XIX.—Review of Berthelot's "Mécanique Chimique.*"

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On witnessing the calorific effects which accompany the act of chemical combination, chemists have at all times sought to determine the relations which exist between these two classes of facts; on the one side, affinity, considered as the cause of all chemical combination; and, on the other side, the heat produced when this combination takes place.

A century ago, Lavoisier explained this relation, by assuming that simple bodies are only known to us in a state of union with a certain quantity of caloric, which is set at liberty when these bodies enter into chemical combinations. Having his attention more exclusively attracted to the phenomena of combustion, he attributed this too exclusively to oxygen. Later, it was admitted for all the elements.

The brilliant discoveries of Davy, on the chemical decompositions effected by the galvanic current, gave rise to the electro-chemical theory, proposed by this scientist, and afterwards adopted and modified by Ampére and Berzelius, which caused heat and affinity to be looked upon in an entirely new light. According to this theory, affinity is merely the reciprocal attraction of the opposite electricities, which exist in either a free, or a polarized state, in the elements which tend to combine, and the heat observed in chemical combinations results from the mutual neutralization of these electricities.

When chemists abandoned the electro-chemical theory, they returned to the system previously adopted, admitting, at the same time, the pre-existence of caloric in all the elements. But, about this time, an important revolution took place in the physical sciences; heat and electricity ceased to be considered as material fluids, combined more or less intimately with ponderable bodies, and came to be regarded as modes of motion. The discoveries of Mayer, of Golding, of Joule, had demonstrated the mechanical equivalent of heat. This new doctrine necessarily modified the ideas entertained by chemists concerning the origin of the heat and the electricity evolved in chemical reactions, and led them to consider these mani-

* Essai de Mécanique Chimique, Fondée sur la Thermo-chemie, par M. Berthelot; Dunod, Editeur; Paris, 1879.

† Published in the Archives des Sciences Physiques et Naturelles, and republished in the Moniteur Scientifique, of February, 1880.

festations as complementary to one another, and as resulting from the loss of molecular impetus attending the act of combination.

Vast erudition, and long bibliographical researches, would be necessary, to follow this change of doctrine, and to apportion to each scientist the share which he had in it. We may, however, cite the memoir of M. Henri Sainte Claire Deville (1860), and those of Babinet (1866).

A Danish chemist, Mr. Thomsen, whose labors have greatly contributed to the progress of thermo-chemistry, published in 1853 a series of memoirs,* in which he explained the principles of this new science. Without deriving them explicitly from the mechanical theory of heat, he expresses the basis on which they rest in terms which recall this theory. He founds them on the two following principles :

1st. The intensity of chemical energy in a given body is constant when the temperature is invariable.

2d. The totality of the heat given out in a chemical reaction, is the measure of the chemical energy brought to bear in this reaction.

The chemical energy of a body, or, what is identical, its capacity of developing heat, is what Mr. Thomsen calls its *thermo-dynamic equivalent.*

Mr. Thomsen has since tried to show that all the laws of thermo-chemistry subsequently established by M. Berthelot, were derived from the second of these principles. It is true that they may be considered as consequences of it, but only by including conditions and restrictions which are not found in the statement of this principle. The best proof of this is that fifteen years later,† when Mr. Thomsen attempted to establish an agreement between his principles and the manner in which bases and acids are divided in a mixture of salts, he had to introduce a new force, *avidity*, which is an inherent property of these bodies, and in which it is difficult to find anything different from chemical affinity under another form, independent of that which is measured by the heat given out in combinations.

It is in reality to M. Berthelot that the honor belongs, of having stated with perfect precision the fundamental principles of thermo-chemistry, and, above all, of having shown, by a prolonged and numerous series of experiments, that these principles are sufficient to account for all chemical reactions.

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* Pogg. Annal., **88**, 349 : **90**, 261.

† Pogg. Annal., **136**, 65 ; also, Archives, 1869, **36**, 301.

Gifted with an eminently philosophical spirit; deeply versed in mathematics and in the physical sciences; trained to the most extended researches by his labors on chemical synthesis, this scientist was better able than any one else to accomplish the task to which he has devoted himself, which is to show the application of the principles of mechanics to the formation of organic compounds, and even to chemical reactions generally.

For this, it was not sufficient merely to determine the heat given out in chemical reactions. A not less important portion of the labors of M. Berthelot has been the study of the conditions under which such reactions take place, and more specially the study of the chemical equilibrium which results from two contrary reactions, which are reciprocally limited. This happens in the formation of ethers, in decompositions and inverse re-combinations produced by electricity, etc.

Through the study of these subjects, the author was led to new and important results in a branch of chemical mechanics, already intimated at the beginning of this century by Berthollet, under the name of *chemical statics*. He has shown that the theory of Berthollet, by which we are enabled to foretell chemical phenomena from the mere knowledge of the physical conditions of insolubility and volatility, has no foundation, except when there already exists a previous equilibrium, which constantly tends to renew itself. But the permanency of this equilibrium, and even its existence, are dependent on a still more general condition, which had never before been pointed out, and which has been defined in the principle of *maximum work* laid down by M. Berthelot.

These researches have taken sixteen years—since 1864. The results have been given in numerous memoirs, published in the *Annales de Chimie et de Physique*. M. Berthelot acknowledges the great help he has had from the labors of his predecessors: Hess, Graham, Andrews, Favre and Silbermann, and in the numerous series of numerical determinations of the quantities of heat given out in combinations, made by Mr. Thomsen, which are generally remarkable for their accuracy.

This subject is not exhausted, and will not be for many years, but M. Berthelot thinks that the time has come for him to state the laws and general principles, the search of which has led him to this long series of experiments, and to show in what manner the ideas recently acquired on the theory of heat, allow us to bring the whole of chemistry, that is, the formation and reactions of organic as well as of mineral substances, under the same principles of mechanics which govern other branches of physics; whence the title of "*Essay on Chemical Mechanics founded on Thermo-chemistry*," given by the author to the work which we are reviewing.

In his introduction, M. Berthelot states the three fundamental principles of thermo-chemistry and chemical mechanics, viz:

I. PRINCIPLE OF MOLECULAR ACTION.—*The quantity of heat given out in any reaction is the measure of the sum of the physical and chemical work accomplished in this reaction.*

This principle gives the measure of chemical affinities.

II. PRINCIPLE OF THE CALORIFIC EQUIVALENCE OF CHEMICAL TRANSFORMATIONS, or, in other words, PRINCIPLE OF THE INITIAL AND FINAL STATE.—*If a system of simple or compound bodies, taken in determinate conditions, suffers physical or chemical changes capable of bringing it to a new state, without giving rise to a mechanical effect exterior to the system, the quantity of heat given out or absorbed by the effect of these changes, depends solely on the initial and final states of the system; it is always the same, independently of the nature and sequence of intermediate states.*

III. PRINCIPLE OF MAXIMUM WORK.—*Every chemical change, accomplished without the intervention of a foreign energy, tends toward the production of the body, or system of bodies, which gives out the greatest quantity of heat.*

The prevision of chemical phenomena is, by this last principle, brought down to the purely physical and mechanical idea of the maximum labor accomplished by molecular action.

The following principle, deduced from the preceding, is applicable to a multitude of phenomena:

Every chemical reaction, which may be accomplished without the help of a preliminary action, and apart from the intervention of any energy foreign to the bodies present in the system, will necessarily take place if it be attended with evolution of heat.

The two first principles, above given, had not heretofore been stated in such precise terms, but, it may be said that they had been implicitly admitted by the previous investigators in thermo-chemistry. It was, however, M. Berthelot, who first called attention to the principle of maximum work, which is the basis of chemical statics.

In the statements made above, we may note the particular care taken by the author in distinguishing, in the calculations of reactions, the heat given out by chemical reactions, properly so called, from that due to change of state, and which is derived more specially from physical energies, such as the liquefaction of gases, the solidification of liquids, changes of volume and of specific heats of gases, of liquids and solids ; changes of tension in vapors, and of fluidity in liquids, of crystallization and of crystalline form in solids ; also, various modifications of the amorphous state.

It is indeed only on the condition of keeping account of all these circumstances, and of eliminating the share of all these physical causes, that we are able to ascertain that the heat given out in a reaction, is the exact measure of the affinities brought into play.

The first volume of M. Berthelot is specially dedicated to *chemical calorimetry*, which is the study of the quantities of heat given out in chemical reactions. It forms the exposition and confirmation of the first two principles stated above.

These principles cannot be demonstrated *a priori*. They are founded on a hypothesis, in itself very probable, that the imperceptible molecular motions developed in chemical reactions, obey the same laws as the motions of mechanical motors, which may be seen and measured. The accuracy of this hypothesis can only be established by long series of experiments, and by the constant conformity of the results obtained with those foreseen by theory.

The first volume is divided into three books. The first book develops the rules and general methods of chemical calorimetry. The author reviews the various reactions, combinations of elements, formation of salts, &c. He gives the calculations for each case, also gives rules for taking into account all the physical actions which intervene in these reactions, and shows, by numerous examples, the agreement of experience with the fundamental principles established by him.

One chapter is devoted to the quantities of heat which come into play in the reactions which take place in living beings. Another chapter treats of the variation of the heat of combination as influenced by temperature.

The second book contains descriptions of experimental processes and of calorimetric apparatus, for the determination of the quantities of heat given out in chemical reactions, of specific heats, and of the heat due to changes of state.

The great experience of the author gives a special interest to this description of the methods and apparatus used by him, in which he has succeeded in uniting simplicity with accuracy, and in which he has tried to eliminate or, at least, to reduce as much as possible, the corrections made necessary by the influence of exterior causes.

The third book is devoted to numerical tables. It includes numbers obtained by experiment, representing the quantities of heat given out or absorbed during physical or chemical changes of state which these bodies undergo in the operations of our laboratories. It therefore contains, besides results of thermo-chemical experiments, all the data relating to specific heats, and to changes of state (latent heats). It forms an extensive and exceedingly useful compendium of the labors of all the scientists who have studied these questions. We also find in this portion very interesting discussions on numerous theoretical questions suggested by the examination of these results. We may cite more specially those which relate to specific heat.

M. Berthelot states that the specific heat is the only physical property by which simple gases differ from compound gases. This property, however, is sufficient to establish between these two groups such an important difference, that it is impossible to suppose that any of the gases, now considered as simple, results from the union of several other elements, such as we admit them at the present time, or from the condensation of several equivalents of the same element. This union or condensation must be understood to be comparable to that which gives rise to compound bodies, such as are now known to us. Simple gases differ from all compound gases formed with condensation, by the constancy of their specific heat, while for these last, the specific heat increases rapidly with the temperature, and always exceeds in a notable manner, at all temperatures, that of simple gases. They also differ from compound gases, formed without condensation of their elements, such as hydrochloric acid and carbonic oxide (corresponding to four volumes, according to the system of notation of the author), whose molecular specific heat is equal to that of simple gases, and also remains constant at all temperatures, by the fact that the molecular volume always corresponds to one equivalent for these compound gases, while it represents two or four equivalents for all the known elements.*

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* This difference is not so much in the specific heats themselves, as in the relations of molecular volumes to equivalents. In this respect, the reasoning of M. Berthelot does not seem to me unobjectionable. It would be so if the determinations of equivalents rested on fixed rules. But, as he himself acknowledges (Introduction, page 21), "equivalents are only determined within an approximation of a multiple," it would only be necessary to change the multiple which has been chosen more or less arbitrarily, for a given body, to change the

In the chapter relating to specific heats of solid bodies, occur very interesting observations on the law of Dulong and Petit,* and on the relations which exist between the specific heats of compound bodies and those of their elements.

The second volume of the work of M. Berthelot, is specially dedicated to establishing the bases of chemical mechanics.

The object at which the author aims is the highest that science can propose to itself. Instead of confining itself to the individual description of the properties, the preparation and transformations of chemical species, science must endeavor to discover the laws governing these transformations ; the causes and proximate conditions which determine them. The complete solution of this problem of chemical mechanics is not yet possible, and will not be possible for many years. To solve it, we should know, in every reaction, the masses of the particles brought into play, their relative positions, the proper motions of each particle, the exact nature, and the laws which govern the forces which react on each other. Most of these data are wanting, and even if they were known, it is doubtful if any method of calculation would allow us to solve such a complicated problem.

However, some portions of the problem may be attempted. Since a long time, all that relates to the proportions in which combinations take place is known by the laws of definite proportions, of multiple proportions, and of equivalents. As to the prevision of reactions, we have only had the laws laid down by Berthollet at the beginning of this century. These only apply to special cases and meet with frequent exceptions. M. Berthelot replaces them by a more general law, by which the prevision of the reciprocal actions between simple and compound bodies is reduced to the determination

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relation between its molecular weight and its equivalent, which the author regards as characteristic of simple and compound gases. As an instance, it is not clear why M. Berthelot considers the molecule of carbonic oxide, C_2O_2 (four volumes), as representing one equivalent. In the combinations of this gas with oxygen, chlorine and sulphur, it would appear that this quantity rather corresponds to two equivalents.

* Although we acknowledge, with M. Berthelot, that the law of Dulong and Petit, when applied to solids, is not rigorously exact, and that it cannot serve, in an absolute manner, for the determination of atomic weights, still we believe that he exaggerates the exceptions which it suffers, and that it must be taken into account in the case of elements whose physical properties are very similar, as in the case of metals whose fusion points are not very far apart.

of the thermic properties of the reacting bodies. We may, by this new law, foresee the reciprocal actions of compounds towards one another and towards simple bodies, when we know the quantities of heat given out in the formation of each compound. This new law is no other than the third principle of the author, which has already been stated, the law of maximum work.

Whence the division of this volume in two parts :

The first treats of what may be called chemical dynamics. It is the study of combination and decomposition, and contains definitions of the opposing actions, on one side, of chemical forces, and on the other side, of calorific, luminous and electric energies, which determine the phenomena. In this way, the conditions are laid down which determine the existence and the stability of combinations for each separate body.

The second part is the study of the final state which results from reciprocal actions between simple and compound bodies ; this is chemical statics. In this part comes into action the principle of maximum work, which is as remarkable for its simplicity as for its generality. It brings everything down to the knowledge of two things : the heat given out by the transformations, and the stability which belongs to each compound.

The author demonstrates the existence of this principle, by the discussion of the general phenomena of chemistry ; afterwards, he develops the application of it to the reciprocal actions of the principal groups of substances, such, for instance, as take place between elements and binary compounds ; the reciprocal displacement of binary compounds, and specially of hydracids, when opposed to one another or to water ; the reciprocal displacements of acids in salts, and, finally, saline double decompositions.

It may be easily understood that it is impossible to give, in a review of this kind, a clear idea of a work of such importance and of such vast extent. We have only tried to give an idea of the subjects treated in it. The theories of M. Berthelot are well known, as they have been developed by him for the last sixteen years in a series of papers, which have been read by all chemists. Nevertheless, the present work forms an important epoch in the history of chemistry, and shows the necessity of transforming its methods. In the future, it will not be sufficient to state the reactions of which a body is susceptible, as if they were mere experimental data. It will be necessary to derive them from the general principles, of which these reactions are consequences. Doubtless, the edifice of chemical mechanics, whose foundations have been laid by M. Berthelot, cannot be considered as complete. Sixty years ago, the laws which govern chemical proportions were established, and nevertheless, the numbers which represent equivalents have frequently to be rectified. We may expect that those which express the quantities of heat of combination, or transformation, will also require change, more especially, as many of them cannot be determined directly by experiment, but result from complicated calculations in which a great number of reactions have to be taken into account.

There are, moreover, many theoretical questions of the highest importance, the solution of which is at present beyond our reach.

If the heat given out in the combination of two bodies, is the immediate consequence of the loss of momentum which comes from the union of their particles, and if it measures at the same time their mutual affinity, what then is the first cause of affinity? Is it a special force as was once believed? Or is it the concordance in the vibratory motions of the particles?

Those combinations which are attended with evolution of heat, are the only ones which can take place directly; but they do not always take place spontaneously. Many of them must be determined by an exterior cause, such as heat, light, electricity, but these agents do not give to the elements an energy of which they have already an excess. How then do they act?

These questions, and many others which will come up, cannot fail to exercise for a long time to come the sagacity of chemists. At any rate, an important step has been made towards their solution when it it has been shown that the physical and chemical energies which come into play in chemical reactions, follow the laws of rational mechanics.