorine, or uranous oxide in hydrochloric acid. It forms metallic, shining, dark green octahedra. In the air it deliquesces, and dissolves in water with hissing. On evaporation of the solution, uranous hydrate remains.

**Uranous Oxide**— $\text{UO}_2$ —is formed when the other oxides are heated in a current of hydrogen. It is a black powder, which, when heated in the air, becomes uranous-uranic oxide  $\text{UO}_2\cdot 2\text{UO}_3$ .

Uranous oxide dissolves with a green color in hydrochloric and concentrated sulphuric acids. Uranous sulphate,  $\text{U}(\text{SO}_4)_2 + 8\text{H}_2\text{O}$ , consists of green crystals. From the salts the alkalis precipitate a brown powder  $\text{U}(\text{OH})_4$ .

## HEXATOMIC URANIUM COMPOUNDS.

**Uranium Hexachloride**— $\text{UCl}_6$ —could not be obtained, but the oxychloride  $\text{UO}_2\text{Cl}_2$  (Uranyl chloride) exists—a yellow crystalline mass, deliquescing in the air—and is obtained by heating  $\text{UO}_2$  in dry chlorine gas.

**Uranic Oxide**  $\text{UO}_3$  or **Uranyl oxide**—is a yellow powder, and is obtained by heating uranyl nitrate to  $250^\circ$ . Warmed with nitric acid it becomes *uranylhydrate* or *uranic acid*,  $\text{UO}_2(\text{OH})_2$ , which is also yellow colored.

**Uranyl nitrate**— $\text{UO}_2(\text{NO}_3)_2$ —results from the solution of uranous or uranic oxide, or more simply of uraninite in nitric acid. It crystallizes with six molecules of water, in large, greenish-yellow prisms, which are readily soluble in water and alcohol. On adding

sulphuric acid to the solution, there crystallizes, on evaporation, **Uranyl sulphate**— $\text{UO}_2\text{SO}_4 + 6\text{H}_2\text{O}$ —in lemon yellow needles.

If sodium or potassium hydrate be added to the solutions of uranyl salts, yellow precipitates of the *uranates*— $\text{U}_2\text{O}_7\text{K}_2$  and  $\text{U}_2\text{O}_7\text{Na}_2$  are obtained. These are soluble in acids. In commerce the sodium salt is known as uranium yellow, and is employed for the yellow coloration of glass (uranium glass) and porcelain.

The so-called uranic-uranous oxide, which constitutes uraninite, and is formed by the ignition of the other oxides in the air, must be viewed as uranous uranate— $2\text{UO}_3 \cdot \text{UO}_2 = (\text{UO}_2, \text{O}_2)_2 \overset{\text{IV}}{\text{U}}$ .

Many uranium salts exhibit magnificent fluorescence. The oxide colors glass fluxes a beautiful greenish yellow (uranium glass). Uranous oxide— $\text{UO}_2$ —imparts a beautiful black color to glass and porcelain.

Besides these compounds, in which it appears tetratomic and hexatomic, uranium forms, like molybdenum and tungsten, also a pentachloride  $\text{UCl}_5$ . The same results by leading chlorine gas over a moderately heated mixture of carbon with one of the uranium oxides, and forms dark needles, which, in direct light, are metallic green, but in transmitted, ruby red. In the air it deliquesces to a yellowish green liquid; upon heating it is dissociated into  $\text{UCl}_4$  and  $\text{Cl}$  (at  $120^\circ$ – $235^\circ$ ).

There is also a tetroxide,  $\text{UO}_4$ , which, like the trioxide,  $\text{UO}_3$ , forms salts with the bases.

## MANGANESE.

Mn = 54.8.

In proportion to its atomic weight, manganese stands in the same relation to the elements of the chlorine group as chromium to the elements of the sulphur group. The relationship manifests itself distinctly in the higher states of oxidation. Permanganic oxide,  $\text{Mn}_2\text{O}_7$ , and acid,  $\text{HMnO}_4$ , are perfectly analogous to  $\text{Cl}_2\text{O}_7$  (or  $\text{I}_2\text{O}_7$ ) and  $\text{HClO}_4$ . The permanganates and the perchlorates are very similar, and for the most part isomorphous. In them manganese, like the halogens in their highest state of oxidation, appears as a heptad. To this, however, is limited the similarity of manganese with the halogens. In its remaining compounds it shows great resemblance to the elements standing in the same horizontal series of the periodic system, viz., with iron and chromium (p. 341). Like these two elements it forms three series of compounds.

1. In the manganous derivatives— $\text{MnX}_2$ —the metal is diatomic. These salts are the more stable, and comprise the

most common manganese compounds. They are very much alike, and usually isomorphous with the *ous* salts of iron and chromium, and the salts of metals of the magnesium group.

2. The manganic compounds— $Mn_2X_6$ —are similar to and isomorphous with the ferric, chromic and aluminium derivatives; however, they are less stable, and easily reduced to the manganous state. Their composition is due to the tetratomic nature of manganese (p. 368).

3. The derivatives of manganic acid— $H_2MnO_4 = MnO_2(OH)_2$  in which manganese is hexatomic, are analogous to those of ferric ( $H_2FeO_4$ ) and chromic ( $H_2CrO_4$ ), also, of course, to those of sulphuric acid ( $H_2SO_4$ ).

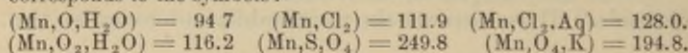
Consequently, in manganese we plainly observe how the similarity of the elements in their compounds is influenced by the valence (see p. 324). In its *ous* condition manganese, like the elements of the magnesium group, has a rather strong basic character, which in the *ic* state diminishes considerably. Hexatomic manganese has a metalloidal, acidic character, and manganic acid approaches sulphur. By further increase of oxygen manganese finally (in permanganic acid) acquires the metalloid character of the halogens. A similar behavior, as we have already noticed, is shown by many other metals, especially chromium and iron.

On the other hand, by addition of hydrogen or hydrocarbon groups ( $CH_3 \cdot C_2H_5$ ), the metalloids and the weak basic metals acquire a strong basic, alkaline character. The groups,  $NH_4$  (ammonium),  $P(CH_3)_4$  (tetramethylphosphonium),  $S(C_2H_5)_3$  (triethylsulphine),  $Sn(C_2H_5)_3$  (tin triethyl), etc., are of metallic nature, because their hydrates,  $P(CH_3)_4 \cdot OH$ ,  $S(C_2H_5)_3 \cdot OH$ ,  $Sn(C_2H_5)_3 \cdot OH$ , are perfectly similar to the alkaline hydrates ( $KOH, NaOH$ ).

Manganese is widely distributed in nature. Native, it is found in meteorites. Its most important ores are pyrolusite,  $MnO_2$ , hausmannite,  $Mn_3O_4$ , braunite,  $Mn_2O_3$ , manganite,  $Mn_2O_3 \cdot H_2O$ , and rhodochrosite,  $MnCO_3$ .

Metallic manganese is obtained by igniting the oxides with charcoal. It has a grayish-white color, is very hard, and difficultly fusible; specific gravity 7.2. In moist air it oxidizes readily. It decomposes water on boiling, and when dissolved in acids forms manganous salts.

The heat of formation of the most important manganese compounds corresponds to the symbols:—





## MANGANOUS COMPOUNDS.

**Manganous Oxide**— $MnO$ —results from ignition of the carbonate, with exclusion of air, and by heating all manganese oxides in hydrogen. It is a greenish, amorphous powder, which, in the air, readily oxidizes to  $Mn_3O_4$ .

**Manganous Hydrate**— $Mn(OH)_2$ —is a voluminous, reddish-white precipitate, formed by the alkalis in manganous solutions. Exposed to the air, it oxidizes to manganic hydrate  $Mn_2(OH)_6$ .

Manganous salts mostly have a pale, reddish color, and are formed by the solution of manganese or manganic oxides in acids.

**Manganous Chloride**— $MnCl_2$ —crystallizes with four molecules of water in reddish tables. On drying, it is decomposed with separation of hydrochloric acid. Anhydrous manganous chloride is made by heating the double salt  $MnCl_2 \cdot 2NH_4Cl + H_2O$  (see Magnesium chloride) or by heating manganese oxides in hydrochloric acid; it is a crystalline, reddish mass, which deliquesces in the air.

**Manganous Sulphate**— $MnSO_4$ —crystallizes below  $+6^\circ$  with 7 molecules of  $H_2O$  (like magnesium and ferrous sulphates), at ordinary temperatures with  $5H_2O$  (like copper sulphate); the last molecule of water does not escape until  $200^\circ$ . It forms double salts with the alkaline sulphates, *e. g.*,  $MnSO_4 \cdot K_2SO_4 + 5H_2O$ .

**Manganous Carbonate**— $MnCO_3$ —exists in nature as rhodochrosite, and is precipitated by alkaline carbonates from manganous solutions, as a white powder, which, on exposure turns brown.

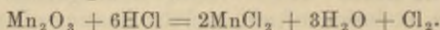
**Manganous Sulphide**— $MnS$ —is found in nature as alabandite or manganese blende. Alkaline sulphides precipitate a flesh-colored sulphide from manganese solutions. In the air it becomes brown.

## MANGANIC SALTS.

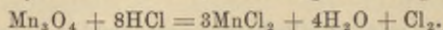
**Manganic Oxide**— $Mn_2O_3$ —is a black powder produced by the ignition of the manganese oxides in a current of oxygen gas.

**Manganic Hydrate**— $Mn_2(OH)_6$ —is precipitated as a blackish-brown powder, from manganic solutions, by ammonium

hydrate. Warmed with hydrochloric acid the oxide and hydrate yield manganous chloride with evolution of chlorine :



**Manganous-manganic Oxide**— $\text{Mn}_3\text{O}_4 = \text{MnO}, \text{Mn}_2\text{O}_3$ . It constitutes the mineral *hausmannite* crystallized in dark brown quadratic octahedra, and is formed by the ignition of all oxides in the air; it is isomorphous with magnetite,  $\text{Fe}_3\text{O}_4$ . It reacts with hydrochloric acid, according to the equation :—

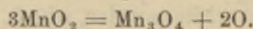


Manganic oxide, like the other sesquioxides, is only a very feeble base; its salts are very unstable, and with separation of oxygen readily become manganous salts.

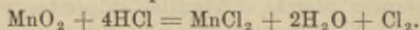
**Manganic Sulphate**— $\text{Mn}_2(\text{SO}_4)_3$ —is a dark green powder. It is produced when concentrated sulphuric acid is poured over hydrated manganic peroxide. It deliquesces in the air and dissolves in cold water with a dark red color. It forms *alums* with potassium and ammonium sulphates—*e. g.*,  $\text{Mn}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 + 24\text{H}_2\text{O}$ .

When the solutions are heated both salts decompose and yield up oxygen.

**Manganese Dioxide**— $\text{MnO}_2$ —peroxide. This is the mineral *pyrolusite* occurring in dark-gray radiating masses, or in almost black rhombic prisms, which possess metallic lustre. When gently heated it is converted into oxide, by strong glowing, into manganous-manganic oxide :—



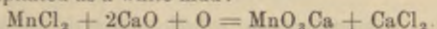
It is used for making oxygen. When warmed with hydrochloric acid chlorine escapes :—



Artificially the dioxide may be obtained in the form of hydrates— $\text{MnO}_2 \cdot \text{H}_2\text{O}, \text{MnO}_2 \cdot 2\text{H}_2\text{O}$ —if a hypochlorite be added to the solution of the manganese salt, or if chlorine be conducted through a solution of manganese containing sodium carbonate. In cold hydrochloric acid the precipitated dioxide dissolves without liberating chlorine, as  $\text{MnCl}_4$  probably is formed, which upon application of heat breaks up into  $\text{MnCl}_2$  and  $\text{Cl}_2$ . This department would indicate that manganese is tetratomic in the dioxide.

Manganese peroxide (as also  $Mn_2O_3$  and  $Mn_3O_4$ ), serves chiefly for the manufacture of chlorine gas, and it is, therefore, technically important to estimate the quantity of chlorine which a given oxide of manganese is able to set free. This is done by boiling the oxide with hydrochloric acid, conducting the liberated chlorine into a potassium iodide solution, and determining the separated equivalent amount of iodine by means of sodium hypochlorite. Or the oxide is heated in a flask with oxalic and sulphuric acids, when the first is oxidized to carbon dioxide. From its quantity we can calculate the quantity of active or available oxygen in the manganese oxide.

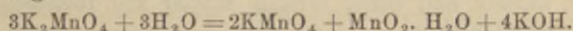
In the chlorine preparation the manganese is found as manganous chloride in the residue. With the relatively high value of pyrolusite, it is important for trade that the peroxide be recovered from the residue. This regeneration is executed, at present, upon a grand scale, according to Weldon's method, in the following manner. The manganous chloride, containing excess of hydrochloric acid, is neutralized with lime, the clear liquid brought into a high iron cylinder (the oxidizer), milk of lime added and air forced in. The mixture becomes warm, and so-called calcium manganite  $MnO_3Ca = MnO_2 \cdot CaO$  is precipitated as a white mud:—



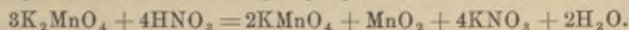
The calcium chloride solution is run off, and the residual calcium manganite employed for the preparation of chlorine, when it conducts itself as a mixture of  $MnO_2 + CaO$ .

#### COMPOUNDS OF MANGANIC AND PERMANGANIC ACIDS.

When oxygen compounds of manganese are heated in the air, in contact with potassium hydrate, or better, with oxidizing substances, like nitre or potassium perchlorate, a dark gray amorphous mass is produced, and this dissolves in cold water with a dark green color. When this solution is evaporated under the air-pump, dark green metallic rhombic prisms of *potassium manganate*— $K_2MnO_4$ —crystallize out. This salt is isomorphous with potassium sulphate and chromate. In potassium or sodium hydrate, potassium manganate dissolves without alteration; it is, however, decomposed by water, hydrated manganese dioxide separating, and the green solution of the manganate changing into a dark red solution of the permanganate:  $KMnO_4$ —



A similar conversion of the green manganate to red permanganate occurs more rapidly by the influence of acids:—

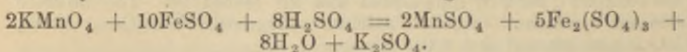




Owing to this ready alteration in color the solution of the manganate, is called mineral chameleon.

**Potassium Permanganate**— $\text{KMnO}_4$ —is best prepared by conducting  $\text{CO}_2$  into the manganate solution until the green color has passed into a red. On concentration the salt crystallizes in dark red rhombic prisms isomorphous with potassium perchlorate,  $\text{KClO}_4$ . It is soluble in 12 parts of water at ordinary temperatures.

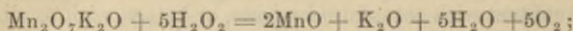
The permanganate solution is strongly oxidizing, as it converts lower oxygen compounds into higher; in this manner the permanganate is reduced to a colorless manganous salt. When a permanganate solution is added to an acidulated ferrous solution, the former is decolorized, and there results a feeble yellow solution of ferric and manganic salts:—



Hence the permanganate solution serves in volumetric analysis for the quantitative estimation of ferrous salts.

In the same manner, the permanganate oxidizes and destroys many organic substances, therefore the solution cannot be filtered through paper; it serves as a disinfectant.

The permanganate is also reduced by hydrogen peroxide (p. 93); the reaction proceeds according to the following equation:—



the formation of oxides requires, for completion of the reaction the presence of acids (sulphuric acid).

The remaining permanganates are also similar to and isomorphous with the perchlorates. The sodium salt is very soluble in water, and crystallizes but poorly.

Strongly cooled sulphuric acid added to dry permanganate causes the separation of **Manganese Heptoxide**— $\text{Mn}_2\text{O}_7$ —an oily, dark-colored liquid. By careful warming it is converted into dark violet vapors, which explode on rapid application of heat. Manganese heptoxide has a violent oxidizing action; paper, alcohol and other organic matter are inflamed by mere contact with it.

## METALS OF GROUP VIII.

Of all known elements, there remain yet for consideration those standing in the VIII column of the periodic system. They arrange themselves into the following three groups, the members of which possess almost agreeing atomic weights and specific gravities :—

Fe = 56.0	Co = 58.6	Ni = 58.6
Ru = 103.0	Rh = 104.0	Pd = 106.7
Os = 198.0 *	Ir = 192.8	Pt = 196.7

These elements represent the middle members of the three great periods, for which, in the two small periods, no analogues exist (pp. 234, 236).

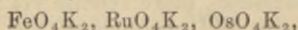
Both as regards atomic weights and in their entire chemical character, the elements of these three groups constitute a transition from the preceding members of the great periods (Mn and Cr Mo W) to the next following members (Cu Ag Au and Zn Cd Ag). The elements standing side by side (heterologous) and belonging to the same periods are very similar in their physical properties, and show, *e. g.*, very close specific gravities. Therefore these are included usually in groups and distinguished : (1) the iron group (Fe Co Ni), with the specific gravity 7.8–8.6 ; (2) group of the light platinum group metals (Ru Rh Pd), with specific gravity 11.8–12.1, and (3) the group of the heavy platinum metals (Os Ir Pt), of specific gravity 21.1–22.4.

On the other hand, the homologous elements (Fe Ru Os, Co Rh Ir and Ni Pd Pt), according to their chemical properties, show a like similarity, as all the other homologous groups, and therefore may be considered in such groups. This resemblance shows itself chiefly in their combination forms, and, of course, too, in the properties of the compounds (p. 324). We observed that the metals of group VI (chromium, molybdenum, wolfram) and of group VII (manganese) form the highest oxides ( $\text{MeO}_3$  and  $\text{Me}_2\text{O}_7$ ) of an acidic nature. Agreeing with

---

\* As already mentioned (p. 238), osmium must, corresponding with its position in the periodic system, have a lower atomic weight than that experimentally determined (198). As, however, in its entire deportment, it bears the same relation to Ir and Pt as Ru to Rh and Pd and Fe to Co and Ni, therefore it is extremely probable that its atomic weight is not correctly determined, and will show itself less, somewhat, than that of iridium (192.7).

this, there exist for the adjacent elements of group VIII (iron, ruthenium and osmium) salts—



which are derived from the unstable trioxides  $\text{FeO}_3$ ,  $\text{RuO}_3$  and  $\text{OsO}_3$ . This acid-forming function disappears in the following members, Co Rh Ir and Ni Pd Pt, the chemical valence of which rapidly diminishes, and which attach themselves to Cu Ag and Au.

Consequently the whole physical and chemical department of the 9 elements to be considered is governed by their position in the periodic system.

As previously mentioned pp. 236, 240 and at other places, the valences of the elements in their highest salt-forming oxides present themselves as periodic functions of the atomic weights. A similar dependence is also seen in the lowest salt-forming oxides, as is visible from the following tabulation of the highest and lowest salt-forming oxides of the middle members of the great periods:—

<sup>v</sup> V <sub>2</sub> O <sub>5</sub>	<sup>vi</sup> CrO <sub>3</sub>	<sup>vii</sup> Mn <sub>2</sub> O <sub>7</sub>	<sup>vi</sup> FeO <sub>3</sub>	<sup>iv</sup> Co <sub>2</sub> O <sub>3</sub>	<sup>ii</sup> NiO	<sup>ii</sup> CuO	<sup>ii</sup> ZnO	<sup>iii</sup> Ga <sub>2</sub> O <sub>3</sub>	<sup>vi</sup> —
<sup>iii</sup> V <sub>2</sub> O <sub>3</sub>	<sup>ii</sup> CrO	<sup>ii</sup> MnO	<sup>ii</sup> FeO	<sup>ii</sup> CoO		<sup>i</sup> Cu <sub>2</sub> O			—
<sup>v</sup> Nb <sub>2</sub> O <sub>5</sub>	<sup>vi</sup> MoO <sub>3</sub>	<sup>vi</sup> —	<sup>vi</sup> RuO <sub>3</sub>	<sup>iv</sup> Rh <sub>2</sub> O <sub>3</sub>	<sup>ii</sup> PdO	<sup>i</sup> Ag <sub>2</sub> O	<sup>ii</sup> CdO	<sup>iii</sup> In <sub>2</sub> O <sub>3</sub>	<sup>iv</sup> SnO <sub>2</sub>
<sup>iii</sup> (Nb <sub>2</sub> O <sub>3</sub> )	<sup>ii</sup> MoO	<sup>ii</sup> —	<sup>ii</sup> RuO	<sup>ii</sup> RhO					<sup>ii</sup> SnO
<sup>v</sup> Ta <sub>2</sub> O <sub>5</sub>	<sup>vi</sup> WO <sub>3</sub>	<sup>vi</sup> —	<sup>vi</sup> OsO <sub>3</sub>	<sup>iv</sup> IrO <sub>2</sub>	<sup>iv</sup> PtO <sub>2</sub>	<sup>iii</sup> Au <sub>2</sub> O <sub>3</sub>	<sup>ii</sup> HgO	<sup>iii</sup> Tl <sub>2</sub> O <sub>3</sub>	<sup>iv</sup> PbO <sub>2</sub>
<sup>iii</sup> (Ta <sub>2</sub> O <sub>3</sub> )	<sup>ii</sup> (WO)	<sup>ii</sup> —	<sup>ii</sup> OsO	<sup>ii</sup> IrO	<sup>ii</sup> PtO	<sup>i</sup> Au <sub>2</sub> O	<sup>i</sup> Hg <sub>2</sub> O	<sup>i</sup> Tl <sub>2</sub> O	<sup>ii</sup> PbO

### METALS OF THE IRON GROUP.

The metals of this group, iron, cobalt and nickel, form a gradual transition from manganese to copper. Their magnetic properties mostly distinguish them from the other elements. Iron forms three series of compounds after the forms,  $\text{FeO}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{FeO}$ .

In its highest combinations iron has an acidic character, and the derivatives of ferric acid ( $\text{H}_2\text{FeO}_4$ ) are entirely similar to those of chromic and manganic acids; they are, however, less stable than the latter. Their analogues with cobalt and nickel are not known.



The ferric compounds— $\text{Fe}_2\text{X}_6$ —containing the hexatomic group  $\text{Fe}_2$  (p. 368) are much like the aluminium, chromic and permanganic derivatives. They are usually isomorphous. Among iron salts they are characterized by their relative stability. The highest oxides of cobalt are much less stable, and only a few double salts of this form are known, while the higher salts with nickel are not known.

Thirdly, iron, cobalt and nickel afford *ous* compounds, ( $\text{FeX}_2$ ,  $\text{CoX}_2$ ,  $\text{NiX}_2$ ) in which they appear to be dyads. They are very much like the compounds of chromium, manganese and copper of the same form, and those of the magnesium metals. The ferrous salts are not as stable as the ferric; they are readily oxidized to the latter.

The cobaltous and nickelous compounds are quite stable, and in this respect these metals ally themselves with copper and zinc.

## 1. IRON.

Fe = 56.

This metal, which is practically of such great importance, is very widely distributed in nature. Native, it is found on the earth's surface almost exclusively in meteorites; however, it is present in great masses in other worlds which (like the sun) are surrounded by an atmosphere of hydrogen.

The most important iron ores are: magnetite ( $\text{Fe}_3\text{O}_4$ ), hematite ( $\text{Fe}_2\text{O}_3$ ), brown iron ore and limonite (hydrate of the oxide), siderite ( $\text{FeCO}_3$ ). These are the almost exclusive materials for the manufacture of iron; the sulphur ores, like pyrite, are not adapted to this end.

In commerce there are three varieties of iron, cast iron, steel and wrought iron, which are principally chemically distinguished by their varying quantities of carbon.

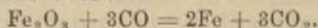
Cast iron contains 3-6% carbon, partly chemically combined and partly mechanically mixed, in the form of graphite. Molten cast iron rapidly cooled yields the so-called *white iron*, in which the greater portion of the carbon is chemically combined with the iron. It has a whitish color, upon fracture exhibits a granular crystalline structure, and is very hard and brittle. Its specific gravity is 7.1. At about  $1200^\circ$  it fuses to a pasty mass. The chemically combined carbon in it can easily be removed by oxidation, for which reason it is suitable for the making of steel or wrought iron.

Manganiferous cast iron has a leafy structure, and is called *Spiegeleisen*. It serves principally for the manufacture of Bessemer steel. By slow cooling of molten cast iron, the greater part of the carbon within separates, in the form of small leaflets of graphite. The thus produced *gray* cast iron has a darker gray color, is not so hard and brittle, fuses more readily (about  $1150^{\circ}$ ) than white cast iron, and serves for the manufacture of castings. Owing to their brittleness, neither variety can be forged or welded.

**Steel** contains 0.8-1.8 of carbon, which is entirely chemically combined with the iron. It has a steel gray color, and a fine-grained structure; its specific gravity equals 7.6-8.0. It is more difficultly fusible (about  $1400^{\circ}$ ) than cast iron, but easier than wrought iron. When glowing steel is rapidly cooled, it becomes very hard and brittle. In this process more carbon is chemically combined. Slowly cooled it is soft and malleable, and may be forged and welded. The weldability diminishes with the addition of carbon.

**Wrought iron** contains the least amount of carbon, 0.2-0.6 %. It possesses a bright gray color, has a specific gravity of 7.6, is rather soft and tough, and, at a red heat, may be readily forged, rolled and welded. The rolled iron possesses a radiating layer, while the forged is fine grained; the former is more compact and tenacious. Wrought iron fuses at a bright white heat ( $1500^{\circ}$ ), while cast iron and steel begin to melt at  $1200^{\circ}$ .

**Metallurgy of Iron.**—The extraction of iron from its oxygen ores is based upon the reduction of the same by carbon at a glowing heat. According to the oldest course, the ores were heated with carbon in wind furnaces; in this way, by the excess of air the greater portion of the carbon was consumed and at once we got an iron poor in carbon, wrought iron, a spongy mass, which was then forged under the hammer. Since the beginning of the previous century, the present methods were adopted, according to which cast iron is first prepared from the ores, and this afterwards converted into steel or wrought iron. The smelting of the ores is executed in large, walled blast furnaces, which permit an uninterrupted process. These are filled, from openings above, with alternating layers of coal, broken ore and fluxes containing silica and lime; these latter facilitate the melting together of the reduced iron. The necessary air for the process is blown into the contracted portion of the furnace by means of a blast engine. By the combustion of the coal, carbon monoxide is produced, which reduces the iron oxide to metal:—



In sinking in the furnace the reduced iron comes in contact with the coal, takes up carbon and forms cast iron, which on further sinking fuses and flows into the hearth of the furnace. By protracted and strong heating, whereby the at first chemically united carbon passes into the graphitic, the formation of the gray cast iron is accelerated. The earthy impurities of the ores combine with the fluxes, forming readily fusible *slag*, which envelops the fused iron and protects it from further oxidation.

To convert the cast iron thus produced into steel or wrought iron, carbon must be withdrawn from it. In making the wrought iron the cast iron is fused in open hearths (refining process), or in reverberatory furnaces with air access, and the mass stirred thoroughly until it has become semi-pasty (puddling process). In this way almost all the carbon is burned to carbon monoxide and the other admixtures, like silicon, sulphur, and phosphorus, present in small quantities, oxidized. The wrought iron is then worked up by rolling, or under the iron hammers (bar iron).

Formerly, steel was manufactured from wrought iron (not cast iron), by cementation. The iron bars were exposed, together with fine charcoal, for some time, to a red heat, whereby the iron takes up carbon from the surface. The bars are then reformed, again heated with fine charcoal, and the process repeated until the mass has become as homogeneous as possible (cementation steel). It can be obtained more uniform by fusion in crucibles (cast steel).

At present, steel is, chiefly, prepared directly from cast iron, by the method invented by Bessemer, somewhere in 1850. It consists in blowing air, under high pressure, into the molten iron, until the necessary amount of carbon has been consumed (Bessemer steel).

Puddle steel is obtained from cast iron through the puddling process, by the less extensive removal of carbon; another variety, by the fusion of cast iron with iron ore and pyrolusite.

Induced by the different more recent processes for manufacturing steel and wrought iron, whereby the same are obtained in a liquid condition, bearing in mind that steel differs from wrought iron essentially in its hardness, that the so-called Bessemer steel, however, is not tempered—there has been accepted, lately, a new division and nomenclature of the ideas of steel and wrought iron (which, in contrast to cast iron, are difficultly fusible and workable). At present we distinguish—

(1) Weld iron as a non-fused, non-tempered mass, formerly wrought iron; (2) weld steel, not fused, tempered, formerly puddle steel; (3) ingot iron, fused, not tempered, formerly Bessemer steel; (4) ingot steel, has been fused and tempered.

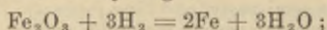
---

The ordinarily occurring iron, even the purest wire, always contains foreign ingredients, principally carbon, and in minute quantities silicon, sulphur, phosphorus and nitrogen, nickel, cobalt, titanium and others. The quantity of manganese is



purposely increased (to 30%), as the iron by this means acquires technically valuable properties; it becomes more compact and solid. When iron containing carbon is dissolved in hydrochloric acid the chemically combined carbon unites with hydrogen, to form hydro-carbons, while the mechanically admixed graphite remains behind. The whole quantity of carbon is determined by solution of the iron in bromine or cupric chloride, when all the carbon remains behind.

To prepare chemically pure iron, pure oxide or the oxalate is heated in a current of hydrogen—

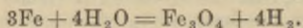


the iron then remains as a fine black powder. In case the reduction occurs at a red heat the powder glows in the air and burns (pyrophoric iron). The strongly ignited powder is not inflammable. Iron obtained by the electrolysis of ferrous sulphate contains some hydrogen.

Chemically pure iron has a grayish-white color, is tolerably soft, and changes but slowly in the air. Its specific gravity is 7.78. It melts in an oxy-hydrogen flame (above 1500°). Ordinary iron rusts rapidly in moist air, as it covers itself with a thin layer of ferric hydrate. Glowed in the air it is coated with a layer of ferrous-ferric oxide ( $\text{Fe}_3\text{O}_4$ ) which is readily loosened. In oxygen it burns with an intense light.

In contact with a magnet iron becomes magnetic; but only steel retains the magnetism, while cast iron and wrought iron, after the removal of the magnet, soon lose the property.

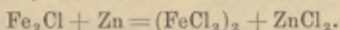
Iron decomposes water at a red heat, with the formation of ferrous-ferric oxide, and the liberation of hydrogen:—



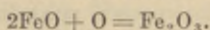
The metal dissolves without trouble in hydrochloric and sulphuric acids, with evolution of hydrogen; the latter has a peculiar odor, due to hydrocarbons simultaneously produced. In nitric acid, iron dissolves with separation of nitrogen oxide. On dipping iron into concentrated nitric acid, and then washing it with water, it is no longer soluble in the acid (passive iron); this phenomenon is due to the production of oxide upon its surface.

## FERROUS COMPOUNDS.

These are formed by the solution of iron in acid, and may also be obtained by the reduction of ferric salts:—

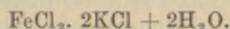


In the hydrous state they are commonly colored green; in the air they oxidize to ferric salts:—



**Ferrous Chloride**— $\text{FeCl}_2$ —crystallizes from hydrochloric acid solutions in green monoclinic prisms, with four molecules of water. They deliquesce in the air, and oxidize. When dried they sustain a partial decomposition. The anhydrous salt is formed by conducting hydrogen chloride over heated iron. It is a white mass, which on application of heat fuses and at a red heat sublimes in white, six-sided leaflets.

It forms double salts with the alkaline chlorides, *e. g.*:—



**Ferrous Iodide**— $\text{FeI}_2$ —is obtained by warming iron with iodine and water. It also crystallizes with four molecules of water.

**Ferrous Oxide**— $\text{FeO}$ —is a black powder, resulting from the reduction of ferric oxide with carbon. When warmed it oxidizes readily. **Ferrous Hydrate**— $\text{Fe}(\text{OH})_2$ —is thrown out of ferrous solutions, as a white precipitate, by the alkalies. Exposed to the air, it oxidizes, becoming green at first, then reddish-brown. It is somewhat soluble in water, and has an alkaline reaction.

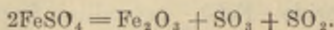
**Ferrous Sulphate**— $\text{FeSO}_4$ —crystallizes with 7 molecules of  $\text{H}_2\text{O}$  in large, greenish, monoclinic prisms, and is generally called *green vitriol*. In dry air, these disintegrate some; in moist air they become coated, by oxidation, with a brown layer of basic ferric sulphate. At  $100^\circ$  they lose 6 molecules of  $\text{H}_2\text{O}$ , and become a white powder. The last molecule of water escapes at  $300^\circ$ . Therefore, ferrous sulphate behaves just like the sulphates of the metals of the magnesium group. Like them, it yields double salts with potassium and ammonium sulphates, which have six molecules of  $\text{H}_2\text{O}$ . They are more stable than ferrous sulphate, and oxidize but very slowly in the air.

Ferrous sulphate is obtained by dissolving iron in sulphuric acid; commercially it is obtained from pyrites ( $\text{FeS}_2$ ). On

roasting, these lose one molecule of sulphur, and are converted into ferrous sulphide ( $\text{FeS}$ ), which, in presence of water, absorbs oxygen from the air, and forms sulphate, which may then be extracted by water.

Iron vitriol has an extended practical application; among other uses, it is employed in the preparation of ink, and in dyeing.

When heated it decomposes according to the following equation:—

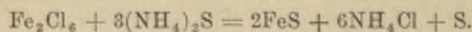


On this is based the production of fuming Nordhausen sulphuric acid and of colcothar.

**Ferrous Carbonate.**— $\text{FeCO}_3$ —exists in nature as *siderite*, crystallized in yellow-colored rhombohedra, isomorphous with calcite and smithsonite. Sodium carbonate added to ferrous solutions precipitates a white voluminous carbonate, which, in the air, rapidly oxidizes to ferric hydrate. Ferrous carbonate is somewhat soluble in water containing carbon dioxide, hence present in many natural waters.

**Ferrous Phosphate**— $\text{Fe}_3(\text{PO}_4)_2 + 8\text{H}_2\text{O}$ —occurs crystallized in bluish leaflets as *Vivianite*. Ferrous phosphate, precipitated by sodium phosphate, is a white amorphous powder, which oxidizes in the air.

**Ferrous Sulphide**— $\text{FeS}$ —is obtained by fusing together iron and sulphur as a dark gray, metallic mass. It is made use of in laboratories for the preparation of hydrogen sulphide. If an intimate mixture of iron filings and sulphur be moistened with water, the union will occur even at ordinary temperatures. Black ferrous sulphide is precipitated from ferrous solutions by alkaline sulphides. In moist condition in the air it oxidizes to ferrous sulphate. The same reagents also precipitate ferrous sulphide from ferric salts, but they first suffer reduction:—



### FERRIC COMPOUNDS.

**Ferric Oxide**—*Sesquioxide of Iron*— $\text{Fe}_2\text{O}_3$ —exists as *hematite* in nature. It may be formed by heating the iron oxygen compounds in the air, and on a large scale is obtained by the ignition of green vitriol. It then is a dark red powder

*Hematite*  
 — \* *Magnetite*  $\text{FeO} \cdot \frac{1}{2}\text{Fe}_2\text{O}_3$  —  $\left\{ \begin{array}{l} \text{Protoxide } 31.03 \\ \text{Sesquiox. } 68.97 \end{array} \right.$



(colcothar or caput mortuum) used as a paint and for polishing glass.

**Ferric Hydrate**— $\text{Fe}_2(\text{OH})_6$ . As a voluminous, reddish-brown mass, it is precipitated by alkalis from ferric solutions. On boiling with water, it becomes more compact, gives up water and is converted into the hydrate,  $\text{Fe}_2\text{O}(\text{OH})_4$ . Many iron ores, like bog-iron ore,  $\text{Fe}_2\text{O}(\text{OH})_4$ , pyrosiderite,  $\text{Fe}_2\text{O}_2(\text{OH})_2$ , and brown hematite,  $\text{Fe}_2\text{O}_3(\text{OH})_6$ , are similarly derived.

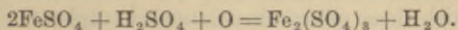
Freshly precipitated ferric hydrate is soluble in a solution of ferric chloride or acetate. When such a solution is subjected to dialysis, the iron salt diffuses, and there remains a pure, aqueous solution of ferric hydrate. From this, by slight quantities of alkalis and acids, all the ferric hydrate is precipitated as a jelly.

\* **Ferrous-Ferric Oxide**— $\text{Fe}_3\text{O}_4 = \text{FeO} \cdot \text{Fe}_2\text{O}_3$ —occurs crystallized in regular octahedra, in nature, as magnetite. It is abundant in Sweden, Norway, and in the Urals. It may be artificially obtained by conducting steam over ignited iron.

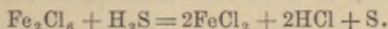
\* Magnetite constitutes the natural magnets.

Ferric hydrate, like other sesquioxides, is only a weak base, which does not yield salts with weak acids, like carbonic or sulphurous (p. 347).

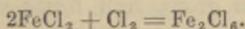
Ferric salts arise by the solution of ferric oxide in acids, or by the oxidation of ferrous salts in the presence of free acids:—



They generally have a yellow-brown color. By reduction, they pass into ferrous salts:—



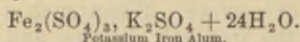
**Ferric Chloride**— $\text{Fe}_2\text{Cl}_6$ . In aqueous solution it is obtained by conducting chlorine into a solution of ferrous chloride:—



Upon evaporation, the hydrate— $\text{Fe}_2\text{Cl}_6 + 6\text{H}_2\text{O}$ —remains as a yellow crystalline mass, readily soluble in water, alcohol and ether. It is partially decomposed when heated; hydrogen chloride escapes and a mixture of chloride and oxide remains.

Anhydrous ferric chloride is made by heating iron in a current of chlorine gas; it sublimes in brownish-green, metallic, shining, six-sided prisms and scales, which deliquesce in the air. The specific gravity of their vapor is 162.5 ( $H = 1$ ) corresponding to the molecular formula  $Fe_2Cl_6 = 325$ .

**Ferric Sulphate**— $Fe_2(SO_4)_3$ —is obtained by dissolving the oxide in sulphuric acid, and remains, on evaporating the solution, as a white mass, which dissolves in water gradually, with a reddish-brown color. With alkaline sulphates it forms alums (p. 341) *e. g.* :—



Potassium Iron Alum.

**Ferric Phosphate**— $Fe_2(PO_4)_2$ —is a white precipitate, thrown out of ferric solutions by sodium phosphate. It is insoluble in water and acetic acid.

**Ferric Sulphide**— $FeS_2$ —occurs in nature as *pyrites*, crystallized in yellow, metallic, shining, regular cubes. It is employed in the manufacture of sulphuric acid and green vitriol. It may be artificially prepared in various ways.

#### COMPOUNDS OF FERRIC ACID.

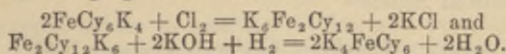
On fusing iron filings with nitre, or by conducting chlorine into potassium hydrate, in which there is suspended ferric hydrate, *Potassium Ferrate*  $K_2FeO_4$  is produced, which crystallizes from the alkaline solution in dark red prisms; they are isomorphous with those of the chromate and sulphate. They are readily soluble in water; the dark red liquid soon decomposing with separation of ferric hydrate and oxygen. The free acid is not known, as it at once decomposes when liberated from its salts.

#### CYANOGEN DERIVATIVES OF IRON.

With the cyanogen group iron forms very characteristic, and for commerce, important compounds. When potassium cyanide is added to aqueous solutions of the ferrous or ferric salts, the cyanides  $Fe(CN)_2$  and  $Fe_2(CN)_6$  are thrown down as white precipitates, which in the air soon break up. In excess of potassium cyanide they dissolve to the double cyanides  $Fe(CN)_2 \cdot 4KCN$  and  $Fe_2(CN)_6 \cdot 6KCN$ . Acids added to these

solutions induce the separation of the hydrogen compounds,  $H_4FeCy_6 = FeCy_2 \cdot 4HCy$  and  $Fe_2Cy_{12}H_6 = Fe_2Cy_6 \cdot 6HCy$ .\*

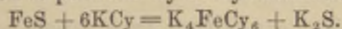
These are of acid nature, and form salts by exchanging their hydrogen for metals. In these salts, and also in the free acids, neither the iron nor the cyanogen group can be detected by the usual reagents (iron is not precipitated, *e. g.*, by the alkalis). It is supposed that in these double cyanides compound groups of peculiar structure are present, and that they conduct themselves analogously with the halogens. The group  $FeCy_6$  in the *ous* compounds is called *ferrocyanogen*, that of  $Fe_2Cy_{12}$  in the *ic*, *ferricyanogen*. The ferro conduct themselves towards the ferri compounds like the ferrous to the ferric salts; by oxidation the first are converted into the latter, and by reducing agents the latter into the former.



Cobalt, manganese, chromium and the platinum metals form similar cyanides.

**Potassium Ferrocyanide**—*Yellow Prussiate of Potash*— $K_4FeCy_6$ , is produced by the action of potassium cyanide upon iron compounds, or upon free iron (in this case the oxygen of the air or of water takes part). Commercially it is prepared by igniting carbonized nitrogenous animal matter (blood, horn, hoofs, leather, offal, etc.,) with potashes and iron.

In this operation first the carbon and nitrogen of the organic matter combine with the potassium of the potashes to form potassium cyanide, while the sulphur present forms iron sulphide with the iron (by means of alcohol, potassium cyanide can be extracted from the fusion). Upon now treating the fusion with water, there arises, through the alternating action of the potassium cyanide and sulphide, ferrocyanide of potassium, which is purified by recrystallization:—

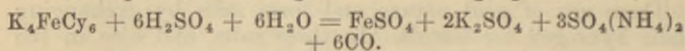


It crystallizes from water in large, yellow, quadratic prisms, having three molecules of water and soluble in 3–4 parts  $H_2O$ . At  $100^\circ$  the crystals lose all their water and become a white powder. At a red heat the ferrocyanide breaks up into cyanide, nitrogen and iron carbide ( $FeC_2$ ). When the salt is warmed with dilute sulphuric acid, half of the cyanogen

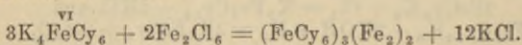
\* The cyanogen group, CN, is usually designated by the letters Cy.



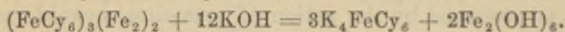
escapes as hydrogen cyanide; by concentrated sulphuric acid it is decomposed, according to the following equation:



When strong hydrochloric acid is added to a concentrated potassium ferrocyanide solution, there separates *hydrogen ferrocyanide*,  $\text{H}_4\text{FeCy}_6$ , as a white crystalline powder, which rapidly turns blue in the air. It has the nature of an acid. Its salts with the alkalis and alkaline earths are very soluble in water. The sodium salt crystallizes with difficulty. The salts of the heavy metals are insoluble, and are obtained by double transposition. Ferrocyanide added to the solution of a ferric salt precipitates a dark blue cyanide  $(\text{FeCy}_6)_3$ ,  $(\text{Fe}_2)_2$  called *Prussian Blue*:—

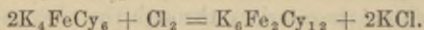


This is the ferric salt of hydroferrocyanic acid; on pouring potassium or sodium hydrate over it ferrocyanide of potassium and ferric hydrate are produced:—



In copper solutions potassium ferrocyanide produces a reddish-brown precipitate of  $\text{FeCy}_6\text{Cu}_2$ .

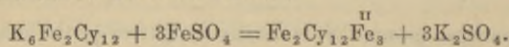
Oxidizing agents convert the ferro into *potassium ferricyanide*— $\text{K}_6\text{Fe}_2\text{Cy}_{12}$ —red prussiate of potash. This conversion is most conveniently effected by conducting chlorine into the solution of the yellow prussiate:—



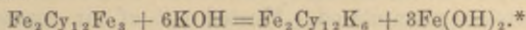
By this the ferrocyanogen group  $\text{FeCy}_6$  is changed to the ferri,  $\text{Fe}_2\text{Cy}_{12}$ .

The red prussiate crystallizes from water in red rhombic prisms. Concentrated hydrochloric acid precipitates the free hydro-ferricyanic acid  $\text{H}_6\text{Fe}_2\text{Cy}_{12}$ , which decomposes very easily.

Potassium ferricyanide with ferrous solutions affords a dark blue precipitate,  $\text{Fe}_2\text{Cy}_{12}\text{Fe}_3$ , very similar to Prussian Blue, and called *Turnbull's Blue*:—



This blue is the ferrous salt of hydroferricyanic acid. Alkalies change it to ferricyanide of potassium and ferrous hydrate:—



In ferric solutions, potassium ferricyanide does not cause precipitation. Ferrocyanide gives Prussian blue, while in ferrous solutions it forms a bluish-white precipitate.

By these reactions, ferric salts may readily be distinguished from the ferrous. Potassium sulphocyanide (CNSK) produces a dark red coloration in ferric solutions, while it leaves the ferrous unaltered.

## 2. COBALT.

Co = 58.6.

Occurs in nature as smaltite ( $\text{CoAs}_2$ ) and cobaltite ( $\text{CoAs}_2$ ,  $\text{CoS}_2$ ). The metal is obtained by the ignition of cobaltous oxide with carbon or in an hydrogen stream. It has a reddish-white color and strong lustre, is very tenacious and difficultly fusible. Its specific gravity is 8.9. It is attracted by magnets, but to a less degree than iron. It is not altered by the air or water. Only slightly attacked by hydrochloric and sulphuric acids; nitric acid dissolves it readily, forming cobalt nitrate.

The predominating compounds have the form  $\text{CoX}_2$ , and are called *cobaltous*. They are very stable and mostly isomorphous with the ferrous salts. The hydrous cobaltous compounds have a reddish color, the anhydrous are blue.

### COBALTOUS COMPOUNDS.

**Cobaltous Chloride**— $\text{CoCl}_2$ —is obtained by the solution of cobaltous oxide in hydrochloric acid, and crystallizes with  $6\text{H}_2\text{O}$  in red monoclinic prisms. When heated, it loses water, and becomes blue in color, and anhydrous. On writing on paper with the solution, the pale reddish characters are almost invisible, but when warmed they appear distinctly blue (Sympathetic ink).

\* According to recent investigations it appears that Turnbull's blue and Prussian blue possess the same composition  $(\text{FeCy}_6)_2 \left\{ \begin{array}{l} \text{VI} \\ \text{Fe}_2 \\ \text{Fe} \end{array} \right.$  The simpler relations are retained here.

**Cobaltous Hydrate**— $\text{Co}(\text{OH})_2$ —a reddish precipitate produced by the alkalis in hot, cobaltous solutions. Exposed to the air, it becomes brown by oxidation. From cold solutions basic salts are precipitated. Heated out of air contact the hydrate passes into green *cobaltous oxide*  $\text{CoO}$ .

**Cobaltous Sulphate**— $\text{SO}_4\text{CO} + 7\text{H}_2\text{O}$ —crystallizes in monoclinic prisms; from a warm solution there separates  $\text{CoSO}_4 + \text{OH}_2\text{O}$ . It is isomorphous with ferrous sulphate, and forms double salts with alkaline sulphates.

**Cobaltous Nitrate**— $\text{Co}(\text{NO}_3)_2 + 6\text{H}_2\text{O}$ —forms red deliquescent prisms.

**Cobaltous Sulphide**— $\text{CoS}$ —is a black precipitate, produced in neutral cobalt solutions by alkaline sulphides, and insoluble in dilute acids.

**Cobalt Silicates.** When glass is fused with a cobalt compound it is colored a dark blue and when pulverized becomes a blue powder which is used as a paint, under the name of *smalt*.

Smalt is commercially prepared by fusing cobalt ores with potashes and quartz, whereby the cobalt forms a silicate (smalt) with the  $\text{SiO}_2$  and potassium, while the other metals accompanying Co in its ores, such as Bi, As, and especially nickel, are thrown out as a speiss. This is called speiss-cobalt and serves for the preparation of nickel.

On igniting cobalt oxide with alumina a dark blue mass is produced—*cobalt ultramarine* or *Thenard's Blue*. When zinc oxide and cobalt oxide are ignited a green color—*green cinnabar*—is obtained.

---

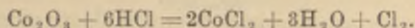
### COBALTIC COMPOUNDS.

**Cobaltic Oxide**— $\text{Co}_2\text{O}_3$ —is left as a black powder on the ignition of cobaltous nitrate. At a red heat it becomes cobaltous-cobaltic oxide,  $\text{Co}_3\text{O}_4$ , and at a white heat cobaltous oxide. The hydrate— $\text{Co}_2(\text{OH})_6$ —separates as a dark brown powder, if chlorine be passed through an alkaline solution having a cobaltous salt in it.

By the action of sulphuric acid upon the oxide and its hydrate there is formed a cobaltous salt and hydrogen set free.



Chlorine is generated when it is heated with hydrochloric acid:—

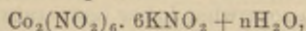


In dilute, cold hydrochloric acid the cobaltic hydrate dissolves almost without any liberation of chlorine; in solution, is probably  $\text{Co}_2\text{Cl}_6$ , which in evaporation is decomposed into  $2\text{CoCl}_2$  and  $\text{Cl}_2$ .

**Cobaltous-Cobaltic Oxide**— $\text{Co}_3\text{O}_4 = \text{Co}_2\text{O}_3\text{CoO}$ —corresponding to magnetite,  $\text{Fe}_3\text{O}_4$ —is formed by the ignition of the oxygen cobalt derivatives, and is a black powder.

Of the oxygen salts of cobalt only a few double salts are known, of which potassio-cobaltic nitrite is worthy of note.

When potassium nitrite  $\text{KNO}_2$  is added to a cobaltous solution acidified with acetic acid, nitrogen is set free, and in course of time there separates the double salt



as a yellow crystalline powder. This reaction is very characteristic, for cobalt, and serves to separate it from nickel.

**Ammonio-Cobalt Compounds.** Cobalt is capable of forming with ammonia a series of peculiar compounds, in which it appears in its highest state of oxidation; the structure of them has not yet been explained. On adding ammonium hydrate to a cobaltous chloride solution, the first formed precipitate dissolves in the excess of the reagent, and when this liquid is permitted to stand exposed to the air, the color, at first brown, passes gradually into red. On adding concentrated hydrochloric acid to this, a brick-red, crystalline powder, of the composition— $\text{Co}_2\text{Cl}_6 \cdot 10\text{NH}_3 + 2\text{H}_2\text{O}$ —called Roseocobalt—is precipitated. If, however, the red solution be boiled with hydrochloric acid, a red powder—purplecobaltic chloride,  $\text{Co}_2\text{Cl}_6 + 10\text{NH}_3$ —separates out. If the ammoniacal red solution contain much ammonium chloride, hydrochloric acid will precipitate a yellowish-brown compound—luteo-cobaltic chloride  $\text{Co}_2\text{Cl}_6 \cdot 12\text{NH}_3$ .

The other salts of cobalt, such as the sulphate and nitrate, yield similar compounds, *e. g.*,  $\text{Co}_2(\text{NO}_3)_6 \cdot 10\text{NH}_3$ , roseocobaltic nitrate.

**Cyanogen Cobalt Compounds.**—In solutions of cobaltous salts, potassium cyanide produces a bright brown precipitate of cobaltocyanide,  $\text{Co}(\text{CN})_2$  soluble in an excess of the reagent. In the air the solution absorbs oxygen and forms potassium cobalticyanide,  $\text{K}_6\text{Co}_2(\text{CN})_{12}$  corresponding to potassium ferricyanide. On evaporation of the solution the cobalticyanide crystallizes in colorless rhombic prisms, very soluble in water. Sulphuric acid precipitates from the concentrated solution, hydrogen cobalticyanide,  $\text{H}_6\text{Co}_2(\text{CN})_{12}$ , crystallizing in needles.

## 3. NICKEL.

Ni = 58.6.

In native condition nickel exists in meteorites; its most important ores are *Nickelite*— $\text{NiAs}$ —and *Gersdorffite*,  $\text{NiS}_2$ .  $\text{NiAs}_2$  (constituted like cobaltite.) In its ores nickel is always accompanied by cobalt, and *vice versa*, cobalt mostly by nickel. The isolation of the latter from its ores, as also from speiss-cobalt (p. 398), is very complicated. Generally nickel appears in commerce in cubical forms; in addition to the chief ingredient, there always are present copper, bismuth and other metals. To get chemically pure nickel, its oxalate or carbonate should be ignited in an hydrogen stream.

Nickel is almost silver white, very lustrous, and very tenacious. Its specific gravity is 9.1 and that of the fused variety 8.8. It fuses at a somewhat lower temperature than iron, and like this is attracted by the magnet. In the air it is not altered; it dissolves with difficulty in hydrochloric and sulphuric acids, but readily in nitric acid.

It forms almost exclusively *ous* compounds of the form  $\text{NiX}_2$ ; nickelic oxide behaves like a peroxide, and does not afford corresponding salts.

**Nickelous Hydrate**— $\text{Ni}(\text{OH})_2$ —is a bright green precipitate produced by alkalis in nickelous solutions. It dissolves in ammonium hydrate, with a blue color. When heated it passes into gray nickelous oxide,  $\text{NiO}$ .

**Nickelous Chloride**— $\text{NiCl}_2 + 6\text{H}_2\text{O}$ —forms green, monoclinic prisms. When heated they lose water and become yellow.

**Nickelous Cyanide**— $\text{Ni}(\text{CN})_2$ —is precipitated, as a green-colored mass, from nickel solutions, by potassium cyanide. It is soluble in excess of the precipitant. From the solution there crystallizes the double cyanide,  $\text{NiCy}_2 \cdot 2\text{KCy} + \text{H}_2\text{O}$ . Acids decompose this readily. Cyanogen compounds, constituted like those of iron and cobalt, are not known with nickel.

**Nickelous Sulphate**— $\text{NiSO}_4 + 7\text{H}_2\text{O}$ —appears in green, rhombic prisms, isomorphous with the sulphates of the magnesium group, and forms analogous double salts.

**Nickelous Sulphide**— $\text{NiS}$ —is precipitated, black-colored, by alkaline sulphides from nickel solutions.

**Nickelic Oxide**— $\text{Ni}_2\text{O}_3$ —and **Hydrate**— $\text{Ni}_2(\text{OH})_6$ —are perfectly similar to the corresponding cobalt salts; when warmed with hydrochloric acid they give up chlorine.

Nickel is used for certain alloys. Argentan consists, ordinarily, of 50% copper, 25% nickel and 25% zinc. The more nickel there is present in the alloy the whiter and harder it is, and the more capable of receiving a high polish. The German nickel coins consist of 75% Cu and 25% Ni. At present, to protect cast iron ware from rusting and to impart to it a beautiful white surface, it is coated with a layer of nickel. This is accomplished in an electrolytic manner, or by boiling the iron ware in a solution of zinc chloride and nickel sulphate.

### GROUP OF THE PLATINUM METALS.

Here belong palladium, rhodium, ruthenium, osmium and iridium—the constant companions of platinum in its ores. On page 385 we observed that these metals are divided into two groups; the group of light platinum metals and the group of heavy ones, which have higher atomic weights and specific gravities:—

Ru, 103.5 sp. gr. 12.26 Rh, 104 sp. gr. 12.1 Rd, 10.6 sp. gr. 11.8  
Os, 198\* " " 22.4 Ir, 192.7 " " 22.38 Pt, 196.7 " " 21.4

The relations of the metals of this group to each other, like those of the iron group, are entirely similar, and they show in their physical and chemical properties a great similarity to the corresponding members of the iron group. Like iron, osmium and ruthenium have a gray color, are very difficultly fusible and readily oxidized in the air. Palladium and platinum, however, like nickel, have an almost silver-white color, are more fusible, and are not oxidized by oxygen. In chemical relations osmium and ruthenium, like iron, show at the same time a metalloidal nature, inasmuch as their highest oxygen compounds form acids. Their derivatives exhibit great similarity to those of iron:—

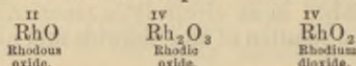
II $\text{OsO}$ Osmious oxide.	IV $\text{Os}_2\text{O}_3$ Osmic oxide.	IV $\text{OsO}_2$ Osmium dioxide.	VI $(\text{OsO}_3)$ Osmic trioxide.
$\text{RuO}$ Ruthenous oxide.	$\text{Ru}_2\text{O}_3$ Ruthenic oxide.	$\text{RuO}_2$ Ruthenium dioxide.	$(\text{RuO}_3)$ Ruthenium trioxide.

\* See note (page 385).



The acid oxides  $\text{OsO}_3$  and  $\text{RuO}_3$  are unknown, but the corresponding acids  $\text{H}_2\text{OsO}_4$  (osmic acid) and  $\text{H}_2\text{RuO}_4$  (ruthenic acid) and derived salts, are known. In addition, osmium and ruthenium exhibit another very high degree of oxidation— $\text{OsO}_4$ , perosmic oxide, and  $\text{RuO}_4$ , per-ruthenic oxide—which are not known with iron; in these derivatives the metals appear to be octads, yet these oxides form no corresponding acids or salts.

Rhodium and iridium, like cobalt, do not form acidic-like derivatives. Their salts correspond to the forms:—



The rhodic compounds are the most stable.

Palladium and platinum, finally, are relatively of more basic nature, as their *ous* derivatives  $\text{PdX}_2$  and  $\text{PtX}_2$  are proportionally more stable than the *ic* forms  $\text{PdX}_4$  and  $\text{PtX}_4$ . Palladium also forms a lower oxide, palladium suboxide  $\text{Pd}_2\text{O}$  in which it approaches silver.

The platinum metals are almost exclusively found in nature in the so-called platinum ore, which usually occurs in small metallic grains in accumulated sands of a few regions (in California, Australia, the Island of Sumatra and chiefly in the Urals). The platinum ore, like that of gold, is obtained by the elutriation of the platiniferous sand with water, whereby the lighter particles are carried away. Platinum ore contains usually 50–80 % platinum, besides palladium (to 2 %), iridium (7 %), osmium ( $1\frac{1}{2}$  %), and ruthenium ( $1\frac{1}{2}$  %), and also different other metals, like gold, copper, iron.

The separation of the platinum metals is generally executed in the following manner: The gold is first removed by dilute aqua regia. Then the ore is treated with concentrated aqua regia, whereby platinum, palladium, rhodium, ruthenium and a portion of iridium are dissolved. Metallic grains or leaflets, an alloy of osmium and iridium—platinum residues—remain. Then ammonium chloride is added to the solution, and platinum and iridium are precipitated as double salts. When the precipitate is ignited a spongy mass of iridium-bearing platinum (platinum sponge) is obtained, which is directly applied in the manufacture of platinum vessels. The filtered

solution from the insoluble chlorides contains palladium, rhodium and ruthenium, which are thrown down as a metallic powder by iron; their further separation is then effected in various ways.

For the manufacture of platinum objects spongy platinum was formerly solely employed; this was pressed into moulds, then glowed and hammered out. Now the fusibility of Pt in the oxy-hydrogen flame is made use of, and the molten metal run into moulds.

By means of the oxy-hydrogen blowpipe iridium and rhodium-bearing platinum may be directly fused out of the platinum ore; osmium and ruthenium, for the most part, are consumed in this operation. The presence of iridium and rhodium makes platinum harder and less readily attacked by many reagents.

### RUTHENIUM and OSMIUM.

Ru = 103.5.

Os = 198.\*

Ruthenium has a steel gray color; it is very hard, brittle, and difficultly fusible. In pulverized condition it oxidizes, when ignited in the air, to  $\text{RuO}$  and  $\text{Ru}_2\text{O}_3$ . It is insoluble in acids, and only slowly dissolved by aqua regia. Fused with potassium hydrate and nitrate, it forms potassium ruthenate  $\text{K}_2\text{RuO}_4$ .

Ruthenium heated in chlorine gas yields ruthenium dichloride  $\text{RuCl}_2$ , a black powder, insoluble in acids. The sesquichloride  $\text{Ru}_2\text{Cl}_6$  is obtained by the solution of  $\text{Ru}_2(\text{OH})_6$ , and is a yellow, crystalline mass, which deliquesces in the air. With potassium and ammonium chlorides, it yields crystalline double chlorides, *e. g.*,  $\text{Ru}_2\text{Cl}_6 \cdot 4\text{KCl}$ . The tetrachloride  $\text{RuCl}_4$  is only known in double salts. Ruthenious oxide  $\text{RuO}$ , the sesquioxide  $\text{Ru}_2\text{O}_3$ , and dioxide  $\text{RuO}_2$ , are black powders, insoluble in acids, and are formed when ruthenium is roasted in the air.

The hydrates  $\text{Ru}_2(\text{OH})_6$  and  $\text{Ru}(\text{OH})_4$  are produced by the action of the alkalis upon the corresponding chlorides, and are very readily soluble in acids. Ruthenic acid  $\text{H}_2\text{RuO}_4$  is not known in free condition. Its potassium salt  $\text{K}_2\text{RuO}_4$  is formed by fusing the metal with potassium hydrate and nitre. It dissolves in water with an orange yellow color. When chlorine is conducted through the solution ruthenium tetroxide  $\text{RuO}_4$  separates as a gold-yellow crystalline mass. It fuses at  $40^\circ$  and boils about  $100^\circ$ , and yields a yellow vapor, the odor of which is similar to nitrogen dioxide,  $\text{NO}_2$ . At  $108^\circ$  it decomposes with explosion. Water breaks it up with formation of  $\text{Ru}_2(\text{OH})_6$ . In concentrated potassium hydrate it dissolves to  $\text{RuO}_4\text{K}_2$ . By less con-

\* Compare note (p. 385).

tinuous introduction of Cl into the solution of  $\text{RuO}_4\text{K}_2$  greenish black crystals separate out, which are isomorphous with potassium permanganate, and appear to be  $\text{RuO}_4\text{K}$ .

Osmium is very much like the preceding. It is not even fusible in the oxy-hydrogen flame; it only sinters together somewhat. As a fine powder it burns when glowed in the air to  $\text{OsO}_4$ . Nitric acid and aqua regia oxidize it to the same. The compounds  $\text{OsCl}_2$ ,  $\text{OsO}$ ,  $\text{Os}_2\text{Cl}_6$  and  $\text{Os}_2\text{O}_3$ ,  $\text{OsO}_2$  and  $\text{OsCl}_4$  are very similar to the corresponding compounds of ruthenium. By fusion with potassium hydrate and nitre we get potassium osmate— $\text{K}_2\text{OsO}_4$ —which crystallizes from aqueous solution with  $2\text{H}_2\text{O}$  in dark-violet octahedra. The most stable and very characteristic derivative of osmium is the tetroxide,  $\text{OsO}_4$ , which is produced by glowing the metal in the air or by the action of chlorine on osmium in presence of water. It crystallizes in large colorless prisms, which fuse below  $100^\circ$  and distill at somewhat higher temperature. It has a very sharp, piercing odor, similar to that of sulphur chloride. Reducing and organic substances precipitate from it pulverulent osmium. On this depends its application in microscopy.  $\text{OsO}_4$  and  $\text{RuO}_4$  do not afford corresponding salts.

### RHODIUM and IRIDIUM.

Rh — 104.

Ir — 192.7.

These have more of a white color and are more easily fusible than ruthenium and osmium. (Iridium fuses at  $1950^\circ$ .) In pure condition they are not attacked by acids or aqua regia; alloyed with platinum they, however, dissolve in aqua regia.

Rhodium forms three oxides:  $\text{RhO}$ ,  $\text{Rh}_2\text{O}_3$  and  $\text{RhO}_2$ , of which the second forms salts with acids. When rhodium is heated with nitre  $\text{RhO}_2$  results.

Of the chlorides only  $\text{Rh}_2\text{Cl}_6$  is known. It results when the metal is heated in chlorine gas. It is a brownish-red mass. With alkaline chlorides it forms readily crystallizing, red-colored double salts.

Iridium has perfectly analogous derivatives:  $\text{IrO}$ ,  $\text{Ir}_2\text{O}_3$ ,  $\text{IrO}_2$  and  $\text{IrCl}_2$ ,  $\text{Ir}_2\text{Cl}_6$ ,  $\text{IrCl}_4$ . The sesquichloride,  $\text{Ir}_2\text{Cl}_6$ , formed by heating Ir in chlorine, is an olive-green, crystalline mass, insoluble in water and acids. It forms double salts with the alkaline chlorides, *e. g.*,  $\text{Ir}_2\text{Cl}_6 \cdot 6\text{KCl} + 6\text{H}_2\text{O}$ , which crystallize from water in green crystals. They are also produced by the action of  $\text{SO}_2$  upon the double salts of  $\text{IrCl}_4$ .

**Iridium Tetrachloride**— $\text{IrCl}_4$ —is formed by the solution of iridium or its oxide in aqua regia, and remains, on evaporation, as a black mass, readily soluble in water (with red color). When alkaline chlorides are added to the solution double chlorides are precipitated, *e. g.*,  $\text{IrCl}_4 \cdot 2\text{NH}_4\text{Cl}$ , isomorphous with the double chlorides of platinum. When a solution of  $\text{IrCl}_4$  is boiled with  $\text{KOH}$ ,  $\text{Ir}(\text{OH})_4$  will be precipitated.



**PALLADIUM.**

Pd = 106.2

Palladium, in addition to occurring in platinum ores, is alloyed with gold (Brazil), and in some selenium ores (Hurtz); it has a silver white color, and is somewhat more fusible than platinum. In finely divided condition it dissolves, in boiling concentrated HCl, sulphuric and nitric acid. When ignited in the air, it, at first, through oxidation, becomes dull; at higher temperature, however, the surface again assumes a metallic appearance.

Palladium possesses, like some other metals (as platinum and silver), but in much higher degree, the ability of absorbing hydrogen gas (occlusion).

Freshly ignited palladium leaf absorbs at ordinary temperatures upwards of 370, at 90–100°C., about 650 vols. of hydrogen. A greater absorption, at ordinary temperatures, may be easily accomplished in the following manner:—

Water is decomposed by the galvanic current, palladium foil being used as negative electrode. The liberated hydrogen is then taken up by the palladium (to 960 vols); the metal expands ( $\frac{1}{6}$  its volume), becomes specifically lighter, but entirely retains, however, its metallic appearance. According to the investigations of Debray, the compound  $\text{Pd}_2\text{H}$  is produced, in which the hydrogen is contained dissolved, and departs itself similar to an alloy (compare p. 39). Palladium charged with hydrogen usually remains unaltered in the air and in a vacuum; sometimes, however, it becomes heated in the air, as the hydrogen is oxidized to water. The same occurs upon heating palladium hydride to 100°; in vacuo, all the hydrogen escapes as gas. Palladium hydride is a strong reducing agent, similar to nascent hydrogen.

Ferric salts are reduced to the ferrous state; chlorine and iodine in aqueous solution are converted into potassium chloride and hydriodic acid.

Palladium black absorbs hydrogen more energetically than the compact variety (at 100° upwards of 980 volumes). This substance is obtained by the reduction or electrolysis of palladic chloride. On heating palladium sponge in the air until the white metallic color becomes black, through the superficial formation of a layer of palladious oxide, it will at ordinary temperatures absorb hydrogen very energetically, with partial oxidation to water.

When palladium sheet or sponge is introduced into the flame of a spirit lamp, it is covered with smoke; this is due to the fact that the metal withdraws the hydrogen of the hydrocarbons, and carbon is set free.

Palladium forms two series of compounds; the palladious  $\text{PdX}_2$  and palladic,  $\text{PdX}_4$ . The first are well characterized and are distinguished by their stability.

**Palladious Chloride**— $\text{PdCl}_2$ —remains as a brown, deliquescent mass, in evaporating the solution of palladium in aqua regia. With alkaline chlorides it yields easily soluble, crystalline double salts, *e. g.*,  $\text{PdCl}_2 \cdot 2\text{KCl}$ .

**Palladious Iodide**— $\text{PdI}_2$ —is precipitated as a black mass, insoluble in water, by potassium iodide, from palladium solution.

**Palladious Oxide**— $\text{PdO}$ —is a black residue left upon careful ignition of the nitrate. It is difficultly soluble in acids. When heated it loses oxygen and forms palladium suboxide  $\text{Pd}_2\text{O}$ .

When palladium dissolves in sulphuric or nitric acids the corresponding salts are produced.

The sulphate,  $\text{PdSO}_4 + 2\text{H}_2\text{O}$ , is composed of brown crystals, readily soluble in water. Much of the latter decomposes it.

**Palladic Chloride**— $\text{PdCl}_4$ —is formed when the metal is dissolved in aqua regia. On evaporation it decomposes into  $\text{PdCl}_2$  and  $\text{Cl}_2$ . On adding potassium or ammonium chloride to the solution, difficultly soluble red double chlorides, similar to the corresponding platinum salts, appear.

---

## PLATINUM.

Pt — 196.7.

Its separation from the ore was described on p. 402. The metal has a grayish-white color and a specific gravity of 21.5. It is very tough and malleable, and may be drawn out into very thin wire and rolled into foil. At a strong heat it becomes soft without melting; in the oxy-hydrogen flame it fuses (about  $1770^\circ$ —Violle) and is somewhat volatile. On fusion it absorbs oxygen, which it again gives up on cooling (like silver). At ordinary temperatures it condenses oxygen too, upon its surface, especially when in finely divided state, as *platinum black* or *sponge*. The first is obtained if reducing

substances, like zinc, be added to solutions of platinic chloride or upon boiling with sugar and sodium carbonate; it absorbs as much as 250 volumes of oxygen. Platinum black remains as a spongy mass upon the ignition of  $\text{PtCl}_4 \cdot 2\text{NH}_4\text{Cl}$ . Upon this property of platinum to condense oxygen, as we have seen, depends the introduction of various reactions: thus hydrogen inflames in the air, if it be conducted upon platinum sponge; sulphur dioxide combines at  $100^\circ$  with O to form the trioxide. At a red heat platinum permits free passage to hydrogen, while it is not permeable by oxygen and other gases.

Platinum is not attacked by acids; it is only soluble in liquids generating free chlorine, as aqua regia. In consequence of this opposition to acids, and also its unalterability upon ignition, this metal answers as an undecomposable material for the production of chemical crucibles, dishes, wire, etc. The usual presence of iridium in ordinary platinum increases its durability.

The alkaline hydrates, sulphides and cyanides attack it strongly at a red heat. With phosphorus, arsenic, and many heavy metals, especially lead, it gives rise to easily fusible alloys; many heavy metals are also reduced from their salts by platinum. Therefore such substances must not be ignited in platinum crucibles, etc.

Platinum, like palladium, forms platinous  $\text{PtX}_2$  and platinic  $\text{PtX}_4$  compounds; in the first it is more basic, in the latter more of an acid nature.

**Platinic Chloride**— $\text{PtCl}_4$ —is obtained by the solution of platinum in aqua regia, and, on evaporation of the solution remains as a red-brown crystalline mass, very deliquescent in the air. It forms characteristic double chlorides,  $\text{PtCl}_4 \cdot 2\text{KCl}$ , with ammonium and potassium chloride. These are difficultly soluble in water; hence, on mixing the solutions, they immediately separate out in form of a crystalline yellow powder. Ignition completely decomposes the ammonium salt, leaving spongy platinum.

Similar insoluble double chlorides are formed by platinum chloride with those of rubidium, caesium and thallium, while that with sodium is very soluble in water. At  $200^\circ$ ,  $\text{PtCl}_4$  breaks up into  $\text{PtCl}_2$  and  $\text{Cl}_2$ .

On adding  $\text{NaOH}$  to platinic chloride and then supersaturating with acetic acid, there separates a reddish-brown pre-



cipitate of platinic hydrate,  $\text{Pt}(\text{OH})_4$ . This dissolves readily in acids (excepting acetic), with formation of salts. The oxygen salts, as  $\text{Pt}(\text{SO}_4)_2$ , are very unstable. The hydrate also has an acidic character (platinic acid), and dissolves in alkalies, forming salts with them. These, also, result in fusing platinum with potassium and sodium hydrate. The barium salt,  $\text{Pt} \left\{ \begin{array}{l} (\text{OH})_2 \\ \text{O}_2\text{Ba} \end{array} \right. + 3\text{H}_2\text{O}$ , is precipitated from platinic chloride, by barium hydrate, as a yellow, crystalline compound. As regards the acidic nature of its hydrate, platinum approaches gold. If hydrogen sulphide be conducted through platinic solutions, black platinum disulphide,  $\text{PtS}_2$ , is precipitated, soluble in alkaline sulphides, with formation of sulpho-salts.

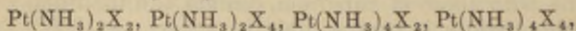
**Platinous Chloride**— $\text{PtCl}_2$ —is a green powder, insoluble in water, remaining after heating  $\text{PtCl}_4$  to  $200^\circ$ . It also affords double salts with alkaline chlorides, *e. g.*,  $\text{PtCl}_2 \cdot 2\text{NaCl}$ . Warmed with potassium hydrate it gives the hydrate  $\text{Pt}(\text{OH})_2$ .

#### CYANOGEN COMPOUNDS.

Like iron and cobalt, platinum yields double cyanides corresponding to ferrocyanides. When platinous chloride is dissolved in potassium cyanide there crystallizes on evaporation platinum-potassium cyanide,  $\text{K}_2\text{PtCy}_4 + 3\text{H}_2\text{O}$ , in large prisms exhibiting magnificent dichroism; in transmitted light they are yellow; in reflected light blue. This salt must be viewed as the potassium compound of hydro-platino-cyanic acid  $\text{H}_2\text{PtCy}_4$ . Separated from its salts it crystallizes in gold-yellow needles. Its salts with the heavy metals are obtained by double replacement, and all show a beautiful play of colors.

#### PLATINUM-AMMONIUM COMPOUNDS.

There is a whole series of these, which must be viewed as platinum bases and their salts. They are constituted according to the following empirical formulas:—



in which X indicates various acid residues, or halogen atoms. They arise by the action of ammonium hydrate upon platinous chloride. The bases are obtained by substituting hy-

droxyl groups for the acid residues, *e. g.*,  $\text{Pt}(\text{NH}_3)_4(\text{OH})_2$ . In their chemical properties these resemble alkaline hydrates. The other platinum metals form similar amine derivatives. The nature and chemical constitution of these interesting compounds is, however, not yet entirely explained.

### SPECTRUM ANALYSIS.\*

We observed that various substances, if introduced into a non-luminous flame, imparted to it a characteristic coloration. Thus the sodium compounds color it yellow, the potassium, violet, thallium, green, etc., etc. Upon the decomposition of the thus formed rays of light, and, indeed, of every light, by means of the prism, and the consideration of the resulting spectrum, depends spectrum analysis, established in 1859 by Kirchhoff and Bunsen, which, by its important applications and universal use, constitutes one of the greatest of scientific achievements of all ages.

As we well know, every substance, solid or liquid, heated to white heat emits rays (*e. g.*, molten platinum; lime heated in the oxy-hydrogen flame; the ordinary flame containing glowing particles of carbon,) of every refrangibility; and hence, furnishes, if the light be conducted through a prism, a *continuous spectrum*, which brings to view all the colors of the rainbow, from red to violet. Glowing gases and vapors, on the contrary, whose molecules can execute unobstructed oscillations, emit light of definite refrangibility, and therefore afford spectra, consisting of single, bright lines. Thus the spectrum of the yellow sodium flame is recognized as composed of one very bright yellow line, which by increased magnifying power is shown to consist of two lines lying very near each other. This reaction is so very delicate, that by means of it  $\frac{1}{1000000}$  of a milligram of sodium may be detected. The violet potassium light affords a spectrum, consisting of a red and a blue line. The crimson strontium light shows in the spectrum several single red and a blue line. (See the spectrum plate.) Each of these lines corresponds to a very definite coefficient of refraction, therefore in the spectrum it occupies a very definite relative position.

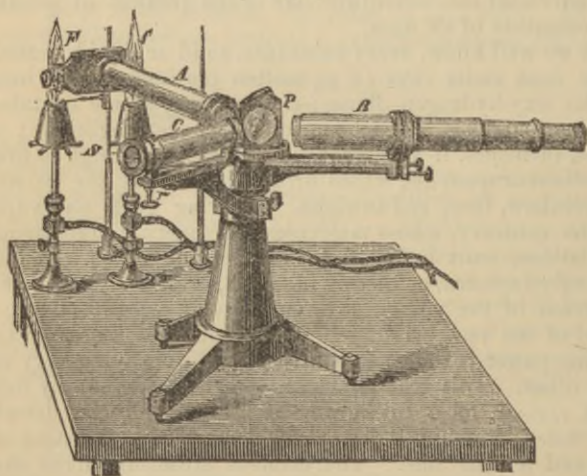
\* A more exhaustive, concise and distinct presentation of the spectrum phenomena may be found in Hermann W. Vogel's "Practische Spectralanalyse iridischer Stoffe." 1877.

If variously coloring substances be introduced into a flame, usually the most intense color obscures the others; in the spectrum, however, each individual substance shows its peculiar bright lines, which appear simultaneously or succeed each other, corresponding to the volatility of the various substances.

The spectrum apparatus or spectroscope, figured in Fig. 89, serves to observe the spectra.

In the middle of the apparatus is a flint-glass prism *P*. At the exterior end of the tube *A* is a movable vertical slit, in front of which is placed the source of light to be investigated. The entering light rays are directed by a collecting lens into the tube *A*, upon the prism, and the refracted rays (the spectrum) observed by the telescope *B*. To ascertain the relative position of the spectrum lines the tube *C* is employed. This at its outer end is provided with a transparent horizontal scale.

FIG. 89.



When a luminous flame is placed before the scale its divisions are reflected from the prism surface and reach into the telescope *B*. We see, then, in *B*, simultaneously, the spectrum to be investigated and the scale divisions, and can then readily determine the relative position of the spectrum lines. To study the spectra at the same time, and compare them, there is attached in front of one-half (the lower and upper) of the slit



of the tube *A* a three-sided, right-angled glass prism, which directs the rays of a light source placed at the side (*f*, Fig. 89) through *A* upon the prism *P*. Then by means of *B*, two horizontal spectra will be observed, one above the other, and between the bright scale divisions.

*Adjustment of the Spectroscope.*—To observe the spectra in the apparatus described, it is necessary to previously adjust the same correctly. The tube *A* contains, besides the slit, also a lens (Collimator lens), which serves to make parallel the bunch of rays proceeding from the slit; hence, the latter must be accurately placed in the focus of the lens. This is best accomplished as follows: The telescope (*B*) is screwed out and adjusted to some distant object, that it may be adapted for the reception of parallel rays; it is then replaced in the stand, pointed towards the slit, illuminated by a sodium chloride flame, and the slit then so far extended as to appear perfectly distinct in the telescope. To observe the spectrum lines as sharply as possible, the slit must be made quite narrow; for feebly luminous lines it must, however, be widened. The horizontal black lines appearing in the spectrum arise from dust particles adhering to the slit.

The proper position of the tube with the slit towards the prisms is usually fixed by the frame on which they rest. It must be so, that the refracted rays pass through the prism as symmetrically as possible, *i. e.*, in the minimum of their deviation, otherwise the spectrum is less distinct and (owing to unequal refraction) will appear distorted. The symmetrical passage of the spectrum rays approximates most nearly if the medial green rays pass through the prism symmetrically. Such a position, therefore, must be given the prism, with reference to the slit-bearing tube, that the middle green rays (line *E* of the sun spectrum) pass through in the minimum of their deviation. Then it is only necessary to so arrange the telescope that the green rays lie in the middle of the field of vision.

The *determination of the position of the lines of the spectra* is usually effected by means of a scale (see above) and so arranging it (according to Bunsen) that the yellow sodium line coincides with the division line 50 on the scale; then the red potassium line (*a*) lies at 17, the violet (*β*) at 152 (apparatus of Desaga). As, however, the refraction and dispersion of the rays are influenced by the quality of the glass of the prism, the scale indications of different forms of apparatus are not directly comparable. Hence they must be referred to an absolute measure. This is most conveniently attained by reduction to the sun spectrum, which, by means of the comparison prism, may be rendered at the same time visible in the telescope. The dark sun lines are now determined, with which the flame lines under investigation coincide. For accurate determinations, the spectrum lines are represented in wave lengths, according to the millionth of a millimeter.

The above described apparatus is that usually employed in chemical laboratories. In addition exist still others, accommodated to special purposes,—for investigation under the microscope, for the observation

of the sun and stars. For accurate observations, to obtain correct detailed, broad spectra, the light is permitted to pass through several (3-9) prisms, consisting of hollow glass filled with carbon disulphide, which refracts light very strongly. Instead of prism spectra, in many instances, diffraction spectra may be advantageously applied.

The *direct line* (*à vision directe*) spectroscopes are very excellent for laboratory purposes, with which the spectra, without deflection, may be seen in the direction in which the luminous objects really are. This is accomplished by a combination of several prisms of crown and flint glass, whereby dispersion, with simultaneous removal of deflection, is attained.

To observe the spectra of metals in many instances, thus with the alkalis and alkaline earths, it is only necessary to introduce their volatile salts into a non-luminous alcohol or gas flame. A reduction of the metal usually takes place, and the spectra of the free metals themselves are obtained; thus, for example, sodium chloride is decomposed in the flame at first into HCl and NaOH, which is then reduced by the carbon of the glowing gases to metallic sodium, which colors the flame yellow. The difficultly decomposable compounds (as the barium salts) frequently yield independent spectra, differing from those of the free metal; this is plainly recognizable in the copper compounds.

However, most metals require for their conversion into gases much higher temperature than that of the gas flame. To vaporize them and observe their spectra, the electric spark is made to pass from electrodes constructed of them. In this manner all metals, even the most non-volatile, like gold, iron and platinum; can be investigated. The spectra of these metals are generally quite complicated, and exhibit a great number of single lines. Thus, for iron, over 450 lines have been established.

Instead of making the electrodes from the metals under study, we can, according to Bunsen (Poggend. Ann., 155), employ carbon points saturated with solutions of the metallic salts. To produce the electric spark, a Ruhmkorf induction apparatus with a dip battery of 4 elements, and an attached Leyden jar, will suffice. Such *spark spectra* frequently distinguish themselves from flame spectra obtained in the gas flame.

A peculiar, very interesting and practical procedure for the production of spark spectra, is due to Lecoq de Boisbaudran (Spectres lumineux, Paris, 1874). He allows the induction sparks to strike into the solution of the metal under consideration. This is placed in a small reagent tube, in the bottom of which is fused a platinum wire. Above the surface of the liquid is the second electrode, a platinum

wire connected with the positive pole of the induction spiral. In this manner the spectra of all the metals may be easily obtained, and indeed, by it Lecoq de Boisbaudran discovered gallium.

The spectra of the elementary gases may be determined by passing electric sparks through them, whereby these will be variously colored. Hydrogen illuminates with a red light, giving in the spectrum a bright red, a blue and a green line. Nitrogen shines with violet light and affords a spectrum of many lines, chief of which are the violet. The spectra of gases may be more conveniently observed by aid of Geissler's tubes, which are filled with very dilute gases and the induction stream then passed through them.

By these methods we can very readily distinguish the individual chemical elements, and even detect them in traces. By means of them, since the year 1860, different new elements: Cæsium, rubidium, thallium, indium, scandium, gallium and several others which have not been accurately studied, have been discovered.

In addition to the just described direct, bright spectra, there are yet *dark absorption spectra*. If a white light giving an uninterrupted spectrum be allowed to pass through different transparent bodies, the latter will absorb rays of definite refrangibility, allowing all others to pass. Therefore, in the spectroscope we observe the sun spectrum interrupted by dark lines or bands. Thus solutions of didymium and erbium absorb certain rays, and in the spectrum give corresponding dark lines. The gases deport themselves similarly. White light that has traversed a broad layer of air shows several dark lines in the spectrum peculiar to nitrogen, oxygen and steam. To a much higher degree is this power of absorption peculiar to all glowing gases or vapors. If a white light, like the Drummond calcium light, be conducted through the yellow sodium flame (through glowing sodium vapors), there will appear in the rainbow spectrum of the white light a dark line, which, as regards position, accurately corresponds to that of the yellow sodium line; the latter thus appears converted into a dark line. If white light be passed through the potassium flame, two dark lines will be visible in the spectrum, corresponding to the red and blue lines of the potassium spectrum. Such spectra are designated the *inverted spectra* of the corresponding metals. In this way the inverted spectra of all elements may be obtained, which accurately correspond to the direct



bright spectra. The cause of these phenomena lies in the proposition deduced by Kirchhoff from the undulatory theory of light, viz., the proportion between the power of emission and absorption for all bodies at equal temperatures is the same. According to this, glowing gases only absorb rays of just the same refrangibility which they emit. For example, bright white light is passed through the yellow sodium flame, the yellow rays of the same are absorbed and retained, while all others, almost entirely unaltered, pass on. Therefore, in the rainbow spectrum of white light the yellow rays of definite refrangibility fail; if, now, the other refracted rays of the white light are brighter than the yellow rays emitted from the sodium flame, the latter will be relatively darker; a dark line will therefore make its appearance.

These phenomena have laid open to spectrum analysis, a new and broad domain, inasmuch as they open up avenues for the investigation of the chemical nature of the sun and other bodies.

As is known, the bright rainbow sun spectrum is intersected by a quantity of dark lines which have been called, from their discoverer, the Fraunhoff lines. The explanation of these becomes simple after what has been given in the preceding paragraphs, as shown by Kirchhoff, with the following hypothesis upon the nature of the sun. The latter is composed of a solid or liquid, luminous nucleus, surrounded by an atmosphere of glowing gases and vapors. Therefore, the uninterrupted spectrum of the glowing nucleus must be intersected by the dark lines of the inverted spectra of these gases and vapors, which are present in the sun's atmosphere. An accurate comparison of the Fraunhoff lines with the spectrum lines of the various elements, has revealed the fact that in the sun's atmosphere are chiefly found iron, sodium, magnesium, calcium, chromium, nickel, barium, copper, zinc and hydrogen. Thus, for all the 450 lines of the iron spectrum have been discovered the corresponding dark lines in the sun's spectrum. The conclusive inferences upon the chemical constitution of the sun, possess just such, indeed, a much higher degree of probability than is peculiar to many other deductions.

The investigation of the sun's spectrum has cleared up many other changes occurring there, and on this was founded an entire sun-meteorology; all the fixed stars thus far investigated

possess a constitution like that of the sun. They give spectra intersected by dark lines; therefore they consist of incandescent nuclei surrounded by gaseous atmospheres. The spectra of nebulae only show bright lines; hence these consist of masses of glowing vapor yet uncondensed.

**Periodicity of the Spectrum Lines.** As all other properties of the elements and their compounds proved themselves to be periodic functions of the atomic weights, the same is to be expected with reference to the spectrum phenomena. As yet but few such regularities have occurred. The most elements, chiefly the metalloids and the difficultly volatile metals, afford very complex spectra, which at the same time frequently vary with the temperature, so that for some of them spectra of 1st, 2d, etc., order are distinguished. It, however, appears that not all the spectra lines are of the same importance, as in several instances it has been possible to refer the various lines of a spectrum to particular fundamental lines whose relations to each other are comparable to that of the harmonies to primary tones. Thus the four lines of the hydrogen spectrum may be looked upon as the harmonies of a single wave. Therefore, in the comparison of spectra only individual lines are to be regarded. This is clearly observed with the easily volatile metals belonging to the homologous groups K Rb Cs, Ca Sr Ba, Ga In Tl, whose lines lying in the violet portion of the spectrum proceed more towards the red end as the atomic weights increase; with the latter, or that of the atomic volumes, the wave lengths (in millionths of a millimeter) become successively greater:—

K 39	Wave length,	404	Ca 40	Wave length,	422
Rb 83	“	420.421	Sr 87	“	461
Cs 132	“	456.459	Ba 137	“	525.550
	Ga 69	Wave length,		403.417	
	In 113	“		410.450	
	Tl 209	“		535.	

By the arrangement of the spectra in the spectrum plate, these relations are made apparent.

A similar shifting of the spectral lines is observed with heterologous elements belonging to the same periods: K Ca, Rb Sr, Ba Cs, so that a conclusion upon the spectra of the succeeding elements appears possible. Indeed, the element scandium (45) succeeding calcium, shows intense violet lines of the wave length 425–440.

## ERRATA.

P. 137, 4th line. Instead of *algar red sand*, "powder of algaroth." P. 233, 22d line. Instead of *Ba*, read "BN." P. 351, 17th line, the number of page omitted in (compare p. ) is 69. P. 256. The page omitted under *Salts* is 169. P. 300. Atomic weight of strontium should be 87.2 not 872.



LIBRARY.

... of the ...  
 ... of the ...  
 ... of the ...

Particulars of the ...  
 ... of the ...  
 ... of the ...  
 ... of the ...  
 ... of the ...

...	...	...	...
...	...	...	...
...	...	...	...
...	...	...	...

... of the ...  
 ... of the ...  
 ... of the ...

... of the ...  
 ... of the ...  
 ... of the ...



FOUNDATIONS OF THE METALS

CHAPTER I OF METALS

Table of Contents (continued)

a	b	c	d
100	100	100	100
101	101	101	101
102	102	102	102
103	103	103	103
104	104	104	104
105	105	105	105
106	106	106	106
107	107	107	107
108	108	108	108
109	109	109	109
110	110	110	110
111	111	111	111
112	112	112	112
113	113	113	113
114	114	114	114
115	115	115	115
116	116	116	116
117	117	117	117
118	118	118	118
119	119	119	119
120	120	120	120
121	121	121	121
122	122	122	122
123	123	123	123
124	124	124	124
125	125	125	125
126	126	126	126
127	127	127	127
128	128	128	128
129	129	129	129
130	130	130	130
131	131	131	131
132	132	132	132
133	133	133	133
134	134	134	134
135	135	135	135
136	136	136	136
137	137	137	137
138	138	138	138
139	139	139	139
140	140	140	140
141	141	141	141
142	142	142	142
143	143	143	143
144	144	144	144
145	145	145	145
146	146	146	146
147	147	147	147
148	148	148	148
149	149	149	149
150	150	150	150









A

	PAGE		PAGE
Absorptiometer.....	111	Animal charcoal.....	141
Acetylene.....	145	Anthracite.....	141
Acids.....50, 75,	168	Antimony.....	185
Acid radicals.....	169	" butter.....	186
Active oxygen.....	76	" chloride.....	186
" chlorine.....	296	" hydride.....	186
Affinity, chemical.....	15	" oxide.....	215
Agate.....	227	" sulphides.....	216, 217
Alabandite.....	381	Antimonic acid.....	216
Algar red, powder.....	137	Antimonyl.....	215
Alkaline metals.....	265	Apatite.....	297
" earths.....	291	Apparatus of Carrè.....	118
Allotropy.....	79	" " Dœbereiner....	38
Alloys.....	252	" " Marsh.....	133
Alum.....347,	382	Aqua regia.....	195, 337
" burned.....	348	Argentan.....	331, 401
" cubic.....	348	Arsenates.....	213
" Roman.....	348	Arsenic.....	131
" shales.....	348	" acid.....	212
Alumina.....	346	" sulphides.....	213, 214
Aluminates.....	345	Arsenious chloride.....	135
Aluminite.....	347	" oxide.....	211
Aluminium.....	342	Arsenites.....	212
" bronze.....	343	Arsine.....	132
" chloride.....	343	Asbestos.....	308
" oxide.....	344	Atmosphere.....	108
" sulphate.....	347	Atomic compounds.....	165
Alunite.....	348	" heat.....	247
Amalgams.....	253	" volume.....	245
Ammonia.....	115	" weights.....	17, 158
" heat of formation of	139	" " thermal.....	250
Ammonium.....	120	Atoms.....	60, 68, 157
" anglesite..	364	Aurates.....	340
" chloride.....	288	Auric acid.....	339
" compounds.....	287	Auripigment.....	213
" salts.....	348	Aurous compounds.....	338
Anatase.....	229	Auric ".....	339
Anhydrides of acids.....	169	Avogadro, law of.....	68
Anhydride.....	296	Azote.....	109
Anhydro-acids.....	186, 206, 227	Azurite.....	330



<b>B</b>		PAGE		PAGE
Barium.....		301	Carbon disulphide.....	223
“ peroxide.....		302	“ group.....	140
“ sulphate.....		302	“ monoxide.....	222
“ chromates.....		373	“ oxychloride.....	223
Baryta water.....		302	Carbonates.....	222
Bases.....	50,	75	Carbonic acid.....	222
Basicity of acids.....	168,	208	Carrè's apparatus.....	118
Bauxite.....		345	Cast iron.....	388
Bell metal.....		331	“ steel.....	389
Blue, Prussian.....		396	Cassiterite—Tin-stone.....	357
Beryllium.....		309	Caustic potash.....	274
Bessemer steel.....		389	“ soda.....	278
Bismuth.....	137,	365	Cement.....	293
Bismuthic acid.....		366	Cementation steel.....	389
Bismuthinite.....		365	Cerium.....	351
Bitter salt.....		307	Cerite.....	350
“ water.....		82	Cerussite.....	361, 364
Bleaching.....	42,	179	Chalk.....	298
Boiler incrustation.....		298	Chamber acid.....	182, 184
Boracite.....		231	Charcoal, animal.....	141
Boron.....		230	Chemical affinity.....	15
“ fluoride.....		232	“ energy.....	15
Brass.....		330	“ structure.....	160
Braunite.....		380	Chloranhydrides.....	187
Bromine.....		43	Chloric acid.....	172
“ hydrate.....		44	Chlorides of sulphur....	101, 102
“ hydride.....		52	Chlorine.....	39
Bromic acid.....		173	“ gas.....	383
Bronze.....		331	“ hydrates.....	41
Brown coal.....		141	“ iodide.....	58
Burned alum.....		348	“ oxides.....	169
			“ water.....	41
<b>C</b>			Chloroform.....	151
Cadmium.....		312	Chlorous acid.....	171
Cæsium.....		276	Chromates.....	371
Calamine.....		312	Chromic acid.....	372
Calcium.....		292	Chromite.....	373
“ carbonate.....		298	Chromium group.....	367
“ manganite.....		383	“ .....	368
“ oxide.....		292	“ alum.....	370
“ silicate.....		298	“ oxychloride.....	374
“ sulphides.....		299	“ yellow.....	374
“ sulphate.....		296	Chrysoberyl.....	346
Calcite.....		392	Cinnabar.....	321
Calomel.....		318	“ green.....	398
Calorie.....	57,	80	Cobalt.....	397
Caput mortuum.....		393	“ cyanides.....	399
Carbon.....		140	Cobalt rose.....	399
“ chlorides.....		151	“ ultramarine.....	398
“ dioxides.....		219	Cobaltite.....	397

	PAGE		PAGE
Cobaltous compounds.....	397	Ekaboron .....	350
Cobaltic .....	398	Eka-aluminium.....	352
Coke.....	141	Electrolysis of salts.....	260
Colcothar.....	393	Elements.....	12
Colloids.....	227	" classification of....	30
Compounds atomic.....	165	Emery .....	344
" definite.....	83	Equivalence.....	162, 164
" endothermic.....	57	" of forces.....	14
" exothermic.....	57	Equivalent weights.....	162
" molecular.....	165	Erbium.....	351
Copper.....	325, 330	Ethyl.....	144
" hydride.....	328	Ethylene.....	144
" vitriol.....	329	Eudiometer .....	111
Corundum.....	242	Euxenite.....	350
Critical temperature.....	219		
Crocoisite.....	361, 368	<b>F</b>	
Cryolite.....	283, 342	Feldspar.....	349
Crystallization, water of.....	83	Ferric acid.....	394
Crystallography.....	20	" compounds.....	392
Crystalloids.....	227	Ferricyanogen .....	395
Cupellation.....	332	Ferrous compounds .....	391
Cuprammonium compounds,	329	Ferrocyanogen.....	395
Cupric compounds.....	328	Flame .....	145
Cuprite .....	327	" illuminating power of.....	147
Cuprous compounds.....	327	" non-luminosity of.....	150
Cyanogen .....	224, 394	Flores zinci.....	311
" compounds.....	408	Flint .....	299
Corrosive sublimate.....	319	Fluorine .....	46
Cubical alum.....	348	Fluorite.....	292
		Fulminating silver.....	333
<b>D</b>			
Davy's lamp.....	150	<b>G</b>	
Decipium .....	341	Gadolinite .....	350
Dialysis.....	227	Gahnite.....	346
Diamond.....	140	Galenite.....	332, 361
Dicyanogen .....	225	Gallium.....	352
Didymium .....	351	" group.....	351
Diffusion of gases.....	113	Gas densities.....	62
Dissociation 85, 96, 130, 184,	198	" laughing .....	204
Disodium phosphate.....	234	" volume .....	64
Disulphuric acid.....	186	Gases, condensation of.....	35
Dithionic acid.....	190	" diffusion of.....	113
Döbereiner's lamp.....	38	" kinetic theory of.....	64
Drummond's light.....	75	" measuring of.....	112
		Gersdorffite .....	400
<b>E</b>		Glass.....	299
Earth metals.....	291	Glover's tower.....	182
Earth alkaline.....	291	Glucinum.....	309
" rare.....	350	Gold.....	337
Epsom salt.....	373	" purple .....	340

	PAGE		PAGE		
Gold fulminating.....	340	Indium .....	353		
“ sulphide.....	340	Iodic acid.....	173		
Granite.....	349	Iodine .....	44		
Graphite..... 140,	141	Iridium.....	402, 404		
Greenockite.....	313	Iron.....	387		
Guignet's green.....	330, 370	“ alum .....	394		
Gypsum.....	296	“ cast.....	388		
<b>H</b>					
Halogen compounds.....	253	“ fused .....	392		
“ hydrides.....	47	“ group .....	386		
Halogens.....	39	“ pyrite.....	391		
Haloid acids.....	51	“ pyrophoric .....	390		
“ salts.....	51	“ vitriol.....	391		
Hausmannite.....	380, 382	“ wrought.....	388		
Heat, latent.....	81	Isomerism.....	79		
“ solution of.....	83	Isomorphism.....	251		
“ specific.....	274	<b>K</b>			
“ unit of.....	80	Kaolin.....	342, 349		
“ atomic .....	274	Kelp.....	45		
Hematite.....	392	Kermes minerale.....	217		
Hornsilver.....	331, 334	Kieserite.....	306		
Hydrargillite .....	345	<b>L</b>			
Hydrates..... 75, 174,	254	Lanthanum.....	341, 350		
“ of acids.....	185	Lapis lazuli.....	349		
Hydrobromic acid.....	52	Laughing gas.....	204		
“ chloric “ .....	47	Lead.....	356, 361		
“ cyanic “ .....	225	“ chamber crystals.....	184		
“ carbons .....	142	“ oxide.....	362		
“ fluoric acid.....	55	“ peroxide.....	363		
“ sulphurous acid.....	180	“ sulphide .....	363		
Hydrogen.....	31	“ tree .....	362		
“ chloride.....	47	“ vitriol (sulphate).....	364		
“ cyanide.....	225	“ white.....	363		
“ fluoride.....	55	“ alloys.....	362		
“ iodide.....	53	Lime .....	293		
“ peroxide.....	90	“ stone .....	292		
“ persulphide.....	100	“ water.....	293		
“ sulphide.....	97	“ chloride of.....	294		
Hydroxides..... 75,	254	Litharge.....	362		
Hydroxylamine.....	121	Lithium.....	286		
Hypochlorites.....	170	Lunar caustic.....	336		
Hypochlorous acid.....	170	Luteocobalt chloride.....	399		
Hypophosphites.....	206	<b>M</b>			
Hypophosphorous acid.....	206	Magnesia.....	306		
Hyponitrous acid.....	204	Magnesite.....	308		
Hyposulphites.....	189	Magnesium.....	305		
Hyposulphurous acid.....	189	“ group.....	303		
<b>I</b>					
Ice machine of Carrè.....	118	Magnetite.....	393		
		Malachite.....	330		



	PAGE		PAGE
Manganese.....	379	Nitrosylsulphuric acid.....	198
Manganic acid.....	380	Nitrous acid.....	197
“ salts .....	381	Nordhausen sulphuric acid...	186
Manganite .....	380		
Marble.....	292	<b>O</b>	
Marsh's apparatus.....	133	Orthoclase.....	349
Marsh gas.....	142	Olefiant gas.....	145
Massicot.....	363	Organic chemistry.....	142
Maximum valence.....	165	Ores.....	310
Mercuric compounds.....	319	Orthite.....	350
Mercurous “ .....	318	Ortho-acids.....	192
Mercury.....	314, 316	“ nitric acid.....	194
Meta-acids .....	192	“ phosphoric acid.....	208
Meta-antimonic acid.....	216	Osmium.....	401, 403
Metahydrates.....	255	Oxidation.....	75
Metals.....	244	Oxides.....	254
Metalloids.....	12, 30	“ basic.....	75
Metaphosphoric acid.....	208	“ acid-forming.....	75
Metastannic acid.....	358	Oxygen.....	71
Methyl.....	142	Ozone.....	76
Mineral waters.....	82		
Molecular theory.....	69	<b>P</b>	
“ compounds.....	165	Palladium.....	401, 405
Molecule.....	68, 69, 157	“ hydride.....	39, 405
Molecules of elements 69; 79, 96, 125		Passive iron.....	390
Molybdenum .....	375	Pattison's method.....	332
Molybdenite.....	375, 376	Pentathionic acid.....	190
Molybdic acid.....	376	Periodates.....	175
Mortar.....	293	Perchloric acid.....	172
Mosaic gold.....	361	Periodic system.....	233
Multiple proportions .....	62	Periodicity of heat of forma- tion.....	242
Magisterium bismuthi.....	367	“ “ spectral lines..	415
		“ “ valence.....	240
<b>N</b>		Periodic acid.....	174
Nickel.....	400	Permanent white.....	365
“ plating.....	401	Permanganic acid.....	379, 383
Niobium.....	137	Peroxides.....	255
Nitrates.....	193	Phillipium.....	341
Nitric acid .....	193	Phlogiston.....	109
“ “ anhydride .....	196	Phosgene.....	223
“ “ fuming.....	195	Phosphates.....	206
Nitrogen.....	106	Phosphine.....	126
Nitrogen chloride.....	122	Phosphites.....	206
“ iodide .....	123	Phosphonium .....	128
“ oxide .....	201	“ iodide.....	128
“ pentoxide .....	196	Phosphorus.....	123
“ tetroxide.....	197	“ bromides.....	131
Nitrosulphuric acid.....	198	“ chlorides.....	129
Nitrosylchloride .....	201	“ iodides.....	131

	PAGE		PAGE
Phosphorus oxychloride.....	131	Radicals s. residues.....	169
“ pentoxide.....	205, 209	Realgar.....	214
“ sulphides.....	211	Reduction.....	76
Phosphorous acid.....	207	Residues.....	169
Phosphoric “.....	208	Respiration.....	221
Phosphorite.....	297	Rhodium.....	404
Photography.....	335	Rhodochroisite.....	380, 381
Platinum.....	406	Rock salt.....	278
“ bases.....	408	Roseo-cobalt.....	399
“ metals.....	401	Rose's metal.....	367
“ ores.....	402	Rubidium.....	276
“ sponge.....	38, 402, 406	Ruby.....	342
Plumbic acid.....	363	Ruthenium.....	401, 403
Polyacids.....	186, 227	Rutile.....	229
“ silicic acid.....	227	Roman alum.....	348
“ thermic “.....	188		
Porcelain.....	349	<b>S</b>	
Potashes.....	273	Safety lamp.....	150
Potassium.....	267	Salts.....	54, 75, 168, 256
“ amide.....	276	“ basic.....	257
“ aurate.....	340	Saltpetre.....	272
“ bromide.....	268	Salt producers.....	39
“ chloride.....	269	“ springs.....	278
“ cyanide.....	270	Sapphire.....	342
“ fluoride.....	270	Sassolite.....	232
“ hydrate.....	268	Scandium.....	350
“ iodide.....	270	Scheele's green.....	330
“ manganate.....	352	Scheelite.....	377
“ oxide.....	268	Schlippe's salt.....	217
“ plumbate.....	363	Schweizer's reagent.....	328
“ saltpetre.....	272	Sea water.....	82
Prussiate of potash, yellow... ..	395	Selenic acid.....	191
“ “ red.....	396	Selenium.....	102
Purpureocobalt chloride.....	399	Silicates.....	227
Pyrolusite.....	380, 382	Silicic acid.....	226
Pyrites.....	181, 394	Silicon.....	152
Pyroacids s. polyacids..	186, 227	“ chloride.....	153
Pyrophosphoric acid.....	208	“ chloroform.....	154
Pyrosulphuric “.....	186	“ dioxide.....	226
		“ disulphide.....	228
<b>Q</b>		“ fluoride.....	155
Quantivalence.....	160	“ hydride.....	152
Quartz.....	226	Silver.....	331
Quadrant oxides.....	256	“ cyanide.....	335
Quicksilver.....	320	“ nitrate.....	335
		“ oxides.....	333
<b>R</b>		Silvering.....	336
Red chromate of potash. ....	373	Slags.....	381
Red lead.....	363	Smaltite.....	397
Rare metals.....	350	Smalts .....	398

	PAGE		PAGE
Smithsonite.....	392	Sulphuric acid.....	181
Soda.....	282	“ anhydride.....	181
“ caustic.....	278	“ “ English..	184
Sodium.....	277	“ “ fuming..	186
“ carbonate.....	282	Sulphides.....	99
“ chloride.....	278	Sulphites.....	179
“ hydrate.....	277	Sulphurous acid.....	179
“ hyposulphite.....	281	Sulphuryl.....	188
“ iodate.....	279	“ chloride.....	188
“ saltpetre.....	284	Sylvanite.....	337
“ sulphate.....	277	Sylvite.....	269
“ oxide.....	277	Sympathetic ink.....	397
“ phosphates.....	284		
“ silicate.....	286	<b>T</b>	
Soft solder.....	362	Talmi gold.....	331
Specific gravity of gases...36,	63	Tantalum.....	187
“ “ “ metals.....	244	Telluric acid.....	191
“ heat.....	247	Telluride, hydrogen.....	104
“ volume.....	245	Tellurium.....	103
Spectrum analysis.....	409	Tension of vapors.....	81
Spiegeleisen.....	388	Terbium.....	341
Stalactite.....	298	Tetanic acid.....	191
Stannates.....	356	Tetranoxide.....	328
Stannic compounds.....	360	Tetrathionic acid.....	190
Stanniol.....	357	Thallic acid.....	356
Stannous compounds.....	359	Thallium.....	354
Stassfurt salts.....	267	“ glass.....	356
Status nascendi.....43,	69	Thenard's blue.....	398
Steel.....	388	Thionyl chloride.....	179
“ cast.....	389	Thiosulphuric acid.....	189
“ Bessemer.....	389	Thorium.....	228, 230
Stibnine.....	186	Thulium.....	18, 341
Stibnite.....	185	Tin.....	356
Stone coal.....	140	“ stone.....	357
Stolzite.....	377	Tinkal.....	285
Strass.....	299	Titanium.....	229
Strontianite.....	300	Tombac.....	331
Strontium.....	300	Trithionic acid.....	190
Structure, chemical.....	160	Turnbull's blue.....	396
Substitution.....	151	Turpetum mineral.....	321
Sulphur auratum.....	217	Type metal.....	362
Sulphates.....	177	Tungsten.....	367, 377
Sulphur.....	94	“ steel.....	377
“ chlorides.....	101	Tungstic acid.....	377
“ dioxide.....	177		
“ heptoxide.....	180	<b>U</b>	
“ sesquioxide.....	180	Ultramarine.....	349
“ trioxide.....	181	Uranates.....	378
Sulpho-stannate.....	359	Uranium.....	378, 367
Sulphuretted hydrogen.....	97	“ yellow.....	379



	PAGE		PAGE
Uranium glass .....	379	White lead.....	364
Uranyl.....	378	Wolfram .....	377
		Wollastonite.....	299
		Wrought iron.....	388
		Wolfenite.....	361
<b>V</b>		<b>Y</b>	
Valence.....	160	Ytterbium.....	351
Vanadium.....	137	Yttrium.....	351
Vapor density.....	45	Yellow prussiate of potash....	395
Varec.....	45		
Vivianite.....	392		
Vitriol, oil of, see Sulphuric acid			
Vitriol, iron.....	391	<b>Z</b>	
		Zinc.....	310
		“ blende.....	312
<b>W</b>		“ dust.....	310
Water.....	80	“ vitriol.....	311
Water glass.....	226	“ white.....	311
“ of constitution.....	307	Zircon.....	228, 230
White iron.....	387		

# INORGANIC CHEMISTRY.

---

## A TEXT-BOOK FOR STUDENTS.

---

By **PROF. VICTOR V. RICHTER,**  
*University of Breslau.*

AUTHORIZED TRANSLATION FROM THE THIRD GERMAN EDITION,

By **EDGAR F. SMITH, M.A., Ph.D.,**

*Prof. of Chemistry in Wittenberg College, Springfield, Ohio; formerly in the Laboratories of the University of Pennsylvania and Muhlenberg College; Member of the Chemical Societies of Berlin and Paris, of the Academy of Natural Sciences of Philadelphia, etc., etc.*

---

89 Wood-cuts and Colored Lithographic Plate of Spectra.  
12mo, Cloth, 421 Pages. Price \$2 50.

---

In most of the chemical text-books of the present day, one of the striking features and difficulties with which teachers have to contend is the separate presentation of the theories and facts of the science. These are usually taught apart, as if entirely independent of each other, and those experienced in teaching the subject know only too well the trouble encountered in attempting to get the student properly interested in the science and in bringing him to a clear comprehension of the same. In this work of **PROF. VON RICHTER**, which has been received abroad with such hearty welcome, and for which there has been a great demand, two editions having been rapidly disposed of, theory and fact are brought close together, and their intimate relation clearly shown. From careful observation of experiments and their results, the student is led to a correct understanding of the interesting principles of chemistry. The descriptions of the various inorganic substances are full, and embody the results of the latest discoveries. The periodic system of **MENDELEJEFF** and **LOTHAR MEYER** constitutes an important feature of the book. The thermo-chemical phenomena of the various groups of elements also receive proper consideration, both in their relation to chemical affinity and the law of periodicity. The matter is so arranged as to adapt the work to the use of the beginner as well as for the more advanced student of chemical science.

The arrangement of types, size of the book, etc., are such as to facilitate its use.

*\*\*Favorable terms will be made for the adoption of this work in schools and colleges. Professors of chemistry are invited to correspond with the publishers in reference to its introduction, and for further information.*

**P. BLAKISTON, SON & CO.,** Publishers and Booksellers,  
MEDICAL AND SCIENTIFIC BOOKS,  
*No. 1012 Walnut Street, Philadelphia.*

316

From JOHN MARSHALL, M.D., NAT. SC.D. (Tübingen), Demonstrator of Chemistry in the University of Pennsylvania.

Knowing the value of the excellent work of Prof. von Richter in the original, I am pleased to hear of a forthcoming English translation, by such an able chemist and admirable translator as Prof. Smith.

The work is of undoubted value. The theory of chemistry, which is generally the bugbear of students, is in this book very clearly explained, and the explanations are so well distributed through the book that students are brought easily from the simplest to the most difficult problems.

That part descriptive of the elements and their compounds is full, and all that could be desired in a text-book, while the cuts, with which the work is profusely illustrated, are an excellent aid to the student. Altogether, it is one of our best modern works on chemistry.

---

MUHLENBERG COLLEGE, CHEMICAL LABORATORY,  
ALLENTOWN, PA.

This volume is especially adapted for use as a text-book; and, if for no other reason than for its superior arrangement, should find its way into our best schools and colleges. The author has apparently accomplished the difficult task of furnishing to the student a book that combines, with the utmost clearness, the two departments of general chemistry, in such a way as to remove the trouble which has for a long time been experienced in applying the theoretical knowledge obtained to the explanation of the inorganic portion of the work. In this volume, however, the two departments are treated at one and the same time. The name of the translator should insure it a cordial reception by all American chemists.

N. WILEY THOMAS.

---

I am well acquainted with von Richter's Inorganic Chemistry in its original German form. Its success abroad has been exceptional, having rapidly run through several large editions in Germany, and having been translated into at least two other languages.

With the large number of text books on Inorganic Chemistry at present in the field, this success could only have been achieved because of distinctive features which merited commendation.

These we find to be the clear presentation of simple underlying theory and succinct statements of illustrative facts; but above all, in the well chosen order in which present views of chemistry are developed in successive steps.

Dr. Smith's previous successes in the role of translator and editor of German works on chemistry insure an accurate reproduction of the original.

We have no doubt that the work will be as well received by American chemists as it has been abroad.

SAM'L P. SADTLER,  
Prof. of General and Organic Chemistry, University of Penn'a.













" " " IV  
H O - su  
cl c  
di

Ammonia  $\text{NH}_3$

H. H. H.







