

of the forty-one known L. P.'s, thirty would be in one semicircle, is about $\frac{1}{806}$; and that of the forty ascending nodes, thirty-one would be in one semicircle, is about $\frac{1}{4021}$. Thus the probability that there is some influence causing a tendency to one semicircle, ascertained from the facts before us, is very strong: for, for the L. P.'s, the odds are about 660 to 1, and for the ascending nodes about 4430 to 1 in favour of such a supposition." But after all it may be an accidental coincidence; as, consistently with the laws of planetary motion, such a congregation of perihelia or nodes may occur at periods exceedingly remote. The further consideration of this subject must be left to analysts, of leisure and inclination to pursue it.

II. "On Circumstances modifying the Action of Chemical Affinity." By J. H. GLADSTONE, Ph.D., F.R.S. Received February 1, 1855.

The question intended to be solved in this communication is,—what takes place when two binary compounds AB and CD are brought together under such circumstances that both they themselves and the products of their mutual action remain free to react? Do they, according to a generally received opinion, remain unaltered, or, should the affinities so preponderate, become simply AB and CB? Or do A and C, according to Berthollet's view, divide themselves in certain proportions between B and D, the said proportions being determined not solely by the difference of energy in the affinities, but also by the difference of the quantities of the bodies? And, supposing the latter to be the correct view, do the amounts of AD and CB produced by the reaction, increase progressively with the relative increase of AB, or do sudden transitions occur, such as Bunsen and Debus have recently observed in certain cases where the products were removed at once from the field of action?

A reply was sought in the colours produced upon mixing different salts in aqueous solution. There were not many coloured salts suitable for the purpose, as it generally happens that a base gives the same colour with whatever acid it is combined, and *vice versâ*; but the compounds of sesquioxide of iron were peculiarly adapted to

the requirements of the experiment, as some are intensely coloured while others are nearly colourless.

The circumstances that attended the formation of the blood-red sulphocyanide were first fully examined. On mixing known quantities of different ferric salts with known quantities of different sulphocyanides, it was found that the whole of the iron was never converted into the red salt; that the amount of it so converted depended on the nature both of the acid combined with the ferric oxide, and of the base combined with the sulphocyanogen; and that it mattered not how the bases and acids had been combined previous to their mixture, so long as the same quantities were brought together into solution. The effect of mass was fully tried by mixing equivalent proportions of ferric salts and sulphocyanides, and then adding known amounts of either one or the other compound. It was found that in either case the amount of red salt was increased; and that when the numbers of equivalents of the salt added were taken as abscissæ, and the amounts of red sulphocyanide produced, as ordinates, the numbers observed in the experiments gave regular curves, though not belonging to the second order. The curves representing the experiments in which sulphocyanide of potassium was mixed with ferric nitrate, chloride, or sulphate, appeared to be the same, but hydrosulphocyanic acid gave a different curve. The deepest colour was given when nitrate of iron was mixed with the sulphocyanide, but even upon the admixture of one equivalent of the former with three of the latter, only 0.194 equiv. of the intensely red ferric salt was formed, and when 375 equivalents of sulphocyanide of potassium had been added there was still a recognizable amount of nitrate of iron undecomposed. It was found that the addition of a colourless salt not only reduced the colour of a solution of ferric sulphocyanide, but also that the reduction increased in a regularly progressive ratio according to the mass of the salt.

Other ferric salts were likewise examined. The black gallate gave results precisely analogous to those obtained by means of the sulphocyanide; the red meconate also confirmed Berthollet's views, but the action of mass was rendered obscure by the formation of double or of acid salts; the red pyromeconate resembled the meconate; the red acetate bore similar testimony; the blue solution of the ferric ferrocyanide in oxalic acid gave results fully corroborative

of the influence both of the nature and of the mass of every substance present at the same time in the mixture; the purple and the red comenamate afforded similar results; while the red bromide (not the oxybromide), though somewhat indistinct in its testimony, corroborated to a certain extent the preceding observations.

Experiments were performed with a view to determine what effect the mass of water might have on the salts operated upon; its influence in reducing the colour of the ferric sulphocyanide was found to be very great, but the nature of it could not be exactly determined. As however it was uniform in its action in whatever manner the sulphocyanide had been produced, it could not affect the results of the preceding experiments. Water did not appear to act in any similar manner upon the other ferric salts.

From the mass of quantitative observations made during the investigation, it was possible to deduce not only the order of affinity of the various acids for sesquioxide of iron as compared with potash, but also to assign approximative numbers. Doubt may rest on the position of some terms in the series, but hydrosulphocyanic acid certainly had the least affinity for ferric oxide in comparison with potash: it was represented by unity: the other acids followed in the order—nitric, 4; hydrochloric, 5; sulphuric, 7; gallic, 10; pyromeconic; meconic; acetic, 20; hydrobromic; comenamic; citric, 100; hydroferrocyanic, 170.

Other coloured salts were submitted to a more cursory investigation. The scarlet bromide of gold when treated with an alkaline chloride gave a striking instance of the effect of mass in gradually overcoming a strong affinity. The intensely red iodide of platinum afforded results which, though somewhat obscure, were not opposed in their testimony. So did the blue sulphate of copper when treated with different chlorides. The “manganoso-manganic oxide” dissolves in sulphuric or phosphoric acid of a red, and in other acids of a deep brown colour; and it was found that hydrochloric acid was capable of changing the colour of the sulphate according to its mass, while on the other hand sulphuric or phosphoric acid altered in like manner the tint of the chloride. Somewhat similar results were obtained by means of the green chloride and the purple fluoride of molybdenum; and the blue solution that forms when gallic acid is brought in contact with both the oxides of iron at once, bore testi-

mony to the same general laws. The peculiar optical character of certain salts of quinine was also taken advantage of for determining what changes took place among the compounds in solution. The amount of fluorescence exhibited by a solution of acid sulphate of quinine was found to be affected by the admixture of a chloride, bromide, or iodide according to the nature and the mass of the salt added, and the addition of sulphuric, phosphoric, nitric and other acids was found to produce a fluorescence in solutions either of hydrochlorate of quinine, or of sulphate which had been rendered non-fluorescent by hydrochloric acid. Similar results were obtained with quinidine; and somewhat analogous ones with the organic bases contained in horse-chestnut bark, and in tincture of stramonium. An experiment is also narrated showing that the same laws hold good in respect to compound ethers as to salts having metallic bases, alcohol being employed as the solvent.

Beside the very diversified substances already mentioned in this abstract, several others, such as lead, mercury, zinc, potash, soda, baryta, lime, and ammonia, are shown by a more indirect proof to enter into compounds which obey the same laws. Hence it is concluded that what was observed in reference to the ferric salts holds good very generally, if not universally.

The bearing of certain other phenomena upon the question at issue was also examined. The fact that precipitation, when it occurs, gives rise to a perfect interchange of bases and acids, is equally consistent with either Bergmann's or Berthollet's theory; but not so is the fact that two soluble salts cannot be mixed without the occurrence of precipitation, if one of the products that may be formed is an insoluble salt. The only recorded exception to this law, which occurs with oxalate of iron in the presence of a salt of yttria, under peculiar circumstances, was found on close examination to be in perfect accordance with the principles laid down by Berthollet. Besides the argument founded on this universal fact, several experiments were devised for the purpose of proving that the complete precipitation of an insoluble salt on the mixing of two soluble salts, was due to the insoluble compound being removed at once out of the field of action on the first distribution of the elements, thus necessitating a redivision, and so on until no more of it could possibly be formed. The phenomena attending volatilization have the same

bearing as those connected with precipitation. If by the mutual action of two salts a substance be formed, which, though soluble in water, requires more water for its solution than is present, it crystallizes out: certain experiments were noted where this action occurs, and it was found that they gave testimony in favour of the same views as have been supported by the preceding observations. The bearing of the phenomenon of diffusion of salts upon the point at issue was also examined: Malaguti's experiments were discussed; and they, as well as some observations on the solution of certain bodies by others set at liberty, were found to bear testimony also in the same direction.

During the whole of the experiments on this subject, most of which were performed quantitatively, no unequivocal instance occurred of two substances having so strong an affinity for one another, that they combined to the exclusion of other bodies of like kind present in the same solution. After showing that some reputed exceptions are really not capable of being proved to be so, and after suggesting some probable limitations of the action of the general law, the paper concludes with the following deductions:—

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

II. That these proportions are independent of the manner in which the different elements were primarily arranged.

III. That these proportions are not merely the resultant of the various strengths of affinity of the several substances for each other, but are dependent also on the mass of each of the substances present in the mixture.

IV. That 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 regular progressive ratio; sudden transitions only occurring where a substance is present which is capable of combining with another in more than one proportion.

V. That this equilibrium of affinities arranges itself in most cases in an inappreciable short space of time, but that in certain instances the elements do not attain their final state of combination for hours.

VI. That totally different phenomena present themselves where

precipitation, volatilization, crystallization, and perhaps other actions occur, 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. That consequently there is 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 substances exist in a solution, drawn from such empirical rules as, that “the strongest acid combines with the strongest base.”

March 15, 1855.

The LORD WROTTESLEY, President, in the Chair.

The following communications were read :—

- I. “Researches on Organo-metallic Bodies.” By E. FRANKLAND, Ph.D., F.R.S., Professor of Chemistry in Owens College, Manchester. Second Memoir.—Zincethyl. Received February 9, 1855.

This compound, whose existence was mentioned in a previous memoir*, is formed by the action of zinc upon iodide of ethyl, or a mixture of iodide of ethyl and anhydrous ether, at a temperature exceeding 100° C. The materials are enclosed in a copper digester capable of resisting great pressure. When purified by rectification in an atmosphere of carbonic acid, zincethyl possesses the following properties :—At ordinary temperatures it is a colourless, transparent and mobile liquid, refracting light strongly and possessing a peculiar odour, rather pleasant than otherwise, and therefore differing greatly from that of zincmethyl. Its specific gravity is 1·182 at 18° C. Exposed to a cold of −22° C. it exhibits no tendency to become

* Philosophical Transactions, 1852, p. 436.