waters. Meanwhile let us be thankful that they have done something to redeem the race to which Cook belonged from the charge of insensibility to his greatness.

THERMO-CHEMICAL INVESTIGATION

THE introduction of a new method of research, or the invention of a new instrument, has repeatedly marked an epoch in the development of more than one branch of natural science. The last few years have witnessed the introduction into chemical research of a new method of examining chemical changes, a method which is founded upon the study of those thermal reactions which accompany these changes.

The older methods of chemical investigation failed to throw any definite light upon many important problems, some at least of which have been brought a step nearer complete solution by the application of the newer method of thermo-chemical measurement.

When solutions of two salts are mixed, the products of the mutual action of which salts remain in solution under the experimental conditions, it is frequently found impossible to determine, by means of the ordinary analytical processes, the chemical distribution of the mass of reacting matter at the expiry of the experiment.

Again, there are certain acids which undoubtedly form two series of well-marked salts, but which appear to be capable, under certain ill-defined conditions, of forming a third series of unstable saline derivatives. How to determine the basicity of such acids has long been one of the unsolved problems of chemistry.

Once more, the ordinary methods of investigation have failed to supply us with any far-reaching generalisation concerning the stabilities of series of compounds. Certain relations have undoubtedly been traced between general chemical properties of compounds, the properties of their constituent elements, and the stability of these compounds, but, nevertheless, the shadowing forth of well-marked generalisations, connecting stability of compounds with chemical structure, from which generalisations exact deductions, capable of experimental investigation, might be made, dates from the introduction of the thermo-chemical method of investigation.

That system of notation which is now employed in chemistry, although of the greatest value, is nevertheless far from being perfect ; it fails to tell anything concerning the changes in forms of energy involved in those changes of distribution of mass which it formulates. Previous to the introduction of the thermo-chemical method little or no exact knowledge regarding these changes of energy was in the possession of chemists.

Chemists were long aware that certain reactions were possible only under stated conditions of temperature, pressure, &c., but until measurements had been made of the amounts of heat evolved or absorbed in these reactions they were unable to generalise the connection between the conditions of the reactions and the possibility of their occurrence.

Such are some of the problems which have been at least partially solved by the new method.

The fundamental position of thermal chemistry may be thus stated : "Every chemical change taking place without the aid of extraneous forces tends to produce that body, or system, in the formation of which the greatest evolution of heat occurs."

As a deduction from this statement Berthelot formulates his law of maximum work as follows :—"That salt, the formation of which is attended with the greatest evolution of heat, is always produced when those salts, from whose mutual action it may be formed, exist in solution in a condition of partial decomposition."

Many special instances illustrative of these generalisations might be cited ; let one or two suffice. Chlorine decomposes dry sulphuretted hydrogen with formation of hydrochloric acid and separation of sulphur ; iodine does not decompose sulphuretted hydrogen under the same conditions. The formation of hydrochloric acid and sulphur in the first change is accompanied with the evolution of a considerable quantity of heat ; the formation of hydriodic acid and sulphur, in the second case, would involve the absorption of much heat. If, however, the action of extraneous forces be allowed to supervene, a new condition of equilibrium is attained ; add water to sulphuretted hydrogen and iodine, hydriodic acid and sulphur are produced. But the solution·in water of hydriodic acid, which is the potential product of the reaction, involves the evolution of more heat than is absorbed in the reaction itself.

Iodine scarcely decomposes water, but if sulphurous acid be added to water, iodine is capable of bringing about decomposition, the products of the reaction being hydriodic and sulphuric acids

$$(H_2O + I_2 + H_2SO_3 = H_2SO_4 + 2HI).$$
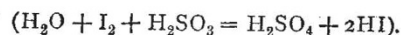
Now it is found that the formation of sulphuric from sulphurous acid is accompanied with the evolution of a considerable amount of heat ; if, then, the decomposition formulated $2H_2O + 2I_2 = 4HI + O_2$ be started, the combination of the oxygen thus produced with the sulphurous acid present causes the evolution of more heat than would be evolved in any other series of chemical changes which could occur among the bodies present.

The applications of the thermal method in general chemistry are many and important. I propose briefly to consider some of the results obtained by this method, as shown in the phenomena attending the neutralisation of acids ; in the changes which occur on mixing solutions of two salts which are capable of undergoing decomposition with the production of salts themselves soluble under the conditions of experiment ; in the measurements of (so-called) affinities between elementary bodies ; and in one or two reactions of general interest.

The neutralisation of an acid by an alkali is attended with the evolution of a constant amount of heat ; in some cases it is noticed that the total amount of heat evolved is independent of the relative quantities of acid and alkali employed, while in other cases the total heat evolution may be divided into two equal portions, one half of the whole accompanying the addition of the first portion, and one-half accompanying the addition of the second portion of alkali. Those results evidently point to the exhaustion of the available energy of the acid (or alkali) as a phenomenon which takes place in regular stages. The thermal results of neutralisation phenomena are rendered more intelligible when we find that an acid, the neutralisation of which is accompanied with the evolution of but one quantity of heat, is also a monobasic acid ; while in the case of a dibasic acid the total amount of heat evolved on neutralisation with alkali is divisible into two distinct portions. Further, a difference is traceable between the thermal phenomena which attend the neutralisation of an acid by caustic potash or soda, on the one hand, and by ammonia on the other.

The reaction formulated

$$2KHO + H_2SO_4 = K_2SO_4 + 2H_2O,$$

involves the expenditure of 31,000 thermal units; but the reaction $2NH_3 + H_2SO_4 = (NH_4)_2SO_4$ is attended with the expenditure of but 28,150 thermal units

If, however, a compound more strictly comparable with caustic potash in its chemical structure be employed to neutralise sulphuric acid, we find that the heat evolved is equal in both cases ; the reaction

$$2N(CH_3)_4OH + H_2SO_4 = (N(CH_3)_4)_2SO_4 + 2H_2O,$$

is attended with the evolution of 31,300 thermal units.

From the point of view of their thermal reactions, the alkalis (including thallium hydroxide) and the alkaline earths, are strictly equivalent, so far as the power of

neutralising one and the same amount of sulphuric acid is concerned.

The effect of substituting various compound radicles for the hydrogen of ammonia, is well shown in the phenomena attending the neutralisation of acid by ammonia, and by those substituted products. The introduction of a C_nH_{2n+1} group (C_2H_5, CH_3, &c.) into the ammonia molecule produces a substituted ammonia, the heat of neutralisation of which is the same as that of the parent body; but if a negative radicle (such as C_6H_5) be substituted for hydrogen, then a compound is produced in the neutralisation of which less heat is evolved than in the neutralisation of the parent body. Thus the neutralisation of hydrochloric acid by ammonia is accompanied with the evolution of 24,540 units of heat, while the neutralisation of the same acid by aniline ($NH_2C_6H_5$) is accompanied with the evolution of only 15,000 to 16,000 thermal units.

When solutions of two salts are mixed under conditions such that the products of their mutual action remain in solution, thermal measurements throw very considerable light on the progress of the chemical change.

The problem presented by the phemonenon now under consideration is one of those which are peculiarly difficult of attack by the older methods. If a third body were introduced into the mixture of salts, which should combine with, or render insoluble, one or more of the possible products of the action, a new configuration would be initiated, new chemical changes would probably occur, and we should be unable to say whether the results obtained were really trustworthy representations of the action which had taken place between the members of the original system.

But measurement of thermal changes involves no disturbance of the equilibrium of the reacting chemical system, and at the same time it yields trustworthy information regarding the changes which have occurred in the distribution of the mass of matter comprising that system. To take an example :—On adding a solution of potassium chloride to dilute hydrochloric acid no thermal change is noticed ; on adding a solution of potassium sulphate to dilute sulphuric acid heat is absorbed, the amount of heat so absorbed increasing with the amount of acid added, until a limiting point is reached. If the solution of potassium sulphate be made more and more dilute less and less heat is absorbed. Now these facts evidently point to the occurrence of two processes of chemical change in the above reaction, viz., the direct action, formulated $H_2SO_4 + K_2SO_4 = 2KHSO_4$; and the inverse action, formulated

$$2KHSO_4 + H_2O = K_2SO_4 + H_2SO_4 + xH_2O$$
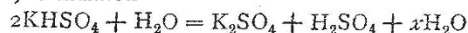
We are thus taught to regard this chemical change as dependent on the conditions of the experiment, and further we obtain a glimpse of the decompositions and recompositions which are continuously occurring among the molecules of our seemingly stable compounds.

If solutions of zinc acetate and sodium sulphate be mixed no thermal change is noticeable, but if solutions of zinc sulphate and sodium acetate be mixed, an evolution of heat occurs, that is to say, a chemical change (or a series of chemical changes) proceeds. Such an experiment as this, besides throwing light upon the special chemical change under consideration, leads to a clearer conception of those phrases " strong acid," " weak base," than were generally to be found before the introduction of the thermal method into chemistry. A strong acid is evidently an acid in the formation of the salts of which much heat is evolved, and a weak acid is one in the formation of whose salts little heat is evolved, or heat is absorbed. If therefore the heats of neutralisation of two acids by given bases be known, it may become possible to predict what chemical changes will occur when given salts of those acids are mixed.

Attempts have been made from time to time to measure the so-called affinities of the elementary atoms. These attempts have been considerably advanced, and the whole problem of affinity has been much defined by applying the results of thermal measurements to chemical reactions.

If chlorine be mixed with hydrogen, and the mixture be exposed to daylight, hydrochloric acid is produced with evolution of a large amount of heat ; the formation of hydrobromic acid from its elements is accompanied with the development of less heat, while less heat is absorbed in the formation of hydriodic acid from its elements. These thermal reactions show that more energy changes form in the first than in the second, and more in the second than in the third of these reactions. The amount of energy of motion which is convertible into thermal energy, under fixed conditions, seems, therefore, to measure the mutual affinities of chemical elements.

But we do not know what is the amount of energy spent in decomposing the molecules of hydrogen and chlorine ; the heat developed in the reaction

$$2H + 2Cl = 2HCl$$
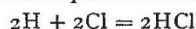
is therefore the sum of the plus and minus thermal changes during the cycle of chemical changes, the initial and final stages of which are chlorine and hydrogen molecules and hydrochloric acid molecules respectively. Therefore it is evident that thermal measurements do not give data which suffice for determining the absolute affinities of the elements.

If the elements comprised in a natural group be converted into similar compounds—say into oxides—and if that element in the formation of whose oxide the greatest amount of heat is developed be said to have the greatest affinity for oxygen, many remarkable relations may be shown to exist between the affinities and the atomic weights of the elements in such a series. Thus Thomsen has shown that in the group comprising magnesium, calcium, strontium, barium, the affinity for chlorine, bromine and iodine increases with increase of atomic weight, while the affinity of the haloid compounds of these elements for water decreases as the atomic weight of the elements increases. Many more exceedingly interesting results are brought out by Thomsen in the same paper.

The results of thermo-chemical investigation—a few of which I have endeavoured to sketch in thinnest outline—suggest one or two considerations regarding chemical action in general, and regarding some of those problems which yet remain to be solved by chemical science.

The older theory of chemical action is based upon the idea that the reacting bodies exert force upon one another ; the word affinity has thus a positive meaning.

Recently the view has gained ground, with some chemists, that a chemical change is but the outward representation of a loss of energy occurring within the reacting system ; that no positive force is exerted between the reacting molecules, but that the system, as it were, falls to pieces because the conditions are realised under which a loss of energy is possible.

The latter view, I think, fails to account for the facts ; there is no doubt that it expresses a truth, but surely only a partial truth.

General considerations, no less than those derived from thermal measurements, compel us to regard the first action between two elementary molecules as consisting in a decomposition of those molecules with the production of their constituent atoms, which afterwards combine with the formation of new molecules. But the decomposition of elementary molecules involves the expenditure of energy ; in other words, there is a mutual action and reaction between these molecules. If this stress be regarded from the point of view of one set of the reacting molecules only, we certainly have positive force exerted.

It is not a mere negative loss of energy, but a positive action of one kind of molecules upon another kind of

molecules; and the amount of force exerted is different for different elementary molecules. Hence chemical affinity is a positive force. The mutual action and reaction between the molecular systems involves the loss (or gain) of energy, but this loss of energy does not furnish a complete account of the action.

Thermal measurements enable us to determine the quantity of energy entering or leaving a given chemical system during its passage from one state to another. These measurements, therefore, give us most valuable information concerning the phenomena exhibited by those chemical systems.

The results obtained by these measurements show how great is our ignorance with regard to the progress of chemical reactions in general; and they suggest many exceedingly interesting problems which will doubtless ere long meet with satisfactory solution. The great problem of chemistry is to determine the connection between the structure and the properties of molecules. To take a special case, it may be asked, why is the hydrogen of acids replaceable by metals under definite conditions? Many facts are known which enable us to give partial answers to this question; doubtless, thermal investigation, taken in conjunction with other methods of research, will some day furnish the complete answer.

Thermal measurements have already shown us that allotropic changes in elementary molecules are accompanied with changes in the energy of these molecules and that the same generalisation holds good with regard to isomeric changes among compound molecules. But the whole question of allotropy is yet in its infancy.

The thermal method promises to throw light upon those phenomena which are classed together under the name of valency, and perhaps to furnish an answer to the query, *why* does the valency of elementary atoms vary? The new method is full of hopeful anticipations.

M. M. Pattison Muir

ARE THERE NO EOCENE FLORAS IN THE ARCTIC REGIONS?

IN NATURE (vol. xix. p. 124) I expressed doubt whether the beds containing fossil plants in or near the Arctic circle, said by Heer to be miocene, are really of that age. It seemed to me then very probable, but now I may say certain, that at least all those said to be *lower* miocene are truly eocene. The article was translated in *Das Ausland*, No. 2, 1879, and replied to by Heer in No. 8 (February 24) of the same journal. In this reply he, as I expected, combats my views, and, although affecting to believe that I had written without thought or previous study, he devotes eight columns to contradicting me, yet without bringing forward any fresh evidence whatever, or indicating any sources of information which I had not already consulted.

Heer contends that all the known fossil floras containing dicotyledons, from all lands within at least 2,000 geographical miles of the Pole, are either cretaceous or miocene. I think, on the contrary, many of them are eocene.

The leading facts for and against the hypothesis of a miocene age for so large a proportion of them may be briefly summarised.

1. The great similarity of the floras (miocene of Heer) of latitude 70° to those of 47° and 46°, 98 species out of 363, or more than 25 per cent. being common to both, even in the present state of our knowledge. This, according to existing plant-distribution, precludes their being of the same age, unless the more southern ones grew in Alpine or even hilly regions; but no one has ever contended that they did do so. No floras so much alike, and assimilating so closely to those of the present day, could have grown simultaneously at the same level in such widely different latitudes.

Against this Heer states that a number of trees extend from the borders of Italy to the 70th parallel, as the firs, birches, aspens, bird-cherry, and mountain-ash. This fact has little bearing on the subject, since the trees are Alpine, or, at least, not in any way characteristic of the lowland flora of North Italy or of that latitude in Europe. Secondly, he says that of the fifty-nine phanerogams found by Feilden in Grinnell Land between 81° 44′ and 83°, forty-five are European, and six of these are not only found in Swiss valleys, but also in Italy. This should not have been advanced, being quite beside the question, unless he wishes to make believe that the present floras of Grinnell Land and Italy resemble each other. They are, in fact, all Alpine herbaceous plants, and have nothing to do with the fossil *forest* floras in question; besides which, the level of the Swiss valleys in which these six grow is not stated, and there is nothing curious in Alpines ranging into Italy. Thirdly, of 559 species of phanerogams of the Isle of Saghalien, 188 are found in Switzerland. Such occasional examples of wide lateral distribution among plants are well known, and might often be adduced, without affecting the question in the remotest degree. The present distribution of the *same* types of plants, trees, &c., as those which are found fossil, have alone any bearing on the subject. Heer, to sustain his theory, must prove that forest floras extend in some other parts of the world with a much less degree of change than we have experience of in our continent, over not less than 30° of latitude, and in about the same longitude.

2. The extreme improbability that the plant remains of the eocene, a far more important formation than the miocene, should have been alone overlooked in a series of deposits abounding in plants of immense extent and thickness, and continuous, it is supposed, from the middle cretaceous to the upper miocene. The absence of any intelligent explanation of the complete break in the sequence, which Heer's nomenclature implies, and of which there is not the least stratigraphical evidence. The vastness and immense extent of the formations which are ascribed to miocene. The universally admitted fact that continuous land existed in the north between Europe and America from early eocene times, as proved by the palæontological records of both continents, and supported by other considerations, and which must have left records at least in proportion to those of the miocene, since volcanic, the preserving agency, was active throughout the whole time.

Heer characteristically meets these important objections by stating that at Eisfiord, in Spitzbergen, there are 1,000 feet of strata between the cretaceous and miocene, which he thinks doubtless represent the eocene. It is strange to find any one with the least knowledge of stratigraphical geology simple enough to advance such evidence as the presence of 1,000 feet of beds at a single spot, in dealing with so colossal an interval as that between the cretaceous and miocene, especially when the latter alone, over the area, is several thousands of feet in thickness. Besides Nordenskjöld,[1] from whom Heer derives his information, says that the miocene (of Heer) habitually rests upon the cretaceous.

Heer further says that there is a deposit with lower miocene mollusca under a miocene deposit. This is exactly what I should expect; for the same reasons that make it improbable that the flora is miocene apply equally to these mollusca.

3. The much higher temperatures which prevailed in the eocene than in the miocene, and which could only have permitted the growth of such temperate floras in such high latitudes in the eocene period, according to existing laws of plant distribution.

Although I showed *seriatim* that a mean temperature higher by 20° F. in the northern hemisphere would inevitably have produced approximately just the series of

[1] Excursion to Greenland, *Geol. Mag.*, vol. ix.