Horsford (E. N.)

INVESTIGATION

OF

GLYCOCOLL

AND SOME OF ITS

PRODUCTS OF DECOMPOSITION.

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To JOHN W. WEBSTER, M.D.,
ERVING PROFESSOR
IN THE
UNIVERSITY AT CAMBRIDGE:
THE FOLLOWING PAPER,
IN TESTIMONY
OF GRATEFUL REMEMBRANCE,
IS RESPECTFULLY DEDICATED,
BY
THE AUTHOR.

INVESTIGATION, &c.

As there are laws in physics, whose evolution, carefully traced, would constitute a general history of this department of science, so there are bodies in chemistry, whose career, if we may employ such an expression, accurately followed out, would acquaint us with the prominent periods through which this science has passed. The history of *sulphuric acid*, for example, may almost be said to be the history of *technical* chemistry, as that of *hydrosulphuric acid* and *ammonia* is of *analytical;* or, as that of *oxygen* is of *theoretical* chemistry.

Among the bodies belonging to organic chemistry, perhaps no one presents itself, whose history, fairly exhibited from the time of its discovery down to this date, contains more obvious and lasting impressions of the periods through which this branch of chemical science has passed, than the sugar of gelatine. It bears the stamp of a period when an organic analysis had scarcely been made; of a time when the substance was not obtained pure; then of a time when, from the perfection of methods and apparatus, analyses enjoyed the whole confidence of the chemist, and it was only necessary that formulæ should coincide with them, in order to their being considered correct; and finally, of a time in which the relations to other substances came in to share in the solution of the problem of the constitution of an organic body. These circumstances may justify a glance at the history of this interesting body.

Braconnot,[*] in 1820, by treating isinglass with sulphuric acid, obtained a body of sweet taste, ready solubility in water, difficult solubility in alcohol, capable of uniting with nitric acid, and in this state of combination uniting with alkalies and alkaline earths; to which substance he gave the name of sugar of gelatine, (*sucre de gelatine.*)

Boussingault,[†] to whom we are indebted for the first analysis of this body, gave it the formula $C_{12}H_{31}N_6O_{11}$, which, expressed in equivalents, is $C_{12}H_{15\frac{1}{2}}N_3O_{11}$.

From this body he obtained a crystallizable compound, with the protoxyd of lead, which, upon analysis, yielded the formula $C_{12}H_{13\frac{1}{2}}N_3O_7+3PbO$. Three atoms of protoxyd of lead had taken the place of two atoms of water.

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[*] Annal. de Chim. et de Phys., T. xiii, p. 113.

[†] L'Institut, No. 245. Phar. Cent. Blatt, No. 50, 1838.

If this be regarded neutral, Boussingault remarks, the body without water would be $C_4H_{4\frac{1}{2}}NO_3$.

The investigation undertaken at this period (1838) was resumed in 1840, '41,* when, from the same chemist, a new formula, obviously based upon a conscientious trust in the results of analysis, was produced.

Meanwhile, Mulder† had obtained the same body with Leucin, by treating glue with caustic potash. His analysis led him to the formula $C_8H_9N_2O_7$. With protoxyd of lead it lost two atoms of water. Its composition would then have been $C_8H_7N_2O_5 + 2HO$, the two atoms of water being replaceable by two atoms of protoxyd of lead. This formula differs from that of Boussingault, chiefly in that it is about two-thirds as large. In that of Boussingault, an equal loss of water was, however, replaced by three atoms of protoxyd of lead, instead of two.

With the gelatine-sugar-nitric acid, (*acide-nitro-saccharique; leim-zucker-salpetersaure,*) Mulder obtained a compound with baryta, of unusual constitution, which he expressed by the following formula—

$$(BaO, C_8H_7N_2O_5) + 2(BaO, NO_5).$$

His formula for gelatine-sugar-nitric acid, is

$$C_8H_{11}N_4O_{19} = C_8H_9N_2O_7 + 2NO_5 + 2HO,$$

while that of Boussingault, for this compound, was

$$C_4H_{6\frac{1}{2}}N_2O_{10} = C_4H_{4\frac{1}{2}}NO_3 + NO_5 + 2HO.$$

These differ from each other in the relative and absolute quantities of hydrogen and oxygen, and yet not so widely but that the want of correspondence might be attributed to slight impurity of substance.

Boussingault analyzed a compound of this acid with oxyd of copper, of the following constitution:—

$$C_4H_{6\frac{1}{2}}N_2O_{10} + 2CuO =$$
$$(C_4H_{4\frac{1}{2}}NO_3, NO_5) + (2CuO, HO).$$

At a temperature of 165° C., [329° F.] this compound lost 17·71 per cent. of water, leaving

$$C_4H_{2\frac{1}{2}}NO, NO_5 + 2CuO.$$

Deducting the two atoms of oxide of copper, there remains a body— $C_4H_{2\frac{1}{2}}NO$.

In this condition of the question, as to the constitution of glycocoll, the investigation was resumed by Boussingault. He analyzed the body itself, and several most interesting compounds of it with oxyds of copper, lead and silver, nitric acid and nitrates of metallic oxyds. From these he derived the formula

$$C_{16}H_{15}N_4O_{11} + 3HO,$$

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* Ann. de Chim. et de Phys., 3d Ser., T. i, p. 257–270.

† Nat. en Scheik. archief, 1838, p. 146.

in which the three atoms of water were replaced with four atoms of metallic oxyd.

The gelatine-sugar-nitric acid he found to be

$$C_{16}H_{15}N_4O_{11}, 4NO_5+9HO,$$

and its compounds with bases to be

$$C_{16}H_{15}N_4O_{11}+4NO_5+4(8)MO+2aq.$$

This exceedingly complicated formula, and its high atomic weight, together with the fact that the several formulæ for gelatine sugar, enumerated above, though differing absolutely from each other, are nevertheless but slight modifications from once, twice, three and four times the following formula,

$$C_4H_4NO_3,$$

led naturally to the conclusion that the differences might be attributed partly to the impurity of the substances analyzed, and partly to the imperfect atomic weights at that time in use.

Beyond the description and analysis of the body itself, and the few salts above enumerated, gelatine sugar had met with no detailed examinations. These considerations gave occasion to the investigation which follows. It is scarcely necessary to add to the statement of its having been conducted at Giessen, that the counsel and coöperation there enjoyed, have united with the recollections of this labor, some of the most grateful memories of a life.

Formula of Glycocoll.

Finding it impossible to obtain as large a per-centage of carbon by the combustion of gelatine sugar, either in chromate of lead or oxyd of copper, as had been found by both Mulder and Boussingault, no conclusion remained, but that the analyses they had recorded, and those we had made, were of different bodies. After the analyses of several compounds of this body with hydrochloric, sulphuric and nitric acids, oxyd of copper, nitrate of silver, and bisulphate of potash, the conviction was established that its constitution was $C_4H_4NO_3$, to which in crystallized gelatine sugar, an atom of water is united.*

Upon comparing the per-centages derived from this formula with the results of analysis in Boussingault's last investigation, the differences will be seen to be scarcely greater than frequently occur in a series of the best determinations.

The body analyzed by Boussingault, was dried at 120° C., [248° F.] That analyzed by us lost nothing in weight at 150° C.,

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* For the anhydrous body, we have adopted the already proposed name GLYCOCOLL. The inappropriateness of the name *sugar*, has been noticed by Dessaigne. The attribute of sweetness it shares with AqO, S_2O_2, oxide of glyceryle and nitrous ether, and beside, it is incapable of fermentation.

We submit the symbol Gl., as least likely to lead to confusion. G. might confound with Glycium, (Glucinum, Beryllium,) and Gly. is already appropriated to *Glycerile*.

[304° F.] When exposed upon a watch crystal to the heat of a lamp, with a metallic screen between, and at such distance that the escape of vapor is barely discernible, a part of the mass in contact with the glass becomes browned, while another portion melts and shoots into crystals. These continue to form even after other portions have become charred. Rubbed together with finely pulverized hydrate of baryta, it becomes almost instantly fluid, the whole dissolving readily in water, from which, in process of time, crystals containing baryta and glycocoll deposit themselves. Here, in the act of combination, the water from one or both the ingredients was given up.

The above circumstances, and others yet to be noted, induced the opinion that at a certain temperature, a lower one longer continued, an atom of water from one half of the hydrated glycocoll might be given up, and the remaining half take its place. This would give almost precisely the analytical results of both Mulder and Boussingault, and yield from the formula determined on by us, precisely the composition given by Mulder.

$$2(C_4\,H_4\,NO_3,\,HO)—HO=C_8\,H_9\,N_2\,O_7.$$

Below, follow the estimated per cent. constitution, according to the above formula, and the average of a series of analyses by Boussingault and Mulder.

	Estimate.	Bous.	Mulder.
8 equiv. Carbon, - - - - -	34·04	33·79	34·17
9 " Hydrogen, - - -	6·38	6·44	6·49
2 " Nitrogen, - - -	19·85	19·90	19·84
7 " Oxygen, - - - - -	39·73	39·70	39·50
	100·00	100·00	100·00

The effort to expel this half atom of water was unsuccessful. A temperature of 150° C. [302° F.] produced scarcely a perceptive diminution in weight. At 170° C. [338° F.] it began to brown with the escape of gaseous products of decomposition. At 190° C. [374° F.] though portions had become quite charred, others had merely melted and crystallized anew.

The support which the analyses of Boussingault give to the formula $C_4\,H_4\,NO_3,\,HO$, will justify the following juxtaposition of the estimated per cents. and the actual results.

Glycocoll and Oxyd of Silver; dried at 110° C. [230° F.]

	Boussingault.			Horsford.	
	$C_{16}H_{15}N_4O_{11}+4AgO.$			$C_4H_4NO_3+AgO.$	
	Equiv.	Estimate.	Result.	Equiv.	Estimate.
Carbon, . . .	16 = 96	13·35	13·62	4 = 24	13·18
Hydrogen, . .	15 = 15	2·08	2·21	4 = 4	2·19
Nitrogen, . .	4 = 56	7·78	8·07	1 = 14	7·69
Oxygen, . .	11 = 88	12·26	12·35	3 = 24	13·21
Ox. silver, . .	4 = 464	64·53	63·75	1 = 116	63·73
	719	100·00	100·00	182	100·00

Glycocoll and Oxyd of Copper; dried at 120° C. [248° F.]

	Boussingault.			Horsford.	
	$C_{16}H_{15}N_4O_{11}+CuO$.			$C_4H_4NO_3+CuO$.	
	Equiv.	Estimate.	Result.	Equiv.	Estimate.
Carbon, . . .	16 = 96	23·19	23·57	4 = 24	22·68
Hydrogen, . .	15 = 15	3·62	3·75	4 = 4	3·77
Nitrogen, . .	4 = 56	13·53	. .	1 = 14	13·24
Oxygen, . .	11 = 88	21·29	. .	3 = 24	22·70
Ox. copper, . .	4 = 158·8	38·37	37·60	1 = 39·7	37·61
	413·8	101·00		105·7	100·00

Glycocoll and Oxyd of Lead; dried at 120°. [248° F.]

	Boussingault.			Horsford.	
	$C_{16}H_{15}N_4O_{11}+4PbO$.			$C_4H_4NO_3+PbO$.	
	Equiv.	Estimate.	Result.	Equiv.	Estimate.
Carbon, . . .	16 = 96	13·67	13·58	4 = 24	13·48
Hydrogen, . .	15 = 15	2·13	2·12	4 = 4	2·24
Nitrogen, . .	4 = 56	7·97	7·78	1 = 14	7·86
Oxygen, . .	11 = 88	12·57	11·62	3 = 24	13·50
Ox. lead, . .	4 = 446·8	63·66	64·90	1 = 111·7	62·92
	701·8	100·00	100·00	177·7	100·00

Glycocoll and Nitric Acid, dried in vacuo by ordinary temperature.

	Boussingault.			Horsford.	
	$C_{16}H_{15}N_4O_{11}+4NO_5+9HO$.			$C_4H_4NO_3$, $HO+NO_5$, HO.	
	Equiv.	Estimate.	Result.	Equiv.	Estimate.
Carbon, .	16 = 96	17·39	17·32	4 = 24	17·39
Hydrogen, .	24 = 24	4·34	4·53	6 = 6	4·34
Nitrogen, .	8 = 112	20·29	20·23	2 = 28	20·29
Oxygen, .	40 = 320	57·98	57·92	10 = 80	57·98
	552	100·00	100·00	138	100·00

At 100° C. [212° F.] this salt lost 9·18 per cent., and at 110° C. [230° F.] 4·5 per cent. more, with which it began to brown. This loss, 13·68 per cent., corresponds nearly with 13·77 per cent., the water in the salt. Its formula would then be

$$C_4H_4NO_3, NO_5.$$

Glycocoll and Nitrate of Silver.

	Boussingault.			Horsford.	
	$C_{16}H_{15}N_4O_{11}+2HO+4(AgO, NO_5)$.			$C_4H_4NO_3+AgO, NO_5$.	
	Equiv.	Estimate.	Result.	Equiv.	Estimate.
Carbon, .	16 = 96	10·07	10·09	4 = 24	10·16
Hydrogen, .	17 = 17	1·78	1·84	4 = 4	1·69
Nitrogen, .	8 = 112	11·75	11·50	2 = 28	11·87
Oxygen, .	33 = 264	27·72	27·87	8 = 64	26·75
Ox. silver, .	4 = 464	48·68	48·70	1 = 116	49·53
	953	100·00	100·00	236	100·00

Glycocoll and Nitrate of Potash.

	Boussingault.			Horsford.	
	$C_{16}H_{15}N_4O_{11}+2HO+4(KO, NO_5)$.			$C_4H_4NO_3KO, NO_5$.	
	Equiv.	Estimate.	Result.	Equiv.	Estimate.
Carbon, .	16 = 96	14·14	14·26	4 = 24	14·35
Hydrogen, .	17 = 17	2·55	2·42	4 = 4	2·39
Nitrogen, .	8 = 112	16·50	. .	2 = 28	16·78
Oxygen, .	33 = 264	38·86	. .	8 = 64	38·21
Potash, .	4 = 189·6	27·95	27·49	1 = 49·4	28·27
	678·6	100·00		167·4	100·00

Glycocoll and Nitrate of Copper.

	Boussingault.			Horsford.	
	$C_{16}H_{15}N_4O_{11}+4NO_5+8CuO+9HO.$			$C_4H_4NO_3,\ HO\left\{\begin{array}{l}CuO,\ HO\\ CuO,\ NO_5\end{array}\right.$	
	Equiv.	Estimate.	Result.	Equiv.	Estimate.
Carbon, .	16 = 96	11·02	11·04	4 = 24	11·02
Hydrogen,	24 = 24	2·75	2·89	6 = 6	2·75
Nitrogen, .	8 = 112	12·86	12·08	2 = 28	12·86
Oxygen, .	40 = 320	36·79	37·45	10 = 80	36·79
Ox. copper,	8 = 317·6	36·58	36·54	2 = 79·4	36·58
	869·6	100·00	100·00	217·4	100·00

If we review the estimates from the two systems of formulæ, and the results of analysis recorded above, it will be seen—

1st. That the analyses of the compounds with nitrate of silver, more nearly correspond with the estimates from Boussingault's formula.

2d. That the analyses of the compounds with nitric acid, nitrate of potash and nitrate of copper, are suited equally well to either formula. And

3d. That the analyses of the remaining compounds, viz: with the oxyds of silver, copper and lead, correspond more nearly with the simpler formula.

As additional reasons for adopting the simpler formula, the following, drawn from our investigation, may be recorded.

4th. The analyses give this constitution: as the average of four combustions for carbon and hydrogen, and two for nitrogen, will show, placed side by side with the estimates from the formula

$$C_4H_4NO_3, HO.$$

		Theory.	Experiment.
Carbon, - - - - -	4 equiv. = 24	32·00	31·98
Hydrogen, - - - -	5 " = 5	6·67	6·87
Nitrogen, - - - -	1 " = 14	18·67	18·79
Oxygen, - - - -	4 " = 32	42·66	42·36
	75	100·00	100·00

5th. It forms a compound in which sulphuric acid replaces the atom of water: $C_4H_4NO_3, SO_3$ corresponding with Boussingault's nitrate, dried at 110° C. [230° F.]: $C_4H_4NO_3, NO_5$.

6th. It forms a compound with oxyd of copper, of this formula:

$$C_4H_4NO_3, CuO, HO,$$

which, at 100° C., [212° F.] loses an atom of water.

7th. It forms a compound in which the atom of water is replaced by an atom of nitrate of silver:

$$C_4H_4NO_3;\ AgO, NO_5.$$

8th. It forms, when long digested with sulphuric acid, a salt of this constitution:

$$\left.\begin{array}{l}C_4H_4NO_3, SO_3\,HO\\ \quad H_4NO, SO_3\,HO.\end{array}\right\}$$

The ammonia is taken from the hydrated glycocoll, which may be considered as fumarate of ammonia:

$$C_4 H_4 NO_3, HO = H_4 NO, C_4 HO_3.$$

9th. It decomposes when subjected to the action of the galvanic battery; an acid (fumaric?) and oxygen appearing at one pole, and an alkali (ammonia) and hydrogen appearing at the other.

10th. It may be derived from hippuric acid by treatment with a mineral acid, in which case a neutral salt of glycocoll is formed and benzoic acid set free: or by treatment with potash, in which case benzoate of potash is formed and glycocoll is set free.

Hippuric acid, - -	$C_{18} H_9 NO_6$
Benzoic acid, - - -	$C_{14} H_5 O_3$
Glycocoll, - - -	$C_4 H_4 NO_3$

We may add also that the formulæ of Boussingault and Mulder have not the advantage of so great simplicity.

Preparation of Glycocoll.

The recent brilliant discovery of Dessaigne,* that by boiling hippuric acid with sulphuric, hydrochloric or any of the stronger acids, this body separates into benzoic acid and a salt of glycocoll, rendered the preparation of the latter, in purity, a task of no difficulty. It was, of course, necessary first of all to obtain a quantity of *hippuric acid.*

This acid was prepared according to the method proposed by Dr. Bensch,† by evaporating in a water bath, the morning urine of stall-fed horses, to from one-eighth to one-tenth of its volume; adding hydrochloric acid till all effervescence ceased; setting aside, in a cool place, for the perfect separation of the hippuric acid; filtering through linen, and pressing; dissolving in freshly prepared solution of hydrate of lime, with addition of boiling water; filtering, as before, and pressing; heating the filtrate to boiling, acidifying with solution of alum, cooling to 40° C. [104° F.], adding solution of bicarbonate of soda till no farther precipitation takes place; filtering and pressing; and precipitation of the filtrate with hydrochloric acid. After washing, filtering and pressing the precipitate of hippuric acid, it was again dissolved in boiling water, and blood coal added in the proportion of half an ounce to a pound of moist acid, again filtered at boiling heat through paper, and set aside to crystallize. By this method prismatic crystals are obtained of the most perfect whiteness, an inch in length, and from one to two lines in diameter.

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* Compt. Rend., xxi, p. 1224–1227. Liebig's Annalen, Bd., lviii, S. 322.

† Liebig's Annalen, Bd., lviii, S. 267.

From three to four ounces of hippuric acid were digested in a flask of one litre* capacity, over a spirit lamp, in four times their weight of concentrated hydrochloric acid, until entirely dissolved. A larger quantity is less manageable, and the subsequent treatment less expeditious. It is well to continue a gentle heat, with the addition of water half an hour after the solution is completed. In this time a part of the benzoic acid gathers into oily drops and sinks to the bottom, becoming, as the whole cools, a solid crystalline mass, not easily removed from the flask. The presence of water retains the hydrochlorate of glycocoll in solution. After the whole mass has become cool, the benzoic acid having for the most part crystallized out, the contents of the flask are poured upon the filter and washed till the filtrate no longer tastes sour. The filtrate is then evaporated in an open porcelain basin over a water bath, nearly to dryness,—by which process the excess of hydrochloric acid and benzoic acid are, for the most part, removed. Redissolving and again evaporating two or three times repeated, at length give the hydrochlorate of glycocoll quite pure. Ammonia is then added to the syrup till it yields an alkaline reaction. Absolute alcohol being then added, the remaining traces of benzoic acid and the salammoniac are dissolved, while the glycocoll is thrown down in the form of a white precipitate, consisting of myriads of minute prismatic crystals. As the body is slightly soluble in alcohol, and more so in alcohol containing salammoniac, it is well to let the fluid stand a few hours. The precipitate is then brought upon a filter and washed with absolute alcohol, till the filtrate no longer gives a precipitate with nitrate of silver.

Properties of Glycocoll.

Thus obtained, hydrate of glycocoll tastes sweet, though less so than cane sugar,—has neither acid nor alkaline reaction; dissolves in from 4·24 to 4·35 parts of water; is more soluble in hot than in cold spirits of wine; is quite insoluble in ether, and scarcely less in absolute alcohol.

When heated with a concentrated solution of caustic potash, in excess, it assumes, with the evolution of ammonia, a fine brilliant red color. If the heat be continued, the color gradually disappears.

Heated with hydrate of baryta or oxyd of lead, the same brilliant color is produced.

With sulphate of copper, a trace of glycocoll prevents the precipitation by potash, and the solution assumes a characteristic blue color. Boiled with oxyd of copper or its hydrate, it yields the same blue solution, which, if concentrated, crystallizes in fine needles.

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* = 0·2201 English gallon.

With nitrate of suboxyd of mercury, it gives a precipitate of metallic mercury.

From a concentrated solution in diluted spirits of wine or in water, in process of time large prismatic crystals are formed, which apparently belong to the monoclinate system, of the combination $\infty P. 0P. +P. \infty P\infty$. Prof. Kopp, to whom I am indebted for an examination of these crystals and of several others of salts of glycocoll, obtained from crystals prepared by Prof. v. Liebig, an admeasurement of the sharper angles of ∞P, (through which the orthodiagonal passes,) giving 66¼°.

The combustions for carbon and hydrogen were made with chromate of lead; those for nitrogen, according to the method of Varrentrapp and Will,—

I. 0·6770 grm. gave 0·7940 carbonic acid and 0·4170 water.
II. 0·5576 " " 0·6607 " " " 0·3474 "
III. 0·4670 " " 0·5455 " " " 0·2882 "
IV. 0·4003 " " 0·4686 " " " 0·2478 "
V. 0·1338 " " 0·4100 platin-salammoniac.
VI. 0·1937 " " 0·5646 " "

These determinations correspond in per cent. with

	I.	II.	III.	IV.	V.	VI.
Carbon,	31·89	32·31	31·81	31·92	. .	. .
Hydrogen,	6·84	6·92	6·85	6·87	. .	. .
Nitrogen,	. .	. .	. .	. .	19·24	18·36

From these may be derived the formula,

$$C_4 H_4 NO_3, HO,$$

as will be seen by comparing the estimated and average actual per cents. of the several elements.

		Theory.	Experiment.
Carbon, - - -	4 equiv. = 24	32·00	31·98
Hydrogen, - - -	5 " = 5	6·66	6·87
Nitrogen, - - -	1 " = 14	18·66	18·79
Oxygen, - - -	4 " = 32	42·68	42·36
	75	100·00	100·00

The atomic weight of glycocoll is, with the above constitution, 66.

GLYCOCOLL AND HYDROCHLORIC ACID.

Neutral Hydrochlorate of Glycocoll.

Gl, HCl, HO.

This is the product of boiling hippuric acid with concentrated hydrochloric acid, as already described. If the filtrate, page 376, be carefully evaporated to syrup consistence, and suffered quietly to cool, the whole mass becomes filled with groups of long, flat prisms, perfectly transparent, and of the greatest brilliancy. The mother liquor poured off, and the crystals washed with spirits of wine, gives the salt in the utmost purity. A second and third portion of crystals may be obtained by concentrating the mother liquor and similar treatment.

This salt slowly absorbs moisture from the air and deliquesces: over sulphuric acid, the crystals retain their form and constitution any length of time. It tastes sour, and slightly but positively stiptic; reacts acid: dissolves readily in water; in hot spirits of wine, and slightly in absolute alcohol.

The substance dried over sulphuric acid, on combustion with chromate of lead,

I. 0·2368 grm. gave 0·1833 carbonic acid and 0·1272 water.
II. 0·3218 " " 0·2555 " " " 0·1711 "
III. 0·2853 " " 0·5698 platin-salammoniac.
IV. 1·5920 " " 2·0562 chlorid of silver.
V. 1·0008 " " 1·2961 " "
VI. 1·5300 " " 1·9300 " "

Expressed in per cents., the above determinations correspond with

	I.	II.	III.	IV.	V.	VI.
Carbon,	21·11	21·28	. .	. .	. .	. .
Hydrogen,	5·96	5·95	. .	. .	. .	. .
Nitrogen,	. .	. .	12·57	. .	. .	. .
Chlorine,	. .	. .	. .	31·91	31·99	31·99

With these numbers, the following formula is in accordance:

$$C_4H_4NO_3, HCl, HO,$$

as the annexed comparison will show.

		Theory.	Experiment.
Carbon, - - -	4 equiv. = 24	21·42	21·20
Hydrogen, - - -	6 " = 6	5·35	5·95
Nitrogen, - - -	1 " = 14	12·56	12·57
Oxygen, - - -	4 " = 32	28·53	28·40
Chlorine, - - -	1 " = 35·4	32·14	31·94
	111·4	100·00	100·00

Basic Hydrochlorate of Glycocoll.

(a.) 2Gl, HCl, HO.

This salt is formed by adding hydrochloric acid to a cold concentrated solution of glycocoll in water, and then pouring in alcohol till the solution becomes slightly turbid. Crystals of the utmost transparency and regularity commence forming immediately. To continue the crystallization, alcohol is added drop by drop, at intervals. It is perhaps better to let the solution in water slowly evaporate over sulphuric acid. In this way larger crystals, of surpassing beauty, were obtained. They are rhombic prisms of 87° and 93°. They do not deliquesce like those of the neutral salt, upon exposure to the air. The salt has a pleasant sour, and at the same time sweet taste, reminding one of fine fresh pippins.

The solution reddens litmus with chromate of lead.

I. 0·3505 grm. gave 0·3550 carbonic acid and 0·1743 water.
II. 0·2758 " " 0·6729 platin-salammoniac.
III. 1·5050 " " 1·1940 chlorid of silver.

These determinations expressed in per cents.:

	I.	II.	III.
Carbon,	27·59	. .	. .
Hydrogen,	5·52	. .	. .
Nitrogen,	. .	15·37	. .
Chlorine,	. .	. .	19·58

Correspond with the formula

$$C_4\ H_4\ NO_3,\ HCl + C_4\ H_4\ NO_3,\ HO,$$

which, calculated, gives:

		Theory.	Experiment.
Carbon, - - -	8 equiv. = 48	27·05	27·59
Hydrogen, - - -	10 " = 10	5·63	5·52
Nitrogen, - - -	2 " = 28	15·78	15·37
Oxygen, - - -	7 " = 56	31·59	31·94
Chlorine, - - -	1 " = 35·4	19·95	19·58
	177·4	100·00	100·00

Basic Hydrochlorate of Glycocoll.

(b.) $2(Gl,\ HO) + HCl$.

This salt was obtained by dissolving glycocoll in hydrochloric acid and leaving the solution to a quiet crystallization. The exact proportions of acid and base necessary to procuring it have not been determined. Indeed, it will appear obvious, after the accounts of the hydrochloric and sulphuric acid compounds, that the task of accurately fixing the temperature, concentration and quantity of the several ingredients necessary to the formation of a given compound of acid, glycocoll and water, will be exceedingly difficult.

Combustion with chromate of lead gave the following results:

I. 1·0290 grm. gave 0·9840 carbonic acid and 0·5580 water.
II. 1·0890 " " 0·8180 chlorid of silver.
III. 0.9760 " " 0·7305 " "
IV. 0·9710 " " 0·7290 " "

In per cents. expressed,	I.	II.	III.	IV.
Carbon,	26·08	. .	. .	. .
Hydrogen,	6·02	. .	. .	. .
Chlorine,	. .	18·53	18·46	18·41

These numbers conduct to the formula,

$$2(C_4\ H_4\ NO_3,\ HO) + HCl,$$

the estimated per cents. of which with the results of analysis are here placed side by side.

		Theory.	Experiment.
Carbon, - - -	8 equiv. = 48	26·46	26·08
Hydrogen, - -	11 " = 11	6·06	6·02
Nitrogen, - -	2 " = 28	15·43	. .
Oxygen, - -	8 " = 64	33·12	. .
Chlorine, - -	1 " = 35·4	18·91	18·47
	186·4	100·00	100·00

The rational constitution of this salt may be considered as one atom of hydrated glycocoll, united to one atom of hydrochlorate of hydrated glycocoll, thus, Gl, HO+Gl, HCl, HO.

Basic Hydrochlorate of Glycocoll.

(c.) 3Gl, 2HCl, 2HO.

This salt was prepared in the same manner as the last; a simple solution of glycocoll in hydrochloric acid, set aside to crystallize. The acid was, however, in excess.

It was also prepared by passing dry hydrochloric acid gas over melted hydrate of glycocoll. For this purpose, a gramme and a half of substance was distributed along the bottom of a Liebig's drying apparatus, and carefully heated with a spirit lamp; at the same time conducting over it hydrochloric acid gas. At a temperature of between 150° C. and 170° C. [between 302° F. and 338° F.] as determined in an oil bath, the glycocoll melts in the acid atmosphere. It was found better, however, to employ the simple lamp. With the latter the apparatus could be readily inclined or half inverted, to spread the molten substance over the interior of the tube, and thus facilitate absorption.

The absorption is attended with the escape of aqueous vapor. The process was continued until no further increase in weight was observed. At each interval the hydrochloric acid was thoroughly removed, by long continued passing of dry air through the tube before weighing. At the end of the absorption, the glycocoll usually became slightly green, owing doubtless to a trace of decomposition and separation of carbon.

From an analysis of crystals obtained by the first method,

I. 1·2560 grm. of substance, gave 1·2520 grm. chlorid of silver.

By the other method,

II. 1·9727 grm. of hydrated glycocoll, increased in weight to 2·4580 grm. Precipitated with silver, this gave 2·3855 grm. chlorid of silver. The increase in weight was 24·60 per cent. The per centages of chlorine, I. 24·59; II. 24·23.

These numbers correspond to the formula,

$$3(C_4 H_4 NO_3)+HCl+2HO,$$

which requires 24·51 per cent. of chlorine.

Basic Hydrochlorate of Glycocoll.

(d.) 3Gl, 2HCl, HO.

This salt is prepared precisely as the last mentioned, both by crystallization from the acid solution and by leading dry hydrochloric acid gas over fused hydrate of glycocoll.

The notice of this salt would scarcely have been ventured upon, had not a precisely corresponding compound with sulphuric acid been analyzed. It will contribute to show how multifarious may be the relations of a body, that combines as a salt, and yet possesses both acid and basic properties.

From crystals of the salt prepared as above mentioned,

I. 1·2864 grm. gave 1·3203 grm. chlorid of silver.

II. By leading dry hydrochloric acid gas over glycocoll in the manner already described, a compound was formed, of which,

1·1370 grm. gave 1·1845 grm. chlorid silver.

In per cent. expressed, these determinations give,

	I.	II.
Chlorine, ...	25·43	25·72

corresponding with the formula

$$3(C_4\ H_4\ NO_3)+2HCl+HO,$$

which requires 25·30 per cent. of chlorine. As the probable rational constitution of the above salt the following is submitted,

$$(Gl\ HCl+Gl,\ HO)+Gl\ HCl.$$

Anhydrous Hydrochlorate of Glycocoll.

Having found a basic hydrochlorate, which might be regarded as a double salt of one atom of hydrate of glycocoll, with one atom of anhydrous hydrochlorate of glycocoll:

$$C_4\ H_4\ NO_3,\ HO+C_4\ H_4\ NO_3,\ HCl,$$

and especially having found as will be seen below, an anhydrous *sulphate* of glycocoll, it was natural to suppose that the anhydrous hydrochlorate might be obtained by itself, viz. $C_4\ H_4\ NO_3$, HCl.

To this end absolute alcohol was saturated with hydrochloric acid gas, and this added to a solution of glycocoll in hot spirits of wine. Upon evaporating the liquid, delicate prismatic crystals appeared which deliquesced with the greatest rapidity. They even dissolved in absolute alcohol. This latter circumstance led to the supposition that the crystals might have been a double salt of hydrate of glycocoll with hydrochlorate of oxide of ethyle. This supposition was further strengthened from an analysis of a sulphate of corresponding constitution soon to be noticed.

Compounds of glycocoll and sulphuric acid are even more remarkable than those with hydrochloric acid. As little success attended the effort to ascertain the precise conditions under which some of them are formed, as rewarded the labors with the compounds already described. Of these, two, the double sulphate of glycocoll and oxyd of ammonium, and the anhydrous sulphate of glycocoll, have especial interest, as they throw much light over the constitution and nature of this body.

Anhydrous Sulphate of Glycocoll.

$$Gl,\ SO_3.$$

By dissolving glycocoll in hot spirits of wine, cooling, adding sulphuric acid drop by drop, and setting aside in a quiet place, after a day or two there are formed beautiful elongated thin flat prisms with right angled terminal planes. From another portion the salt crystallized in the most delicate attenuated tables of the greatest brilliancy. It is soluble in water and hot diluted alcohol, and quite insoluble in absolute alcohol and ether. It tastes sour and reddens litmus paper, does not change upon exposure to the air, and loses no weight by 100° C. (212° F.)

Combustion with chromate of lead gave the following results:

I. 0·5147 grm. gave 0·4257 carbonic acid and 0·2509 water.
II. 0·3134 " " 0·2574 " " " 0·1616 "
III. 0·1541 " " 0·1260 " "
IV. 0·3397 " " 0·7039 platin-salammoniac.
V. 0·4248 " " with chlorid of barium 0·4673 grm. sulphate of baryta.

In per cent. expressed agreeing with,

	I.	II.	III.	IV.	V.
Carbon,	22·55	22·40	22·30	. .	. .
Hydrogen,	5·41	5·72	. .	. .	. .
Nitrogen,	. .	. .	. .	13·05	. .
Sulphuric acid,	. .	. .	. .	. .	37·97

Which give the formula

$$C_4 H_4 NO_3, SO_3,$$

as the comparison of estimated and analytical results shows.

		Theory.	Experiment.
Carbon, - - - - -	4 equiv. = 24	22·66	22 42
Hydrogen, - - - -	4 " = 4	3·77	5·56
Nitrogen, - - - -	1 " = 14	13·20	13·05
Oxygen, - - - -	3 " = 24	22·64	21·00
Sulphuric acid, - - -	1 " = 40	37·73	37·97
	106	100·00	100·00

Repeated combustions did not enable us to lessen the per-centage of hydrogen. The variation from the theory is, doubtless, to be attributed to the absorption in the chlorid of calcium tube, of a small quantity of sulphurous acid, which escaped from the combustion tube. This explanation unfortunately occurred after repeated analyses had consumed the stock of salt.

This constitution is remarkable in the field of organic chemistry. On its borders we have a similar instance in anhydrous sulphate of ammonia, NH_3+SO_3.

Sulphate of Hydrate of Glycocoll.

$$Gl, SO_3, HO.$$

This salt was obtained from a solution similarly prepared to that which yielded the anhydrous salt, except that the solution was boiled with sulphuric acid, instead of the latter being added to the cold solution. It crystallizes in short prisms, reminding one of sulphate of copper, and the crystals, though small, are of exceeding beauty and perfection of form. They do not change upon exposure to the air.

A single determination only was made, and *that* of the nitrogen. The other determinations were not made, from want of substance, all subsequent efforts to form the salt having failed. By Varrentrapp and Will's method:—

0·3367 grm. gave 0·2943 grm. platin-salammoniac.

In per cent. expressed, Nitrogen 12·37.

This corresponds with the formula

$$C_4\ H_4\ NO_3,\ SO_3,\ HO,$$

which requires 12·17 per cent. of nitrogen.

Basic Sulphate of Glycocoll.

(a.) $3Gl\ HO,\ 2SO_3,\ 2HO.$

If to a solution of glycocoll in diluted spirits of wine, sulphuric acid in excess be added, and set aside, in twenty-four hours long rectangular prismatic crystals form upon the bottom of the containing vessel. A very considerable excess of sulphuric acid did not change the constitution of the crystals.

They taste and react acid, and like the salts already described suffer nothing from exposure to the air.

Combustion with chromate of lead gave the following results:

I. 0·4199 grm. gave 0·3528 carbonic acid and 0·2149 water.
II. 0·3944 “ “ 0·3219 “ “ “ 0·1974 “
III. 0·2399 “ “ by Varrentrapp and Will's method, 0·5067 grm. platin-salammoniac.
IV. 0·6866 grm. gave 0·4928 sulphate of baryta.
V. 0·5808 “ “ 0·4170 “ “
VI. 0·4532 “ “ 0·3225 “ “
VII. 0·4960 “ “ 0·3500 “ “

In per cent. expressed the above determinations correspond with

	I.	II.	III.	IV.	V.	VI.	VII.
Carbon,	22·91	22·25					
Hydrogen,	5·68	5·56					
Nitrogen,			13·31				
Sulphuric acid,				24·62	24·62	24·20	24·40

These numbers give the formula,

$$3(C_4\ H_4\ NO_3,\ HO)+2(SO_3,\ HO).$$

The juxtaposition of the estimated per cents. and analytical results follows:—

		Theory.	Experiment.
Carbon, - - - - -	12 equiv. = 72	22·29	22·58
Hydrogen, - - - -	17 “ = 17	5·26	5·62
Nitrogen, - - - -	3 “ = 42	13·00	13·31
Oxygen, - - - -	14 “ = 112	34·69	34·03
Sulphuric acid, - - -	2 “ = 80	24·76	24·46
	323	100·00	100·00

The following formula is submitted as expressing the rational constitution of this salt:—

$$(Gl\ HO,\ SO_3\ HO+Gl\ HO)+(Gl\ HO,\ SO_3\ HO).$$

The following sulphuric acid compounds were none of them completely analyzed. They were prepared in small portions while seeking to obtain a neutral sulphate of hydrate of glycocoll; and it was not until the capacity of this body to combine with others of such different nature, and in such varied proportions became fully apparent, that the existence of so complex and unusual compounds was believed.

The crystallized salts were for the most part groups of elongated prisms.

Basic Sulphate of Glycocoll.

(b.) $3Gl, 2SO_3, HO$.

The constitution of this salt differs from that of the preceding in the amount of water. As both of them were dried in the air over sulphuric acid, and suffered no change, this difference is attributable doubtless to the degree of concentration, or difference of temperature. It will be observed that it corresponds precisely with a basic hydrochlorate (d), whose constitution is given on page 16.

With chlorid of barium, 0·2182 grm. of crystals, gave 0·1940 grm. sulphate of baryta.

In per cent. sulphuric acid 27·74.

This corresponds with the formula

$$3(C_4\,H_4\,NO_3)+2SO_3+HO,$$

which requires 27·87 parts in 100. As the probable rational constitution of this salt the following is submitted:

$$(Gl, SO_3+Gl, HO)+Gl, SO_3.$$

Basic Sulphate of Glycocoll.

(c.) $3(Gl, HO)2SO_3, HO$.

A mixture of the salt (b) with the previously described one (a), doubtless gave the crystals for the following determination:

0·3076 grm. gave 0·2300 grm. sulphate of baryta, which gives in per cent. expressed, sulphuric acid 25·65; corresponding with the above formula. The following is more rational.

$$(Gl, SO_3, HO+Gl, HO)+(Gl, HO+SO_3\,HO).$$

This requires 25·47 parts of sulphuric acid in 100.

(d.) $2(Gl, HO)+SO_3$.

Another salt gave by combustion with chromate of lead,—

From 0·3039 grm., 0·2872 grm. carbonic acid, and 0·1680 grm. water; which expressed in per cent., give carbon 25·77, hydrogen 6·01. These numbers correspond with the formula

$$2(C_4\,H_4\,NO_3, HO)+SO_3,$$

which requires carbon 25·26, and hydrogen 5·26.

Glycocoll and Sulphate of Oxyd of Ethyl.

Gl, HO, AeO, SO_3.

The particular circumstances of the formation of this salt, beyond those already given, viz. a solution in hot spirits of wine, or in water to which absolute alcohol was added, are not ascertained. With chlorid of barium, 0·6470 grm. gave 0·3036 grm. sulphate of baryta; which in per cent. give of sulphuric acid 17·27. This quantity of acid corresponds with the formula

$$C_4 H_4 NO_3, HO + C_4 H_5 O, SO_3,$$

which requires 17·62 per cent. of sulphuric acid.

Nitrate of Glycocoll.

$$Gl, HO + NO_5, HO.$$

The capability which this compound possesses of uniting with bases enveloped the earlier conceptions of the nature of glycocoll in obscurity:—an obscurity from which the changes the nitrate of copper salt experienced upon subjection to heat, and the simple combinations with the oxyds of silver, copper and lead, did not in any degree relieve it. It was then suggested that the glycocoll played the part of the water of crystallization in the salts that were formed. From the analysis below, it will be seen that the salts were double salts, in which glycocoll with or without water, as a *base*, united with hydrated nitric acid, or as a salt with nitrates of metallic oxyds.

Braconnot obtained this compound by direct combination of nitric acid with glycocoll prepared from isinglass. Dessaigne procured it directly from hippuric acid, employing nitric instead of hydrochloric acid for its decomposition.

We prepared it by dissolving glycocoll in strong nitric acid, and setting the solution over sulphuric acid to crystallize. Occasionally large tabular crystals, apparently belonging to the monoclinate system, are formed. Not unfrequently, however, the salt crystallizes in needles, especially if the fluid has been warmed.

They do not deliquesce upon exposure to the air. They taste and react acid. They were dried over sulphuric acid. Combustion with chromate of lead gave the following results:—

I. 0·4509 grm. substance gave 0·2954 grm. carbonic acid, and 0·1963 grm. water.

II. 0·4968 grm. substance gave 0·3122 grm. carbonic acid and 0·2054 grm. water.

Two analyses, according to Varrentrapp and Will's method, gave respectively 10·04 per cent. and 10·64 per cent. of nitrogen. From this it is evident that this method cannot here be employed:—a fact with regard to nitrates, to which attention has already been drawn by the chemists just mentioned.

Failing in this, a determination was made by the quantitative method of Prof. v. Liebig.

The proportions of carbonic acid to nitrogen in four tubes, were: 17 : 9, 14 : 7, 10 : 5, 24 : 11; or, together 65 : 32 = 2 : 1.

In per cent. expressed the above determinations give

	I.	II.	III.
Carbon, - - -	17·86	17·15	. .
Hydrogen, - - -	4·83	4·59	. .
Nitrogen, - - -	. .	. .	20·50

These correspond with the formula

$$C_4\ H_4\ NO_3,\ HO+NO_5\ HO,$$

as will be seen by the annexed estimates and results of analysis.

		Theory.	Experiment.
Carbon, - - - - -	4 equiv. = 24	17·38	17·49
Hydrogen, - - - -	6 " = 6	4·32	4·71
Nitrogen, - - - -	2 " = 28	20·29	20·50
Oxygen, - - - -	10 " = 80	58·01	57·30
	138	100·00	100·00

Boussingault by drying the salt at 110° C. (230° F.) obtained as already noticed the anhydrous compound $C_4\ H_4\ NO_3,\ NO_5$.

Oxalate of Glycocoll.

$$Gl,\ \bar{O},\ HO.$$

An aqueous solution of glycocoll with oxalic acid, evaporated upon a watch glass, crystallizes in rays reminding one of a cross section of wavellite. If alcohol be added to a solution of glycocoll in oxalic acid, the latter in excess, the solution becomes milky, with the separation of oxalate of glycocoll. If added in small quantities and successively, it crystallizes with the beauty that characterizes all or nearly all the compounds of this body. Dessaigne obtained the salt directly from hippuric acid by employing oxalic instead of a stronger acid, to effect the decomposition. It does not alter upon exposure to the air.

Combustion with chromate of lead gave the following :—0·3600 grm. gave 0·4227 grm. carbonic acid, which in per cent. expressed, gives carbon 32·02, corresponding with the formula

$$C_4\ H_4\ NO_3,\ C_2\ O_3,\ HO,$$

which requires 32·43 per cent. of carbon.

Acetate of Glycocoll.

$$Gl,\ HO,\ \bar{A},\ 2HO.$$

This salt is readily prepared by dissolving glycocoll in acetic acid, and adding absolute alcohol drop by drop, till the solution becomes turbid, and then afterward at intervals, as the crystallization proceeds. The salt analyzed was prepared by adding absolute alcohol in excess to a concentrated solution of glycocoll in acetic acid, (the latter in excess,) by which the salt was thrown down. It was then redissolved by heat, and set aside to cool and crystallize, by which slender prismatic crystals of great beauty were obtained.

On combustion with chromate of lead, 0·2981 grm. gave 0·3644 grm. carbonic acid and 0·2031 grm. water, which in per cent.

expressed correspond with carbon 33·33, hydrogen 7·57. The formula

$$C_4H_4NO_3, HO+C_4H_3O_3+2HO,$$

requires of carbon 33·33 per cent. and of hydrogen 6·94 per cent.

Tartrate of Glycocoll.

By dissolving glycocoll in tartaric acid and adding absolute alcohol in excess to the solution, an oily appearing liquid separates and settles to the bottom. Repeated and protracted agitation with alcohol and ether effect no change. This liquid dried upon a watch glass gave a gummy mass which was not further investigated.

Palmatinate of Glycocoll.

By dissolving palmitinic acid and glycocoll in hot spirits of wine, and setting aside to cool, the excess of acid rises to the surface in the form of an oil, while the salt crystallizes in white, thin, silky, radiating scales or blades of the greatest brilliancy. The oily layer, above, which with the whole mass becomes solid, may be readily removed, and the remainder pressed in silk and dried in the air over sulphuric acid. Combustion with chromate of lead gave the following results:

	I.	II.	III.
Carbon, -	51·30	51·23	50·84
Hydrogen, -	9·45	. .	9·44

With these, no formula embracing palmitinic acid and glycocoll has been found. The formula

$$C_4H_4NO_3, C_{32}H_{31}O_3+12HO,$$

requires 51·31 per cent. of carbon and 11·16 per cent. hydrogen, which would correspond with the carbon, but not with the hydrogen determinations.

Glycocoll and Bi-chlorid of Platinum.

$$Gl, PtCl_2, 2HO.$$

When to a concentrated solution of glycocoll in water, a concentrated solution of bi-chlorid of platinum is added, and then absolute alcohol drop by drop, the solution becomes turbid, and in a very short time, regular cherry-red crystals attach themselves to the sides of the vessel. Or if the concentrated aqueous solution be evaporated over sulphuric acid, after a time, groups of prismatic crystals are formed.

They become instantly covered with a light colored crust upon exposure to the air, manifestly with the loss of water.

0·3679 grm. substance gave 0·0872 grm. platinum.

In per cent. expressed = 33·03, which corresponds with the formula

$$C_4H_4NO_3, PtCl_2+2HO,$$

which requires 33·26 per cent. of platinum.

Glycocoll and Chlorid of Barium.

Gl, BaCl, 2HO.

To obtain this salt, equivalents of crystallized chlorid of barium ($=$BaCl$+$2HO) and glycocoll were dissolved in the least quantity of hot water, and suffered to crystallize quietly in the cold. In a few moments the salt crystallized in groups of short prisms of extreme beauty. None were sufficiently perfect to admit of measurement. They appeared to belong to the rhombic system, of the combination $\infty P . \breve{P}\infty . \infty\breve{P}\infty$.

The addition of alcohol to the solution changed the form to that of slender flat needles.

The salt is soluble in water, more so in hot than in cold, tastes bitter, gives neither acid nor alkaline reaction, does not deliquesce or change upon exposure to the air.

Dried over sulphuric acid, 0·6715 grm. substance gave 0·3833 grm. sulphate of baryta, $=$55·34 per cent. of chlorid of barium, giving the formula $C_4H_4NO_3$, BaCl, 2HO, which requires 55·31 per cent. of chlorid of barium.

Glycocoll and Chlorid of Potassium.

Gl, KCl.

This compound was prepared by dissolving glycocoll and chlorid of potassium in water, and evaporating over sulphuric acid.

When the solution had become very concentrated, fine needle-formed crystals filled the whole mass. They deliquesce readily in the air.

A single combustion with chromate of lead, gave from 0·4992 grm., 0·3055 grm. carbonic acid$=$16·58 per cent. of carbon.

The formula $C_4H_4NO_3$, KCl, requires 16·92 per cent. of carbon.

Glycocoll and Chlorid of Sodium.

A concentrated solution of glycocoll and chlorid of sodium in water, gave upon addition of absolute alcohol and standing a length of time, crystals containing both of the above mentioned ingredients. A quantitative examination was not made.

Glycocoll and Bi-chlorid of Tin.

By dissolving glycocoll in the least quantity of water, and adding bi-chlorid of tin, after a time, crystals containing both ingredients of the solution are formed. They were not more particularly examined.

Glycocoll and Hydrochlorate of Berberin.

Gl, Ber, HCl.

This salt is obtained by adding a hot solution of hydrochlorate of berberin in spirits of wine, to a concentrated solution, in excess, of glycocoll in the same menstruum. Upon cooling, the whole mass becomes solid, and consists of myriads of the most delicate needles, of a brilliant orange color and bitter taste. The salt may be washed with water, as glycocoll is therein readily soluble, while the salt of berberin is not.

The salt dried at 100° C. [212° Fah.] and burned with chromate of lead, gave the following results:

0·1563 grm. substance gave 0·3485 grm. carbonic acid and 0·0826 grm. water, which expressed in per cent. give carbon 60·80, hydrogen 5·87. These correspond with the formula

$$C_4\,H_4\,NO_3+C_{42}\,H_{18}\,NO_9,\ HCl,$$

which, containing berberin with the constitution given by Fleitmann,* requires 60·21 per cent. of carbon and 5·03 per cent. of hydrogen.

Glycocoll and Potash.

By dissolving glycocoll in diluted caustic potash and evaporating to syrup consistence over a water bath, crystals in the form of long delicate needles, containing the two ingredients, are formed. They may be rapidly washed with spirits of wine. They deliquesce rapidly in the air, even over sulphuric acid. Dissolved in water, the salt gives a very strong alkaline reaction. It was not further examined.

Glycocoll and Hydrate of Baryta.

It has already been mentioned, that glycocoll rubbed with pulverized hydrate of baryta, in a mortar, becomes almost instantaneously semifluid. Upon diluting the solution, and setting aside, after a time crystals containing both baryta and glycocoll were deposited. The salt was not analyzed. Its composition, in all probability, corresponds with that of the oxyd of copper, silver and lead, noticed below, and there exist, doubtless, similar salts of strontia, lime and magnesia.

Glycocoll and Oxyd of Copper.

Gl, CuO, HO.

This salt may be prepared by adding to a solution of glycocoll sulphate of copper and caustic potash—and addition of absolute alcohol,—or by dissolving hydrated oxyd of copper, with the aid of heat, in a solution of glycocoll, and adding absolute alcohol:—or lastly by boiling the anhydrous oxyd of copper, in excess, with glycocoll. If the latter be concentrated it must be filtered hot. In this case, the filtrate in a few moments is resolved into a solid mass of the most exquisite cerulean blue color. More carefully examined, it is found to consist of exceedingly delicate

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* Liebig's Annalen, Bd. lix, s. 166.

needles. The addition of absolute alcohol to the concentrated solution precipitates the whole salt; to the diluted, less perfectly.

At 100° C. [212° F.] 0·5443 grm., at the conclusion of several days, had lost 0·0438 grm. =8·04 per cent. =one atom of water. With this loss the color passed through a light green to a shade in which a lavender or violet tint is discernible.

The analysis was made with the substance dried in the air over sulphuric acid.

Combustion with chromate of lead gave the following results:—

I. 0·2030 grm. of substance gave 0·1538 grm. carbonic acid and 0·0912 grm. water.

II. 0·2373 grm. by the method of Varrentrapp and Will, gave 0·4762 grm. platin-salammoniac.

III. 0·1745 grm. gave 0·0592 grm. oxyd of copper.

IV. 0·2871 grm. gave 0·0972 grm. oxyd of copper.

Which expressed in per cent. give

	I.	II.	III.	IV.
Carbon,	20·66	. .	. .	. .
Hydrogen,	4·99	. .	. .	. .
Nitrogen,	. .	12·65	. .	. .
Oxyd of copper,		. .	33·85	33·92

These give the formula $C_4 H_4 NO_3$, CuO, HO, as will be seen by comparing the theoretical and analytical results.

		Theory.	Experiment.
Carbon, - - - -	4 equiv. = 24	20·92	20·66
Hydrogen, - - -	5 " = 5	4·35	4·99
Nitrogen, - - -	1 " = 14	12·20	12·65
Oxygen, - - -	4 " = 32	27·92	27·81
Oxyd of copper, - -	1 " = 39·7	34·61	33·89
	114·7	100·00	100·00

With the loss of an atom of water, we have the salt

$C_4 H_4 NO_3$, CuO,

which it will be seen is precisely the composition derived from Boussingault's analysis of the salt dried at 120° C. = [248° F.] See page 9.

Glycocoll and Protoxyd of Lead.

Gl, PbO, HO.

This salt was prepared by dissolving with the aid of heat, protoxyd of lead (obtained from the peroxyd by long continued heat) in a concentrated aqueous solution of glycocoll, and the addition of alcohol till it began to be turbid. In a few hours it separated in prismatic crystals that slowly increased in size for several days, particularly with successive additions of absolute alcohol. The crystals remind one of cyanid of mercury.

A single combustion with chromate of lead gave from 1·3967 grm. substance, 0·6182 grm. carbonic acid, equal to 12·07 per cent. of carbon, corresponding with the formula derived from Boussingault's analysis with the addition of an atom of water,

$$C_4 H_4 NO_3, PbO, HO,$$

which requires 12·83 per cent. of carbon.

Boussingault's analysis was made from the salt, dried at 120° C., [248° F.,] leaving $C_4 H_4 NO_3, PbO$.

Glycocoll and Oxyd of Silver.

$$Gl, AgO, HO.$$

If oxyd of silver be added to a solution of glycocoll, it readily dissolves with the application of heat. With the addition of alcohol the above compound crystallizes in wartform crystals, which become dark upon exposure to light.

This salt was not analyzed, as Boussingault's analysis of it, dried at 110° C. [230° F.] as already noticed, gave the formula

$$C_4 H_4 NO_3, AgO.$$

There is scarcely a doubt that corresponding compounds of cobalt, nickel, manganese and iron protoxyds with glycocoll, might with nearly equal facility be prepared.

These compounds are perhaps analogous to those of ammonia with copper and nickel oxyds, when the latter are dissolved in the volatile alkali.

Glycocoll and Nitrate of Silver.

$$Gl, AgO, NO_5.$$

If the filtrate from a chlorine determination of the hydrochlorate of glycocoll be evaporated to concentration, and set aside over sulphuric acid, in a little time tolerably regular crystals of the above salt may be obtained.

It may be procured by dissolving glycocoll in nitrate of silver: or by dissolving oxyd of silver in the solution of the nitrate of glycocoll.

Upon melting, it explodes with violence. When exposed to moist air it deliquesces; though it remains unchanged over sulphuric acid.

The salt dried over sulphuric acid, on combustion with chromate of lead:—

I. 0·9300 grm. of substance gave 0·3550 grm. carbonic acid and 0·1880 grm. water.

II. 0·7840 grm. of the same gave 0·2950 grm. carbonic acid and 0·1560 grm. water.

III. 0·6469 grm. of the same gave 0·0258 grm. chlorid of silver.

In per cent. expressed,

	I.	II.	III.
Carbon,	10·11	10·26	. .
Hydrogen,	2·24	2·21	. .
Silver,	. .	. .	49·83

giving the formula $C_4 H_4 NO_3, AgO, NO_5$,
as the annexed estimates and results of analysis will show:

		Theory.	Experiment.
Carbon, - - - -	4 equiv. = 24	10·16	10·18
Hydrogen, - - -	4 " = 4	1·69	2·22
Nitrogen, - - -	2 " = 28	11·86	. .
Oxygen, - - -	8 " = 64	26·76	. .
Ox. silver, - - -	1 " = 116	49·53	49·83
	236	100·00	

Glycocoll and Nitrate of Copper.

$$Gl, HO, CuO, NO_5, CuO, HO.$$

This salt was analyzed by Boussingault, and may be considered as a compound of hydrate of glycocoll with nitrate of copper, united to hydrate of oxyd of copper.

$$(Gl, HO + CuO\,NO_5) + CuO, HO.$$

Glycocoll and Nitrate of Potash.

$$Gl, KO, NO_5.$$

This salt forms readily from a solution of glycocoll in nitrate of potash, upon the addition of absolute alcohol. No quantitative analysis of it was made. The above formula is derived from the analyses on page 9.

Glycocoll and Bi-sulphate of Potash.

$$Gl, SO_3 + Gl, KO, SO_3.$$

By dissolving bi-sulphate of potash in water and adding a solution of glycocoll, throwing the whole down with alcohol, redissolving by heat and setting aside to cool and crystallize, the above salt is obtained in semi-opaque prismatic crystals.

A single determination from the salt dried over sulphuric acid gave from 0·6873 grm. of substance 0·6200 grm. sulph. baryta. In per cent. giving sulphuric acid =30·94. The formula

$$C_4 H_4 NO_3, SO_3 + C_4 H_4 NO_3, KO, SO_3,$$

requires of sulphuric acid 30·83 per cent.

Glycocoll and Bi-chromate of Potash.

If glycocoll be dissolved in an aqueous solution of bi-chromate of potash, and absolute alcohol be added till the liquid becomes turbid, and the whole set aside, in a little time crystals will be formed.

These, even under the liquid, in a few days become decomposed, with the deposition of carbon. They were not further examined.

Glycocoll and Urate of Ammonia.

$$Gl, \bar{U}, AmO, \bar{U}.$$

When to a hot filtered solution of urate of ammonia, glycocoll is added, in a little time as the liquid cools, long semi-opaque needles shoot out from the sides of the vessel. The addition of alcohol after the first crystallization, causes the separation of a second portion.

Upon dissolving in hot water equivalents of glycocoll and urate of ammonia, and cooling, a flocculent mass was thrown down, which the addition of alcohol increased, and which, when examined with the microscope, proved to consist of exceedingly minute prisms.

The salt dried over sulphuric acid and burned with chromate of lead, gave from 0·2926 grm. substance, 0·3463 grm. carbonic acid and 0·1144 grm. water, which equal carbon 32·46, hydrogen 4·40. The formula

$$C_4 H_4 NO_3, C_5 N_2 H_2 O_3 + NH_4 O, C_5 N_2 H_2 O_3,$$

requires carbon 32·30, hydrogen 4·61.

Similar flocculent precipitates were obtained from solutions of glycocoll in both urates of potash and soda.

Glycocoll and Uric Acid.

The importance of finding a compound of uric acid that would readily dissolve in water, suggested the effort to combine it with glycocoll.

Two atoms of glycocoll united to two of uric acid would equal three atoms of cyanate of glycocoll:

$$C_8 H_8 N_2 O_6 + C_{10} N_4 H_4 O_6 = 3(C_4 H_4 NO_3, C_2 NO),$$

a compound that may be presumed readily to dissolve in water.

All effort to this end, however, proved unsuccessful. Uric acid remained unchanged in the most concentrated solution of glycocoll, even with the long continued application of heat.

Glycocoll and Benzoic Acid.

As these two bodies exist in combination in hippuric acid, it was to be presumed that a reunion might be effected. To this end, solutions of the two in spirits of wine were made and poured together. After a time the glycocoll on the one hand and the benzoic acid on the other crystallized out.

The same result attended the effort to combine cinnamic acid, cane sugar and neutral phosphate of lime with glycocoll.

Products of Decomposition of Glycocoll.

Action of Sulphuric Acid.

As glycocoll contains the elements of fumarate of ammonia,

$$C_4\,H_4\,NO_3, HO{=}NH_4\,O, C_4\,HO_3,$$

it was conceivable that the employment of the appropriate agencies might effect a simple decomposition into these two members. Neither potash nor baryta, however, were found capable of expelling the ammonia. But upon dissolving in diluted sulphuric acid, and evaporation by heat to syrup consistence, redissolving with water, again evaporating, and repeating this process several times, at a certain stage, not definitely ascertained, the whole crystallizes in forms of great beauty;—which when washed with alcohol and pulverized, with addition of potash yield ammonia.

Some of the crystals were nearly cubic, reminding one of chlorid of sodium, others were rhombic with feathered margins. They taste and react acid, and do not change upon exposure to the air.

Dried over sulphuric acid and analyzed, they gave the following results.

I. 0·4302 grm. of sub. gave 0·2031 carb. acid and 0·2099 water.
II. 0·3526 " " " 0·8062 platin-salammoniac.
III. 0·3574 " " 0·8300 platin-salammoniac.
IV. 0·4958 " " 0·6090 sulphate of baryta.

Expressed in per cents.

	I.	II.	III.	IV.
Carbon,	12·87	. .	. .	. .
Hydrogen,	5·42	. .	. .	. .
Nitrogen,	. .	14·40	14·63	. .
Sulph. acid,	. .	. .	. .	41·85

These numbers give the formula:

$$C_4\,H_4\,NO_3, SO_3, HO+NH_4O, SO_3\,HO,$$

as the juxtaposition of the per cents. of analysis and those derived from direct estimate will show:

		Theory.	Experiment.
Carbon, - - - -	4 equiv. = 24	12·36	12·87
Hydrogen, - - -	10 " = 10	5·26	5·42
Nitrogen, - - - -	2 " = 28	14·73	14·52
Oxygen, - - - -	6 " = 48	25·04	25·58
Sulphuric acid, - - .	2 " = 80	42·10	41·85
	190	100·00	100·00

This result supported the view that glycocoll contained not only the elements of fumaric acid and ammonia, but contained them in such form or arrangement, as would yield to an active affinity aided by heat.

It was highly probable, therefore, that galvanic action alone would be adequate to the task of decomposition.

To submit this query to the test of experiment, a solution of glycocoll was exposed to the *action of a galvanic battery*, consisting of four of Bunsen's pairs. The solution was separated by a membrane from the water. Upon closing the circle and plunging the poles terminated with platinum plate, one into the solution of glycocoll and the other into the water without, an instantaneous evolution of gas bubbles, at each pole succeded. After the action had continued a short time the fluid about the negative pole gave an alkaline reaction, while that about the positive pole gave an acid reaction. There could then scarcely a doubt remain, that glycocoll was a salt of which the base was ammonia and the acid a body identical in constitution with fumaric acid.

To obtain this acid, glycocoll was treated several hours, over a moderate heat with sulphuric acid, in the manner above described—repeatedly diluting and evaporating. The sulphuric acid for the most part was thrown down with oxyd of lead, and the last traces accurately removed with solution of baryta. The filtrate was then evaporated to concentration over sulphuric acid. In a few hours rhombic prisms of unexampled beauty and perfection, of the combination, ∞P, OP, crystallized from the solution.

Their taste was exceedingly sour. In water they dissolved with difficulty and in ether and alcohol they were absolutely insoluble. With potash, ammonia was evolved from them.

Combustion with chromate of lead, gave the following results.

I. 0·1922 grm. of sub. gave 0·1048 carb. acid and 0·1008 water.
II. 0·2350 " " " 0·5700 platin-salammoniac.

or in per cent.:

	I.	II.
Carbon,	14·86	. .
Hydrogen,	5·82	. .
Nitrogen,	. .	15·28

With these results it was found impossible to construct any formula, containing only the elements of glycocoll, that could have been derived from the action of sulphuric acid. The first action of the acid would be the abstraction of ammonia.

$$C_4\,H_5\,NO_4 - NH_3 = C_4\,H_2\,O_4.$$

If in excess it was conceivable that the remaining member would be subdivided, giving oxalic acid and an oxyd of the radical of Dumas' alcohol and ether series.

$$C_4\,H_2\,O_4 = C_2\,O_3 + C_2\,H_2\,O.$$

The latter uniting with sulphuric acid would give a compound that might not be thrown down by baryta and which with the ammonia, after the precipitation of oxalic acid would give—

$$C_2 H_2 O, SO_3, NH_4 O.$$

Upon heating the body with potash—dissolving in hydrochloric acid and adding baryta, a copious precipitate followed, establishing the presence of sulphuric acid. The small quantity prepared, prevented a determination of the quantity of acid. This formula requires 13·86 p. c. of carbon, 16·36 of nitrogen, and 6·81 p. c. of hydrogen.

It is not considered as established but merely as indicating approximately the action of sulphuric acid.

A concentrated solution of the crystals gave with baryta a crystalline precipitate that redissolved in hydrochloric acid.

With chlorid of calcium, upon the addition of ammonia, a crystalline precipitate was thrown down.

Want of time as well as of substance, postponed the further examination of this interesting body.

*Action of Chlorine.**

When a moderately concentrated solution of glycocoll is subjected to a current of chlorine gas, the latter is rapidly absorbed, and an instantaneous and copious evolution of carbonic acid succeeds. Heat and sunlight both facilitate the action. A convenient method was found in connecting with a stream of dry chlorine gas, a Liebig's potash apparatus, filled, as far as is usual for a combustion, with a solution of glycocoll. It is only necessary that the rapidity of evolution equal that of absorption.

At the end of the third day the process was interrupted, and the liquid evaporated to a syrup consistence. A drop of this syrup yielded, upon the addition of ammonia, a white crystalline precipitate with both chlorids of barium and calcium.

Upon saturating with baryta, filtering and washing with absolute alcohol, it was found that but a small fraction of the glycocoll had been oxydated.

It was again returned to the potash apparatus, and exposed to a slow but uninterrupted stream of chlorine gas for a week. At the conclusion of this period there was still glycocoll unchanged. Chlorid of barium gave the precipitate from the concentrated solution after neutralization with ammonia. This precipitate redissolved in water. It also redissolved in nitric acid, from which it was not thrown down by ammonia.

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* Mulder did not observe any action of chlorine upon glycocoll; a circumstance attributable possibly to the presence of an impurity rich in hydrogen, or to the action not being continued sufficiently long.

When washed and dried the baryta compound was no longer soluble in water, not even with long continued boiling. It was however promptly dissolved in dilute hydrochloric acid. It contains neither chlorine nor nitrogen.

The baryta salt alone was analyzed.

Combustion with chromate of lead gave from—

I. 0·3218 grm. of sub. 0·1544 carb. acid and 0·0547 water.
II. 0·6627 " " 0·5210 sulphate of baryta.

The only formula which can be derived from these determinations is—

$$C_3 H_3 O_6 + BaO.$$

Which requires:

			Estimated.	Found.
Carbon, - - - -	3 equiv.	= 18	12·36	13·08
Hydrogen, - - - -	3 "	= 3	2·05	1·89
Oxygen, - - - -	6 "	= 48	32·99	33·38
Baryta, - - - -	1 "	= 76·6	52·60	51·65
		145·6	100·00	100·00

The same remarks are applicable to this formula that have been made concerning the preceding.

It is recorded chiefly to show that chlorine does not act upon glycocoll as upon many other bodies, by which a certain number of atoms of hydrogen are replaced by an equal number of atoms of chlorine.

The action may be conceived to be the following:—

$$C_4 H_4 No_3 + 5HO + 3Cl = C_3 H_3 O_6 + NH_4 Cl + Co_2 + 2HCl.$$

The same body was obtained by direct addition of a solution of *permanganate of potassa* to an aqueous solution of glycocoll.

After boiling a length of time with *nitric acid*, the same product of decomposition was formed.

When pulverized *chlorate of potash* in small quantity and at intervals is added to a solution of glycocoll in hydrochloric acid, a slow oxydation goes forward, and a product is obtained, in which, as in the cases above noticed, baryta gives apparently the same white crystalline precipitate.

Action of Caustic Potash.

The brilliant fire red color assumed by glycocoll when heated with caustic potash, has already been noticed. If the solution be evaporated to extreme concentration, the evolution of ammonia and hydrogen continues, until at length the mass becomes solid. When treated with hydrochloric acid, hydrocyanic acid is evolved, and if iron salts be present Berlin blue is formed. When dissolved in water the addition of chlorid of calcium is followed by an instantaneous white precipitate, which does not dissolve in acetic acid—a precipitate of oxalate of lime.

The decomposition may be illustrated by the following scheme:—

1 equiv.	cyanogen,	C_2	. .	N	. .
1 "	ammonia,	. .	H_3	N	. .
2 "	oxalic acid,	C_4	. .	. .	O_6
2 "	carbonic oxyd,	C_2	. .	. .	O_2
7 "	hydrogen,	. .	H_7	. .	. .
2 "	glycocoll,	C_8	H_{10}	N_2	O_8

Glycocoll and Hydrosulphuric Acid.

The readiness with which glycocoll enters into combination, and the interest attaching to sulphur compounds in the products of decomposition in the organism, suggested the treatment with hydrosulphuric acid.

Taurin, according to Redtenbacher,* is—

$$C_4\,H_7\,NO_6\,S_2$$

which he observed contained the elements of two atoms of sulphurous acid, aldehyde, and ammonia:

$$C_4\,H_7\,NO_6\,S_2 = C_4\,H_3\,O, NH_4\,O, S_2\,O_4.$$

The union of these several ingredients he succeeded in effecting.

Taurin also contains the elements of hydrated glycocoll, two atoms of water and two of sulphur:

$$C_4\,H_7\,NO_6, S_2 = C_4\,H_5\,NO_4, 2HO, S_2.$$

It was conceivable that by treating a solution of glycocoll with hydrosulphuric acid, and exposing the product to oxydation, a compound, consisting of glycocoll, water, and sulphur in the above relations, might be obtained.

Two atoms of Cystine:

$$2(C_6\,H_6\,NO_4\,S_2)$$

contain the elements of three atoms of hydrated glycocoll, from which ammonia has been withdrawn, and in which four atoms of oxygen have been replaced by an equal number of atoms of sulphur:

$$C_{12}\,H_{12}\,N_2O_8\,S_4 = C_{12}\,H_{15}\,N_3\,O_{12} + S_4 - NH_3 - O_4$$
$$= 2(C_6\,H_6\,NO_4\,S_2).$$

The evolution of the latter product was also not impossible.

Long continued and repeated efforts, however, gave no awaited result; the hydrated glycocoll recrystallizing from the solution with neither accession nor loss.

To obtain either of the above results another experiment was made.

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* Liebig's Annalen, Bd. lvii, s. 170.

Glycocoll was dissolved in quinqui-sulphid of potassium, spirits of wine added, and the solution evaporated through several weeks, over sulphuric acid, to dryness.

An efflorescence had crept up the sides of the containing vessel and the bottom was covered with crystals. Upon treating the whole with hot water, sulphur was separated, which was filtered off and the filtrate slowly evaporated to syrup consistence, from which the whole became a solid crystalline mass.

To a solution of the crystals, addition of sulphuric acid caused the evolution of sulphurous acid and the separation of sulphur. Here was the usual product of exposing the quinqui-sulphid of potassium to the air—hyposulphite of potash.

Upon adding bi-chlorid of platinum to a second portion, a precipitate of platin-chlorid of potassium followed, without the evolution of sulphurous acid or separation of sulphur. There was then left in the solution—

$$C_4\,H_4\,NO_3,\,HO,\,S_2\,O_2,$$

which equals,

$$C_4\,H_7\,NO_6\,S_2 - H_2.$$

CONSTITUTION OF GLYCOCOLL.

The enquiry presses itself, where in the general subdivisions of chemistry does glycocoll belong? Is it a base? Is it an acid? Or is it a salt?

The combinations into which it is capable of entering seem only to embarrass reply.

The following table of the principal compounds of glycocoll that have been analyzed, and the adjoining table of corresponding compounds, chiefly from inorganic chemistry, will not be without interest in the determination of this question.

As an Acid.

$C_4\,H_4\,NO_3$, CuO (Aq)	SO_3, CuO
$C_4\,H_4\,NO_3$, PbO "	SO_3, PbO
$C_4\,H_4\,NO_3$, AqO "	SO_3, AgO

As a Base.

a.

$C_4\,H_4\,NO_3,\,SO_3$	AgO, SO_3
$C_4\,H_4\,NO_3,\,NO_5$	AgO, NO_5

b.

$C_4\,H_4\,NO_3,\,SO_3$, HO	ZnO, SO_3, HO
$C_4\,H_4\,NO_3$, HCl, HO	BaO, HCl, HO
$C_4\,H_4\,NO_3,\,\bar{O}$, HO	KO, $\bar{O}$, HO

c.

$$C_4\,H_4\,NO_3,\ HO,\ \bar{A},\ 2HO \mid NH_3,\ \bar{A},\ 2HO$$

As a Haloid Salt.

$$C_4\,H_4\,NO_3,\ KCl \mid Hg\ Cl,\ KCl.$$

As a Bi-chlorid of Platinum.

$$\begin{array}{l|l} C_4\,H_4\,NO_3,\ \overset{+}{Ber},\ \ HCl & Pt\ Cl_2,\ \overset{+}{Ber},\ HCl \\ C_4\,H_4\,NO_3,\ BaCl,\ (2aq) & Pt\ Cl_2,\ Ba\ \ Cl \end{array}$$

As Ammonia.

$$\begin{array}{l|l} C_4\,H_4\,NO_3,\ PtCl_2\ (2aq) & H_6\,N_2,\ PtCl_2\ \ (\text{Gros.}) \\ & \text{or as haloid salt,} \\ & NH_4\ Cl,\ PtCl_2 \end{array}$$

As an Amphid Salt.

$$\begin{array}{l|l} C_4\,H_4\,NO_3,\ AgO,\ NO_5 & HgO,\ NO_5+AgO,\ NO_5 \\ C_4\,H_4\,NO_3,\ KO,\ NO_5 & \end{array}$$

As of the Magnesia Series.

$$\begin{array}{llr} C_4\,H_4\,NO_3,\ SO_3,\ KO,\ SO_8 & \ldots\ldots & 1 \\ C_4\,H_4\,NO_3,\ SO_3,\ NH_4\ O,\ SO_3+(2aq) & \ldots & 2 \\ 1\ \ldots\ldots & MgO,\ SO_3\ KO,\ SO_3+(6aq) & \\ 2\ \ldots\ldots & MgO,\ SO_3\ NH_4\ O,\ SO_3+(6aq) & \end{array}$$

Basic Salts.

$$\left.\begin{array}{l} C_4\,H_4\,NO_3,\ HO \\ 2\ CuO \end{array}\right\} NO_5\ HO \mid 3\ CuO,\ NO_5\ HO$$

$$2\,(C_4\,H_4\,NO_3)\ HCl,\ HO \mid 2NH_3,\ Zn\ Cl,\ HO$$

$$3\,(C_4\,H_4\,NO_3),\ 2SO_3,\ 2HO \mid 3Hg_2\ O,\ 2NO_5,\ 3HO$$

And further:

$$C_4\,H_4\,NO_3,\ HO,\ AeO,\ SO_3 \mid SO_3\ HO,\ AeO,\ SO_3$$

$$C_4\,H_5\,NO_3,\ \bar{U}\ NH_4O,\ \bar{U} \mid HO,\ \bar{U},\ NH_4O,\ \bar{U}$$

In the above tables we have representatives from almost every class of compounds in the domain of chemistry, and yet they are severally typified in the combinations of glycocoll.

We have it uniting with bases;—a characteristic of acids: uniting with acids;—a characteristic of bases: uniting with amphid salts; a characteristic of amphid salts.

We have it replacing a haloid salt in a binary chlorine compound; playing the part of bichlorid of platinum in another; now appearing in the magnesia series and again replacing water.

It will not be out of place to trace this relationship to other bodies in chemistry a little further, if it may aid in arriving at a nearer conception of the place glycocoll should hold.

The great truth that *the distinguishing properties of bodies depend upon the form, volume and density of their atoms*, or to use another form of expression, that *with every change of these attributes of the atoms, there is a corresponding change in the distinguishing properties of the masses*, is every day acquiring a more profound significance.

The chemical and physical differences between *phosphoric*, *pyrophosphoric* and *metaphosphoric* acids, are but the counterparts of different forms, volumes and densities assumed by the same elements in the same relative proportions.

The same is true of *cyanic*, *fulminic* and *cyanuric acids:* of *oxyd of methyle* and *alcohol:* of *hydrated acetic acid* and formate of *oxyd of methyle.*

It is well known that the several members of groups of isomorphous bodies;—the *alums* for example, have many chemical and physical attributes in common. They have also common *form* and *volume.**

It requires but a little expansion of the thought naturally arising from the consideration of these facts, to come upon the enquiry: *are not acids as such, indebted for their distinguishing characteristic to a common peculiarity of form among their atoms; and bases to another for theirs, and salts to another for theirs ?*†

Let this conception be entertained for the moment, and connect with the peculiarities of glycocoll the following considerations.

1. We have already seen that glycocoll contains the elements of *fumarate of ammonia;*

$$C_4\ H_4\ NO_3 = NH_3,\ C_4\ HO_3.$$

2. It may also be regarded as *cyanate of hydrated oxyd of methyl:*

$$C_4\ H_4\ NO_3 = C_2\ H_4\ O_2,\ C_2\ NO,$$

a sugar in which alcohol and carbonic acid are replaced by wood-spirit and cyanic acid.

The effort to obtain methyl alcohol by slow distillation of glycocoll from a solution in strong potash, failed.

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* Mitscherlich and Kopp.

† The following interesting relationship may be worth recording.

$$C_4\ H_3\ \substack{H \\ N}\ O_3 = \text{glycocoll.}$$

$$C_4\ H_3\ \substack{H \\ O}\ O_3 \times 3 = \text{grape sugar.}$$

$$C_4\ H_3\ \substack{Pb \\ O}\ O_3 = \text{sugar of lead.}$$

$$C_4\ H_3\ \substack{H \\ H_{\frac{2}{3}}O_{\frac{1}{3}}}\ O_3 = \tfrac{2}{3}\ \text{oxyd of glyceryle.}$$

$$C_4\ H_3\ \substack{H \\ N}\ O_3\ HO = \text{nitrous ether.}$$

These bodies have similar taste. Is it dependent upon the similar arrangement of their smallest particles?

One is here reminded of the large number of acids of this formula $(R) + O_3$. Is the sourness of this class dependent upon a common peculiarity of form?

Dumas has suggested that the compound produced when anhydrous sulphuric acid is conducted into an atmosphere of dry ammonia, may be considered *hydrated sulphite of amidogen:*

$$NH_3, SO_3 = HO, NH_2, SO_2.$$

Kane on the other hand, suggests that it be regarded as *hydrated sulphuric acid,* in which one atom of oxygen is replaced by one atom of amidogen.

$$NH_3, SO_3 = S \left\{ \begin{matrix} O_3 \\ NH_2 \end{matrix} \right\} H.$$

3. Glycocoll may be regarded as a *succinate of amidogen,*

$$C_4\ H_4\ NO_3 = NH_2, C_4\ H_2\ O_3,$$

4. Or as *malic acid* in which one atom of oxygen is replaced by amidogen.

$$C_4\ H_2\ O_4 = \text{atom of malic acid.}$$

$$C_4\ H_4\ NO_3 = C_4\ H_2 \left. \begin{matrix} O_3 \\ NH_2 \end{matrix} \right\}$$

5. If doubled it becomes *asparagin.*

$$2\,(C_4\ H_4\ NO_3) = C_8\ H_8\ N_2\ O_6.$$

Since the atom of water in crystallized glycocoll is replaced by both acids and bases, it may not be impossible to obtain from glycocoll a body identical in elementary composition with asparagin. Instances of metamorphosis of this description are not infrequent in the records of chemical investigation.

The conversion of *styrol* into *metastyrol* by heat* and by vibratory motion† in connection with machinery, is among the most remarkable. The spontaneous change of cyanate of ammonia into urea:‡ of aldehyd into metaldehyd:§ of hydrated cyanic acid into cyammelide:|| and the reconversion by distillation of cyammelide and cyanuric acid into cyanic acid: the change of allōxan into alloxanic acid: the metamorphoses of phosphoric acid by heat, and other similar phenomena by *contact* with alkalies, lend support to the supposition, that it may yet be possible to effect some of the metamorphoses above suggested—or some which follow.

6. It would not be more unexpected, than was the artificial preparation of urea, to make glycocoll by combining *urea* and *grape sugar.*

$$\underbrace{C_2\ H_4\ N_2\ O_2}_{\text{Urea.}} + \underbrace{C_6\ H_6\ O_6}_{\text{Half atom of grape sugar.}} = \underbrace{2(C_4\ H_5\ NO_4)}_{\text{Hydrated glycocoll.}}$$

7. The circumstance that in the preparation of the bisulphate of glycocoll and ammonia, fumaric acid is driven out, leads to

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* Blythe and Hoffman, Liebig's Annalen, Bd. liii, s. 311.

† Sullivan, Phil. Mag., 1845.

‡ Wöhler. § Liebig. || Liebig and Wöhler.

the following consideration. If upon separating the fumaric acid, it were to unite with uncombined glycocoll, there would arise a compound containing the elements of *asparaginic acid.*

$$\underbrace{C_4\,H_4\,NO_3 + C_4\,HO_3}_{\text{Fumarate of glycocoll.}} = \underbrace{C_8\,H_5\,NO_6}_{\text{Asparaginic acid.}}$$

8. Two atoms of glycocoll contain also the elements of *allophanic ether.**

$$\underbrace{2\,(C_4\,H_4\,NO_3)}_{\text{Glycocoll.}} = \underbrace{C_4\,H_5\,O,}_{\text{Ether.}}\ \underbrace{C_4\,H_3\,N_2\,O_5}_{\text{Allophanic acid.}}$$

9. Hydrated glycocoll contains the elements of *nitric ether.*

$$C_4\,H_4\,NO_3,\,HO = C_4\,H_5\,O,\,NO_3.$$

Here are two bodies of the most opposite properties, one fluid and volatile, the other solid and cannot be sublimed.

We have a similar instance in the two forms of chlorid of cyanogen; the volatile discovered by Gay Lussac and the solid by Serrullas.

We have another in aldehyd and metaldehyd—a liquid and a solid body.

10. Two atoms of glycocoll and one of ammonia contain the elements of the *creatine* of Chevreul, recently analyzed by Liebig.

$$\underbrace{2(C_4\,H_4\,NO_3)}_{\text{Glycocoll.}} + NH_3 = \underbrace{C_8\,H_{11}\,N_3\,O_6}_{\text{Creatine.}}$$

11. The base derived, by Liebig, from creatine, by boiling with baryta water, which separates urea (as CO_2 and NH_3), contains the elements of glycocoll and oxyd of methyl. It contains also the elements of the Lactamide of Pelouze.

$$\underbrace{C_8\,H_{11}\,N_3\,O_6}_{\text{Creatine.}} - \underbrace{C_2\,H_4\,N_2\,O_2}_{\text{Urea.}} = \underbrace{C_6\,H_7\,NO_4}_{\text{New base.}} = \underbrace{C_4\,H_4\,NO_3,}_{\text{Glycocoll.}}$$

$$\underbrace{C_2\,H_3O}_{\text{Oxyd of methyl.}} = \underbrace{C_6\,H_5\,O_4,\,NH_2}_{\text{Lactamide.}}$$

It will no longer seem strange that a body having so many relationships as are here exhibited, should find its place in the established classes of chemical compounds with difficulty.

The conclusion to which we have arrived in the progress of the investigation above recorded, is, that glycocoll may at the same time be an *acid*, a *base*, and a *salt*, since it has properties in common with each, that distinguish each from the other two.

In the possession of such a variety of attributes as attach to these three classes of bodies, glycocoll is without example in chemistry.

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* Liebig's Annalen, Bd. lix, s. 292.

Constitution of Hippuric Acid.

It has long been observed that in the preparation of hippuric acid, if the heat be too high or the evaporation too rapid, benzoic acid alone is obtained.*

If it be treated with sulphuric acid and peroxyd of manganese, carbonic acid is evolved, benzoic acid crystallizes from the hot filtered solution, and in the filtrate from the crystals sulphate of ammonia is formed.†

Berzelius‡ has remarked that sulphuric acid may be considered as a compound of benzoic acid and a body of this constitution:—

$$C_4\,H_4\,NO_3.$$

Pelouze had attempted to prove that hippuric acid consisted of one atom of hydrocyanic acid, one of oil of bitter almonds, and one of formic acid:

Hydrocyanic acid	=	C_2	H	N	. .
Hydrobenzoylic acid	=	C_{14}	H_6	. .	O_2
Formic acid	=	C_2	H	. .	O_3
Hippuric acid	=	C_{18}	H_8	N	O_5

Fehling§ entertained the view that it consisted of benzamide and fumaric acid.

Benzamide	=	C_{14}	H_7	N	O_2
Fumaric acid	=	C_4	H	. .	O_3
Hippuric acid	=	C_{18}	H_8	N	O_5

Over all this field of speculation Dessaigne's discovery has thrown the most grateful light.

Hippuric acid contains benzoic acid and glycocoll. With the aid of heat and a strong acid or alkali, the two members may be separated.

$$C_{13}H_9NO_6+HCl+2HO=C_{14}H_5O_3,HO+C_4H_4NO_3,HCl,HO.$$

or $C_{18}H_9NO_6+KO+HO=C_{14}H_5O_3$, $KO+C_4H_4NO_3$, HO.

By treating glycocoll with caustic potash, we obtain, among other products, cyanid of potassium and ammonia. If a stronger acid be applied to the former it yields hydrocyanic acid, which with water falls apart into formic acid and ammonia:

$$C_2\,NK+3HO+HCl=KCl+NH_3+C_2\,HO_3.$$

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[*] Schwartz, Annalen der Chem. u. Phar., liv, s. 30. Erdmann, Jour. für Practische Chemie, xiii, s. 422. Dumas, by treating hippuric acid with hypochlorous acid, Annales de Chem. et de Phys., lvii, p. 327.

[†] Berzelius Jahresbericht, 1840, s. 701.

[‡] Jahresbericht, 1836, s. 462. In the Bericht for 1831, s. 240, a similar suggestion from a less perfect analysis of hippuric acid, is to be found. It is again repeated in the Bericht for 1840, s. 704.

[§] Leibig's Annalen, Bd. xxvi, s. 60.

Glycocoll contains the elements of fumaric acid and ammonia. If the former alone be taken from hippuric acid there remains benzamide.

$$\underbrace{C_{18}H_8NO_5}_{\text{Hippuric acid.}} - \underbrace{C_4HO_3}_{\text{Fumaric acid.}} = \underbrace{C_{14}H_7NO_3}_{\text{Benzamide.}}.$$

Physiological Relations of Glycocoll.

Ure* observed that when benzoic acid is taken into the alimentary canal, it reappears in the urine as hippuric acid. This at the time startling announcement, has been verified in the most satisfactory manner by Garrod,† by Keller,‡ in the laboratory of Prof. Booth, Philadelphia, and in the Giessen laboratory.

Pettenkofer§ found in the medical examination of the urine of a girl, who suffered from St. Vitus' dance, and ate nothing but apples and bread, an unusually large quantity of hippuric acid. With the return to animal food, the abnormal proportion of this ingredient diminished.

The occurrence of this acid in the urine of horses and cattle, and of men who live chiefly upon vegetable food, is well known.

These facts taken in connexion with the newly developed constitution of hippuric acid, suggest an inquiry that may not be without interest, viz :—

Are glycocoll and benzoic acid, as such, a part of the tissues of the animal body?—of the albumen, caseine, and fibrine, supplied to it as food? and finally of the corresponding bodies in the seeds and juices of plants.

1. Braconnot obtained glycocoll by treating glue with sulphuric acid; Mulder and Boussingault by treating glue with caustic potash; and Keller obtained it by treating the tissues or the fluids of the body with benzoic acid.

The group of atoms constituting glycocoll resisted more firmly the destructive action of sulphuric acid and potash with the aid of heat, than the remaining members composing glue. These were for the most part oxydated or consumed.

The albumen, fibrine, and caseine received into, and secreted from the blood, no sooner become parts of the living organism, than they commence their return to the original carbonic acid, ammonia, sulphates, phosphates, water, etc., from which they were derived. They commence oxydation. This, however, does not affect all members of the complex compounds alike. In some instances glycocoll *escapes oxydation*, appearing in the urine

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* L'Institut, No. 399, 279, and No. 401, 294. Journal de Pharmacy, xxviii, p. 646.

† Phil. Mag., xx, p. 501.

‡ Pogg. Ann., Bd. lvi, 638. Liebig's Ann., Bd. xliii, s. 108. Central Blatt. 1844, s. 879.

§ Liebig's Ann., Bd. liii, s. 86.

as a member of hippuric acid, as it escaped oxydation with the potash and sulphuric acid.

2. Fumaric acid is present in a great variety of plants.[*] In asparagine[†] we have the elements of fumaric acid and ammonia, which with the requisite metamorphosis would become glycocoll.

$$2(NH_3, C_4\ HO_3)=C_8\ H_8\ N_2\ O_6=2(C_4\ H_4\ NO_3).$$

3. Schlieper[‡] by treating isinglass with chromic acid, obtained among a variety of products benzoic acid.

It is found frequently in the vegetable kingdom, for example in gum-benzoin.

We have then benzoic acid and glycocoll (asparagine) in the vegetable kingdom, in the tissues of the animal body, and in the form of hippuric acid in the urine.

It remains to be ascertained if they be present in the *animal and vegetable albumen, fibrine, and caseine.*

Formation of Uric Acid Concretions.

Keller observed both urea and uric acid in the urine after the separation of hippuric acid, and therefrom concludes that Ure's suggestion that benzoic acid might be employed to prevent the formation of uric acid concretions, is too hasty.

The following experiment may have in connection with this subject sufficient interest to justify its being recorded.

The morning urine from mixed animal and vegetable diet, was evaporated over a water bath to thick syrup consistence, and tested for glycocoll. Neither in the alcoholic extract, nor in the residue, could a trace be recognized with the oxyd of copper test. Nitric acid gave a precipitate of urea, not, however, in large quantity.

At ten o'clock the next evening, four grammes of glycocoll were dissolved and taken in water. No consciousness of having taken any thing unusual was felt. The next morning urine reacted acid. Its color was the same as that of the previous day. Upon evaporation to syrup consistence, it presented a much larger quantity than before. One portion was supersaturated with concentrated oxalic acid, accurately neutralized with carbonate of soda and extracted with spirits of wine. Another portion was supersaturated with acetate of lead and treated with hydro-sulphuric acid. Upon evaporating to syrup the extract of the first, and the filtrate of the second, and testing both with the oxyd of copper, no trace of glycocoll was discovered. The glycocoll had

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[*] If we include malic acid, the number will be greatly increased.

Buchner's Report, Bd. xxxiv, s. 368. Liebig's Ann., Bd. xxxi, s. 241; Bd. xxxviii, s. 257; Bd. li, s. 246.

[†] Geiger's Mag., xxxv, 42.

[‡] Liebig's Annalen, Bd. lviii, s. 1.

then disappeared. In its place were urea and uric acid, both in larger proportion, as compared with the quantities of the previous day.

If we deduct, as has already been shown, half an atom of grape sugar from two atoms of hydrated glycocoll, we obtain urea:—

$$C_8 H_{10} N_2 O_8 - C_6 H_6 O_6 = C_2 H_4 N_2 O_2.$$

It is conceivable that glycocoll should thus divide, and that the sugar should disappear in the products of oxydation.

By treating it with nitric acid, with this view, no such result was obtained. Concentration or dilution, a strong heat or a moderate and long continued heat, gave no urea and no oxalic acid. One of the products is noticed on page 329.

Uric acid (as bibasic) may be contemplated as a cyanurate of glycocoll:—

$$C_{10} H_4 N_4 O_6 = C_6 N_3 O_3, C_4 H_4 NO_3.$$

If benzoic acid be capable of withdrawing glycocoll from uric acid, the remaining member, in the presence of water, would furnish the materials for carbonic acid and ammonia:

$$C_6 N_3 O_3 + 9HO = 6CO_2 + 3NH_3.$$

No great confidence can be placed in a single result of this description. Still whatever worth it has, seems to support the suggestion of Ure. Uric acid is found where the products of decomposition are too imperfectly oxydated.* Those who suffer from uric acid concretions are principally sedentary persons. Exercise by increasing the supply and furthering the action of oxygen, more perfectly secures the oxydation of the products of decomposition.

Could a part of the products destined to consume oxygen be withdrawn, the usual supply through the lungs might be adequate to the complete oxydation of the remainder, and thus the formation of uric acid concretions be rendered impossible. Glycocoll is one of these products. If united to benzoic acid, a consumer of oxygen is withdrawn from the blood.

A series of experiments upon given diet, with and without benzoic acid, could not fail to solve this important question.

With this investigation, and particularly with the products of decomposition of glycocoll, which so far as here recorded, may be considered rather as qualitative than quantitative, it is our purpose to proceed with as little delay as possible.

Note.—It may not be improper to state that Baron Liebig employs his own time and that of his assistants, and the appliances of his private laboratory, in great part, in labors to ascertain methods of cheap and expeditious preparation, that he may spare

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* Liebig's Thier Chimie, 2e. Ausg. s. 125.

the time, means, and patience of the young chemists in his school. He brings to bear his vast experience in this most difficult of all chemical labor—the preparation in their purity of chemical substances.

He had been employed six months in finding out a better method than that of Braconnot or Mulder, for obtaining gelatine sugar, when in the winter semestre of 1845–46, I expressed a wish that he would give me, for a change from the labors in which I had been for some months engaged, a crystalline body, whose study would increase my knowledge of organic chemistry. In compliance with this request he gave me some three ounces of exquisitely beautiful transparent prismatic crystals, whose analysis I employed myself immediately in making. He remarked to me of the method of preparation and of some of its properties, and of much more that I could not retain, and I went to the back journals to ascertain what investigation of it had been made; at the same time making repeated analyses of the pure body, its hydrochlorate and anhydrous sulphate.

The result of this labor and a review of Boussingault's analyses, satisfied me that the constitution of the body, combining with acids, bases, and salts, was—

$$C_4 H_4 NO_3.$$

When I had come to this conclusion I had not read the article in the Comptes Rendus, containing Dessaigne's discovery, and felt indebted to no one for the constitution of the body.

Gerhardt's suggestion that the body was—

$$C_2 H_5 NO_2 = C_4 H_{10} N_2 O_4 . \tfrac{1}{2}$$

with his annotation, or $C_4 H_5 NO_4 . \tfrac{1}{2}$, according to that of Liebig and Gmelin, I could not reconcile with the analysis of the anhydrous sulphate; and this also came under my eye after my opinion of the constitution had been formed.

Dessaigne had the honor of having made one of the most brilliant of recent discoveries, but he made no analysis. Laurent made an analysis in the wake of Dessaigne's announcement, confirming the suggestion of Dessaigne, that hippuric acid was a compound of benzoic acid and gelatine sugar. The latter however is not *the body*, glycocoll, but its *hydrate*.

After my paper went into the hands of the conductor of Liebig's Annalen, Mulder's paper, giving the constitution as

$$C_8 H_{10} N_2 O_8$$

in Erdmann and Marchand's Journal, appeared. This however was not the body, but its *hydrate* doubled.