PHILOSOPHICAL TRANSACTIONS.

VIII. *On Circumstances modifying the Action of Chemical Affinity.*

By J. H. Gladstone, *Ph.D., F.R.S.*

Received February 1,—Read March 8, 1855.

It is among the facts in chemical science which admit of no dispute, that a substance frequently shows a greater tendency to combine with one body than with another. This has usually received the appellation "elective attraction," or "elective affinity." It is also perhaps universally allowed that the manifestations of this elective affinity are greatly influenced by the insolubility, or the volatility of the original substances, or of the resulting compounds. The degree of temperature, the respective masses of the different substances, the presence of other bodies, and many circumstances beside these, are supposed to modify the result.

The attempt has frequently been made to construct tables showing the relative strength of affinity of different substances for some particular body, and Guyton de Morveau even endeavoured to give a numerical expression to them. In treating of this subject the elaborate disquisition of Bergman, 'De Attractionibus Electivis,' must be referred to; in which he illustrates at once the chemical fact, and the meaning of the term, by supposing A to be a substance united to *c*, and that on the addition of *b*, the *c* is excluded, and the union of the latter substance with A is brought about; in which case he says *b* has a stronger elective attraction for A than *c* has*. He, in common with most chemists both of his own and of later times, takes it for granted that if *b* decomposes A*c*, it does so completely. The Swedish chemist gives the results of nearly 2000 reactions in one table, the first column of which exhibits the following substances arranged according to their affinity for sulphuric acid, commencing with what he conceived the most powerful:—baryta, potash, soda, lime, magnesia, am-

---

* The whole passage runs thus:—"Sit A materies, quam aliæ heterogeneæ *a*, *b*, *c*, &c. adpetunt: ponatur ulterius A τῷ *c* unitum ad saturationem (quod per A*c* in sequentibus indicamus), addito *b*, ejusdem ambire unionem cum exclusione του *c*, A dicitur fortius adtrahere *b*, quam *c*, vel etiam *b* gaudere attractione electiva fortiori, quam *c*: tandem A*b*, addito *a*, priora vincula laxet, *b* respuat, et ejus loco *a* eligat, hinc intelligitur *a* τῷ *b* vi attractiva præpollere, et ratione efficaciæ seriem quamdam constituere *a*, *b*, et *c*."

monia, zinc, manganese, iron, lead, tin, cobalt, copper, nickel, bismuth, arsenic, mercury, antimony, silver, gold, platinum, alumina, sesquioxide of iron, water, phlogiston. The suitability of some of the methods employed for arriving at these results has never, as far as I know, been questioned; for instance, that zinc has a stronger affinity for sulphuric acid than manganese, or iron, or lead has, because it will separate any one of these metals from its solution in the said acid. Other methods however are more open to objection, such, for example, as that which led BERGMAN to place baryta at the head of the series, because it took sulphuric acid from every other base. To such deductions as this, drawn from precipitation, it may be objected, that the tendency of the two bodies to combine has arisen more or less from the insolubility of the compound. BERTHOLLET adopted this view; and in his 'Recherches sur les Lois de l'Affinité,' he endeavoured to prove "que les affinités électives n'agissent pas comme des forces absolues par lesquelles une substance seroit déplacée par une autre dans une combinaison; mais que, dans toutes les compositions et les décompositions qui sont dues à l'affinité élective, il se fait un partage de l'objet de la combinaison entre les substances dont l'action est opposée, et que les proportions de ce partage sont déterminées non seulement par l'énergie de l'affinité de ces substances, mais aussi par la quantité avec laquelle elles agissent, de sorte que la quantité peut suppléer à la force de l'affinité pour produire un même degré de saturation*."

These two conflicting views were much discussed at the time when they were propounded; the attention subsequently paid to the laws of stoichiometry has removed much of the difficulty in which the subject was then involved; GAY-LUSSAC has pointed out the erroneous idea of cohesion that obscured the reasoning of BERTHOLLET; and yet the amount of truth contained in either of these opposite opinions remains still an open question.

It is now some years since I first began to reason, and occasionally to experiment upon this subject. Since that time MALAGUTI has published a paper bearing upon it, which will be referred to subsequently; BUNSEN and DEBUS have experimented, and independently arrived at a very remarkable law; and WILLIAMSON has on more than one occasion vindicated the views of BERTHOLLET.

BUNSEN† exploded together carbonic oxide, hydrogen or cyanogen with oxygen, and, after varying his experiments greatly, deduced the following conclusions:— 1. When two or more bodies B, B′, ... are presented in excess to the body A, under the circumstances most favourable to their union, the body A takes from each of them B, B′, ... quantities which always stand to one another in a simple relation; so that for 1, 2, 3, 4 .... atoms of the one compound, there are formed 1, 2, 3, 4 .... atoms of the

---

* BERGMAN even had some perception of the influence of quantity, as when he says,—"Jam ulterius restat explorandum, num omne *d* sufficiente *c* possit unione pristina extrudi. Probe hoc in genere notetur oportet, decomponentis *c* duplo, triplo, immo interdum sextuplo majore opus esse quantitate, quam quæ τῷ A libero saturando sufficit." He failed, however, to see any particular significancy in this fact.

† Ann. Ch. Pharm. lxxxv. 137.

other. 2. If in this manner there is formed one atom of the compound $A+B$, and one atom of the compound $A+B'$, the mass of the body B may be increased in the presence of that of B' up to a certain point, without any change in that atomic proportion: but if a certain limit be passed, the relation of the atoms, which was that of 1 : 1, changes suddenly and becomes 1 : 2, 1 : 3, 2 : 3, and so on. 3. When a body A, acting on an excess of the compound BC, reduces it, so that AB is formed, and C is set at liberty; then if C can, in its turn, reduce the newly-formed compound, the final result is that the reduced part of $B+C$ is in a simple atomic proportion to the unreduced part. 4. The second observation applies also to these reductions. DEBUS* examined the phenomena presented in the precipitation of a mixture of the hydrates of lime and baryta by carbonic acid, and of the hydrochlorates of these earths by carbonate of soda, and arrived at results analogous to those given above.

In each of these cases, however, the first products of the chemical combination have been removed at once from the field of action. In BUNSEN's experiment the carbonic acid and water will not react on one another; in that of DEBUS the carbonates separate immediately in an insoluble condition. It is evidently quite another case when the products themselves of the chemical action remain free to react. A mixture of two salts in solution, which do not produce a precipitate, affords a case where this requisite is fulfilled. Let AB and CD be such salts. According to the one view, when mixed they will either remain without mutual action, or, should the affinities so preponderate, they will become simply AC and BD, the excess of either original salt remaining inactive. According to the other view, A will divide itself in certain proportions between B and D, while C will do the same in the inverse ratio, the said proportions being determined not solely by the differences of energy in the affinities, but also by the differences of the quantities of the bodies. Again, supposing the latter view to be correct, another question will arise—Does the amount of AD or CB produced increase in a gradual manner with the relative increase of AB, or do sudden transitions take place under these circumstances, such as BUNSEN and DEBUS observed in their experiments?

It was to the elucidation of these questions that I applied myself. In the majority of instances it is impossible to ascertain what has taken place when a mixture of the kind alluded to has been made; but the physical properties of salts will sometimes give an indication. Colour seemed to offer the best means of solving the problem; yet even here a difficulty arose from the fact that many bases, such as nickel, give the same coloured solution when combined with different acids, and *vice versâ*. Sesquioxide of iron, however, appeared to promise good results, since many of its salts are intensely coloured, while others are almost colourless. The formation of the sulphocyanide was first submitted to a full investigation; after which other ferric salts were more cursorily examined; and after them a number of other binary compounds in order to extend the range of observation.

---

* Ann. Ch. Pharm. lxxxv. 103; lxxxvi. 156; lxxxvii. 238.

Ferric Sulphocyanide.

If a soluble sulphocyanide be mixed with a ferric salt, a red solution results indicating the formation of the ferric sulphocyanide. Suppose three equivalents of the sulphocyanide be mixed with one equivalent of the metallic salt, we have the exact proportions theoretically necessary for the production of $Fe_2, 3S_2Cy$. The first question to be solved is,—In such a case does the whole of the iron and of the sulphocyanogen combine as ferric sulphocyanide, or does it not? If **Bergman**'s view be correct, the decomposition will be in accordance with the following simple formula (Rd standing for any salt radicle, and M for any metal)—

$$Fe_2Rd_3+3M, S_2Cy=Fe_2, 3S_2Cy+3M\,Rd;$$

and it will not matter what metal is represented by M, or what salt radicle by Rd, provided only that a double decomposition *does* take place. Beside which, the addition of a larger quantity of either one of the original compounds will not increase the colour, for there is but one sesquisulphocyanide of iron, and the whole of the iron, or of the sulphocyanogen (as the case may be), has been already saturated. If, however, **Berthollet**'s view be correct, the decomposition will not be so complete as to form merely $Fe_2, 3S_2Cy$ and 3M Rd, but in addition to these two salts there will be certain portions of the two original salts still remaining as such in the solution. This will become manifest by an amount of colour being obtained which is not equal to what would have been produced had the whole of the iron entered into combination with the sulphocyanogen: and the requirements of the theory will lead us moreover to expect that the amount of ferric sulphocyanide (and consequently the depth of colour) will depend in a great measure on the nature of M or Rd, and will be increased by each addition of either the soluble sulphocyanide or the ferric salt.

The following were the preliminaries for the complete determination of this question:—

Solutions of the ferric chloride, nitrate, sulphate, acetate, and citrate were prepared, each containing an amount of iron equivalent to 0·162 grm. of sesquioxide in every 1000 grain measures of water. The salts were made principally by dissolving pure hydrated ferric oxide in the pure acid; but it was found very difficult to obtain them of a definite constitution. Yet those employed, if not absolutely coinciding with the expression Fe_2Rd_3, came very close to it; and fortunately the general result will be found not to depend upon great precision in the perfectly atomic composition of the iron salts. A solution of pure sulphocyanide of potassium was prepared containing 2·376 grms. of the salt in every 1000 gr. measures, that is to say, twelve equivalents in the same quantity of solution as contained one equivalent of the ferric salts. Solutions of other potash salts, containing the same amount of potassium in 1000 gr. measures, were prepared; as also solutions of known strength of sulphocyanide of barium and of mercury, and of hydrosulphocyanic acid.

In order to compare the depth of colour produced on the admixture of these solutions, it was necessary to have vessels of colourless glass of a uniform character. Ordinary precipitating glasses, holding about five ounces, were found peculiarly fitted for the purpose: being blown, and not moulded, they are very translucent; they are easily obtained devoid of colour; and, although not strictly uniform in size, it was easy to pick out a sufficient number which would furnish every requisite for the experiment. This was tested by dividing a coloured solution into two equal parts, and pouring one-half into one glass, and the other half into another; if the two solutions appeared then of a perfect equality of tint, nothing more could be desired. When two or more coloured solutions were to be compared, the best method was found to be to place the glasses containing them on a stand before the window, across the pane of which was stretched a piece of tissue-paper about 3 inches in depth. The experiments were almost always performed when the sun was shining, but not on the window itself, as that was found to be disadvantageous. By observing the coloured solutions against the evenly illuminated tissue-paper, most exact results could be obtained, especially after a little practice. If the object was to observe the amount of dilution necessary to reduce one coloured solution to the same tint as another, distilled water was added, and thoroughly mixed with it, until equal bulks of the two solutions appeared alike. The amount of water added was of course easily measured in a graduated vessel. My own observation was always checked by that of my assistant, and if we differed I generally adopted his view, since having no idea of what result was to be expected, his judgment was the more impartial. I may also state in this place, that it was found unnecessary to let a freshly mixed solution containing a sulphocyanide stand any length of time, for it assumed instantaneously its proper amount of colour: two mixtures, similarly prepared, were always found to be of precisely the same shade; and everything conspired to give me great and increasing confidence in the validity of testimony drawn from the colour of a solution.

The first object to be determined evidently was, whether on mixing three equivalents of sulphocyanide of potassium with one equivalent of the ferric salt, say the chloride, the full depth of colour possible from the combination of all the sulphocyanogen with all the iron was actually obtained. That this was not the case was seen at once, for on the addition to such a mixture of either more sulphocyanide of potassium, or more chloride of iron, the colour was increased. This showed also the influence of mass, which will be exhibited quantitatively in due course; but before doing so it is necessary to advert to another part of the inquiry, viz.—

The dependence of the amount of the coloured salt on the nature of the other substances present in the solution, but which are not immediately concerned in its formation.—In order to investigate this point, 25 gr. meas. of each of the ferric salts, which it will be remembered contained exactly the same amount of iron, were mixed with 6·25 gr. meas. of the sulphocyanide of potassium solution, that is one equiv. of the former to three of the latter. The five mixtures were equally diluted. At a glance it was evident that a widely different amount of red sulphocyanide of iron had been formed. The solution containing the ferric citrate was still green; that containing the acetate was red, but by no means deep in colour, and of a yellowish tint; while those containing the sulphate, nitrate, or chloride were of an intense red. The following are the relative amounts of dilution required to bring these four last-mentioned solutions to the same tint:—

3 equivs. sulphocyan. potassium+1 equiv. ferric nitrate diluted to 100 parts.
3 equivs. sulphocyan. potassium+1 equiv. ferric chloride diluted to 89·4 parts.
3 equivs. sulphocyan. potassium+1 equiv. ferric sulphate diluted to 65·2 parts.
3 equivs. sulphocyan. potassium+1 equiv. ferric acetate diluted to 20 parts.

The numbers 100, 89·4, 65·2, and 20 therefore represent the relative amounts of the ferric sulphocyanide contained in these several mixtures*.

In reference to the mixture of ferric citrate with sulphocyanide of potassium, the question presents itself,—Does absolutely no interchange take place between them, or does a partial though very minute formation of ferric sulphocyanide occur in accordance both with the law of BERTHOLLET and the analogy of the other cases? The latter conclusion will appear probable from the following observations. Although the yellowish-green tint of the citrate still remains after the addition of three equivalents of the sulphocyanide, six equivalents almost remove it, and a larger quantity renders the solution colourless. No red colour ever appears in a very dilute solution, but this destruction of the green appears to point to the presence of a sufficient amount of the complementary colour to neutralize it; and if sulphocyanide of potassium be added in large excess to a strong solution of citrate of iron, an unmistakeable red ensues.

Similar experiments were tried in which the same ferric salt was employed, but different sulphocyanides. Two portions of nitrate of iron, each representing one equivalent, were mixed, the one with six equivalents of sulphocyanide of barium, the other with a corresponding amount of the potassium salt. A deep red resulted in both instances, but 1000 gr. meas. of the solution containing the potassium compound required the dilution of that containing the barium salt to only 880 gr. meas. to bring it to an equality of colour. The solution of sulphocyanide of mercury produced a scarcely perceptible reddening when added to the ferric nitrate.

These experiments suffice to show, that on mixing together solutions of soluble sulphocyanides and of ferric salts, the amount of sesquisulphocyanide of iron formed depends in a great measure on the nature of the substances previously combined with the sulphocyanogen and with the metallic oxide. The question naturally arises,—Does the converse of this hold good? If a solution of sesquisulphocyanide of iron be mixed with some other salt, not capable of forming a precipitate with it, will that also cause the distribution of the elements into *four* salts, manifesting itself by a diminution of the colour? and if so, will that vary according to the nature of the other salt?

---

* See Note A.

In order to test this, pure sesquisulphocyanide of iron was required; but I found the greatest difficulty in preparing such a salt; and even when obtained in tolerable purity, it was always liable to spontaneous decomposition, giving rise to protoxide of iron and a yellow powder (hydropersulphocyanic acid or pseudo-sulphocyanogen). The nearest approach to a pure salt was made by decomposing sulphocyanide of barium by an equivalent quantity of ferric sulphate, but this was not absolutely free from either protoxide of iron or sulphuric acid. Six equal portions of this were taken: one was kept as a standard; to the other five were added respectively equal portions of the nitrate, hydrochlorate, sulphate, acetate, and citrate of potash. In each case the colour was reduced. Column I. in the annexed Table shows the amount to which the standard had to be diluted before it was brought down to an equality in colour with the different mixtures. Column II. represents a similar experiment, in which a red mixture of one equivalent of sesquichloride iron, and twelve equivalents of sulphocyanide of potassium, was employed instead of the actual ferric sulphocyanide. The two following columns give the results of two experiments selected from a number of very early ones, the testimony of all of which was similar In III. a mixture of ferric sulphate and sulphocyanide of potassium was employed in IV. the same, with a large excess of sulphuric acid.

	I.	II.	III.	IV.
Volume of original solution + salt added ...	70 m.	64 m.	34 m.	60 m.
Mixture containing the nitrate	80	77	41	62
Mixture containing the chloride	90	90	56	68
Mixture containing the sulphate	150	160	124	85
Mixture containing the acetate...............	270	220	164	120
Mixture containing the citrate	trace of red	green		

These experiments might be varied *ad infinitum*, all proving the influence on the resulting colour of the *nature* of a substance mixed with the ferric sulphocyanide. Other organic acids, such as the oxalic and the tartaric, were found to reduce the red very rapidly*. As might be expected also, the diversity of effect is not confined to differences in the *acid* present. The addition of a protosalt of iron has a very great effect in reducing the colour of the ferric sulphocyanide: baryta salts act powerfully; lime salts have so much influence that the experiments here detailed would have been rendered abortive if spring water had been used for dilution, and even the quality of the distilled water employed could be detected by its effect on some of the succeeding experiments. A solution of chloride of mercury (as was observed long ago) very speedily removes the colour.

The colour of a mixture not dependent on the manner in which the constituents were originally arranged.—On more closely examining the above results, it will be seen that whether ferric citrate be mixed with sulphocyanide of potassium, or ferric sulphocyanide with citrate of potash, the resulting liquids contain but the merest trace of

---

* Pelouze has observed the different effects of different acids, Ann. Chim. et Phys. xliv. 216.

the red salt; it appears also that the deepest colour is obtained on mixing either ferric nitrate with sulphocyanide of potassium, or ferric sulphocyanide with nitrate of potash; whilst the mixtures containing compounds of acetic, sulphuric, and hydrochloric acids are intermediate in colour in regular order. Mercury also seems to exert the most powerful affinity for sulphocyanogen in whatever way they are brought together. This suggests the conclusion that the amount of sulphocyanide of iron in a mixture of salts does not depend on the *manner* in which the different substances were at first combined. The experiment above described was incapable of affording a quantitative demonstration of this, as a perfectly pure and definite sulphocyanide of iron was not obtained; but the following arrangement was made to put it to a rigid test. Two solutions were made; the first by mixing together 50 grain measures of ferric nitrate, and 12·5 gr. meas. of sulphate of potash; the second by mixing 50 gr. meas. of ferric sulphate, and 12·5 gr. meas. of nitrate of potash; so that each contained one equiv. of ferric oxide, three equivs. of potash, three equivs. of nitric acid, and three equivs. of sulphuric acid. To each was added 6·25 gr. meas., that is, 1·5 equiv. of sulphocyanide of potassium. The colours resulting in the two cases were so nearly identical, that the first diluted to 1770 gr. meas. just equalled the second diluted to 1820 gr. meas. Another 6·25 gr. meas. of sulphocyanide of potassium were added to each. The two solutions appeared now identical in colour; they certainly did not differ by 1 degree in 80. The amount of sulphocyanide of potassium in each was then doubled: the resulting colours could not be distinguished from each other. It appears, therefore, that it makes no difference whether there be mixed in solution

$$Fe_2O_3,\ 3NO_5+3(KO,SO_3)+3KS_2Cy \quad \text{or} \quad Fe_2O_3,\ 3SO_3+3(KO,NO_5)+3KS_2Cy.$$

The influence of the mass of one of the substances that produce the coloured salt.— The influence of mass has yet to be considered quantitatively. For this purpose two mixtures were prepared, each containing 25 gr. meas. of the ferric nitrate, and 6·25 gr. meas. of the sulphocyanide of potassium solution. They were both diluted so as to occupy 880 gr. meas. The one was kept as a standard of comparison; with the other additional portions of sulphocyanide of potassium were mixed; and as that increased the colour, it was diluted till brought to an equality with the standard solution.

Original solution.	Additional sulphocyanide of potassium.	Dilution required*.	Original solution.	Additional sulphocyanide of potassium.	Dilution required*.
880 gr. m.	6·25 gr. m.	390 gr. m.	880 gr. m.	125 gr. m.	2680 gr. m.
880 gr. m.	13·75 gr. m.	680 gr. m.	880 gr. m.	200 gr. m.	3310 gr. m.
880 gr. m.	20 gr. m.	880 gr. m.	880 gr. m.	275 gr. m.	3690 gr. m.
880 gr. m.	27·5 gr. m.	1070 gr. m.	880 gr. m.	387·5 gr. m.	4200 gr. m.
880 gr. m.	33·75 gr. m.	1250 gr. m.	880 gr. m.	500 gr. m.	4510 gr. m.
880 gr. m.	52·5 gr. m.	1780 gr. m.	880 gr. m.	612·5 gr. m.	4720 gr. m.
880 gr. m.	90 gr. m.	2300 gr. m.	880 gr. m.	775 gr. m.	4990 gr. m.

Beyond this the experiment could not be carried, although evidently no termination of the action of additional sulphocyanide had been arrived at.

---

* This includes the water in which the sulphocyanide of potassium was dissolved.

But the original 880 gr. meas. expressed the amount of ferric sulphocyanide produced by the mixture of one equiv. of ferric nitrate and three equivs. of sulphocyanide of potassium. Every addition also of 6·25 gr. meas. of sulphocyanide of potassium is an addition of three equivalents. Hence the first line of the preceding Table signifies that, considering the amount of the aforesaid ferric sulphocyanide as 880 (or for greater convenience 88), the amount formed when the same *one* equivalent of ferric nitrate is mixed with *six* equivalents of sulphocyanide of potassium is 880+390, that is 1270 (or 127)*. On this principle the foregoing experimental results may be thus tabulated :—

Ferric nitrate.	Sulphocyan. of potassium.	Red salt produced.	Ferric nitrate.	Sulphocyan. of potassium.	Red salt produced.
1 equiv.+	3 equivs.	88	1 equiv.+	63 equivs.	356
1 equiv.+	6 equivs.	127	1 equiv.+	99 equivs.	419
1 equiv.+	9·6 equivs.	156	1 equiv.+	135 equivs.	457
1 equiv.+	12·6 equivs.	176	1 equiv.+	189 equivs.	508
1 equiv.+	16·2 equivs	195	1 equiv.+	243 equivs.	539
1 equiv.+	19·2 equivs.	213	1 equiv.+	297 equivs.	560
1 equiv.+	28·2 equivs.	266	1 equiv.+	375 equivs.	587
1 equiv.+	46·2 equivs.	318			

On comparing these numbers, it will be at once evident that each addition of the sulphocyanide produced relatively a smaller increase of colour. The numbers in fact give the long curve of Plate VII. fig. 1, where the ordinates express the proportionate amount of red salt, and the abscissæ the number of equivalents of the sulphocyanide.

The influence of mass was again tried by means of additional portions of ferric nitrate instead of additional sulphocyanide of potassium. The experiment was conducted in a precisely similar manner to the last. I have not thought it necessary to record the amounts of the salts and the water employed: the following are the results of the observations reduced as before :—

Sulphocyan. of potassium.	Ferric nitrate.	Red salt produced.	Sulphocyan. of potassium.	Ferric nitrate.	Red salt produced.
3 equivs.+	1 equiv.	88	3 equivs.+	5 equivs.	138
3 equivs.+	2 equivs.	110·5	3 equivs.+	6 equivs.	144
3 equivs.+	3 equivs.	122	3 equivs.+	10 equivs.	161
3 equivs.+	4 equivs.	131	3 equivs.+	14 equivs.	174

These numbers also give a curve. It is that designed in Plate VII. fig. 11.

It is not difficult to bring this experiment into uniformity with the preceding so as to form in fact a continuation of it, one equiv. of ferric nitrate being combined with less than three equivs. of sulphocyanide of potassium. For, expressing the number of equivalents of the iron salt by x, and the comparative amount of ferric sulphocyanide by y, the general formula of the terms in the above Table will be, K denoting the potassium and F the iron salt,—

$$3K+xF=y,$$

---

* See Note A.

which may evidently be reduced to a unity of F by dividing by x, thus—

$$F+\frac{3}{x}K=\frac{y}{x}.$$

On this principle the experiment may be thus tabulated:—

Ferric nitrate.	Sulphocyan. of potassium.	Red salt produced.	Ferric nitrate.	Sulphocyan. of potassium.	Red salt produced.
1 equiv.+	3 equivs.	88	1 equiv.+	0·6 equiv.	27·6
1 equiv.+	1·5 equiv.	55·25	1 equiv.+	0·5 equiv.	24
1 equiv.+	1 equiv.	40·66	1 equiv.+	0·3 equiv.	16·1
1 equiv.+	0·75 equiv.	32·75	1 equiv.+	0·21 equiv.	12·43

which numbers are represented by the broken line in Plate VIII. fig. 1.

It need scarcely be explained, that had the whole of the sulphocyanogen present in the above experiment united itself with the iron, the second term would have indicated 44 degrees instead of 55·25, the third 29·33, and so on; and the diagram would have presented a straight line joining 0×0 and 3×88; while no excess of sulphocyanide would cause the line to sink below 88.

In order to confirm, by a more direct experiment, the result just arrived at, two mixtures were made, each consisting of 100 gr. meas. of ferric nitrate, and 2 gr. meas. of sulphocyanide of potassium; that is, one equiv. of the former to 0·24 equiv. of the latter. The experiment was conducted precisely as in the previous cases, additional quantities of the sulphocyanide being mixed with one of the red solutions. The results form the subjoined Table. The comparative amount of red salt produced is given in two columns: in the first 88 is taken as the starting-point (which was the case in the actual experiment), in the second 88 is assumed as the expression of the amount produced when one equiv. of ferric salt is mixed with three of the sulphocyanide, and the numbers are calculated accordingly, so that this column should tally with those of the previous experiments.

Ferric nitrate.	Sulphocyan. of potassium.	Red salt produced.		Ferric nitrate.	Sulphocyan. of potassium.	Red salt produced.	
1 equiv.+	0·24 equiv.	88	19	1 equiv.+	3·57 equivs.	450	97·8
1 equiv.+	0·48 equiv.	138	29·7	1 equiv.+	4·44 equivs.	502	108·2
1 equiv.+	0·78 equiv.	183	39·4	1 equiv.+	5·58 equivs.	552	119
1 equiv.+	1·05 equiv.	226	48·7	1 equiv.+	7·08 equivs.	623	134·3
1 equiv.+	1·31 equiv.	279	60·2	1 equiv.+	8·64 equivs.	683	147·3
1 equiv.+	1·83 equiv.	320	69	1 equiv.+	10·29 equivs.	733	158·1
1 equiv.+	2·22 equivs.	355	76·5	1 equiv.+	11·79 equivs.	778	167·8
1 equiv.+	2·88 equivs.	400	86·3				

These numbers form the long curve projected in Plate VIII. fig. 1. The dotted line is that of the previous experiment (vide above), showing an almost perfect agreement. The broken line seems to follow the more continuous course. Where the sulphocyanide was not in excess, there appears a slight discrepancy between the two experiments.

The regularity of this increase of colour (as exhibited to the eye in the curves) is a proof that no law obtains under the circumstances of the experiment, similar to that observed and enunciated by Bunsen. There is nowhere any sudden increase in the amount of ferric sulphocyanide formed. If the partition of the bases and acids in the mixture really take place at first in atomic proportions, it is evident that, being at full liberty to act and react, the salts arrange themselves according to their respective mass, without reference to their respective atomic weights.

The effect of mass on the formation of ferric sulphocyanide in a mixture of salts, where other substances replaced the nitric acid or the potash, was also tried.

Two solutions were prepared, each containing 50 gr. meas. of the ferric sulphate mixed with 12·5 gr. meas. of sulphocyanide of potassium, and the experiment was conducted as in the former instances. The weakness of the colour produced when a sulphate is present was the reason why the amount of the salts employed was doubled. The following are the results deduced from the observations:—

Ferric sulphate.	Sulphocyan. of potassium.	Red salt produced.	Ferric sulphate.	Sulphocyan. of potassium.	Red salt produced.
1 equiv.+	3 equivs.	88	1 equiv.+	45 equivs.	318
1 equiv.+	6 equivs.	128	1 equiv.+	57 equivs.	355
1 equiv.+	9 equivs.	153	1 equiv.+	69 equivs.	390
1 equiv.+	12 equivs.	177	1 equiv.+	81 equivs.	418
1 equiv.+	15 equivs.	198	1 equiv.+	93 equivs.	440
1 equiv.+	20 equivs.	223	1 equiv.+	105 equivs.	458
1 equiv.+	24 equivs.	241	1 equiv.+	123 equivs.	486
1 equiv.+	30 equivs.	263	1 equiv.+	147 equivs.	513
1 equiv.+	36 equivs.	288	1 equiv.+	195 equivs.	538

An experiment precisely analogous to the preceding was tried with the ferric chloride in the place of the sulphate. The results were:—

Ferric chloride.	Sulphocyan. of potassium.	Red salt produced.	Ferric chloride.	Sulphocyan. of potassium.	Red salt produced.
1 equiv.+	3 equivs.	88	1 equiv.+	65·4 equivs.	338
1 equiv.+	9 equivs.	148	1 equiv.+	83·4 equivs.	370
1 equiv.+	15 equivs.	190	1 equiv.+	107·4 equivs.	400
1 equiv.+	21 equivs.	216	1 equiv.+	131·4 equivs.	428
1 equiv.+	28·8 equivs.	246	1 equiv.+	155·4 equivs.	456
1 equiv.+	41·4 equivs.	286	1 equiv.+	191·4 equivs.	488
1 equiv.+	53·4 equivs.	312	1 equiv.+	239·4 equivs.	528

These two series of numbers give respectively the broken and the dotted lines in Plate VII. fig. 1.

A glance at these curves will show that, although the actual amount of ferric sulphocyanide produced from the same quantity of the sesquinitrate, chloride, or sulphate of iron varies greatly, yet the increase of colour on the addition of more sulphocyanide of potassium maintains a somewhat similar ratio in each case. In Plate VIII. fig. 11 the commencement of the three curves is shown on an enlarged scale, and their close approximation becomes still more evident. The variations that do exist arise, I am disposed to think, mainly from errors in the experiment; and this opinion is founded not only on the observations above detailed, but upon others of a shorter range, which it was not considered necessary to record, especially as the three given were the last of their respective kinds which I made, and on that account, I believe, worthy of the greater reliance. None of the others, I may remark, differed materially from them.

I have in vain endeavoured, by the aid of my friend, Mr. HENRY WATTS, to find an equation which will resolve the curves deduced from the above observations. They do not appear to belong to the second order.

For the purpose of seeing whether the same ratio was maintained where a much smaller proportion of red sulphocyanide was formed, the experiment was repeated with the ferric acetate. The following results were obtained:—

Ferric acetate.	Sulphocyan. of potassium.	Red salt produced.
1 equiv.+	1 equiv.	62·4
1 equiv.+	3 equivs.	88
1 equiv.+	5 equivs.	108
1 equiv.+	7 equivs.	133
1 equiv.+	9 equivs.	187
1 equiv.+	11 equivs.	232
1 equiv.+	13 equivs.	304
1 equiv.+	15 equivs.	352
1 equiv.+	19 equivs.	398

Here we have not only an entirely different ratio, but the curve represented by these numbers (see the line composed of alternate lines and dots in Plate VIII. fig. 11) is of an irregular character. It is evident there is some interfering action; what that is will be seen when the ferric acetate itself is made the subject of experiment.

A similar experiment on the influence of mass was tried with hydrogen in the place of potassium; that is to say, nitrate of iron was mixed with successive portions of a solution of hydrosulphocyanic acid of known strength. The following are the results reduced to the same unit of comparison as in the preceding cases:—

Ferric nitrate.	Hydrosulpho-cyanic acid.	Red salt produced.
1 equiv.+	2 equivs.	66
1 equiv.+	4 equivs.	108
1 equiv.+	6 equivs.	142
1 equiv.+	8 equivs.	168
1 equiv.+	12 equivs.	217
1 equiv.+	16 equivs.	257
1 equiv.+	20 equivs.	288
1 equiv.+	24 equivs.	315
1 equiv.+	30 equivs.	353
1 equiv.+	38 equivs.	400
1 equiv.+	46 equivs.	440

The curve represented by these numbers is the line broken by three dots in Plate VIII. fig. 11. It is as regular as the corresponding one from the ferric nitrate, the continuous line in the same Plate, but the curve is quite different, showing a more rapid ratio according to which the coloured salt is formed when hydrogen is substituted for potassium.

Method of determining the actual amount of the coloured salt in a given mixture.—From the experiments above recorded, it would seem probable that no amount of sulphocyanide of potassium added to a ferric salt will absolutely convert the whole of it into the sesquisulphocyanide of iron. Yet we can easily judge where this result will be very nearly attained. Thus 400 equivalents of the sulphocyanide, added to one of the ferric nitrate, must give a close approximation. A somewhat larger quantity will do the same with the sulphate. Indeed, it was found by experiment that 500 equivalents of the sulphocyanide added to each of the three principal ferric compounds, caused as nearly as possible the same intensity of colour. Such a mixture was made, assumed to be the proper tint for an equivalent of the ferric sulphocyanide, and employed as a standard. Mixtures were then made of three equivalents of sulphocyanide of potassium with one equivalent of the various ferric salts, each occupying 330 gr. meas. The standard red was then diluted till it was equal in colour to these several mixtures. The annexed Table gives the different amounts of dilution required.

1 eq. ferric nitrate+3 eq. sulphocyanide of potassium . .	1700 gr. m.
1 eq. ferric chloride+3 eq. sulphocyanide of potassium . .	1900 gr. m.
1 eq. ferric sulphate+3 eq. sulphocyanide of potassium . .	2650 gr. m.
1 eq. ferric acetate+3 eq. sulphocyanide of potassium . .	7000 gr. m. (about)

This affords us the elements requisite for a calculation of the actual amount of ferric sulphocyanide present in each of these mixtures; and had it been desirable, almost every observation given above might have been thus reckoned. The ratio between the volumes of the diluted standard ferric sulphocyanide, and that of any one of the other red mixtures (330 gr. meas.), gives the ratio between one equivalent and the fractional part existing in the said mixture. The four observations calculated on this principle give the following results:—

1 eq. ferric nitrate+3 eq. sulphocyan. of potas. give 0·1941 eq. ferric sulphocy.
1 eq. ferric chloride+3 eq. sulphocyan. of potas. give 0·1737 eq. ferric sulphocy.
1 eq. ferric sulphate+3 eq. sulphocyan. of potas. give 0·1245 eq. ferric sulphocy.
1 eq. ferric acetate+3 eq. sulphocyan. of potas. give 0·0471 eq. ferric sulphocy. (about)

If this mode of reckoning involve no fallacy, the proportion between these four numbers should be the same as that given near the commencement of this inquiry, where the colours produced on a different occasion by adding three equivalents of sulphocyanide of potassium to one equivalent of the ferric salts, were directly compared. That they do agree almost exactly will be seen from the following Table, where column I. gives the numbers of the former experiment, and column II. those of the last calculation reduced to the same unit of comparison.

	I.	II.
1 equiv. ferric nitrate+3 equivs. sulphocyanide of potassium	100	100
1 equiv. ferric chloride+3 equivs. sulphocyanide of potassium	89·4	89·5
1 equiv. ferric sulphate+3 equivs. sulphocyanide of potassium	65·2	64·2
1 equiv. ferric acetate+3 equivs. sulphocyanide of potassium	20	24·2?

This close agreement proves not only the correctness of the two independent experiments, but also the correctness of this method of reckoning the amount of the coloured salt in any given mixture.

Influence of the mass of a substance present in the solution, but which is not one of the constituents of the coloured salt.—It has already been remarked that the addition of a colourless salt will reduce the colour of a solution of ferric sulphocyanide. The influence of mass in this kind of action remains to be examined.

A mixture was made of ferric sulphate and sulphocyanide of potassium. The red solution that resulted contained of course sulphate of potash. Successive portions of a solution of this salt were added, and the amount of decomposition effected was determined by means similar to those employed in previous experiments.

Sulphate of potash added.	Water added to comparative solution.	Sulphate of potash added.	Water added to comparative solution.
5 measures=	22 measures.	30 measures=	92 measures.
10 measures=	38 measures.	40 measures=	115 measures.
15 measures=	52 measures.	60 measures=	155 measures.
20 measures=	67 measures.		

This action then proceeds in a gradually decreasing ratio. The above results give the curve projected in Plate VII. fig. 3, which, like those formerly examined, does not belong to the second order.

These very diversified experiments have put to a rigid test the truth of BERTHOLLET's view. Whatever were the circumstances under which the reactions were tried, they invariably showed that the results were dependent both upon the nature and upon the quantity of all the substances in solution.

I have purposely investigated, at considerable length, the reactions made evident by the colour of ferric sulphocyanide, both because I desired to prove the matter thoroughly, and because the scientific public will probably require (as indeed I did when I commenced the investigation) a greater amount of testimony, where it depends on the colour of a solution, than if it had depended on substances actually separated and weighed. I now proceed to the examination of reactions made evident by means of other coloured iron salts; but I shall not dwell at any length on these, unless there be some apparent anomaly to call for more particular attention.

Ferric Gallate.

A solution of gallic acid was made of known strength. Equal portions of it were added to equal portions of the different ferric salts.

1 equiv. ferric nitrate with 1 equiv. gallic acid gave 100 parts of black salt.
1 equiv. ferric chloride with 1 equiv. gallic acid gave 88 parts of black salt.
1 equiv. ferric sulphate with 1 equiv. gallic acid gave 70 parts of black salt.
1 equiv. ferric citrate with 1 equiv. gallic acid gave 10? parts of black salt.

The mixture containing the citrate could not be accurately compared on account of its greenish hue. That made from the acetate was of an intense blue.

When single equivalents of nitrate of iron and gallic acid were mixed, a solution resulted in which the gallic acid had to such an extent combined with the sesquioxide of iron, that the addition of several equivalents of either one of the constituent substances caused a scarcely perceptible increase of colour.

The ferric chloride was then tried.

Ferric chloride.	Gallic acid.	Black salt produced.	Ferric chloride.	Gallic acid.	Black salt produced.
1 equiv. +	1 equiv.	88	1 equiv. +	4 equivs.	128
1 equiv. +	2 equivs.	108	1 equiv. +	6 equivs.	133
1 equiv. +	3 equivs.	120			

These numbers are represented by the dotted curve in Plate IX. fig. 1.

The citrate afforded a better opportunity of obtaining a numerical result representing the influence of the mass of one of the constituents. The following are two observations made by means of it. A difficulty was experienced from the greenish hue of the mixture of single equivalents gradually changing to black as fresh acid was added; hence the observations given below do not commence at unity.

Ferric citrate.	Gallic acid.	Black salt produced.	Ferric citrate.	Gallic acid.	Black salt produced.
1 equiv. +	4 equivs.	88	1 equiv. +	12 equivs.	256
1 equiv. +	6 equivs.	133	1 equiv. +	16 equivs.	310
1 equiv. +	8 equivs.	176	1 equiv. +	18·6 equivs.	346
1 equiv. +	10 equivs.	220			

These numbers are represented by the broken line in Plate IX. fig. 1.

Ferric citrate.	Gallic acid.	Black salt produced.	Ferric citrate.	Gallic acid.	Black salt produced.
1 equiv. +	5 equivs.	155	1 equiv. +	13 equivs.	297
1 equiv. +	7 equivs.	200	1 equiv. +	17 equivs.	353
1 equiv. +	9 equivs.	237	1 equiv. +	25 equivs.	445
1 equiv. +	11 equivs.	270	1 equiv. +	33 equivs.	509

This is represented by the continuous line in the same Plate.

Experiments were also tried with gallate of potash in the place of gallic acid.

1 eq. ferric nitrate + 1 eq. gallate of potash gave 100 parts of black salt.
1 eq. ferric chloride + 1 eq. gallate of potash gave 97 parts of black salt.
1 eq. ferric sulphate + 1 eq. gallate of potash gave 68 parts of black salt.
1 eq. ferric citrate + 1 eq. gallate of potash gave a blue solution.
1 eq. ferric acetate + 1 eq. gallate of potash gave a precipitate.

A mixture of single equivalents of gallate of potash and ferric nitrate gave nearly, but apparently not quite the same depth of colour as when an equivalent of gallic acid was mixed with the same iron salt.

Ferric gallate was prepared by dissolving the hydrated sesquioxide of iron in gallic acid. It was divided into two equal parts, to one of which successive portions of hydrochloric acid were added, while the other was diluted after each addition till it had been reduced to the colour of the acid mixture.

Hydrochloric acid added.	Water added to comparative solution.	Hydrochloric acid added.	Water added to comparative solution.
1 measure =	3·4 measures.	3·25 measures =	10·1 measures.
2 measures =	6·6 measures.	4·5 measures =	12·0 measures.

It requires no further experiments to show that the ferric gallate bears the same testimony as the sulphocyanide.

Ferric Meconate.

Similar experiments were made with meconic acid and the iron salts. After mixing these substances it was found necessary to allow the solutions to stand a minute or two before observation, in order that the full colour might be developed.

1 eq. ferric nitrate + 1 eq. meconic acid ($3HO, C_{14} H_4 O_{14}$) gave 100 parts of red salt.
1 eq. ferric chloride + 1 eq. meconic acid ($3HO, C_{14} H_4 O_{14}$) gave 96 parts of red salt.
1 eq. ferric sulphate + 1 eq. meconic acid ($3HO, C_{14} H_4 O_{14}$) gave 72 parts of red salt.
1 eq. ferric citrate + 1 eq. meconic acid ($3HO, C_{14} H_4 O_{14}$) gave 42 parts of red salt.
1 eq. ferric acetate + 1 eq. meconic acid ($3HO, C_{14} H_4 O_{14}$) gave a red precipitate.

The influence of successive additions of meconic acid to a mixture of single equivalents of that substance and ferric nitrate was tried. The results were as follows:—

Ferric nitrate.	Meconic acid.	Red salt produced.	Ferric nitrate.	Meconic acid.	Red salt produced.
1 equiv. +	1 equiv.	88	1 equiv. +	4 equivs.	75
1 equiv. +	2 equivs.	80	1 equiv. +	6 equivs.	73
1 equiv. +	3 equivs.	76	1 equiv. +	8 equivs.	74

Here, instead of finding an increase of colour, as might have been expected by analogy, there is a distinct though small decrease. On examining the action more fully, and by repeated experiments, it was found that the maximum colour was obtained when the ferric nitrate and the meconic acid were mixed in single equivalents (or rather in the proportion of 12 atoms of the former to 11 of the latter); that the addition of more ferric nitrate to such a mixture did not notably increase the colour; that the addition to it of 0·25 equivalent of meconic acid made little change; and that a greater addition caused a decided diminution of the tint.

A mixture of one equivalent of meconic acid with one equivalent of sesquichloride of iron was examined in a similar manner. The addition of meconic acid was found in this case also to diminish the colour. The effect of successive additions of the ferric salt was more particularly tried.

Meconic acid.	Ferric chloride.	Red salt produced.	Meconic acid.	Ferric chloride.	Red salt produced.
1 equiv. +	1 equiv.	88	1 equiv. +	5 equivs.	99
1 equiv. +	1·2 equiv.	96	1 equiv. +	7 equivs.	93
1 equiv. +	1·8 equiv.	108	1 equiv. +	9 equivs.	99
1 equiv. +	2·6 equivs.	118	1 equiv. +	13 equivs.	119
1 equiv. +	3·8 equivs.	106			

These different determinations are exhibited by the continuous line in Plate IX. fig. 2. No regular curve can be described passing through these points; it is evident that there is some action which twice changes the order of the series.

When ferric sulphate and meconic acid are mixed, it requires about seven atoms of the former to five of the latter to produce the greatest intensity of colour. It then just about equals in tint the mixture of five atoms of the ferric nitrate with the same amount of meconic acid, and made up to the same volume.

No amount of ferric citrate added to the above-mentioned amount of meconic acid is capable of bringing the colour up to that of the former mixtures. This is partly, if not wholly, due to the greenish tint of the citrate neutralizing the red of the meconate.

There is then, in the case of the ferric meconate, some action interfering with the proper exhibition of the law of mass, which did not occur with the sulphocyanide or gallate. It seemed a natural supposition that this might arise from the power of meconic acid to form several compounds of different degrees of redness with ferric oxide. With a view to ascertain if meconate of iron itself entered into any such combination with meconic acid, the red salt was prepared by allowing hydrated sesquioxide to stand some hours with meconic acid. The experiment never gave the result anticipated, but this may have arisen from the more acid compound being always formed under such circumstances.

Thinking it would be desirable to repeat these experiments with meconate of potash instead of the acid, that salt was prepared by neutralizing meconic acid with the carbonate of the alkali. Three atoms of the base were found to combine with one of the acid. Single equivalents of this salt and of the various ferric salts were mixed.

1 eq. ferric nitrate $+3KO, C_{14}H_4O_{14}$ gave 100 parts of red salt.
1 eq. ferric chloride $+3KO, C_{14}H_4O_{14}$ gave 73 parts of red salt.
1 eq. ferric sulphate $+3KO, C_{14}H_4O_{14}$ gave 84 parts of red salt.
1 eq. ferric citrate $+3KO, C_{14}H_4O_{14}$ gave a trace of red salt.
1 eq. ferric acetate $+3KO, C_{14}H_4O_{14}$ gave a red precipitate.

These proportions differ considerably from those observed where meconic acid itself was employed.

The effect of successive additions of meconate of potash to the ferric nitrate was also tried.

Ferric nitrate.	Meconate of potash.	Red salt produced.	Ferric nitrate.	Meconate of potash.	Red salt produced.
1 equiv. +	0·33 equiv.	34	1 equiv. +	1 equiv.	88
1 equiv. +	0·5 equiv.	50	1 equiv. +	1·2 equiv.	84
1 equiv. +	0·8 equiv.	74	1 equiv. +	1·5 equiv.	69

Here the greatest intensity of colour evidently occurs when about single equivalents are mixed, the addition of a larger quantity of meconate of potash producing a rapid diminution of the colour.

The same was observed in respect to the ferric chloride. When single equivalents had been mixed, the addition of more ferric salt was not found to make any great difference in colour. This action, however, was examined quantitatively by means of the citrate.

Meconate of potash.	Ferric citrate.	Red salt produced.	Meconate of potash.	Ferric citrate.	Red salt produced.
1 equiv. +	0·8 equiv.	97	1 equiv. +	3·8 equivs.	102
1 equiv. +	1·2 equiv.	80	1 equiv. +	5 equivs.	125
1 equiv. +	1·8 equiv.	69	1 equiv. +	7 equivs.	154
1 equiv. +	2·6 equivs.	74	1 equiv. +	9·2 equivs.	165

These numbers are represented by the broken line in Plate IX. fig. 2.

Imagining that the rapid decrease of colour manifested when meconate of potash was added in excess to the ferric salt, might be due to the formation of some paler double compound, I added the potash salt to a solution of pure meconate. The colour was greatly diminished.

These results show satisfactorily enough that the amount of meconate of iron formed depends upon the nature of the various substances in solution, but their testimony in respect to the mass of these substances is obscured by the formation of these double compounds. Thinking to avoid this by always using the same amount of meconic acid and iron, and yet to exhibit the effect of mass, the following experiments were performed. Pure meconate of iron was treated with acetate of potash; it was quickly reduced to a pale yellow. Oxalate or phosphate of potash had the same effect. A saturated solution of sulphate of potash was tried, and gave these results:—

Sulphate of potash added.	Water added to comparative solution.
5 measures =	12 measures.
12 measures =	30 measures.

A strong solution of sulphate of soda was tried:—

Sulphate of soda added.	Water added to comparative solution.	Sulphate of soda added.	Water added to comparative solution.
5 measures =	16 measures.	40 measures =	58 measures.
10 measures =	26 measures.	60 measures =	80 measures.
20 measures =	36 measures.		

Another solution of meconate of iron was similarly treated with dilute hydrochloric acid :—

Hydrochloric acid added.	Water added to comparative solution.	Hydrochloric acid added.	Water added to comparative solution.
2 measures =	3·6 measures.	7 measures =	15 measures.
3 measures =	5 measures.	9 measures =	20 measures.
5 measures =	10 measures.		

It is evident, that although a reduction of the amount of ferric meconate always takes place, there is some cause interfering with the regularity of the decrease of colour.

The amount of ferric meconate depends therefore upon the nature and upon the quantity of all the substances present at the same time in the solution; but the regularity of the action of mass, which was observed with the sulphocyanide and gallate, is not confirmed in this instance.

Ferric Pyromeconate.

Thinking that the irregularity in the influence of mass might be more or less connected with the tribasic character of meconic acid, it occurred to me that an examination of ferric pyromeconate would be desirable, since pyromeconic acid is monobasic, and yet strikes an intense red with the sesquioxide of iron, and in many other respects resembles the substance from which it is derived. Accordingly, some pyromeconic acid was prepared by submitting meconic acid to dry distillation :—

1 eq. ferric nitrate + 3 eq. pyromeconic acid gave 100 parts of red salt.
1 eq. ferric chloride + 3 eq. pyromeconic acid gave 86 parts of red salt.
1 eq. ferric sulphate + 3 eq. pyromeconic acid gave 39 parts of red salt.
1 eq. ferric citrate + 3 eq. pyromeconic acid gave 27 parts of red salt.
1 eq. ferric acetate + 3 eq. pyromeconic acid gave a red precipitate.

1 eq. ferric nitrate + 3 eq. pyromeconate of potash gave 100 parts of red salt.
1 eq. ferric chloride + 3 eq. pyromeconate of potash gave 74 parts of red salt.
1 eq. ferric sulphate + 3 eq. pyromeconate of potash gave 36 parts of red salt.
1 eq. ferric citrate + 3 eq. pyromeconate of potash gave 26 parts of red salt.
1 eq. ferric acetate + 3 eq. pyromeconate of potash gave a red precipitate.

On trying the influence of mass, it was found that the addition of pyromeconic acid rapidly *diminished* the colour of ferric pyromeconate; and that the colour was the deepest when the base was in large excess.

Thinking that the effect of a colourless salt upon the red pyromeconate might display more clearly the influence of mass, a mixture of ferric chloride and pyromeconic acid was experimented on with a solution of sulphate of potash :—

Sulphate of potash added.	Water added to comparative solution.	Sulphate of potash added.	Water added to comparative solution.
3·7 measures =	12·5 measures.	20 measures =	37·5 measures.
11·2 measures =	27·5 measures.	30 measures =	47·5 measures.

This is exhibited in Plate IX. fig. 3.

The monobasic pyromeconate appears therefore to be similar in its testimony to the tribasic meconate.

Ferric Acetate.

Similar experiments to those already described were made with the acetate of iron. As the red colour of this salt is very slight, as compared with that of the preceding compounds, it necessitated the employment of tolerably strong solutions.

Twelve equivalents of acetate of potash were added to one equivalent of each of the ferric salts, and gave the following proportions:—

1 eq. ferric nitrate + 12 eq. acetate of potash gave 100 parts of red salt.
1 eq. ferric chloride + 12 eq. acetate of potash gave 139 parts of red salt.
1 eq. ferric sulphate + 12 eq. acetate of potash gave 112 parts of red salt.
1 eq. ferric citrate + 12 eq. acetate of potash gave no red salt.

These proportions differ greatly from those which have been previously observed.

The effect of successive additions of acetate of potash was tried:—

Ferric nitrate.	Acetate of potash.	Red salt produced.	Ferric nitrate.	Acetate of potash.	Red salt produced.
1 equiv. +	3 equivs.	88	1 equiv. +	21 equivs.	87
1 equiv. +	6 equivs.	109	1 equiv. +	30 equivs.	64
1 equiv. +	9 equivs.	109	1 equiv. +	39 equivs.	61
1 equiv. +	12 equivs.	102	1 equiv. +	48 equivs.	52
1 equiv. +	15 equivs.	96	1 equiv. +	63 equivs.	46

Plate IX. fig. 4 exhibits these numbers; and here again, as in the case of the meconate, there is something producing a great irregularity of action.

To a mixture of one equivalent of ferric nitrate and three of acetate of potash, successive portions of the iron salt were added. They rendered the mixture much paler, reducing it at last almost to the colour of the nitrate itself.

In order to ascertain whether these changes of colour were due to the formation of double salts containing both iron and potash, three equal portions of the ferric acetate employed in the previous experiments were treated respectively with solutions of acetate of potash, acetic acid, and water. The potash salt caused a slight *increase* of colour, and the pure acid a great *decrease*, as compared with the effect of mere dilution. It is clear that there exist different combinations of acetic acid and sesquioxide of iron; indeed, it has been observed before by others, that a highly coloured solution of ferric acetate will spontaneously deposit red oxide and become almost colourless.

This irregularity of colour accounts for the extraordinary appearance when successive portions of sulphocyanide of potassium were added to the ferric acetate (*vide* Plate VIII. fig. 2); for, it must be remembered, the red colour observed in that experiment was due to the colour of the acetate as well as of the sulphocyanide.

The ferric acetate then confirms BERTHOLLET's view, but, like the meconate, its testimony in respect to the influence of mass is equivocal.

Ferric Ferrocyanide.

The ferric ferrocyanide, though insoluble in pure water, is soluble in the presence of oxalic acid, giving a deep blue. A mixture was made of a known amount of ferrocyanide of potassium with that acid, and it was added to the various ferric salts. The blue from the nitrate, chloride, or sulphate was very intense; the mixture containing the acetate was colourless the first minute, but gradually became blue; while that containing the citrate also deepened in tint on standing. After remaining about two hours, the coloured mixtures were in the following proportions:—

1 eq. ferric nitrate + 3 eq. ferrocyanide of potassium gave 100 parts of blue salt.
1 eq. ferric chloride + 3 eq. ferrocyanide of potassium gave 87 parts of blue salt.
1 eq. ferric sulphate + 3 eq. ferrocyanide of potassium gave 89 parts of blue salt.
1 eq. ferric acetate + 3 eq. ferrocyanide of potassium gave 45 parts of blue salt.
1 eq. ferric citrate + 3 eq. ferrocyanide of potassium gave 60 parts of blue salt.

The effect of mass was also tried. The addition of more ferrocyanide of potassium to a mixture of one equivalent of ferric nitrate and three of the ferrocyanide produced no appreciable increase of colour. With the citrate, however, the following numerical results were obtained:—

Ferric citrate.	Ferrocyanide of potassium.	Blue salt produced.	Ferric citrate.	Ferrocyanide of potassium.	Blue salt produced.
1 equiv. +	3 equivs.	88	1 equiv. +	9 equivs.	113
1 equiv. +	6 equivs.	107	1 equiv. +	15 equivs.	120

These numbers give rise to the curve in Plate IX. fig. 5.

Acetate or citrate of potash added to a mixture of ferric nitrate and ferrocyanide of potassium in oxalic acid, produces no perceptible change at the moment of mixing; but a decrease of colour becomes apparent after a few minutes, and continues, becoming more and more marked for some hours.

The ferrocyanide then bears a similar testimony to the truth of BERTHOLLET's position to what the ferric sulphocyanide and gallate do.

Ferric Comenamate.

Single equivalents of comenamic acid ($C_{12}H_5NO_8+4HO$) were mixed with single equivalents of the different ferric salts. With the nitrate, chloride, and sulphate it gave a most intense purple, with the citrate a wine-red solution, and with the acetate a precipitate.

The three purple solutions were about equally deep in colour; they were unaffected by the addition of any amount of iron salt, but were reddened by the addition of comenamic acid. The mixture containing the citrate was uninfluenced in the character of the tint, and almost so in the depth of it, by the addition of any amount of either the acid or the iron salt. It was quite evident from this, that comenamic acid has a great tendency to combine with sesquioxide of iron in place of water, and that it is capable of forming two distinct compounds. Indeed it was found that one equivalent, or less, of comenamic acid uniformly gave with one equivalent of nitrate of iron a deep bluish-purple compound; and that two equivalents, or more, gave a wine-red compound; whilst any proportion intermediate between one and two equivalents gave an intermediate tint.

Comenamate of potash and of ammonia gave similar results to comenamic acid itself; but the colour produced with the citrate at least was not so deep. The following were the ratios:—

1 eq. ferric citrate + 1 eq. comenamic acid gave . . .	5 parts of red salt.
1 eq. ferric citrate + 1 eq. comenamate of ammonia gave	4 parts of red salt.
1 eq. ferric citrate + 1 eq. comenamate of potash gave .	2·9 parts of red salt.

The addition of citrate of iron to a mixture of single equivalents of it and comenamate of potash caused an increase of colour, but no amount turned the solution purple.

Comenamic acid then is able to overcome the great affinity of citric acid for ferric oxide only so far as to produce the more acid salt. The purple comenamate was reddened instantly by citrate of potash, yet a large addition of that substance did not wholly destroy the colour.

That comenamic acid has not so great an affinity for sesquioxide of iron as to be unaffected by the presence of nitric, hydrochloric or sulphuric acid, was easily demonstrated. The following experiment illustrates the action of such a substance. To a solution consisting of single equivalents of ferric chloride and comenamic acid, successive portions of hydrochloric acid were added. The original mixture was bluish-purple.

Hydrochloric acid added.	Colour of mixture.
3 measures.	Bluish purple, but paler by an amount equiv. to 25 measures of water.
6 measures.	Bluish purple, but paler by an amount equiv. to 40 measures of water.
9 measures.	Bluish purple, but paler by an amount equiv. to 54 measures of water.
15 measures.	Visibly redder, and paler by an amount equiv. to 80? measures of water.
21 measures.	Red purple.
31 measures.	Pink.
55 measures.	Still perceptibly pink.

The affinity then of comenamic acid for sesquioxide of iron, though very great, is influenced both by the nature and by the quantity of other substances present in the same solution.

Ferric Bromide.

Experiments were also made on the ferric bromide. The iron salts were employed without dilution, as the bromide itself is but little redder than the chloride. Three equivalents of hydrobromic acid added to one of ferric nitrate produced a distinct red; added to the ferric citrate they produced little change in the colour. Yet the bromine has evidently a great tendency to combine with the iron; for, though the addition of a larger quantity of hydrobromic acid to the nitrate did perceptibly increase the colour, a maximum effect seemed attained when only about twelve equivalents were added. The addition of twelve equivalents in the case of the citrate produced likewise a red tint similar to that from the nitrate. Bromide of potassium did not redden the ferric citrate. Numerical results could not be obtained on account of the paleness of the colour.

If sesquioxide of iron be dissolved in hydrobromic acid, a very deep red solution is obtained, which is scarcely affected in colour by the addition of any potash salts in any quantity, unless, indeed, they decompose it with the formation of a red precipitate. Strong citric acid even has little effect upon it. It gives an intense blue with ferrocyanide of potassium in oxalic acid. This compound, however, is not a true ferric salt; it is an oxybromide.

The Ferric Salts in general.

Effect of mass of solvent.—In connexion with these experiments on ferric salts, it became a matter of interest to ascertain whether changes in the mass of water itself had any influence on the composition of the salts contained in these coloured solutions.

The only methods which occurred to me of obtaining an answer to this inquiry, were, to ascertain whether dilution caused any greater or less decrease of colour in some substances than in others of the same tint; and whether the decrease of colour by dilution was uniform in the same salt, by whatever mixture it might be produced.

It has frequently been noticed that a red solution of ferric sulphocyanide is reduced by the addition of water more than the simple dilution seemed capable of accounting for, and more than the red meconate is. In examining this matter, it seemed desirable first to ascertain how far it might be the fact. For this purpose two solutions were taken; the one of the purest sesquisulphocyanide of iron I could obtain, the other of pure ferric meconate. They were made up to the same colour and the same volume, and were then equally diluted. It became at once evident that the addition of water produced far greater difference in the colour of the sulphocyanide than in that of the meconate; but the exact proportion could not be determined, as, although the two reds were almost identical in shade at first, the sulphocyanide assumed on dilution a yellowish, and the meconate a pink hue. Numerical results, however, were obtained from the comparison of two mixtures, the one consisting of four equivalents of sulphocyanide of potassium and one of ferric chloride, the other of four equivalents of meconate of potash to one of the chloride of iron. They were made up to the same depth of colour, each occupying 200 grain measures.

200 gr. m. of the sulphocyanide equalled in colour 200 gr. m. of the meconate.
400 gr. m. of the sulphocyanide equalled in colour 730 gr. m. of the meconate.
720 gr. m. of the sulphocyanide equalled in colour 2460 gr. m. of the meconate.
1440 gr. m. of the sulphocyanide equalled in colour 7540 gr. m. of the meconate.

The disparity here is very great, and takes place at an increasing ratio.

It seemed desirable to test, if possible, whether this diversity was due entirely to the sulphocyanide, or whether the meconate might not also be departing from the ratio of decrease in colour which mere dilution would cause. For this purpose five solutions were taken of equal bulk and of the same depth of colour. They consisted respectively of meconate of iron, a mixture of ferric chloride and sulphocyanide of potassium, port wine and water, red ink, and infusion of cochineal. These solutions, though not identical in colour, were sufficiently near for the purpose. On repeated dilution of each with equal amounts of water, they all retained the same colour relatively, except the sulphocyanide, which became yellowish and much lighter.

It may fairly be concluded then, without predicating anything as to the action of water on dry salts, that large quantities of water have no specific action on meconate of iron, but that in some way they affect the sulphocyanide. Is this a mere physical effect upon the particular colour; or does some change take place in the composition of the salt itself*? In order to test whether this action of water was influenced by the presence of other substances, red solutions of equal volume and equal depth of colour were prepared by the following admixtures:—ferric chloride with sulphocyanide of potassium in large excess; sulphocyanide of potassium with ferric chloride in large excess; ferric nitrate with sulphocyanide of potassium; the same salts with the addition of a large quantity of sulphate of potash; sulphocyanide of potassium with ferric acetate; ferrous and ferric sulphocyanide with sulphocyanide of lead; and nearly pure sesquisulphocyanide of iron. On repeated dilution with equal amounts of water these all appeared to retain the same relative colour.

It seems then, as far as this experiment can prove it, that the action of water, whatever it be, is exerted equally upon red sulphocyanide of iron, with whatever other substance it may be mixed. This removes any doubt that might have rested from this cause on some of the original experiments with ferric sulphocyanide: and the fact that those experiments were always comparative, leaves little ground for any possible objection.

An experiment was likewise tried in order to determine whether the presence of

---

* See Note B.

other substances had any influence in the dilution of meconate of iron. Solutions were taken of pure ferric meconate; and of mixtures of ferric chloride with meconic acid; of the same with meconate of potash, both in large excess and otherwise; of ferric nitrate with meconic acid; of the same with meconate of potash; and of ferric citrate with meconic acid. On repeated dilution with equal amounts of water, no notable difference was observed in the relative depths of colour of these several solutions, except in the case of the citrate, which, on standing for some hours after dilution, lost colour considerably. The red also was of a more pure crimson where there was nitric acid.

Pyromeconate of iron prepared by double decomposition was affected in colour by dilution in a similar manner to the meconate. Water, too, seemed to have the same effect on the blue ferrocyanide as on ammoniacal sulphate of copper. In these cases, however, the salts compared were not of precisely the same tint.

Relative strength of affinity.—Having considered the evidence borne by eight coloured and soluble ferric salts as to the truth of certain views of the laws that regulate chemical combination, we have found their testimony on the main points uniform. We may now go further, and by examining the results above given determine the relative degree of affinity exerted by the different acids for sesquioxide of iron as compared with potash. Thus it is evident that citric acid has a much stronger affinity for ferric oxide, or a weaker affinity for potash, than nitric acid has; and again, it is evident that an equivalent amount of ferrocyanide of potassium removes the greater proportion of ferric oxide from citric acid, while sulphocyanide of potassium takes only 0·194 part from the nitrate.

The following is the order of affinity of the different acids experimented with for sesquioxide of iron and an equivalent amount of potash.

Least affinity for sesquioxide of iron as compared with potash

Hydrosulphocyanic acid	1
Nitric acid	4
Hydrochloric acid	5
Sulphuric acid	7
Gallic acid	10 ?
Pyromeconic acid ?	
Meconic acid ?	
Acetic acid	20 ?
Hydrobromic acid	
Comenamic acid	
Citric acid	100
Hydroferrocyanic acid	170 ?

Greatest affinity for sesquioxide of iron as compared with potash.

The numbers in the preceding table are deduced from the experimental data, but they must be considered as only rough approximations to the truth. The notes of interrogation indicate that the means of determination were themselves open to doubt.

Effect of differences of temperature.—The experiments narrated in this paper were all performed at the ordinary temperature. The slight changes that may have taken place in that respect from one day to another were incapable of affecting visibly the coloured solutions. Much greater variations had a perceptible effect, but whether this ever arose from changes in the balance of affinities I am not prepared to say.

I now pass on to consider the testimony borne by other coloured salts, not ferric compounds, in respect to the question at issue.

Gold salts.

The bromide of gold is of an intense scarlet, whilst the chloride is of a yellow colour. Dr. G. Wilson has made use of this difference in examining the question as to whether haloid salts exist as such in solution*; which suggested to me the employment of the same salts for my own purpose. In respect to the relative merits of the two hypotheses about haloid salts, it may be as well to state that I desire to express at present no opinion. If I write *bromide of gold* or *sesquichloride of iron* for the dissolved salts, I do so because that is the ordinary nomenclature.

Pure chloride of gold free from hydrochloric acid was prepared. To a portion of this three equivalents of bromide of potassium were added. The formation of the scarlet terbromide of gold was so complete, that the addition of either of the salts employed caused, singly, too small an increase of colour to be readily appreciated. Is it to be considered, then, that the decomposition in this case has been complete? may it be represented thus—

$$Au\,Cl_3+3K\,Br=Au\,Br_3+3K\,Cl\,?$$

This was more rigidly tested by adding chloride of potassium in large excess to bromide of gold. This latter salt was prepared by dissolving gold leaf in bromine water, evaporating to dryness, and redissolving in water.

Strong chloride of potassium added.	Water added to comparative solution.	Strong chloride of potassium added.	Water added to comparative solution.
5 measures	=30 measures.	35 measures	=105 measures.
10 measures	=48 measures.	50 measures	=135 measures.
20 measures	=70 measures.	75 measures	=180 measures.

Some difficulty was felt in determining the last numbers of this experiment, from the fact that the chloride of potassium had by its great excess converted nearly the whole of the bromide of gold into the yellow chloride, or still paler double chloride.

---

* *Vide* Athenæum, 1839, and the Edinburgh Academic Annual for 1840, p. 187.

The gradual diminution of power of the chloride of potassium added is exhibited by the curve in Plate IX. fig. 6.

It was found that bromide of gold was reduced in colour by very small quantities of hydrochloric acid, or even of the common yellow crystals of the chloride of gold, which are, as is well known, the hydrochlorate of that salt. Bromide of gold, as might have been anticipated, was not affected in colour by admixture with *neutral* chloride of gold.

These gold salts then have afforded a good example of the influence of mass in gradually counterbalancing and overcoming a strong affinity.

Platinum salts.

Neutral bichloride of platinum and different amounts of iodide of potassium were mixed in a series of vessels, diluted to an equality of bulk, and allowed to stand some hours for the colour to develope itself properly—a precaution which in this instance was necessary. The following were the appearances noted:—

Bichloride of platinum.	Iodide of potassium.	Character of mixture.
1 equiv.+	0·5 equiv.	Very pale brown solution.
1 equiv.+	1 equiv.	Reddish brown, and opalescent.
1 equiv.+	2 equivs.	The same, but deeper.
1 equiv.+	3 equivs.	The same; some biniodide of platinum deposited on the glass.
1 equiv.+	4 equivs.	Red; opalescence slight; biniodide of platinum deposited.
1 equiv.+	6 equivs.	Bright red; scarcely any opalescence or deposit.
1 equiv.+	8 equivs.	Brighter red; no opalescence or deposit.
1 equiv.+	10 equivs.	Still brighter red.
1 equiv.+	15 equivs.	Still brighter.

The formation of the insoluble iodide of platinum renders some of these cases less distinct in their testimony than the instances previously considered. The opalescence too was doubtless owing to a minute trace of solid matter. This, however, is perfectly clear, that the two salts, though they have mutually decomposed each other, have not done so in the atomic proportions; not according to the schemes

$$\mathrm{Pt\,Cl_2+2Kl=Pt\,I_2+2KCl}$$

and

$$\mathrm{Pt\,Cl_2+3Kl=Pt\,I_2,\,KI+2KCl.}$$

It has required, in fact, about four equivalents of iodide of potassium to produce the maximum amount of the platinic iodide; and the latter terms of the series exhibit a still increasing amount of the intensely red double iodide of platinum and potassium. It may be expected that the double chloride is one of the salts produced in such a mixture*. Successive additions of a strong solution of chloride of potassium to a mixture of one equivalent of bichloride of platinum with two of iodide of potassium, were found to reduce the colour greatly, making it browner.

---

* See Note C.

Copper salts.

Soluble copper salts are, I believe, all of a blue colour when dissolved in a large amount of water; but a strong solution of the chloride, and of one or two others, is green. It has frequently been observed, that on the addition of strong hydrochloric acid to a concentrated solution of sulphate of copper, a green colour takes the place of blue; and it has been naturally concluded that chloride of copper was then formed. This reaction was likewise investigated.

A solution of sulphate of copper was made, containing 125 grm. of the crystals in 1000 gr. measures of water. Hydrochloric acid was taken, having a specific gravity of 1139 at 58° F., and therefore containing 28 per cent. of real acid. Hence, as may be easily calculated, equal bulks of the hydrochloric acid and sulphate of copper solutions represent eight equivalents of the former to one of the latter. A number of equal portions of the blue salt were mixed with respectively one-eighth, one-quarter, one-half, &c. of their volume of the hydrochloric acid in a series of glass tubes of the same size. The following colours resulted:—

Sulphate of copper.	Hydrochloric acid.	Colour of mixture.
1 equiv.+	1 equiv.	Blue.
1 equiv.+	2 equivs.	Blue with a tinge of green.
1 equiv.+	3 equivs.	Dull green.
1 equiv.+	4 equivs.	Dull green.
1 equiv.+	6 equivs.	Bright green.
1 equiv.+	8 equivs.	Bright green.
1 equiv.+	16 equivs.	Very bright green.

The tint designated as "bright green" is of a very vivid hue, in which yellow seemed to preponderate: it arises from the formation of a hydrochlorate of the chloride of copper.

From this it is evident that single equivalents of sulphate of copper and of hydrochloric acid are not resolved wholly (nor indeed to any great extent) into chloride of copper and sulphuric acid; and that the relative mass of the two substances influences the result.

In order to observe the influence of the mass of water, the following experiments were instituted. Eight portions were taken of a saturated solution of sulphate of copper at 60° F., and were mixed with progressively increasing amounts of the hydrochloric acid solution. The colours produced were noted. They are given in column I. of the subjoined table. Each of the mixtures was then diluted with half its volume of water. The resulting shades are given in column II. Column III. represents the shades when the water was doubled; column IV. when the solutions were of three times their original volume:—

Sulphate of copper solution.	Hydrochloric acid solution.	I.	II.	III.	IV.
50 measures	+10 measures.	Perfectly blue.	Perfectly blue.	As Column II, but all paler and more blue.	Pure blue.
50 measures	+12·5 measures.	Greenish blue.	Blue.		Pure blue.
50 measures	+15 measures.	Distinctly green.	Blue, with trace of green.		Pure blue.
50 measures	+20 measures.	Clear green.	Just a shade greener.		Pure blue.
50 measures	+30 measures.	Bright green.	Dull bluish green.		Pure blue.
50 measures	+40 measures.	Bright green.	Green Scarcely distinguishable.		Blue, with a trace of green.
50 measures	+50 measures.	Brighter green.	Green		Blue, with a trace of green.
50 measures	+70 measures.	Still brighter.	Green		Blue, with a trace of green.

It is not to be inferred that the sulphate of copper was in larger quantity in column IV. than in column I., for water acts according to its mass upon pure chloride of copper, converting it from a green into a blue compound. For some time I imagined that the changes of colour in the preceding mixtures of sulphate of copper and hydrochloric acid did not take place in regular gradation, but that something occurred analogous to what Bunsen discovered in his experiments; yet, after repeated endeavours to fix the apparent points of transition, I arrived at the conclusion that they might arise merely from the great difficulty of comparing greens of different characters.

To seven portions of the standard solution of sulphate of copper, each measuring 50 parts, were added respectively 10, 20, 30, 40, 50, 70, and 100 parts of a saturated solution of chloride of sodium. There resulted a series of tints passing gradually from blue to almost pure green, without any sudden transition.

A strong solution of chloride of zinc added to a solution of sulphate of copper also produced a greenish colour, which increased as more chloride was added.

Knowing the disposition of oxide of lead and acetic acid to combine, it occurred to me that chloride of lead might decompose the acetate of copper very readily. Accordingly, two equal portions of the blue acetate were mixed with equivalent amounts of chloride of lead and chloride of sodium in solution; and it was indeed found that the former caused a greater diminution of the colour than the latter did. In this experiment much water was necessarily employed, but chloride of copper always gives a far paler blue solution than an equivalent amount of the acetate does.

These reactions with copper salts bear additional testimony, therefore, to the truth of the previous views*.

Molybdous salts.

As the molybdous fluoride gives a purple, and the chloride a green solution, these salts offered another means of testing whether complete or partial decomposition ensued on the mixing of binary compounds. Molybdous oxide was dissolved in hydrofluoric acid, and the resulting purple solution was treated with hydrochloric acid. It changed gradually to a greenish blue; and, on adding more hydrochloric acid, to a positive green. Time entered as an appreciable element into this change.

---

* See Note D.

The converse of this experiment was also tried. The molybdous oxide dissolved in hydrochloric acid of a green colour. The addition of hydrofluoric acid to this gave at the first moment a rich purple, which was immediately succeeded by a white precipitate, insoluble in any excess of hydrofluoric acid, but readily soluble in hydrochloric acid with the reproduction of the green.

Manganese salts.

Intermediate between the protoxide of manganese and the non-basic oxides, there exists a brownish-red salifiable compound, of the formula Mn_3O_4. It is described in GMELIN's Handbook under the designation "manganoso-manganic oxide." Its solution in hot phosphoric acid or cold oil of vitriol is red, but it dissolves in other acids with a deep brown colour.

I prepared the sulphate and hydrochlorate of this base, and found that the addition of hydrochloric acid in excess caused a change in the colour of the sulphate from red to reddish brown, and eventually brown; while, on the other hand, the addition of sulphuric or phosphoric acid in excess to a solution of the brown chloride converted it into the red salt. Thus it appears that the oxide in question has no such affinity for either one of these acids, but that it is displaced more or less by the other.

Blue Gallate of Iron.

Gallic acid, when added to iron salts, is apt to strike a deep blue colour, from the formation of a very stable compound of the organic acid with both the basic oxides of iron at once.

A portion of this compound was produced by allowing gallic acid to stand for eighteen hours with the hydrated sesquioxide. The effect of successive portions of a strong solution of sulphate of soda was tried.

Sulphate of soda added.	Water added to comparative solution.	Sulphate of soda added.	Water added to comparative solution.
5 measures=	10 measures.	25 measures=	36 measures.
15 measures=	24 measures.	35 measures=	46 measures.

Another blue solution was prepared by mixing solutions of gallic acid and of green vitriol that had been exposed to the air. The effect of sulphuric acid was tried.

Sulphuric acid added.	Water added to comparative solution.	Sulphuric acid added.	Water added to comparative solution.
1 measure =	9 measures.	10 measures=	63 measures.
2 measures=	18 measures.	14 measures=	105 measures.
4 measures=	34 measures.	16 measures=	136 measures.
6 measures=	46 measures.	18 measures=	174 measures.
8 measures=	55 measures.	20 measures=	204 measures.

These numbers give the singular curve in Plate IX. fig. 7. The mixture is of far too complicated a character to admit of a full understanding of the cause of the remarkable change in ratio.

These two experiments suffice to prove the influence upon the production of this blue gallate, both of the nature and quantity of other substances present in the solution at the same time.

Quinine salts.

In his elaborate paper "On the Change of Refrangibility of Light[*]," Professor STOKES has shown that various acid salts of quinine exhibit that remarkable internal dispersion of light which is now known by the name "fluorescence." He mentions the acid sulphate, phosphate, nitrate, acetate, citrate, tartrate, oxalate, and hydrocyanate, as giving rise to the phenomenon; while quinine dissolved in hydrochloric acid did not present any such appearance. He found, moreover, that the addition of hydrochloric acid, or chloride of sodium, to one of the fluorescent salts destroyed the colour. Hence he concluded, and no doubt correctly, that in these cases muriate of quinine was formed; and to obviate the objection that possibly the non-fluorescent salt in solution might be a sort of double salt, in which the quinine was combined with the hydrochloric and the other acid in atomic proportion, he devised the following elegant experiment. To a strong warm solution of neutral sulphate of quinine, which displays no fluorescence, a very small quantity of hydrochloric acid was added; it produced the blue appearance: more hydrochloric acid was added; the blue was destroyed. This seemed intelligible only on the supposition that the small quantity of acid first added displaced an equivalent amount of sulphuric acid, which, combining with the undecomposed sulphate, formed the acid salt which displays fluorescence to such a remarkable degree; and that the larger quantity of hydrochloric acid decomposed this again, setting free the sulphuric acid, and leaving the quinine in solution as hydrochlorate.

From the manner in which Professor STOKES describes and comments on these experiments, it is evident that he imagined (as most others would have done) that the decomposition was perfect, and that, in the particular experiment just mentioned, every particle of the quinine existed in the solution in the form of hydrochlorate, on account of the stronger affinity of that acid for the base. He states, moreover, that "even sulphuric acid is incapable of developing the blue colour in a solution of quinine in hydrochloric acid." If this be true, it evidently militates against the conclusions that double decomposition does not take place perfectly in solution, unless aided by the insolubility or volatility of one or more of the compounds produced, and that great mass counterbalances weak affinity. Accordingly, I repeated the experiments *quantitatively*, and performed some additional ones[†].

---

[*] Philosophical Transactions, 1852.

[†] Since writing the above, my attention has been drawn to a paragraph in Professor STOKES's second paper (Philosophical Transactions for 1853, p. 394), in which he remarks that the neutral hydrochlorate of quinine is not absolutely non-fluorescent, as first stated, and that the hydrocyanate is like the hydrochlorate.

Solutions of known strength were prepared of neutral sulphate of quinine and of hydrochloric acid. The quinine salt was employed warm, and it exhibited only a trace of fluorescence. The solutions were mixed in definite proportions, and the amount of visible fluorescence was noted.

Sulphate of quinine.	Hydrochloric acid.	Character of fluorescence.
1 equiv.+	0·5 equiv.	A deep blue entering far into the liquid.
1 equiv.+	1 equiv.	A more intense blue, and confined to the edges.
1 equiv.+	1·5 equiv.	Much as the preceding.
1 equiv.+	2 equivs.	Rather fainter blue.
1 equiv.+	3 equivs.	Decreasing.
1 equiv.+	4 equivs.	Still decreasing.
1 equiv.+	6 equivs.	Fainter.
1 equiv.+	8 equivs.	Still fainter.
1 equiv.+	12 equivs.	Very faint.
1 equiv.+	20 equivs.	Just visible.
1 equiv.+	30 equivs.	As above.
1 equiv.+	50 equivs.	Invisible except under the most favourable circumstances.

It will be seen at once, that the double decomposition between the sulphate of quinine and the hydrochloric acid was not perfect. Had it been so, the first line of the experiment would have been represented by the formula—

$$2(C_{44}H_{28}N_2O_4, HO, SO_3)+HCl=C_{44}H_{28}N_2O_4, HCl+C_{44}H_{28}N_2O_4, 2(HO, SO_3),$$

and the largest possible amount of fluorescence would have been obtained: while the second line would have been according to the formula—

$$C_{44}H_{28}N_2O_4, HO, SO_3+HCl=C_{44}H_{28}N_2O_4, HCl+HO, SO_3,$$

and there would have been no fluorescence visible with this or any higher proportion of hydrochloric acid. But instead of single equivalents of sulphate of quinine and hydrochloric acid giving a non-fluorescent mixture, the blueness was only then attaining its maximum. After the addition of 1·5 equivalent, more hydrochloric acid caused a gradual diminution of the amount of bisulphate of quinine; and although the presence of undecomposed bisulphate was only observed as far as fifty equivalents of acid added, yet it was doubtless only the imperfection of vision that prevented the experiment being carried further.

If this be the true method of interpreting the observed phenomena, and I imagine there can be no reasonable doubt that it is so, it shows that instead of hydrochloric acid having such an overwhelming tendency to combine with quinine, it is scarcely so strong in its affinity for that base as sulphuric acid is. Chloride of sodium was found to have even less power of decreasing the blue colour than an equivalent amount of the acid has.

There is a slight source of error in the experiment just detailed, arising from the constant dilution of the liquid by the addition of the hydrochloric acid solution. This dilution, however, was very trifling, since strong acid was employed with a view to obviate it as far as possible. It will be evident that it cannot affect the general conclusion; or rather, that if this source of error had not existed, the general conclusion would have been somewhat more strikingly brought out.

The influence of mass is very apparent in the experiment just described, but in order to observe it in the opposite direction, a considerable quantity of sulphuric acid was added to liquids where one equivalent of sulphate of quinine had been mixed with sufficient hydrochloric acid or chloride of sodium to render the fluorescence just invisible. The blue instantly became apparent in each case.

In order to examine this matter still more closely, some neutral hydrochlorate of quinine was prepared by dissolving the organic alkali in the acid, and evaporating gently to dryness. Its solution diluted showed a mere trace of blue, which was removed on the addition of a drop or two of free hydrochloric acid. Portions of this solution were mixed with all the acids mentioned by STOKES as giving fluorescent compounds with quinine. The addition of sulphuric, nitric, phosphoric, acetic or oxalic acid, instantly reproduced the blue colour in a very marked manner. Citric or tartaric acid added in very large excess also produced the blue, but it was faint. I failed to detect any change on the addition of a considerable amount of hydrocyanic acid.

Similarly, a solution of sulphate of soda in considerable excess was added to an acid solution of hydrochlorate of quinine. A very perceptible amount of blue made its appearance. This also is in perfect consonance with what might theoretically be expected, and indicates that not only had the commixture of sulphate of soda converted a portion of the hydrochlorate of quinine into sulphate, but the free hydrochloric acid had decomposed some of the sulphate of soda, liberating sulphuric acid, which had combined with the quinine salt to form the bisulphate. That a mixture of neutral sulphate of quinine with sulphate of soda does not give the blue tint, unless some free acid be added, was verified by previous experiment.

STOKES also states that iodide or bromide of potassium added to a solution of bisulphate of quinine, or the acid phosphate, destroys the fluorescence. On examining these reactions, I found that these haloid salts behaved precisely as the chloride did. A solution containing bisulphate of quinine had its blue tint gradually diminished by the addition of either the bromide or the iodide of potassium; and, where the fluorescence had been thus rendered barely if at all perceptible, it was restored on the addition of dilute sulphuric acid.

This accumulation of evidence all goes to prove that quinine follows the same laws as the substances previously considered.

Other fluorescent Organic Substances.

The beautiful fluorescence exhibited by a solution of the inner bark of the horse-chestnut is due to the presence of the vegeto-alkali æsculine in a free state. When combined with hydrochloric acid it loses its peculiar optical properties, which are restored again on the addition of ammonia*. It occurred to me, that though ammonia is capable of displacing æsculine from its combinations, æsculine ought to be able to decompose more or less the ammoniacal salt. Accordingly a large quantity of hydrochlorate of ammonia was added to a solution of horse-chestnut bark, and it certainly did reduce the blue more than a similar amount of water did in a comparative experiment, while the addition of ammonia to the mixture revived it.

Tincture of stramonium owes its fluorescent properties also to a free alkaloid, and the blue is similarly destroyed by hydrochloric acid, and restored by ammonia. The action of hydrochlorate of ammonia was tried in like manner with this tincture, and it seemed to give the same results as in the case of horse-chestnut bark; but they were more decided.

Compound Ethers.

Compound ethers may be regarded as organic salts in which certain compound radicles take the place of metals, and it is to be expected that they will follow the same general laws as the binary compounds that have been previously examined. Their insolubility in water precludes the use of aqueous solutions of the substances intended to act upon them, but alcohol affords a convenient medium for the reaction, and when this is employed, results are obtained which are perfectly analogous to those already described in the case of different metallic salts. The following experiment may be taken as an example. A large excess of oxalic acid was dissolved in alcohol along with acetic ether, warmed, and allowed to stand for some hours. The mixture was then submitted to gentle distillation, and there passed over acetic ether mixed with alcohol and with oxalic ether, as was proved by decomposing the distillate by hydrate of potash, and testing the resulting salt in the usual manner, when both acids were detected in considerable quantity. The oxalic acid had therefore displaced a certain amount of acetic acid; but though it existed in such large excess that it began to crystallize out, it had not displaced the whole.

I have not examined these reactions among compound ethers to any considerable extent, nor have I performed any of the experiments quantitatively, because I was aware that Professor WILLIAMSON (to whom this branch of the subject more particularly belongs) has been pursuing some investigations in the same direction.

GENERAL INFERENCES FROM THE PRECEDING EXPERIMENTS.

The concurrent testimony of the diversified experiments here detailed is in favour of the view, that when two binary compounds are mixed in solution, there ensues a partition of the two electro-positive between the two electro-negative elements, according to certain proportions regulated both by the difference of strength in the affinities, and by the relative quantities of the different bodies. The reverse of this does indeed appear at first sight to be the case in certain instances, as for instance,

---

* See the paper of STOKES already referred to.

when equivalent portions of sulphocyanide of potassium and ferric citrate are mixed, or of chloride of gold and bromide of potassium. But it makes all the difference whether there be a small, though inappreciable, quantity of the other salt formed at the same time, or whether the decomposition be absolute; and a consideration of the whole series of experiments, and of the influence of mass in these very instances, will leave, I think, a strong conviction on the mind that such cases differ from the others only in degree, and that if we possessed the means of observing minuter differences of colour we should find evidence of traces of the original salts still remaining. But of this each reader will form his independent judgment. Among those instances where evidently four salts were produced by the mixture of two, the following substances took part in the reaction:—

Iron (in both basic conditions), gold, platinum, mercury, copper, zinc, lead, molybdenum, manganese, baryta, lime, potash, soda, ammonia, hydrogen, ethyl, quinine, æsculine (?), base in stramonium (?).

Sulphuric, nitric, phosphoric, hydrochloric, hydrobromic, hydriodic, hydrofluoric, hydrosulphocyanic, hydroferrocyanic, acetic, oxalic, citric, tartaric, gallic, meconic, pyromeconic, and comenamic acids.

It must be borne in mind, that when, in studying the mutual action of AB and CD, we have determined the laws according to which A and D combine, we have equally ascertained them in reference to C and B; that is to say, to take a particular instance, if we find, on mixing ferric nitrate and sulphocyanide of potassium, that ferric sulphocyanide is formed in certain proportions according to the relative force of affinity and mass, we have determined this also in respect to the nitric acid and the potash. We know indeed that for every portion of ferric sulphocyanide produced, an exactly equivalent portion of nitrate of potash must be formed, so that in fact the long curve in Plate VII. fig. 1 will express the amount of nitrate of potash in the experiment equally well with that which it primarily represents. And not only this, but in any such mixture, where we know the original amounts of the two salts, and the amount of any one of the four into which they are resolved, we have the data for determining the amounts of the other three likewise. This may be illustrated from the reaction just alluded to. Suppose (which is about the truth) that one equivalent of ferric nitrate mixed with three equivalents of sulphocyanide of potassium produce one-fifth of an equivalent of ferric sulphocyanide, the following is the only formula which can represent the reaction. The amounts are multiplied by five to avoid decimals:

$$5(Fe_2O_3, 3NO_5)+15KS_2Cy=Fe_2, 3S_2Cy+12KS_2Cy+4(Fe_2O_3, 3NO_5)+3(KO, NO_5),$$

or more simply,

$$5AB+5CD=AD+4AB+4CD+CB.$$

Of course this method of reckoning is inapplicable where polybasic acids are concerned.

TESTIMONY FROM OTHER CHEMICAL PHENOMENA.

There are many chemical phenomena, beside those connected with colour, which bear testimony respecting the question whether two salts in solution resolve themselves into four.

The testimony of precipitation.—The idea that when double decomposition occurs, the acids and bases make a perfect exchange, arose doubtless from what is constantly observed when a precipitate ensues. In that case A combines wholly with D, and C with B. Yet this will be the inevitable result under the one theory as well as under the other. A mixture of single equivalents of nitrate of baryta and sulphate of potash may be taken as an illustration. Here, as has frequently been shown, if Berthollet's views be correct, at the first moment of mixing a portion of the baryta combines with sulphuric acid, but that compound being insoluble is instantly put out of the field of action, and the resulting mixture really consists of nitrate of baryta, nitrate of potash, and sulphate of potash, which of course gives rise to a redistribution of the bases and acids, and a further production of insoluble sulphate of baryta, and so on, till the amount of nitrate of baryta remaining is infinitesimally small; while at the same time the whole of the potash must necessarily combine with the whole of the nitric acid. It is scarcely necessary to observe, that this division and precipitation will take place continuously until complete; and that it may be so rapid as to elude our notice*. The fact then that precipitation when it occurs is complete, decides nothing as to the relative merits of the two theories of elective affinity. Yet there is an important difference to be noted. On Bergman's supposition, it can hardly be imagined but that cases will sometimes occur, where A has so strong an affinity for B, or C so powerful an attraction for D, that on mixing AB and CD, no interchange will take place, although AD may be an insoluble body. On Berthollet's supposition, the insoluble compound will always be wholly precipitated whenever by the interchange of acids and bases such a compound can be formed, even though it be against the preponderating direction of the affinities. Now this can be put at once to the test of experience: and what is the testimony of the thousands of double decompositions which chemists are in the habit of meeting with? Graham† says, "It is a general law to which there is no exception, that two soluble salts cannot be mixed without the occurrence of decomposition, if one of the products that may be formed is an insoluble salt." Gmelin‡, even when arguing against Berthollet's views, admits the same fact, adding, "the only case which

---

* Yet it is easily conceivable that when the affinity for each other of the two substances that produce the insoluble compound is very weak, the action may last some time, and become evident to our senses. Is not this actually the case when sulphate of lime in solution is added to nitrate of strontia, or carbonate of soda to chloride of calcium, or an alkaline carbonate to tartrate of yttria, or oxalate of ammonia to sulphate of magnesia, &c.?

† Elements of Chemistry.

‡ Handbook of Chemistry.

appears to present an exception is that observed by TH. SCHERER*, and this requires further examination." The case referred to is this:—if yttria and sesquioxide of iron be dissolved together in hydrochloric acid, nearly neutralized with ammonia, then treated with acetate of ammonia, and afterwards with a few drops of oxalate of ammonia, no precipitate falls, but the solution is to a considerable extent decolorized; but the addition of more oxalate of ammonia determines the formation of a white curdy precipitate. "It follows from this," says SCHERER, "that hydrochlorate and acetate of yttria can be present in a solution simultaneously with ferric oxalate, without a precipitate resulting; which indeed is very remarkable, and appears to contradict the fundamental laws of chemistry, since oxalic acid gives an insoluble precipitate with yttria." I examined this reaction. The white precipitate which was first formed on dropping oxalate of ammonia into the aforesaid mixture, was certainly dissipated on further mixing; yet on repeated trials I always found that after standing some hours a small quantity of oxalate of yttria was deposited, while the solution still retained the red colour of acetate of iron. However, there is no doubt that ferric oxalate, and the yttria salt, did coexist in the same solution; yet in order to prove that no oxalate of yttria was present along with them, it would be necessary to show that the salt in question is not dissolved by any of the other substances present in the mixture. Now it is by no means insoluble in either hydrochloric or acetic acid, and the conditions of the experiment require the acid to be in slight excess. Thus the experiment merely shows that oxalic acid left free to act on the ferric and the yttria salts, will combine with the former oxide in very much the larger proportion; a fact which is in perfect consonance with the strong affinity between that acid and the sesquioxide of iron, which has been previously remarked in this paper.

It is then a law, without a single known exception, that if AB, CD, EF, &c., by any interchange of bases and acids can possibly produce an insoluble substance, that insoluble compound does actually make its appearance. This seems to me almost conclusive evidence that the interchange always takes place originally to a greater or less degree; for I cannot believe, with one chemist of high repute, that "when bodies are brought into intimate contact, all the forces which exist, not only in themselves, but in all their possible compounds, are called into action at the same time," unless indeed it be by these compounds being actually formed.

The following experiments may illustrate more fully the truth of the explanation of complete precipitation which has been given above.

I. Strong solutions of sulphocyanide of potassium and ferric sulphate were mixed. The resulting intensely red liquid was divided into two equal parts. The one portion was largely diluted with water; and to the other portion a little strong alcohol was added, which caused the precipitation of sulphate of potash while ferric sulphocyanide was dissolved. The alcohol was poured off, and diluted with water

---

* POGGENDORFF, li. 470.

till of the same volume as the first portion. It was far deeper in colour, indicating evidently that the insolubility of sulphate of potash in alcohol had removed it out of the sphere of action, and had caused a much larger proportion of ferric sulphocyanide to be formed than would otherwise have been produced. Only a small quantity of alcohol was employed, and it was mixed with a large amount of water in order to obviate as much as possible the objection that the same amount of ferric sulphocyanide might appear darker in alcoholic than in aqueous solution, which is indeed the fact.

II. Another red solution was prepared by mixing sulphocyanide of potassium and ferric sulphate, and it was divided into two equal portions. To one of these hydrochloric acid was added, which of course reduced the colour somewhat. To each was then added an equal portion of neutral phosphate of soda. The acid solution remained red, though paler than before; the neutral solution became colourless, and turbid from the formation of a flocculent precipitate of ferric phosphate. That the insolubility of this salt in the neutral solution was the cause of the complete combination of the oxide of iron with the phosphoric acid, was further elucidated by adding phosphoric acid to the colourless mixture, which restored a faint red tint to the solution, doubtless because it had set free some of the sulphuric acid, which, redissolving the ferric phosphate, allowed of the formation of a small amount of the red sulphocyanide.

III. A mixture of three parts of ferric citrate, and four of ferrocyanide of potassium was prepared, and divided into two equal parts. To the one there was added a few drops of hydrochloric acid, to the other a few drops of oxalic acid. In the one case, the ferric ferrocyanide, being insoluble in hydrochloric acid, was precipitated, leaving no trace of iron in the solution; in the other case there was a blue solution, but the whole of the iron was not in the condition of ferric ferrocyanide, for the addition of more prussiate of potash caused it to become bluer. That this was due, not to the affinity of the oxalic acid for the ferric oxide, but to that of the citric acid, will be evident from the fact ascertained by the previous experiments on the ferrocyanide, that this result would not have been obtained had the nitrate been employed.

IV. It is well known that if hydrosulphuric acid gas be passed through a solution of arsenious acid in water containing a mineral acid a perfect separation of the yellow sulphuret takes place, but if there be no free acid the *solution* remains yellow. The question suggested itself—Is the whole of the arsenious and hydrosulphuric acids converted in the latter case into sulphide of arsenic and water? In order to ascertain this, a stream of sulphuretted hydrogen was passed through a solution of arsenious acid in water till it was saturated, then it was allowed to stand awhile for the excess of sulphuretted hydrogen to be dissipated, and hydrochloric acid was added. The yellow sulphide was of course precipitated, but on repeated trials I always found more or less arsenious acid still remaining in the solution.

The testimony of volatilization.—The argument that has been employed in the case of precipitation will apply *mutatis mutandis* with equal force in the case of volatilization. I am not acquainted with any exceptional instance.

The testimony of crystallization.—It will sometimes happen that certain quantities of AB and CD are mixed in an amount of water which is insufficient to keep in perfect solution AD, should the whole of A combine with the whole of D, although the salt itself is a soluble one*. In such a case, if BERGMAN's view be correct, either no AD will form, however concentrated the solution, or, should double decomposition ensue, it will form to the fullest extent possible, and may be expected to crystallize out at once with something like the rapidity with which precipitation usually takes place. If, however, BERTHOLLET's theory be a true expression of the fact, a certain amount of AD will always be formed, but it may remain dissolved in the liquid, although if the whole of A had entered into combination with D it must have separated: yet on concentration AD will make its appearance; and should this, or anything else, determine the formation of crystals, or should they ensue on the primary mixing, the crystallizable salt is *pro tanto* put out of the field of action, and a redistribution of the acids and bases will take place with further crystallization, until an equilibrium is obtained. Now the latter of these deductions describes what actually does take place, but there are several circumstances attending crystallization from a mixture of salts which are not readily explained, and which I have as yet but imperfectly investigated.

The testimony of diffusion.—Professor GRAHAM has shown† that binary compounds vary greatly in the rates at which they diffuse through water. Let it be supposed that AB and CD are mixed in one of his diffusion-cells, and that the compounds of A diffuse more rapidly than those of C. If no decomposition take place upon mixing, the amounts of A and B in the diffusate will be in equivalent proportions; and so will likewise the smaller amounts of C and D. If a complete interchange of acids and bases take place, the amount of A in the diffusate will exactly correspond with that of D, and in a similar manner C with B. If, however, A and C divide themselves between B and D, as the four compounds will be unequally diffusive, it will be very improbable that the amount of either A or C in the diffusate should happen just to correspond with the amount of either B or D. There is nothing in Professor GRAHAM's published researches that will indicate which of these is the case, nor have I made any experiments on the subject; but I entertain little doubt that the latter result would be arrived at were the matter to be investigated.

Yet diffusion will never serve as a means of determining numerically the strength of the affinities in a mixture; for, supposing the four compounds are actually produced, the more diffusive one will speedily pass away from the field of action, which

---

* Few if any salts are absolutely insoluble in water, but this will not affect the reasoning in a previous section, for the action of insolubility in a case of crystallization produces the same consequences as in a case of amorphous precipitation.

† Philosophical Transactions, Part I. 1850.

will necessitate a fresh distribution, and so on. Thus a state of things will ensue analogous to what is observed where one of the salts is so sparingly soluble as to separate by crystallization; great diffusibility will compensate for weak affinity; and the mutual attraction of the two components of the more diffusible salt will always be exaggerated.

The testimony of MALAGUTI'S *experiments.*—MALAGUTI* examined the present question by taking two salts, both of which were soluble in water, but only one of which was soluble in alcohol, mixing them in equivalent proportions in water, and then pouring the aqueous solution into a large quantity of alcohol. Some of the resulting salts were precipitated, others remained in solution; and the proportion in which one acid divided itself between the two bases was thence ascertained. This afforded him the data for determining what he denominates "coefficients of decomposition," a large number of which are tabulated; yet he attached no importance to the absolute value of these coefficients on account of the objection that, if there be really four salts in the aqueous solution, their proportions may change when they are thrown into alcohol. However, on considering these experiments, three important results may be arrived at:—1st, that two salts on being mixed resolve themselves into four; 2nd, that this partition takes place in a definite manner; 3rd, that the proportions of the resulting salts are independent of the manner in which the different elements were originally combined†.

The testimony of substances acted on by one of the compounds liberated in a mixture of salts.—It is to be expected that if two binary compounds be mixed, the formation of a new compound, though it remain in solution, may often be ascertained by certain chemical powers which it is capable of exerting. Instances of this are not wanting. Thus gold, as every one knows, is not attacked by hydrochloric or nitric acid singly, but is dissolved by a combination of the two; neutral potash salts of course have no action upon it; and yet gold dissolves readily in a mixture of either nitrate of potash and hydrochloric acid, or of chloride of potassium and nitric acid; whence it appears to me the conclusion may be fairly drawn, that in both mixtures the potash relinquishes a portion of the acid with which it was originally combined, or (which is the same thing) that it divides itself between the two.

Such experiments as this have no quantitative value, since the liberated substance immediately enters into a new combination, which must give rise to a fresh distribution of the different elements, and so on until no more of the active substance can be produced. A mere solvent action of the liberated body would be preferable to an action where positive chemical combination or decomposition takes place; but such cases scarcely exist. Among the actions which appear to answer this requirement most fully, is when a salt insoluble in water is dissolved in an acid, as for instance,

---

* "Exposition de quelques faits relatifs à l'action réciproque des sels solubles," Ann. de Chim. et de Phys. 3. t xxxvii. p. 198.

† See Note E.

ferric phosphate in hydrochloric acid; yet even here a partial decomposition in all probability ensues. The only instructive numerical results which I have obtained were by mixing a saturated solution of oxalate of lime in hydrochloric acid with various proportions of acetate of potash or soda. The hydrochloric acid combining with the alkali caused a deposition of oxalate of lime, since that salt is not soluble in the acetic acid that was liberated at the same time. The following were the results, every separate term of which was of necessity a separate experiment, though conducted at the same time and under similar circumstances.

Acetate of soda series.		Acetate of potash series.	
Salt added.	Oxalate of lime deposited.	Salt added.	Oxalate of lime deposited.
3 measures.	0·075 grm.	20 measures.	0·359 grm.
6 measures.	0·10 grm.	40 measures.	0·345 grm.
9 measures.	0·11 grm.	80 measures.	0·410 grm.
12 measures.	0·13·5 grm.	120 measures.	0·445 grm.
18 measures.	0·14·5 grm.	160 measures.	0·503 grm.
30 measures.	0·11 grm.	240 measures.	0·564 grm.
45 measures.	0·14·5 grm.		
90 measures.	0·19 grm.		

Notwithstanding certain irregularities in these series of numbers, it is sufficiently evident in both instances that the amount of oxalate deposited increased with the amount of acetate added, though not in direct ratio. In the series of experiments with the potash salt each portion of the original hydrochloric acid solution contained 0·730 grm. of oxalate of lime, therefore even in the last term of the series, where 240 measures of acetate were added, there still remained 0·166 grm. in solution. Plate IX. fig. 8. exhibits these results.

Supposed exceptions and limitations.—With this mass of evidence, and that of a very diversified character, the question arises,—Are we justified in concluding that the principles, which are so general, are *universal* in their application? Are there no exceptions? Is there no limitation?

As to exceptions, in the whole range of my experiments upon this subject, I have never met with a single instance of two substances having so strong an affinity for one another, that they combined to the exclusion of other bodies of like kind and present in the same solution, even if in large excess*. Sometimes this rests not on demonstrative but upon moral evidence, as for instance when sulphocyanide of potassium and dissolved ferric ferrocyanide are mixed, where unquestionably the amount of ferric sulphocyanide produced must be quite inappreciable, yet that some is produced may be safely inferred I think from the fact, that sulphocyanide of potassium does give a red with the ferric acetate, and acetate of potash is capable of decomposing the ferric ferrocyanide to a well-marked extent.

---

* Oxybromide of iron certainly appeared to resist even citric acid; but then it is not a binary compound. Anomalous results too were sometimes obtained on examining the solubility of such substances as phosphate of iron in mixtures of salts and acids, but the phenomena were always of an obscure character.

During the controversy that ensued after the publication of **Berthollet**'s treatise, many reactions were brought forward to prove the falsity of his views. Most of these were directed against certain positions of the French philosopher which were certainly untenable, while others were founded on a misapprehension of the question at issue. Those which appear the most formidable against the conclusions arrived at in this paper are, that boracic acid, or carbonic acid, or hydrosulphuric acid, are incapable of decomposing in the least degree sulphate of potash, or any analogous salt; and that chloride of sodium is not affected at all by iodine. The proof of these statements rests in each instance upon the testimony of blue litmus paper. In the first case the vegetable colour is not reddened; which is supposed to prove that no sulphuric acid has been liberated; yet if any had been set free there must have been formed at the same instant an equivalent amount of borate, or carbonate, or hydrosulphate of potash, each of which has an alkaline reaction, and would have restored the blue, or rather prevented the litmus from reddening. So in the case of the common salt and iodine (where by the way only one base is concerned), the chlorine, supposing it liberated, would not have bleached the litmus, but would have combined at the moment of its separation with some of the iodine present to form the terchloride of iodine which has a neutral reaction. That very little decomposition does take place in these instances I have no doubt, but that there is actually none is not proved.

There is however one difficulty not so easily overcome. Water is a binary compound, and it might be expected that on mixing a hydrated acid and base, or on dissolving in water a salt, such as nitrate of potash, or nitrate of ammonia, a certain amount of both the acid and the base would remain in combination merely with water. That it is not so, is proved by the fact that solutions of the salts just named do not give up any portion of their volatile base or acid, even on boiling. Has a limit to the action of the general law been here arrived at? Is water an exception standing by itself? Or is there not an assumption in supposing that water is not an integral part of the constitution of every salt when in a state of aqueous solution? To these queries I do not feel myself in a position as yet to make a reply.

Conclusions.

The general conclusions arrived at in this paper may be summed up as follows:—

I. Where two or more binary compounds are mixed under such circumstances that all the resulting bodies are free to act and react, each electro-positive element arranges itself in combination with each electro-negative element in certain constant proportions.

II. These proportions are independent of the manner in which the different elements were originally combined.

III. These proportions are not merely the resultant of the various strengths of affinity of the several substances for one another, but are dependent also on the mass of each of the substances in the mixture.

IV. An alteration in the mass of any one of the binary compounds present alters the amount of every one of the other binary compounds, and that in a regularly progressive ratio; sudden transitions only occurring where a substance is present which is capable of combining with another in more than one proportion.

V. This equilibrium of affinities arranges itself in most cases in an inappreciably short space of time, but in certain instances the elements do not attain their final state of combination for hours, or even days.

VI. The phenomena that present themselves where precipitation, volatilization, crystallization, and perhaps other actions occur, are of an opposite character, simply because one of the substances is thus removed from the field of action, and the equilibrium that was first established is thus destroyed.

VII. There is consequently a fundamental error in all attempts to determine the relative strength of affinity by precipitation; in all methods of quantitative analysis founded on the colour of a solution in which colourless salts are also present; and in all conclusions as to what compounds exist in a solution drawn from such empirical rules as that "the strongest base combines with the strongest acid."

NOTES ADDED AFTER THE PAPER HAD BEEN READ.

Note A.

That two or more solutions of the same salt in the same solvent and of equal depth of colour are of the same strength, requires no proof. Hence I apprehend no objection can be raised against the conclusion, that the gross amounts of salt dissolved in the different solutions are directly proportional to their volume. But it may be objected, that though this is true of the solutions when diluted to an equality of colour, it is not necessarily true of the solutions before they were diluted, for the solvent may exercise some chemical action on the coloured salt, absolutely increasing or diminishing its quantity. Should such be the case, it appears to me actually the most correct plan of proceeding to reckon the result when the solutions of the coloured salt are of equal strength, that is to say, when the solvent is in each case in the same proportion to the dissolved salt; for the disturbing influence of the solvent is thus practically got rid of, by its reduction to an equality in all the solutions compared.

There is however a more serious objection, namely, that the solvent may act differently on the coloured salt, according to the nature or the quantity of the colourless salts present at the same time in the several solutions, or that these salts may act differently according to the amount of solvent with which they are conjoined. That this may be the case to a slight extent is very possible, but the experiment recorded on page 202, shows that it was too inconsiderable to be appreciated in the cases there submitted to examination. As this is an important matter, I have repeated the experiment in a great variety of ways, and have satisfied my mind that the amount of error arising from this cause must be quite insignificant—at any rate as far as the ferric sulphocyanide is concerned. The slight differences that do occur are rather in the character than in the intensity of the colour.

NOTE B.

Acting upon a suggestion of Professor STOKES, I examined more fully whether this apparent diminution of colour on dilution might possibly be due to some peculiarity in the manner in which this salt in different states of dilution absorbs certain rays and transmits others, and whether it exhibited the same depth of colour when the amount of dilution was compensated for by the thickness of the stratum through which the light passed. In two flat-bottomed beaker glasses were placed two portions of the same solution of ferric sulphocyanide, and beneath them at the distance of a few inches was laid a sheet of white paper. The solutions appeared of the same depth of colour, as I looked down through them. On adding water to one of these and still looking down through the whole liquid, it appeared far lighter in colour, and on the addition of much water it assumed the yellowish tint. Meconate of iron, on the contrary, when looked through in the same manner, presented the same depth of colour, whatever amount of water was added to it.

The ferric sulphocyanide appears then to be really acted on by water, in a manner somewhat analogous perhaps to that in which chloride of copper and several similar salts are.

NOTE C.

An experiment was subsequently made by adding different proportions of iodide of potassium to a solution of the double chloride of platinum and potassium, in hopes of obtaining a result undisturbed by the separation of any solid matter. Such however was not the case. On mixing single equivalents a precipitate instantly resulted; and a deposit was gradually formed when the iodide of potassium was added in proportions of 2, 3, 4, or 5 equivalents to one of the double chloride. These solutions, as also those containing a larger amount of iodide, were intensely red. It was evident that the decomposition was far more complicated than

$$PtCl_2, KCl+2KI=PtI_2+3KCl \text{ and } PtCl_2, KCl+3KI=PtI_2, KI+3KCl.$$

NOTE D.

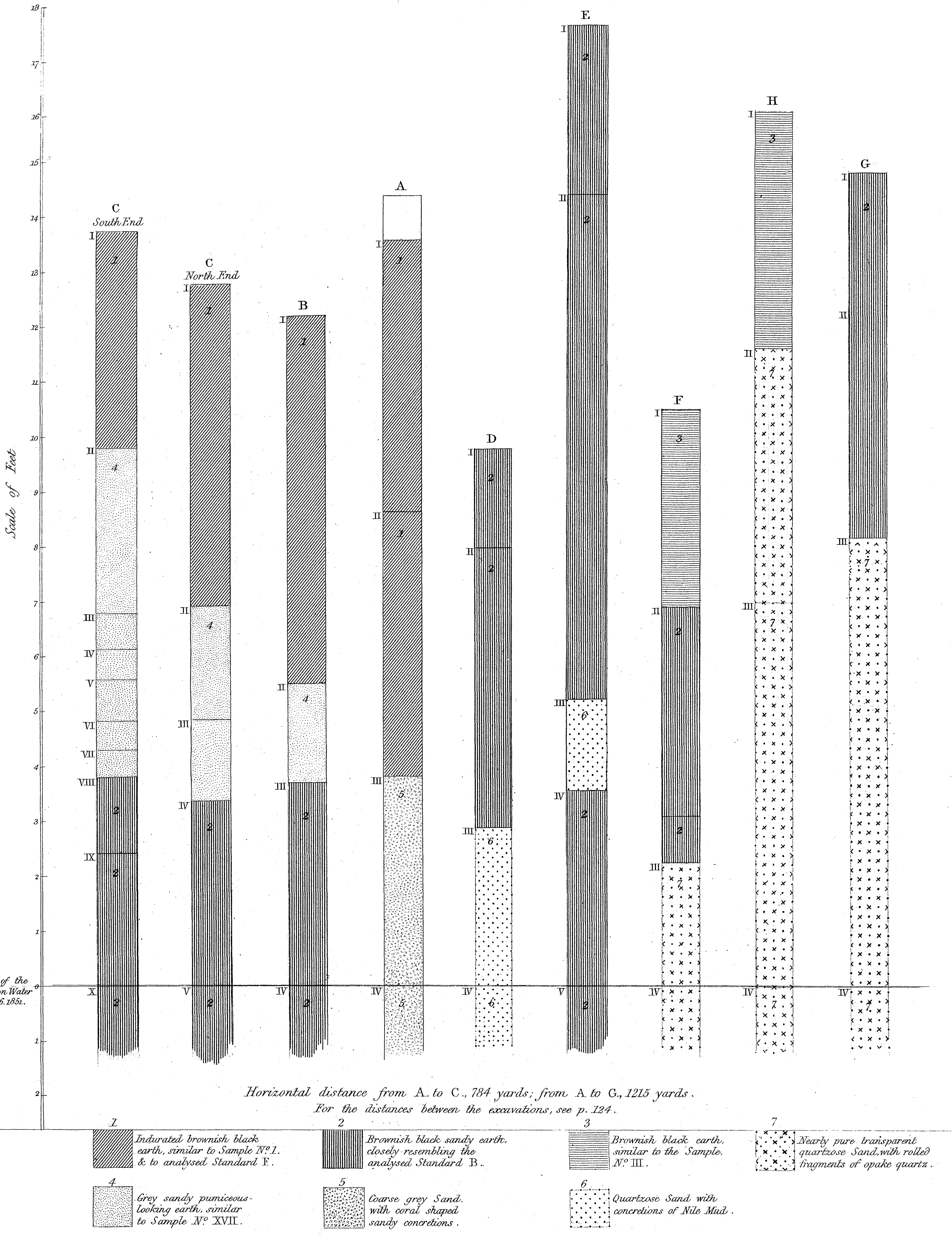
Changes in the state of combination of an element may be rendered visible by a change in the intensity of a colour, even where no change in its character occurs. Thus oxide of copper dissolved in acetic acid gives a much more intense blue than when the same amount is dissolved in sulphuric acid. This fact was taken advantage of in the following experiment, which affords additional evidence of the truth of my main deduction. Sulphuric acid was added to a solution of acetate of copper; it reduced the colour greatly. The experiment was reversed, acetic acid being added to a solution of sulphate of copper; it deepened the colour, but considerable excess of the acid was required to make a very evident difference.

Note E.

After my paper had been sent to the Royal Society, I observed the notice of M. Margueritte's "Recherches sur les affinités chimiques" in the Comptes Rendus, xxxviii. 304. He too has examined Berthollet's views, but by means of some ingenious experiments totally different from those which suggested themselves to me. His results are in perfect harmony with my conclusions, and are just such as might have been deduced from the proposition of Berthollet which is quoted near the commencement of my paper. He finds, for instance, that on dissolving chloride of sodium in a saturated solution of chlorate of potash, it will take up more chlorate of potash; which he naturally considers to be due to the formation of the more soluble chlorate of soda together with chloride of potassium. Again, chloride of ammonium is precipitated from its saturated solution by a very small quantity of nitrate of ammonia, but this does not take place when chlorate of potash has been mixed with it. He has obtained many analogous results. The conclusion he arrives at is, "Lorsque par le mélange de deux sels qui ont satisfaits à la loi d'insolubilité, il peut se former un sel plus soluble que le moins soluble d'entre eux, l'action de l'eau en détermine toujours la formation dans certaines limites." It will be seen that this conclusion is a particular case comprehended in my more general one. With some of his deductions, however, I cannot agree. He appears to have misunderstood Berthollet, perhaps because that chemist himself is not always consistent. He speaks also of an actual "affinity of the solvent," and of the "force of solubility," and the "force of insolubility," as though they were two efficient physical forces.

On repeating some of M. Margueritte's experiments quantitatively, I have obtained interesting results; but they are not described now, as I have not yet seen his more extended memoir.

Vertical Sections of the Excavations at Heliopolis from the surface of the ground at the mouth of each Pit, to the level of the filtration water, shewing the variety in the soils passed through at the same levels.



Horizontal distance from A. to C., 784 yards; from A. to G., 1215 yards.

For the distances between the excavations, see p. 124.

J. Basire sc.

Phil. Trans. MDCCCLV. Plate. VII.

Ferric Sulphocyanide.

Fig. I.

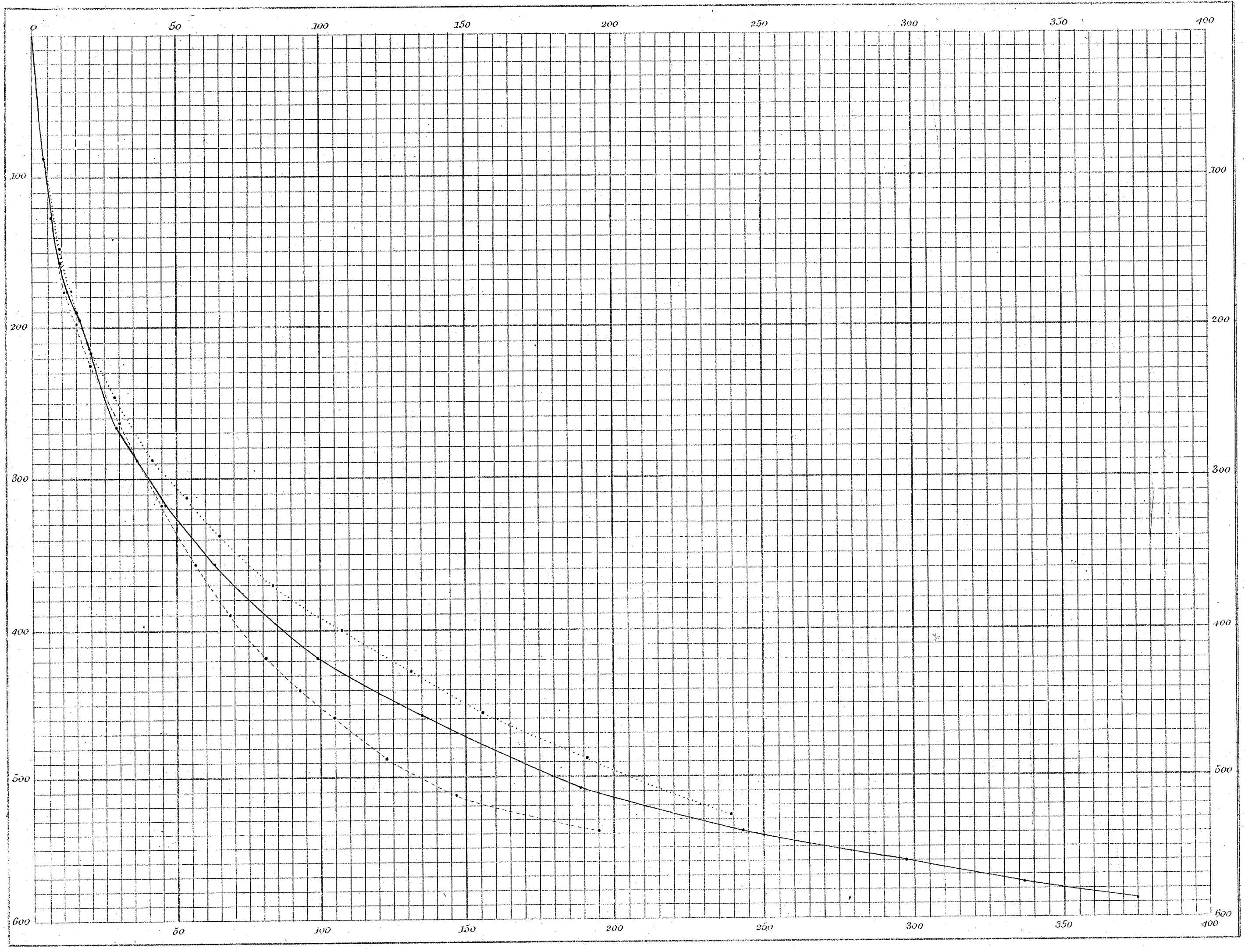
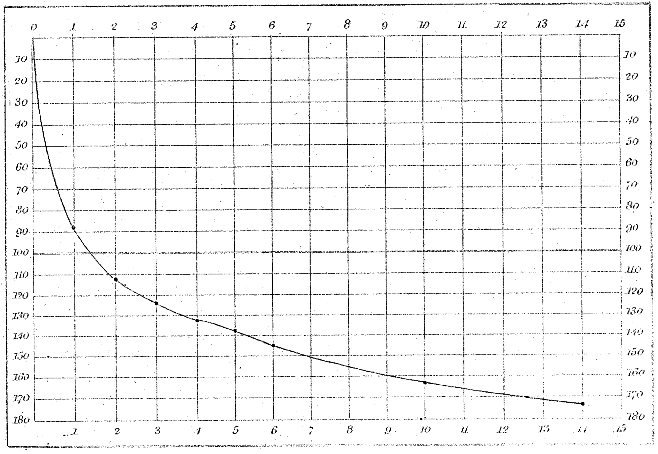


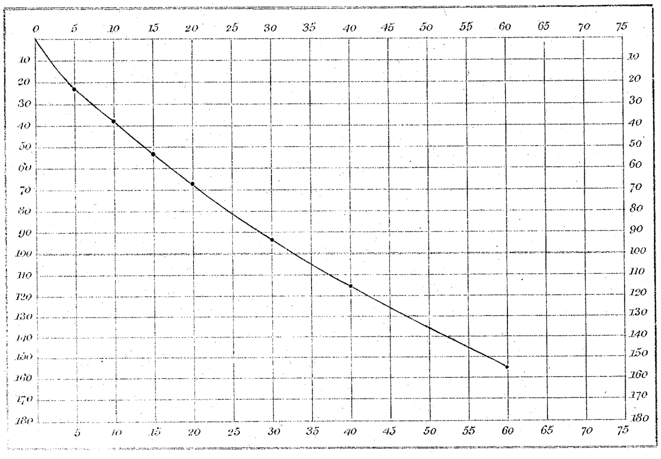
Fig. II.

Ferric Sulphocyanide.



Ferric Sulphocyanide.

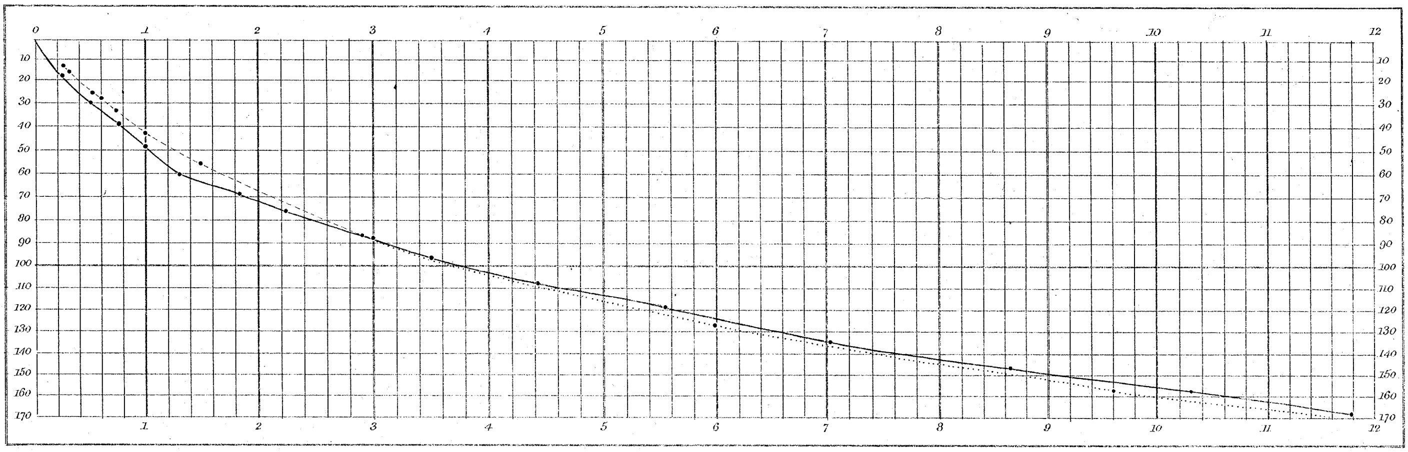
Fig. III.



J. Basire. sc.

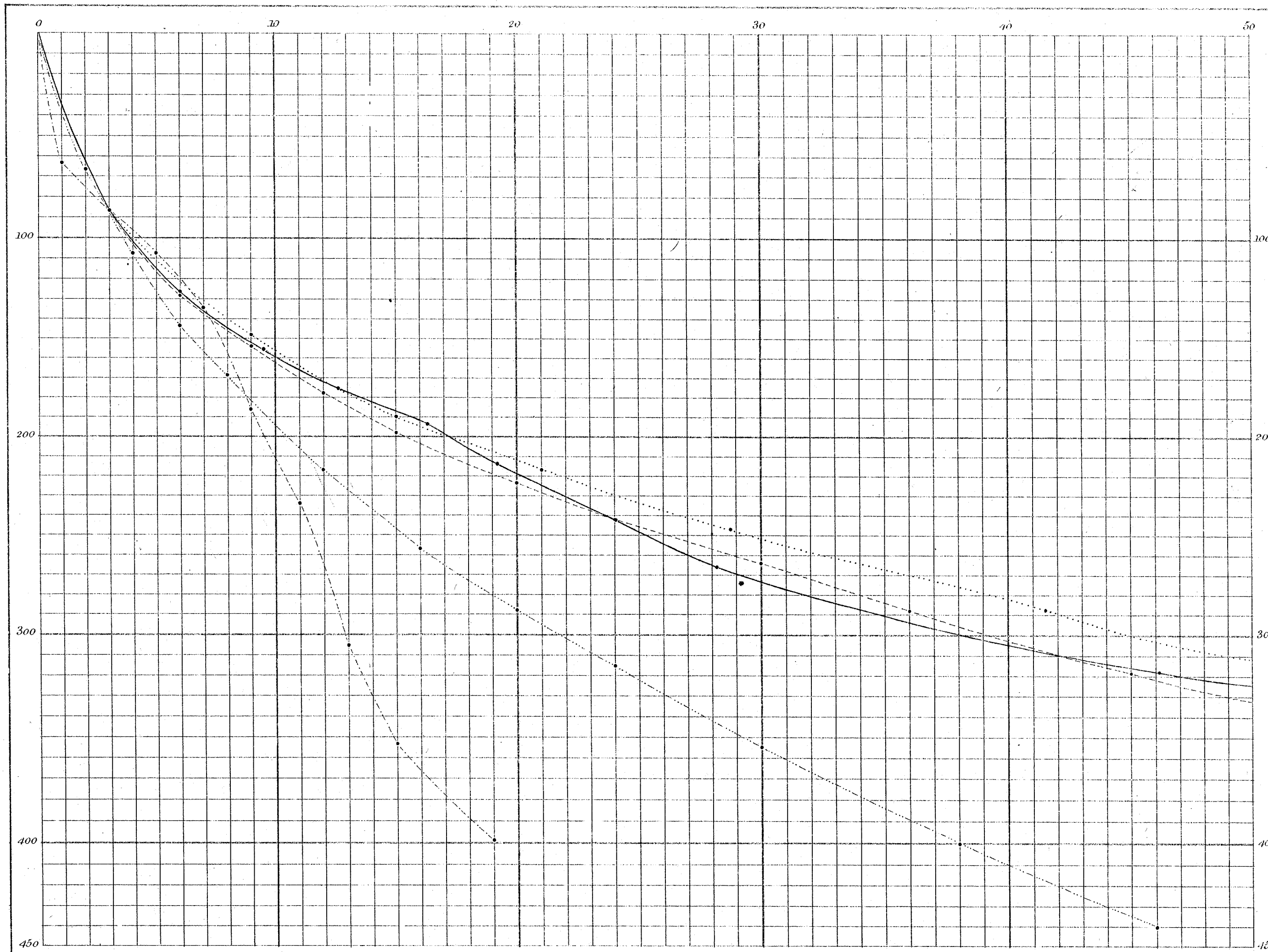
Ferric Sulphocyanide.

Fig. I.



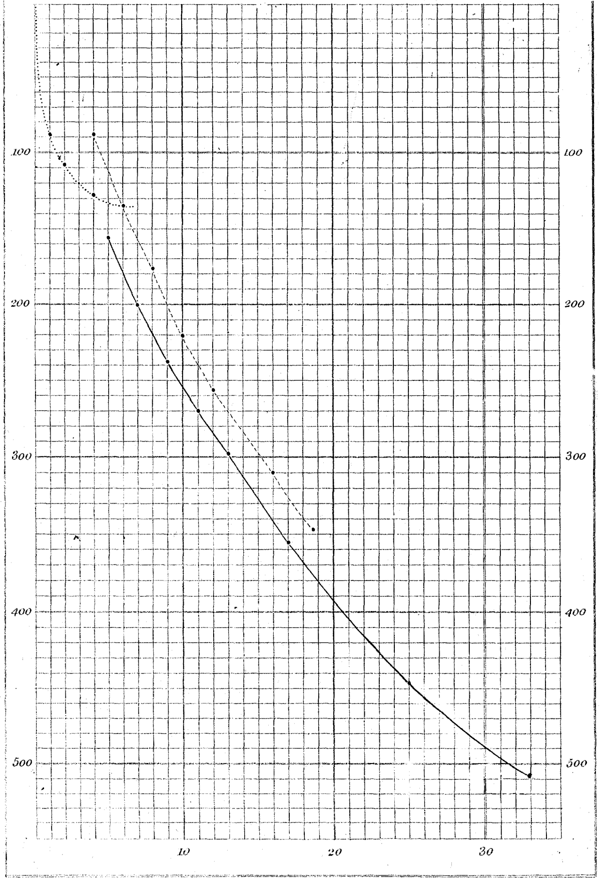
Ferric Sulphocyanide.

Fig. II.

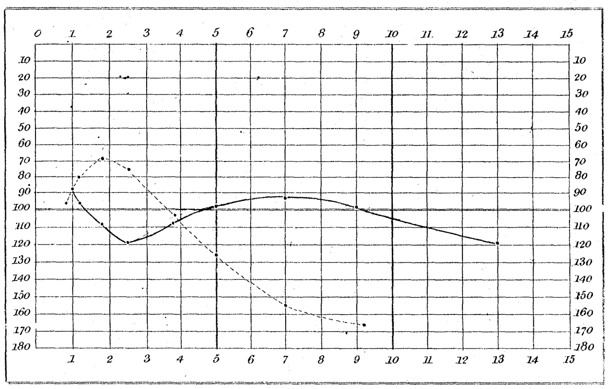


J. Basire. sc

Fig. I. *Ferric Gallate.*



Ferric Meconate. Fig. II.



Ferric Acetate. Fig. IV.

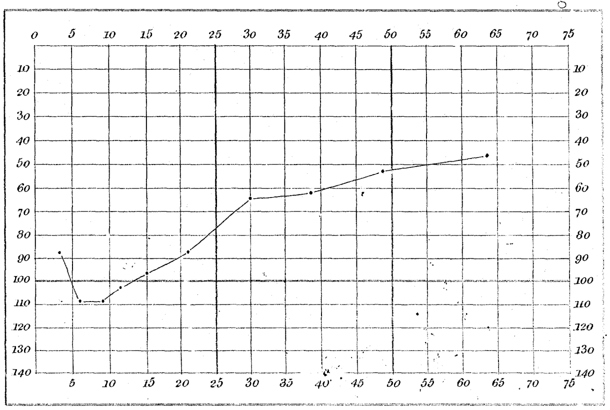
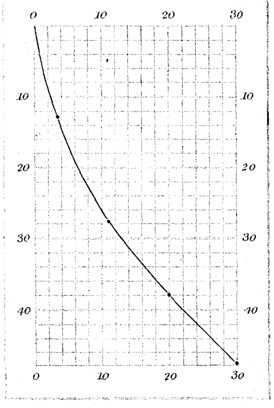
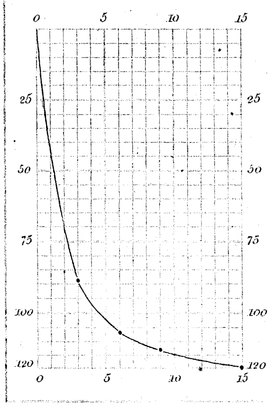


Fig. III. *Pyromeconate of Iron.*



Ferric Ferrocyanide. Fig. V.



Bromide of Gold. Fig. VI.

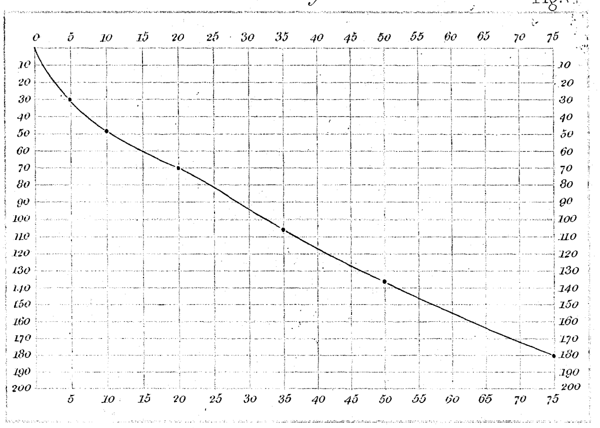
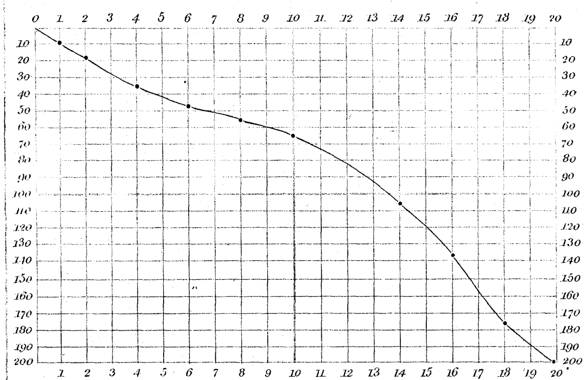
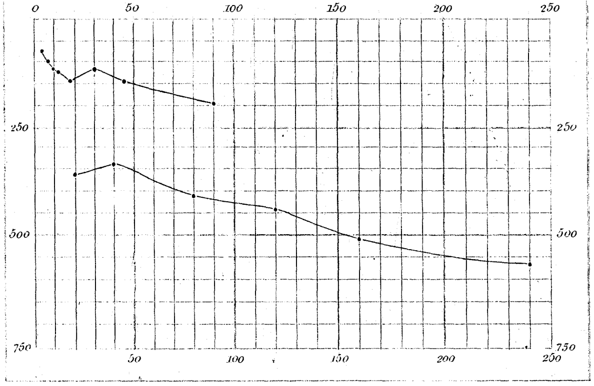


Fig. VII. *Blue Gallate of Iron.*



Deposited Oxalate of Lime. Fig. VIII.



J. Basire. sc.