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ON CHEMICAL ENERGY.¹

BY DR. W. OSTWALD, OF THE UNIVERSITY OF LEIPZIG.

DURING the scientific development of chemistry, the hypotheses which have served as a primary foundation have always been borrowed from a prominent sister science. At the time of the most rapid development of mechanics as founded by Galileo and advanced by his pupils and successors, chemistry was mechanical; the solvent action of acids upon metals was explained by assuming that the former possessed points and edges by means of which they disintegrated the latter; bodies which combine were supposed to have hooks by means of which they attached themselves to each other. When Newton based his theory of astronomical movements upon the assumption of a force acting inversely as the square of the distance, chemistry shortly appropriated this idea, and traced all processes to the attraction and repulsion of particles. It is, therefore, not surprising that the phenomena of the Voltaic pile (which later proved to be so intimately connected with chemical changes) were at once utilized to serve as a foundation for a theory of chemical processes. These theories, especially that of Berzelius, have prevailed a long time, but finally have proved themselves just as insufficient to represent chemical phenomena as the mechanical and the attraction theory.

Thus the theory of chemical combinations is to-day a strange

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and contradictory conglomerate of the fossil constituents of the earlier theories. The rudiments of the theory of attractions still play the most important role, while there is also considerable discussion about positive and negative elements, *i. e.*, the residues of the electro-chemical theory, and in most recent times we see the long-forgotten mechanical conceptions again stepping to the front in stereo-chemistry and being accepted by many as a new step in the progress of science.

In such times it is of great value on the one hand to recall the historical development and the evanescence of theories; on the other hand to find in the older theories that which is useful and correct, so as to obtain sound building material for a new theory.

Especially are we forced to conclude from the fate of past theories, that chemical phenomena must be explained by their own interrelations, that is, must be logically arranged. The use of analogies from other fields of natural science has indeed often led to suppositions which for the moment seemed satisfactory; on trial, however, such analogies have always proved themselves more a drawback than a help, since they hindered the unbiased comprehension of facts, and they could not (or will not in the future) be cast aside without a great struggle and considerable sacrifice of time and labor.

It is scarcely needful, at present, to prove that the several provinces of quantitative science possess in a single conception both the principle which distinguishes them and that common principle which unites them, namely, the conception of energy. Mechanical energy is distinct from thermal; similarly, chemical energy is distinct from electrical; and in each province progress can only be made by studying the various properties which the form of energy under examination possesses.

At the same time, however, the laws which determine the correlation and conservation of energy constitute the only bond which unites the various fields. If heat could not be changed into mechanical energy, and chemical into electrical, these provinces would stand distinct and isolated from each other; and neither thermodynamics nor electro-chemistry would be possible. This shows that progress in the scientific conception of chemical phenomena depends upon primarily determining the

several properties of chemical energy as such, and then its relation to other forms of energy; this done, we will be able to cope in a scientific manner with each chemical process, no matter whether it leads to other chemical changes or causes the appearance or destruction of other forms of energy.

The knowledge of the laws of chemical energy is not only scientifically but also practically of the greatest interest. All energy which is employed in accomplishing the various purposes of industry is derived from chemical sources, the combustion of fuel. Besides each step that we take, every word that we speak, in fact every thought formulated by our brain, leads to sources of chemical energy; animals and plants throughout their whole existence are based primarily upon chemical energy and its laws, and the ultimate problems of biology are in every respect chemical.

All forms of energy have this in common, that they may be resolved into two factors, both of which have definite properties. The one, which we call intensity, determines whether the energy may remain at rest, or must undergo an exchange. Thus, for instance, the factor of intensity for heat is temperature, since we know that two bodies can be at rest with reference to their heat only when their temperatures are equal. The second factor we call capacity; it determines how much energy at a given intensity is present in the object under consideration. With heat, for instance, this is called heat capacity.

What now are the factors of chemical energy? If we had a measure for its factor of intensity, as the thermometer is a measure of the intensity of heat, we would be able to determine for each substance with reference to another whether it could react with the latter or not, just as the thermometer shows us whether or no heat can be transmitted from one body to another. Our answer is that this question has not been completely solved, but that for many phenomena we already possess a chemometer, as we might call the instrument—in analogy to the thermometer.

In order, however, to be able to explain the theory of the chemometer, the factors of chemical energy must first be more precisely determined. The factor of capacity is in this case most easily discovered. The chemical energy which is present under given circumstances is proportional to the weight or mass

of the substances involved. Hence we sell and buy chemical energy according to weight. This becomes more clear from the following consideration: When we buy coal, we do not consider the carbon present, but rather the chemical energy, since in the use of the fuel we allow the carbon to escape quietly through the chimney as carbon dioxide, without making any effort to retain it; that, however, which we husband with the greatest care, is the chemical energy of the coal, obtained as heat. I have stated with due consideration that the factor of capacity of chemical energy is proportional to the mass; yet it is not mass, since this conception belongs solely to mechanics. It is therefore by no means more correct to say "atomic mass" instead of "atomic weight," since in this case the degree of chemical capacity is concerned which is proportional to both weight and mass, without being one or the other.

The term "degree of intensity" of chemical energy has something in common with the conception which has become familiar in the field of chemistry under the term of "chemical affinity," more to denote that field in which a more accurate knowledge was especially desirable than to combine by such a word sufficiently definite ideas. The word was there, just as the name of a future street stands on a signboard in the outskirts of a city, in a waste field; tents and barracks of the most curious kind have been erected from time to time only to be deserted again; only in most recent times solid buildings and permanent settlements have found a place on this site, and soon a new section of the city will be created there, whose importance threatens to throw the older portions of the city in the shade.

J. Willard Gibbs called the degree of intensity of chemical energy the chemical potential; analogous to the degree of intensity of electrical energy, which is called the electrical potential. So, to avoid the vagueness of the term *affinity*, we will make use of the term chemical potential, or in brief potential.

Now it follows from the definition of the degree of intensity, that two substances with like potential can not act on each other; and, conversely, that when two substances act on each other, their potential must be different.

That general law which can be regarded as expressive of the

Second Theorem holds also for the chemical potential, namely: Two potentials which individually are equal to a third are equal to each other. This proposition seems quite self-evident, and therefore equally meaningless. Yet we can draw from it conclusions that are very far reaching. It says that two bodies or groups of bodies, which are in equilibrium with each other, can mutually replace each other at pleasure towards a third system in every reaction in which this third system (towards which equilibrium has been established) can react. Thus, for example, every soluble body can be replaced by its saturated solution, every liquid by its saturated vapor, every solid body at its fusing point by the melted body without causing any alteration in the equilibrium depending upon the former. Among other things, this shows that while the heat of solution, fusion, and evaporation change the evolution of heat during a chemical process they do not thus affect the equilibrium. The thermal theory of affinity, which is even to-day championed by Berthelot and others, is by this circumstance proved to be quite untenable.

It is natural, in the case of such a far-reaching proposition, to require proofs. This proof is found in the fact that it is impossible to create a perpetuum mobile. To have a perpetuum mobile it is not necessary to create energy from nothing, but only to transform potential energy into kinetic. If it were, for instance, possible to transform the constant heat which is present in enormous amounts in the ocean into work which then could change back into heat, we would require no more coal to propel our steamships, since all the work which we required for their propulsion would be transformed into heat by friction and could return to the ocean in unchanged amounts. Such a perpetuum mobile will be instantly possible when two substances which individually are in equilibrium with a third are not in equilibrium with each other. If we assume that a substance, A, when in contact with a large body, B (the ocean), assumes a temperature which is different from that imparted to a body, B, simultaneously in contact and equilibrium with the ocean, we would cause a transmission of heat between A and B which would be capable of driving a machine. This proof is equally

true for every other form of equilibrium and for every form of energy, and thus we also prove our chemical proposition.

When we have thus recognized the conditions under which energy is in equilibrium or at rest, we can directly reason that energy can not be at rest when its potentials are different. A process must then take place by means of which they become equal. This is the most common phenomenon with which we are acquainted; everything which takes place is based in the last instance upon an equalization of energies of different potentials.

Since, however, energy, as is a fact, has a never-ceasing tendency to equalize itself, the question arises why it has not done so long ago during the many thousand years which our system of worlds has existed. We continually see differences of potential existing in nature—compressed air, galvanic elements; all these contain stores of energy which are ever ready to act and must therefore be unequal. Likewise the fossil fuels and the sulphides of the metals are able in conjunction with the oxygen of the air to bring forth large amounts of energy during their interaction, and can not, therefore, be in equilibrium. Aside from the tendency for equalization, which is peculiar to energy, other forces are therefore active in nature which hinder or detain this, and an accurate understanding of these natural phenomena can only be attained when these opposing and detaining causes are known.

For mechanical and electrical energy such hindrances can be easily created. A spring may be kept wound by a weight; two electrically charged bodies, which tend to approach each other, can be kept from attaining their equilibrium by the dielectric resistance of an interposed medium. All these hindrances, however, have but this explanation, that the differences of energy present are compensated by the use of other energies, so that their equalization is prevented; at the same time, we can prove that, according to the method employed, large quantities of one form of energy of any magnitude can be compensated by equally small quantities of another form of energy, for by means of a small switch, enormous currents of electricity can be interrupted and closed at will.

In the case of chemical energy we are, however, very often

unable to prove such compensations by the application of other energies. When a piece of wood is exposed to the air, it would be in accordance with the general tendency to equalize the energy present, if combustion took place and the wood combined with the oxygen of the air. The same would apply to organized bodies. Our body consists of combustible substances; and, in accordance with the chemical affinities present, it should combine with the oxygen of the air and burn without cessation. Why is it not consumed?

If we should attempt to answer this question we should soon become entangled in inexplicable contradictions. We can not ask: "Why is our body not consumed?" since it does actually burn. It continually takes up oxygen and gives off carbon dioxide. The same answer applies to other chemical phenomena. A stick of sulphur exposed to the air seems unchanged, but it is only apparently so. In reality it is oxidized; slowly, however, and so slowly, in fact, that we would not notice it in weeks or months. If the process were, however, continued for years or decades of years, the oxidation could be measured. The rapidity of reaction is clearly proportioned to the surface. If we take finely powdered sulphur, flower or milk of sulphur, whose total surface is much greater, we can prove the formation of sulphuric acid in hours and days.

What has here been stated for a few cases is a general truth. In every case where different substances which could act upon one another are in contact without having, practically speaking, any apparent action upon each other, we can bring the requirements of the teachings of energy into unison with the actual conditions by actually ascribing to these substances an action which is, however, so slow that it lies beyond the possibilities of measurement.

We have here the means of entering upon one of the most important and mysterious problems, namely, the search after the chemical activity of organized bodies. For, as all the activity of organisms depends upon changes in their chemical energy, all knowledge in this case depends upon a correct elucidation of the character of the chemical changes. If we can understand how the chemical processes of combustion, to which all physiological sources of energy finally lead, can be so regulated that

they are able at any moment to adapt themselves to the ever-changing requirements of the organism, we have taken a step in every respect most important in the knowledge of life.

Let us take, for instance, a mixture of oxygen and hydrogen. Under ordinary circumstances we can preserve this mixture for a long time without the formation of a measurable amount of water. If, however, we place a piece of platinum sponge into it, the formation of water immediately begins; and it is as suddenly terminated when we remove the sponge. The platinum sponge has, moreover, undergone no change and is able to exert this action for an unbounded space of time.

At first, it seems as if we had here the first proposition of our later natural science; to rudely dispute "*causa arguat effectuum*," since we have here a cause which can bring forth extended and large effects at pleasure without becoming exhausted. If we ask, however, what this proposition means by cause and effect we find it to be degrees of energy. No energy of any kind can be created without the consumption of an equal amount of energy, and no difference in the potential of energies can be called forth without the simultaneous disappearance of equivalent differences in the potential of other energies. The truth of these propositions is not cast in doubt by the experiment with the mixture of oxygen and hydrogen, since the heat of combustion remains the same both when combination is effected by an electric spark and when it is brought about at the ordinary temperature by means of platinum sponge. While, therefore, the law of cause, clothed in the form of a principle of energy, regulates the final result of the action in an unchangeable manner, the time during which this action takes place remains absolutely independent of this principle, and we have side by side with the absolute necessity of this law of cause the freedom with reference to the time during which it exerts its influence. Therefore we see that all possible phenomena which, originating from the same substances, reach the same products, arrive at these with a very different rapidity. The object to be arrived at is unchangeable; whether it is, however, to be accomplished in a second or in several thousand years is a circumstance over which we have full control.

The name "catalytic bodies" has been given to substances which cause chemical reactions without experiencing any change themselves. We will now change this definition so as to read thus: Catalytic substances are those which modify the rapidity of a definite chemical reaction without changing their own content of energy. To place a catalytic substance into the reacting bodies, and to remove it, requires theoretically no work. This proves that within the strict province of the law of energy, there still remains room for the greatest variation in the temporal extent of the phenomena.

This peculiar circumstance has its foundation in the fact that in the expression of most degrees of energy time is not mentioned, and that, therefore, the equation of energy does not determine the extent of time involved in the phenomena.

One exception is made in the case of kinetic energy which depends upon the rapidity. What has been stated above does not therefore apply to this form of energy. Upon what the action of catalytic substances depends is still a mystery, the solution of which is the more difficult, since it can only be explained by means of new principles, which are beyond the law of energy. At present, we must be satisfied with the knowledge that it is a fact, and must seek to become acquainted with the laws involved. A beginning has already been made; from a large number of various investigations it has been found that many chemical reactions, which usually take place very slowly, are hastened by the presence of free acids; or, to speak in the language of the modern theories, by the presence of free hydrogen-ions, and that this action is proportional to the concentration of the latter. The greatest variety of phenomena have been examined in this respect, partly by me, partly by my pupils, and I have as yet found no case where this statement did not apply. Free hydrogen-ions are therefore without doubt exceedingly active catalysators of a general character.

At the same time numberless *specific* catalysators exist which act only upon certain phenomena. These are the ferments, organized and unorganized. These also are unable to do more than to change the rapidity of certain reactions in one or the other respect, and all attempts to explain their action must be

based upon this, their sole property. The laws which they obey appear to be of an extremely complicated nature, especially with the more complex constituted ferments; this is probably due to the fact that they undergo a change themselves while influencing a certain chemical reaction.

I need not show in an extended manner that the wonderful action of living organisms can be traced to a regular impulse upon the chemical processes which take place among their constituents in accordance with general chemical laws, and that these again may be traced to the action of catalytic substances. If the rapidity of reaction in a muscle is hastened which may be regulated from a central organ, this muscle will accomplish a corresponding amount of work. When, however, the supply of energy is exhausted, the influence of a catalysator cannot force it to any further manifestations. The same is true for all other activities of organisms.

I cannot assume to have made clear the mystery of life in the previous pages, but I believe that I have solved a more apparent problem, namely, to show that the science which is seemingly abstract and foreign to actual life, and which has developed during the last years under the name of physical chemistry, is a science of the highest real importance. If it will be possible for this science to throw light upon that most difficult of all the problems of nature, the mystery of life, how much easier will it be to explain by means of the new principles the by far much easier problems of technical chemistry which have not been solved so far. It is quite natural and self-implied, but we must nevertheless repeat again and again that—"The more perfect the theoretical evolution of the sciences becomes, the greater will be the scope of their explanations and at the same time the greater their practical importance."

THE FUNDAMENTS OF CHEMICAL THEORY.¹

BY J. E. TREVOR.

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The Development of Science.—The general course of development of the sciences which deal with natural phenomena follows,

¹[This paper was delivered in the form of a lecture at Cornell University. It has been substituted by Prof. Trevor for his paper before the World's Congress of Chemists, read August 26th, entitled "The Energy Theory of Chemistry: Comment upon Ostwald's paper on Chemical Energy."—EDITOR.]