# ON AN APPARENT PERTURBATION OF THE LAW OF DEFINITE PROPORTIONS OBSERVED IN THE COMPOUNDS OF ZINC AND ANTIMONY.

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# ON AN APPARENT PERTURBATION, &c.

In a former paper in this Journal* I described two new compounds of zinc and antimony $Sb\,Zn_3$ and $Sb\,Zn_2$ which I named respectively, Stibiotrizincyle and Stibiobizincyle, because they resemble in their composition the metallic radicals of organic chemistry, and because the first decomposes water rapidly at 100° C. I there stated that crystals of $Sb\,Zn_3$ could be obtained containing a much larger amount of zinc than that required by the law of definite proportions, and that this change was not accompanied by any alteration of crystalline form. A similar variation of composition was afterwards observed in the crystals of $Sb\,Zn_2$, and it is the object of the present paper to describe the law of the variation in both cases and to explain its cause.

In the course of my investigations on this subject, crystallizations were made or attempted of alloys differing in composition by one half to five per cent., according to circumstances, from the alloy containing 95 per cent. of zinc to that containing 95 per cent. of antimony; but only two crystalline forms were observed, that of $Sb\,Zn_3$ and that of $Sb\,Zn_2$. Well defined crystals, like those described under $Sb\,Zn_3$ in the former paper,† were obtained from the alloys between 43 and 60 per cent. of zinc; and even in alloys of a higher zinc per-centage, crystals of the same form were still seen, although they were no longer well defined. In the alloys between 20 and 33 per cent. of zinc, well defined crystals, like those described under $Sb\,Zn_2$ in the same paper, were formed; and finally there separated from the alloys between 33 and 42 per cent. of zinc thin metallic plates, which evidently belonged to the same crystalline form. In making the alloys from 43 to 95 per cent. of zinc, the zinc was melted first,

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* This Journal, vol. xviii, p. 234.

† Ibid.

and when in fusion the antimony was added. As the melting point of antimony is much above that of zinc, the fluid zinc acted on the solid antimony as a solvent, dissolving the pure metal, but not the impurities, which rose to the surface forming a scum. This scum seemed to take with it some of the antimony and thus caused a loss, which, together with the impurity, was found by experiment to be about three per cent. of the antimony used. This resulted in raising the per-centage of zinc in the alloy at most about eight-tenths of one per cent. The alloys below 43 per cent. of zinc were made by melting the antimony first, and then adding zinc. By this method the loss of antimony was very greatly diminished, and, counting the impurity, was found to be only about one per cent. and a half of the antimony used. In preparing the alloys this loss was always allowed for, and the crystallizations were all made as nearly as possible under the same circumstances, so that any unexpected cause of error should affect all equally. The crystals formed in the alloys were all analyzed in my laboratory under my direction and immediate supervision, and the greater part of them by myself. The rest were by my assistants, Mr. F. H. Storer, Mr. C. W. Eliot, and Mr. C. S. Homer, to whose care and accuracy I take pleasure in bearing witness. Their work is in all respects as reliable as my own. The results are collected in the following table which will explain itself.

*Analyses of the Crystals formed in the Alloys of Zinc and Antimony.*

| STIBIOTRIZINCYLE. | | | | | | STIBIOBIZINCYLE. | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Composition of the Alloys by Synthesis. | | Composition of the Crystals by Analysis. | | | Name of the Analyst. | Composition of the Alloys by Synthesis. | | Composition of the Crystals by Analysis. | | | Name of the Analyst. |
| Per ct. of Zn. | Per ct. of Sb. | Per ct. of Zn. | Per ct. of Sb. | Sum. | | Per ct. of Zn. | Per ct. of Sb. | Per ct. of Zn. | Per ct. of Sb. | Sum. | |
| 70·40 | 29·60 | 64·15 | 35·77 | 99·92 | Cooke. | 33·00 | 67·00 | 35·37 | 64·57 | 99·94 | Cooke. |
| 66·50 | 33·50 | 61·00 | 39·00 | *100·00 | Cooke. | do. | do. | 35·40 | 64·60 | †100·00 | Cooke. |
| 64·50 | 35·50 | 53·50 | 41·44 | 99·94 | Cooke. | 32·50 | 67·50 | 34·62 | 64·92 | 99·54 | Storer |
| · · | · · | 55·49 | 44·42 | 99·91 | Homer. | do. | do. | 34·61 | 65·39 | †100·00 | Eliot. |
| 60·60 | 39·40 | 55·00 | 45·09 | 100·09 | Homer. | 31·50 | 68·50 | 33·95 | 66·09 | 100·04 | Storer. |
| 58·60 | 41·40 | 50·39 | 49·29 | 99·68 | Eliot. | 29·50 | 70·50 | 33·62 | 66·38 | †100·00 | Storer. |
| 56·60 | 43·40 | 49·92 | 50·05 | 99·97 | Eliot. | do. | do. | 33·62 | 66·38 | †100·00 | Storer. |
| 54·70 | 45·30 | 48·26 | 51·42 | 99·68 | Storer. | 27·50 | 72·50 | 33·85 | 65·81 | 99·66 | Storer. |
| 52·70 | 47·30 | 47·47 | 52·53 | †100·00 | Cooke. | 26·50 | 73·50 | 32·08 | 67·60 | 99·68 | Storer. |
| · · | · · | · · | · · | · · | · · | 26·00 | 74·00 | 30·74 | 69·06 | 99·80 | Cooke. |
| 50·70 | 49·30 | 46·89 | 53·11 | †100·00 | Cooke. | 25·50 | 74·50 | 30·43 | 69·51 | 99·94 | Storer. |
| do. | do. | 46·45 | 53·55 | †100·00 | Cooke. | 25·00 | 75·00 | 29·88 | 70·20 | 100·08 | Cooke. |
| 48·70 | 51·30 | 48·66 | 51·34 | †100·00 | Eliot. | 24·50 | 75·50 | 28·76 | 71·24 | 100·00 | Cooke. |
| 46·70 | 53·30 | 46·77 | 53·23 | †100·00 | Eliot. | 23·50 | 76·50 | 27·93 | 71·85 | 99·78 | Cooke. |
| 44·80 | 55·20 | 44·26 | 55·73 | †100·00 | Eliot. | 22·50 | 77·50 | 26·62 | 73·27 | 99·89 | Storer. |
| 43·80 | 56·20 | 44·04 | 55·96 | †100·00 | Cooke. | 21·50 | 78·50 | 24·83 | 74·74 | 99·57 | Cooke. |
| 42·80 | 58·20 | 43·15 | 56·93 | 100·08 | Cooke. | 20·12 | 79·88 | 20·58 | 79·42 | 100·00 | Cooke. |
| do. | do. | 43·06 | 56·50 | 99·56 | Cooke. | | | | | | |
| do. | do. | 42·83 | 57·24 | 100·07 | Cooke. | | | | | | |

* In this analysis the antimony only was determined.
† In this analysis the zinc only was determined.

*Curve of Variation in Composition.*—In order to compare together the composition of the crystals and that of the alloy in which they form, I have resorted to the usual method of Analytical Geometry, and in the plate illustrating this paper, the lower horizontal line is the axis of abcissas, and the vertical line at the extreme left the axis of ordinates. The first has been divided into equal parts, which denote the per cents. of zinc in the crystals and the last into parts of the same size, which stand for the per cents. of zinc in the alloys. The zinc rather than the antimony determinations have been selected for comparison, as being generally more accurate, and as having been all made in exactly the same way. The points determined by analysis are indicated with dots, and the double line drawn through these dots is a curve, which represents the relation of the composition of the crystals to that of the alloy in which they form. In order to make clear the connection between the two, it will be well to discuss this curve, commencing with what may be termed the two centres of crystallization, the alloys of 42·8 and 31·5 per cents. of zinc, and examining the effect produced on the crystals by diminishing or increasing the amount of zinc in the alloy.

It has already been stated that the crystals of $Sb\,Zn_3$ are obtained in their greatest perfection from the alloy of 42·8 p. c. of zinc. They are then comparatively large, generally aggregated, and, as the three analyses cited in the former paper prove, have the same composition as the alloy. On increasing gradually the amount of zinc in the alloy up to 48·7, the crystals continued to have the composition of the alloy, and the only difference, which could be observed in their character, was, that they were smaller and more frequently isolated. Between these limits, the whole mass of the alloy exhibited a strong tendency to crystallize, and, by pouring it, as it cooled, from one vessel to another, it could be crystallized to the last drop. The portion *a*, *b*, of the curve is therefore a straight line equally inclined to the two axes. On increasing the amount of zinc in the alloy to 50·7 p. c., the amount of zinc found in the crystals was only 46 89 p. c., and above this it was uniformly less than it was in the alloy; but no closer relation between the two could be detected, owing undoubtedly to the unavoidable irregularity in the crystallizations of the alloys, which contained more than 50 p. c. of zinc. This arose from a peculiar pasty condition, which the fluid mass assumed, at the point of crystallization, apparently caused by the separation of the excess of zinc. Definite crystals however were obtained even from the alloy of 60 p. c. of zinc, which contained 55 p. c.; above this, the crystals became less and less abundant, and gradually faded out, although the alloy even of 86 p. c. of zinc exhibited a radiated crystalline texture; and a trace of this structure could still be discovered even in the alloy containing only 4 p. c. of antimony. It might be supposed that on returning to the alloy of 42·8 p. c. of zinc, and increasing the amount of antimony we should obtain crystals containing an excess of antimony; but so far is this from being true that the slightest excess of antimony entirely changes the character of the crystallization. On crystallizing an alloy containing 41·8 p. c. of zinc not a trace of any prismatic crystals could be seen, but in their place there was found a confused mass of thin metallic scales, which, as will soon be shown, are imperfect crystals of $Sb\,Zn_2$. Thus it appears that although perfectly formed crystals of $Sb\,Zn_3$ can be obtained containing 55 p. c. of zinc they can not be made to take up the slightest excess of antimony.

In order to obtain crystals having the composition of $Sb\,Zn_2$, that is, containing 33·5 p. c. of zinc, it is necessary to crystallize an alloy at least as low as 31·5 p. c. of zinc. At this point large compound crystals are obtained corresponding to the large crystals of $Sb\,Zn_3$. On increasing the amount of zinc in the alloy up to 33 p. c., the proportion of zinc in the crystals appeared to increase in the same ratio, so that the curve of $Sb\,Zn_2$ is at this part a straight line parallel to the curve of $Sb\,Zn_3$. It should however be noticed that the extent of this line $k\ i$ is so limited that a very small error in the analyses might change very considerably its direction. The crystals of $Sb\,Zn_2$ containing an excess of zinc, are smaller and more frequently isolated than those containing exactly two equivalents. A similar fact, it will be remembered, is true of the crystals of $Sb\,Zn_3$. At the alloy of 33 p. c. of zinc, the definite crystals of $Sb\,Zn_2$ begin to disappear and are succeeded by thin metallic scales, which, as the two following facts will prove, are imperfect crystals of the same crystalline form. First, the scales from the alloy of 33 p. c. are frequently found having a definite crystal as a nucleus, when it is evident that their surfaces are extensions of the basal plane O of fig. 2 of the former memoir. Secondly, the scales twin together like the large tabular crystals of $Sb\,Zn_2$, forming a cellular structure, and the angle between two scales thus united, measured with an application goniometer approximately 115° 30′, and was therefore equal to the basal angle of the definite crystals. These scales continue up to the alloy of 41·8 p. c. of zinc, becoming however constantly less abundant and less distinct. Several specimens of them were analyzed, but no regularity in their composition could be detected except that they all contained a very much larger amount of zinc than the alloys in which they formed. This irregularity and the imperfection in the crystallization seem to be caused by the interference of $Sb\,Zn_3$, that is, by a tendency to form $Sb\,Zn_3$ which exhibits itself in a proneness of the crystals of $Sb\,Zn_2$ to an excess of zinc. The line *k i* has been continued with dots in order to show that the influence of $Sb\,Zn_2$ extends as far as the alloy of 42·8 p. c. of zinc. On returning to the alloy of 31·5 p. c. of zinc and adding an excess of antimony it was fonnd that the crystals formed continued to have the theoretical composition of $Sb\,Zn_2$ until the amount of zinc in the alloy had fallen to 27 p. c., so that the tendency towards the theoretical composition was so great, that in the alloys between 31·5 and 27 p. c. of zinc, crystals were formed having very nearly this composition. On still further increasing the amount of antimony in the alloy, the composition of the crystals gradually approached that of the alloy, and from the alloy of 20·2 p. c. of zinc, very imperfect crystals were obtained having almost the same composition as the menstruum. At the same time, the crystals became less and less perfect and finally disappeared altogether in the alloys below 20 p. c. of zinc.

The portion of the curve *k m n h*, is the most important result of this investigation and therefore deserves especial notice. It has been shown that crystals of the form of $Sb\,Zn_2$, or at least crystalline scales of the same character, are formed in the alloys between 20 and 43 p. c. of zinc, the first per cent. corresponding to Sb Zn and the second to $Sb\,Zn_3$. Half way between these two points, that is the alloy of 31·5 p. c., is the point where crystals having the calculated composition of $Sb\,Zn_2$ are first obtained. Were the variations in the composition of the crystals of $Sb\,Zn_2$ exactly proportioned to the excess of zinc or of antimony in the alloy, as is the case with $Sb\,Zn_3$, then the curve of variation would be the straight line formed by the continuation of the line *a b*. From this line *b h* the course of the curve is deflected by the force which determines the union of the elements in definite proportions, and which for the want of a special term, I will call the Chemical Force. This is so strong that the curve runs parallel to the axis of ordinates through the distance *k m*. Beyond this point, the influence of the excess of antimony in the alloy becomes stronger than the chemical force, and the curve gradually bends towards the line *h b* which it finally meets at *h*. In the portion *h n* of the curve, the analyses are best represented by the arc of a circle, of which the radius equals *h e* or one-half of *h b*, and to which the line *k m* is tangent. In the portion *n m* the points determined by analysis may also be connected by the arc of a circle of which the radius *o′ n* equals the difference between the radius *o n* and twice *g n*, so that the two centres are at the same distance from the line *a h*. The whole curve is evidently the result of two forces; one acting along the chord in the direction *b h*, a force tending to increase the amount of antimony in the crystals proportional to the amount in the alloy, the same force in fact, which acts undisturbed in forming the portion of the curve *b a*; the other the chemical force acting in the direction of the tangent *k m*. It has already been stated that crystals having the calculated composition of $SbZn_2$ are not first formed in the alloy of the same composition 33·5 p. c. of zinc, but in an alloy containing two per cent. less; so that the line *m k*, instead of extending to *e*, changes from this direction at *k*, and afterwards runs parallel to the line *b h*. Unless this fact can be explained by a tendency in $SbZn_2$ to an excess of zinc caused by the influence of $SbZn_3$ as suggested above, the reason of this difference between $SbZn_2$ and $SbZn_3$ in this respect is not clear; but as some evidence that it is not accidental it may be stated, that the distance *k c* equals *c i*, the last point being the one, at which the tangent line *m k* extended meets the curve. Another remarkable fact whose bearing cannot be at present seen, but which like the last serves to corroborate the general accuracy of the result was pointed out by my colleague, Prof. Peirce, after the plate had been engraved. The distances of the three most important points of the curve of $SbZn_2$ from the line *a h*, viz. *k d*, *m f*, and *n g*, are simple multiples of the first; *n g* is twice and *m f* three times *k d*. The curve has been fixed, as will be noticed from the dots, by a large number of points determined throughout the greater part of its length at every per cent., and in the portion *m n* at every half per cent.; they certainly coincide with the curve as closely as could possibly be expected, and the very agreement of so many different determinations by three separate analysts is a strong proof of the general correctness of the work.

By making hypotheses in regard to the nature of the two forces, which have generated the curve just described, it would not be difficult to obtain for it a mathematical expression; but as such hypotheses, in our ignorance of the nature of these forces, would be premature, I must content myself with giving its geometrical construction on a chart ruled like the plate illustrating the memoir. Let the coördinates of any point of the curve be, $x =$ per cent. of zinc in the crystals, and $z =$ per cent. of zinc in the alloy. In order to construct the curve of $SbZn_3$, find a point (*a*) of which $x = z = 43$ p. c. (the calculated per cent. of $SbZn_3$) and draw a straight line *a b* equally inclined to the two axes in the direction from the origin. To construct the curve of $SbZn_2$, produce the line *a b* in the opposite direction to the point $x = z = 20$, which will be the lowest point of the curve. Find next a point (*k*) of which $x = 33·7$ p. c. (the calculated per cent. of $SbZn_2$ is 33·5) and $z = 31·5$ p. c., which is one-half of $43 + 20$. Through this point draw a line *m k* parallel to the axis of ordinates and intersecting the line *a b h* at *c*. The line *m i* is the tangent, and the line *b h* the chord of the required arc. On the line *m i* take $c i = c k$, and *i* is the point at which the arc should touch the tangent. Erect a perpendicular on the tangent at the point *i*, take $o i = \frac{1}{2}\, b h$, and from *o* as a centre, with a radius = $o\,i$, describe the arc $h\,i$. Also from the centre $o$ let fall a perpendicular $o\,g$ on the chord $b\,h$, and produce it to a point $o'$ making $o'\,g = o\,g$. It will intersect the arc at $(n)$. From $o'$ as a centre with a radius $o'\,n$ describe a second arc $n\,m$ intersecting the tangent at $m$. Finally, draw from $k$, a straight line $k\,l$, parallel to $b\,h$, then the broken line $l\,k\,m\,n\,h$ will be the required curve.

It will be noticed that the tangent which has been drawn on the plate through the points determined by analysis is two-tenths of a per cent. in advance of the line which would correspond to $SbZn_2$. This position is essential to the equality of $k\,c$ and $c\,i$, if we retain as the value of the radius of the larger arc $R = \frac{1}{2}\,b\,h$. If the analyses should have given erroneously too much zinc so that the true position of the line should be at $x = 33{\cdot}5$ per cent., then this equality would be destroyed, and the conditions for finding the centre $o$ would be reduced to the coördinates of the point $h$, the length of the radius and the position of the tangent, from which by a very simple construction the curve might be drawn. It should however be remarked that the position of the tangent in advance of the line $x = 33{\cdot}5$ is in accordance with the fact, already noticed, that the crystals of $SbZn_2$ have throughout a proneness to an excess of zinc caused apparently by the influence of $SbZn_3$; but it is also true that the tendency of the error in the zinc determinations is in the same direction.

Before discussing the conclusions to which the facts already stated seem directly to point, it will be well to see how far the variation in composition corresponds to a variation in the properties of the two compounds. Three classes of properties have been examined in this connection, viz., Specific Gravity, Crystalline Form, and Affinity for Oxygen, which will be treated of in order.

*Specific Gravity.*—The specific gravities of all the crystals analyzed, as well as that of the zinc and antimony used in the investigation, were taken with the greatest care. The determinations were made with a nicely constructed specific gravity bottle, as this method was found susceptible of greater accuracy than any other, when the temperature was observed with precision. In calculating the specific gravity, the weight of the water was corrected for the temperature, so that the unit is in all cases distilled water at 4° C. A similar correction could not be made for the temperature of the substance, as the coefficients of expansion of the crystals are not known. The results of the determination all made by myself are collected in the following table in the column headed "Sp. Gr. by Experiment." In the column headed "Mean Sp. Gr. of Zinc and Antimony" are given the cal-

*Specific Gravities of Crystals, formed in the Alloys of Zinc and Antimony.*

| Composition of the Alloys. | | Composition of the Crystals | | Sp.Gr. of Crystals by Experiment. | Mean Sp. Gr. of Zinc and Antimony. | Expansion in Crystallizing. |
|---|---|---|---|---|---|---|
| Per ct. of Zn. | Per ct. of Sb. | Per ct. of Zn | Per ct. of Sb. | | | |
| 100·00 | | | | 7·153 | 7·153 | 0·000 |
| *96·00 | 4·00 | | | 7·069 | 7·134 | 0·065 |
| *86·20 | 13·80 | | | 6·898 | 7·086 | 0·188 |
| *76·30 | 23·70 | | | 6·769 | 7·039 | 0·270 |
| 70·40 | 29·60 | 64·20 | 35·80 | 6·699 | 6·982 | 0-283 |
| 66·50 | 33·50 | 61·00 | 39·00 | 6·628 | 6·967 | 0·339 |
| 64·50 | 35·50 | 58·56 | 41·44 | 6·596 | 6·956 | 0·360 |
| 62·50 | 37·50 | 55·53 | 44·47 | 6·506 | 6·941 | 0·435 |
| 60·60 | 39·40 | 55·00 | 45·00 | 6·440 | 6·939 | 0·499 |
| 58·60 | 41·40 | 50·39 | 49·61 | 6·396 | 6·917 | 0·521 |
| 56·60 | 43·40 | 49·95 | 50·05 | 6·388 | 6·915 | 0·527 |
| 48·70 | 51·30 | 48·66 | 51·34 | 6·404 | 6·909 | 0·505 |
| 46·70 | 53·30 | 46·77 | 53·23 | 6·376 | 6·900 | 0·524 |
| 44·80 | 55·20 | 44·26 | 55·74 | 6·341 | 6·888 | 0·547 |
| 42·80 | 57·20 | 43·09 | 56·91 | 6·327 | 6·882 | 0·555 |
| *40·00 | 60·00 | | | 6·386 | 6·867 | 0·481 |
| *35·00 | 65·00 | | | 6·404 | 6·844 | 0·440 |
| 33·00 | 67·00 | 35·37 | 64·63 | 6·401 | 6·845 | 0·444 |
| 29·50 | 70·50 | 33·62 | 66·38 | 6·384 | 6·837 | 0·453 |
| 27·50 | 72·50 | 33·85 | 66·15 | 6·383 | 6·838 | 0·455 |
| 26·50 | 73·50 | 32·08 | 67·92 | 6·400 | 6·829 | 0·429 |
| 26·00 | 74·00 | 31·07 | 68·93 | 6·418 | 6·824 | 0·406 |
| 25·50 | 74·50 | 30·43 | 69·57 | 6·428 | 6·822 | 0·394 |
| 24·50 | 75·50 | 28·76 | 71·24 | 6·449 | 6·813 | 0·364 |
| 22·50 | 77·50 | 26·62 | 73·38 | 6·453 | 6·803 | 0·350 |
| 21·50 | 78·50 | 24·83 | 75·17 | 6·467 | 6·795 | 0·328 |
| *15·00 | 85·00 | | | 6·564 | 6·748 | 0·184 |
| *10·00 | 90·00 | | | 6·603 | 6·725 | 0·122 |
| *5·00 | 95·00 | | | 6·655 | 6·701 | 0·046 |
| | 100·00 | | | 6·677 | 6·677 | 0·000 |

culated specific gravities of the same crystals on the supposition that the two metals had undergone no expansion on uniting. The last column was obtained by subtracting the numbers of the former from those of the latter, and therefore shows the relative amount of expansion. On examining the table, it will be found 1st. Than the union of antimony and zinc is accompanied by expansion. 2nd. That the specific gravity of the crystals varies slightly with the composition. 3d. That the two minimum specific gravities correspond precisely to the composition of $Sb\,Zn_2$ and $Sb\,Zn_3$, so that the specific gravity increases and the expansion diminishes as you depart on either side from these two centres. 4th. That the specific gravity of $Sb\,Zn_3$ is smaller than that of $Sb\,Zn_2$. We find then that the specific gravity determinations confirm in general the results of the analysis pointing out the same two centres of crystallization.

*Crystalline Form.*—It has already been stated that only two crystalline forms can be obtained from the alloys of zinc and antimony, that of $Sb\,Zn_3$ and that of $Sb\,Zn_2$. A large number of

* Alloys not crystallized.

crystals of $Sb\,Zn_3$ from different alloys, and therefore containing different proportions of zinc, were carefully measured for the purpose of ascertaining whether the angle was at all affected by the variation of composition. Fortunately four different crystallizations afforded excellent crystals, the angles of which could be measured to a minute. The crystals contained respectively 43·15, 44·14, 46·90 and 55·00 per cents. of zinc, and on all these by repeated measurements the angles were found to be *identical* with those given under figs. 1 and 2. Crystals from many of the other alloys were also measured, but on account of the imperfections of their surfaces the angles could not be determined within five or ten minutes. In all these cases however the values of the angles given above were included within the limits of uncertainty.

The faces of the crystals of $Sb\,Zn_2$ are not generally so perfect as those of $Sb\,Zn_3$, nor is their tabular form so well adapted for measurement; moreover variations in some of the angles have been noticed in crystals from the same crystallization amounting even to ten minutes. The angle 0 on 1 however appeared to be very constant for in all cases where it could be accurately measured the same value was obtained. As none of the crystals of $Sb\,Zn_2$, containing an excess of antimony, could be measured with precision, no constant variation of angle could be detected and on the other hand it could not be proved to be invariable.

*Affinity for Oxygen.*—The affinity of the crystals of $Sb\,Zn_3$, of different compositions, for oxygen, may be estimated by comparing the amounts of hydrogen gas evolved in a given time on boiling alloys of the same composition with water. The results of such experiments were given in the former memoir in a table, a mere glance at which will discover the two following facts—

1st, That up to 40 per cent no great increase in the amount of hydrogen evolved is obtained by increasing the amount of zinc in the alloy.

2nd, That at the alloy containing 42 per cent. of zinc there is an immense maximum confined at most between two per cent on either side.

*General Conclusions.*—Before stating the conclusions to which as I think the facts now established directly point, it will be well to consider the only two admitted principles of chemical science which could possibly be brought forward to explain similar variations. They are, first, that of impurities in crystals; second, that of isomorphous mixtures. It will not be difficult to show that the variations in composition of $Sb\,Zn_2$ and $Sb\,Zn_3$ cannot be caused by either of these principles.

It is a well known fact that crystals frequently take up impurities which are either dissolved or mechanically suspended in the menstruum in which they form, and it might be supposed at first sight that the excess of zinc or antimony in $Sb Zn_3$ or $Sb Zn_2$, bore the same relation to their crystals that the sand does to the rhombohedron of calcite from Fontainebleau, or oxyd of iron and chlorite to crystals of quartz; but, in the first place, in all cases where a considerable amount of impurity is present the crystals are either imperfect or else the angle is considerably changed at times even as much as two or three degrees; and secondly, as such impurities are merely mechanical, the amount in the crystals would in all probability be proportional to the amount present in the menstruum at the time of their formation. Now in the crystals of $Sb Zn_3$, from the alloy of 60 p. c. of zinc, there is present an excess of zinc amounting to 15 p. c. and nevertheless the crystals are as perfect as, and their angles identical with, those obtained from the alloy of 43 per cent. In the crystals of $Sb Zn_3$ the excess of zinc is to a certain limit directly proportional to the excess in the alloy, but in those of $Sb Zn_2$ the excess of antimony is far from obeying this rule; and were the excess in both cases a mechanical mixture the variation in both cases would undoubtedly follow the same law: again, the crystals of $Sb Zn_3$, take up an excess of zinc but do not take up an excess of antimony, while those of $Sb Zn_2$ crystallize with an excess of either, —facts which are as inconsistent with the idea of mechanical impurity as the last: finally the form of the curve of $Sb Zn_2$ of itself alone proves that the excess of antimony in the crystals is not in the condition of mechanical impurity; for in that case the variation of composition would not be influenced, as the curve shows that it is, by the chemical force.

A theory that the variation in composition resulted from the mixture of two or more isomorphous compounds would be even less tenable than the one just discussed. For in the first place it would be necessary to assume the existence of two other compounds of zinc and antimony isomorphous with $Sb Zn_2$ and of one other, if not more, isomorphous with $Sb Zn_3$. Not only would such an assumption be contrary to all the analogies of chemistry and therefore require strong evidence to sustain it; but in the second place it can almost be demonstrated that no such compounds exist. The crystals having the calculated composition of either $Sb Zn_3$ or $Sb Zn_2$ are marked as has been shown by striking peculiarities, and with one possible exception similar peculiarities were not observed throughout the whole series of crystals which have been examined. The crystals containing 50 per ct. of zinc and of the composition of $Sb Zn_4$ were found to have a slightly smaller sp. gr., than those just above or just below them, but the difference is so small that it may be accidental, and as the crystals exhibited none of the other peculiarities, which characterize crystals having the calculated composition of $Sb Zn_3$ or

$Sb\,Zn_2$, I could not attach sufficient weight to the one circumstance to feel authorized in admitting a third compound of zinc and antimony. Admitting however the existence of $Sb\,Zn_4$ yet, as exactly the same angle has been observed in crystals containing 55 per cent. as on those containing 43 per cent of zinc, it would be necessary in order to explain the variation in composition by the principle of isomorphous mixtures, to assume the existence of still a third compound isomorphous with $Sb\,Zn_3$, and containing more zinc than $Sb\,Zn_4$, which would increase greatly the improbability of the theory in question. Again, the only probable compound of zinc and antimony containing less zinc than $Sb\,Zn_2$ would be $Sb\,Zn$ ; and it will be remembered that the crystals of $Sb\,Zn_2$ which contained the largest excess of antimony corresponded very nearly to this compound. In like manner the crystals of $Sb\,Zn_2$ which contained the largest excess of zinc corresponded very nearly to $Sb\,Zn_3$. If then the excess of antimony or zinc in the crystals of $Sb\,Zn_2$, arises from a mixture of isomorphous compounds, it must be that $Sb\,Zn_3$, $Sb\,Zn_2$ and $Sb\,Zn$ are isomorphous. That the first two are not isomorphous may be seen by turning back to the description of their crystalline form ; and that there is no crystalline compound $Sb\,Zn$ is sufficiently proved by the fact that the crystals of $Sb\,Zn_2$, which correspond most closely to it, are so very imperfect that they would hardly be recognized as crystals did they not form the lower limit of a series. Several other facts pointing in the same direction might be added, but sufficient it is thought has been said to show that the variations of composition described in this paper can not be explained either by mechanical impurities in the crystals or by the mixture of isomorphous compounds.

In the absence of any known principle of chemical science by which the remarkable variations of composition, that have been demonstrated in this memoir, can be explained, the conclusion is almost forced upon us that zinc and antimony are capable of uniting and producing definite crystalline forms in other proportions than those of their chemical equivalents: in other words, that the law of definite proportions is not so absolute as has been hitherto supposed. The explanation then of the variation of composition which I would offer is: that it is due to an actual perturbation of the law of definite proportions produced by the influence of mass. I suppose for example that in the crystals of $Sb\,Zn_3$, containing 55 per cent. of zinc, the zinc and antimony are united in exactly the same way as in those containing 43 per cent., or in other words, just as if the equivalent of zinc were increased to 52·57, that of antimony remaining the same. In support of this position I would offer two considerations. The first is that if the variation is not caused by mechanical impurities or by the mixture of isomorphous compounds, we can conceive of no other explanation for the phenomenon than the one offered. This of course is merely negative evidence; for although science as yet presents us with no principle for explaining variations of composition other than those which have been discussed, and although we can conceive of none others, it does not follow that others may not exist or may not hereafter be discovered; but, nevertheless, this consideration is important inasmuch as it meets an obvious objection, which would be urged against any new doctrine, which conflicts with a generally received canon of chemical philosophy. The second consideration has the character of demonstration. It is that the curve of variation is evidently generated by a second force counteracting directly the chemical force. This second force, as has been shown, is exerted by the excess of one or the other element present in the menstruum, and it may therefore be appropriately termed the force of mass. While the chemical force tends to make the curve a straight line parallel to the axis of ordinates, the force of mass would reduce it to a straight line making an angle of 45° with the axis; under the influence of both these forces it follows the arc of a circle between the two. Now I urge that the character of this curve proves that the chemical force has been directly influenced by what we have called, the force of mass, in the same way that the irregularities of the orbits of the planets prove that the force of gravitation exerted by the sun has been disturbed in its action by the influence of the other members of the system. As the details in the form of the curve have been fully discussed in the previous part of the memoir, it does not seem to be necessary to dwell upon this argument, and I would therefore without further comment offer the curve as it has been laid down on the plate as the proof of the validity of the explanation of the variation in composition here advanced.

It is worthy of remark that while the curve of variation may be said almost to demonstrate that the law of definite proportions may be disturbed in its action, it also most clearly sustains the integrity of the law itself; for, as may be seen on inspection, the chemical force is sufficiently strong to retain the curve of $SbZn_2$ parallel to the axis of ordinates through a variation in the menstruum of nearly five per cent., and it is only when the excess of antimony present in the alloy exceeds six per cent. that the force which it exerts becomes strong enough to disturb the action of the law. What the nature of the disturbing force is must be for the present a matter of theory. I am inclined to think that it is a phase of the chemical force itself, in the same way that the perturbations in the motions of the planets are a secondary result of the force of gravitation.

Accepting the view of the subject, which has been offered, it will be obvious that the very large extent of the variation in the compounds of zinc and antimony is due to the very weak affinity between these elements. Were the chemical force stronger in proportion to the disturbing force the variation would be lessened; were it weaker, the variation would be increased. This is illustrated in the difference between the curve of $Sb\,Zn_3$ and that of $Sb\,Zn_2$. It is evident from the action of chemical agents on the two compounds, that one equivalent of antimony and two of zinc are united by a stronger force than one equivalent of antimony and three of zinc, and we find that the crystals of $Sb\,Zn_2$ retain the calculated composition under a considerable variation in the composition of the menstruum, while the composition of those of $Sb\,Zn_3$ varies with the slightest increase of the amount of zinc in the alloy.

To what extent this perturbation of the law of definite proportions prevails among chemical compounds it must remain for future investigation to determine. There are however a number of facts which tend to prove that it is very general whenever chemical affinity is weak. Four of these I will cite as being remarkably analogous to the facts under discussion.

1. Rieffel, to whose investigation of the compounds of tin and copper we have already referred, says, after the paragraph quoted in the introduction to this memoir, "Les aiguilles de $CuSn_{24}$ sont plus grosses que celles de $CuSn_{48}$". "*On croit, sans oser l'affirmer, qu'elles sont, par compensation, en nombre moindre, et que des differences analogues ont lieu dans les autres* $CuSn_\varphi$ *à mesure que* $\varphi$ *augmente jusqu' à* $\varphi=\infty$, *ou jusqu' à l'étain pur.*" It will be noticed that the difference between these needles is precisely the same as the difference between the crystals of $Sb\,Zn_3$ containing a small and a large amount of zinc, and I think that no one after reading Rieffel's paper can doubt that the compounds of copper and tin vary in composition like those of zinc and antimony.

2. The mineral Discrasite, a compound of silver and antimony, crystallizes in trimetric prisms, of which $I$ on $I = 119^\circ\,59'$.* The analyses given below are copied from Dana's System of Mineralogy, changing slightly the order.

$Sb\,Ag_3$ = Antimony 28·5 Silver, 71·5=100. $Sb\,Ag_4$ = Antimony 23, Silver 77=100.

| | | | | | | |
|---|---|---|---|---|---|---|
| 1. | Andreasberg (foliated granular), | Antimony | 24·25 | Silver | 75·25=99.5, | *Abich.* |
| 2. | Wolfach (coarse granular), | " | 24 | " | 76=100, | *Klaproth.* |
| 3. | Andreasberg (foliated granular), | " | 23 | " | 77=100, | " |
| 4. | " " " | " | 22 | " | 78=100, | *Vauquelin.* |
| 5. | Wolfach (fine granular), | " | 16 | " | 84=100, | *Klaproth.* |

It needs no comment on these results to show that Discrasite is homœomorphous with $Sb\,Zn_3$, and varies like it in composition.

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* Dana's System of Mineralogy, 4th ed., vol. ii, p. 35.

3. In a paper recently published,* W. Sartorius von Waltershausen gives descriptions and then analyses of a new mineral occurring with Dufrenoysite in the Binnen Valley, Switzerland, in Dolomite. As the analyses do not agree with each other and do not correspond to a simple formula, von Waltershausen regards the compound as consisting of two hypothetical isomorphous compounds $PbS + AsS_3$ and $2PbS + AsS_3$ and calculates the proportions in which these compounds are mixed in the specimens analyzed. He infers that they are isomorphous from their analogy in composition to Zinkenite and Heteromorphite, $PbS + SbS_3$ and $2PbS + SbS_3$ which he regards as isomorphous. Prof. J. D. Dana questions the isomorphism of the last and thinks that the hypothesis that the new compounds are isomorphous requires further evidence.†

4. It is stated by Staedeler‡ that crystals of the compound of grape sugar and common salt can be obtained containing for every equivalent of grape sugar one or two equivalents of chlorid of sodium and also of intermediate composition. He states moreover that "Calloud, who first observed that the grape sugar of honey combined with chlorid of sodium, found that the amount of the latter varied between 8·3 and 25 per cent." Staedeler refers the variation in composition to a mixture of the compound of one with the compound of two equivalents of chorid of sodium which he assumes to be isomorphous. He adds that it may be caused by "enclosed crystals of chlorid of sodium although the eye could not distinguish any heterogeneous constituents."

All the above compounds are examples of weak chemical affinity accompanied by large variations in composition without any change in the general crystalline form. It is not meant to assert that the variations are identical in character with those of $SbZn_3$ and $SbZn_2$, but only that there is a strong probability that this is the case, which in the first two instances amounts almost to a certainty.

If variations in composition of such magnitude are possible when the force of chemical affinity is weak, it is highly probable that some variation may occur when the force is strong, and, whatever view may be taken of the cause of the variation it will now become a matter of importance to ascertain whether many discrepancies in analyses hitherto referred to imperfections in the process, may not be owing to the same cause which influences the composition of the crystals of zinc and antimony. For this purpose, it will be best to make several analyses of the same compound, prepared under circumstances differing as widely as possible, and then to apply to the results "Peirce's Criterion for

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* Poggendorff's Annalen, vol. xciv, p. 115.

† American Journ. of Science, vol. xix, p. 355.

‡ Chemical Gazette, vol. xiii, p. 44.

the rejection of doubtful observations." Such investigations will be greatly simplified by tables prepared by Dr. B. A. Gould* for facilitating the application of this criterion to which I would refer all chemists who are inclined to take up this line of investigation.

I am well aware that in announcing the existence of perturbations of the law of definite proportions I am calling in question one of the most fundamental dogmas of chemical philosophy, and that the new doctrine will have to encounter prejudice on this very ground. This law is so intimately associated in many minds with the atomic theory, that, to such, absolute definiteness seems to be its essential characteristic; nevertheless, I can not but believe that, laying aside the prejudices which the theory begets, it will be seen by all, that the analogies of nature support the doctrine of variation as maintained in this memoir. The phenomena of some of the phenomenal† laws of nature have that definiteness of character which is claimed for those of the chemical law. The planetary orbits are not perfect ellipses. The ratios of the harmony scale are but approximately realized. The arrangement of leaves on the stem is not perfectly regular. Isomorphism is seldom absolute. In all we observe only a tendency towards a maximum effect which is the perfect expression of the law, but which is rarely fully reached. The limits of variation are broader in some instances than in others, but we find no case in which there is absolutely none. This same character which pervades the other phenomenal laws of nature, I claim for the great law of chemistry. The definite proportion I regard as a maximum toward which the chemical force strives, a maximum, from which the deviations in most cases are small, although in others it may be very large; and I maintain that this view of the subject, which the memoir has aimed to establish, is supported by the analogies of nature.

When the dynamical law has been discovered, of which the phenomenal law was merely the outward manifestation, as Kepler's laws were merely the phenomena of the law of universal gravitation, the very variations have been seen to be necessary consequences of the law itself, and if even the dynamical law, which governs chemical phenomena, shall be discovered, it is most probable that the variations from the law of definite proportions will become as much a matter of calculation as the perturbations of Astronomy. In both cases the perturbation is apparently due to the influence of an extraneous mass of matter.

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* Astronomical Journal, vol. iv, p. 81.

† I have used the term phenomenal laws to designate a class of laws of nature which are empirical in their character inasmuch as they are obviously not ultimate, although their deviation has not been discovered, but which are more universal than those to which the term empirical is commonly applied.

The argument from analogy becomes stronger, when we consider the equivalent numbers. I have shown in a former memoir* that these numbers may be connected by a very simple numerical law, but here, as in other cases, we find merely a tendency towards the law, not an absolute agreement with it, the differences between the theoretical and the experimental equivalents being in many cases too great to be covered by errors of observation. The present memoir may throw light upon these discrepancies; for, to say the least, it is possible that the differences may originate in variations of the equivalent itself, and that the theoretical equivalent may be the maximum towards which the chemical force tends. On comparing carefully the different determinations of the chemical equivalents, many facts may be noticed supporting this view; those equivalents for example, which coincide with or very nearly approach whole numbers such as those of oxygen, carbon and sulphur, will be found as a general rule to have been determined by the analysis or synthesis of compounds whose elements are united by a strong force; also when the equivalents have been determined by essentially different processes it will be noticed that they seldom perfectly agree; so that whatever view may be taken of the subject it will now become a matter of the highest importance to ascertain how far, if at all, the determinations of the chemical equivalents have been influenced by similar causes to those which have produced the variations described in this memoir. This influence can only be detected by multiplying the determinations, by as many different processes as possible, and submitting the results to a rigorous mathematical scrutiny.

If the doctrine of this memoir is correct and the chemical equivalents are really liable to variation it will have an important influence on chemical philosophy. The atomic theory as at present interpreted by chemists is irreconcilable with it, and our present ideas in regard to isomorphism must be materially changed. But it must be remembered that the conclusions of the memoir are drawn from the examination of only two compounds, and therefore that it would be premature to dwell on these obvious consequences of the principle until it has been substantiated by further investigations. In conclusion, I would express my obligation to the gentlemen who have assisted me in the labor of the investigation which on account of the large number of analyses has been very great and could not have been concluded so soon had it not been for their great industry and zeal.

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* This Journal, vol. xviii, p. 229.

CURVE EXHIBITING THE VARIATION IN COMPOSITION OF THE CRYSTALS FORMED IN THE ALLOYS OF ZINC AND ANTIMONY.