PHYSICAL CHEMISTRY

Ostwald on Chemical Energy

"A Classic of Science"

Wilhelm Ostwald, Who Died in Germany April 4, Pioneered In Applying the Laws of Energy to Problems of Chemistry

ON CHEMICAL ENERGY. By Dr. W. Ostwald. Read before the World's Congress of Chemists, August 26, 1893. Published in the Journal of the American Chemical Society, vol. XV., August, 1893.

THE knowledge of the laws of chemical energy is not only scientifically but 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.

Factors of Chemical Energy . . .

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 not heat can be transmitted from one body to another. Our answer is that this question has not been completely solved, but that from 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 kinds 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 portion 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.

Equally Meaningless . . .

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,

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In addition to his work on the laws of physical chemistry, he invented a process of oxidizing ammonia which is fundamental to one of the methods of obtaining nitrogen from the atmosphere.

they do not thus affect the equilibrium. The thermal theory of affinity, which is even today 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 quantities 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 arisese 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 inter-action, 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.

Equalization is Prevented . . .

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 suface. 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 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 effectum," 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.

Science News Letter, April 30, 1932

ARCHAEOLOGY

Shakespeare's Knowledge Defended by Archaeologist

NEW TRIBUTE to Shakespeare as a historian is paid by an archaeologist of the British Museum, Christopher Hawkes, who is in charge of excavations at the city of Shakespeare's King Cymbeline.

Ruins on the edge of the modern city of Colchester are identified as the capital of the British King Cymbeline. The reign of Cymbeline lasted 40 years while Roman Emperors laid their plans to conquer the barbarian Britons.

"The more we come to know of Britain on the eve of the Roman conquest, the clearer it becomes that Shakespeare, searching among the chronicler's welter of fact and fiction for the outlines of the play he was conceiving, brought out the main features of it with the instinct of genius for truth," declares Mr. Hawkes in a report of the excavations at Colchester, in *Art and Archaeology*.

Latest excavations have unearthed some of the homes in Cymbeline's capital city. The excavations were undertaken, speedily, when the site was threatened by road building and real estate developments. Some years ago, archaeologists had dug into a mound on the land and discovered a Celtic burial so magnificent that it may be that of King Cymbeline himself. The palace of the king is still being sought. Cymbeline's mint, which issued coinage of great historic interest, is another future discovery.

Cymbeline's capital, the metropolis of southeastern Britain, covered a huge area, Mr. Hawkes explains. Excavations reveal the foundations of homes made of timber framework with walls of wattle and daub. Houses and town changed somewhat during Cymbeline's reign, and Mr. Hawkes suggests that Cymbeline may have made an early effort at town planning in his capital.

Showing primitive features of the Celtic capital, Mr. Hawkes tells of a great ditch which was dug with shovels made of the blade bones of oxen.

"Thirty or forty of these crude tools—the type was in use as long ago as the Stone Age—were found discarded in a heap on the gravel bottom," he writes.

The huddled mass of primitive dwellings may give place to more ambitious structures, Mr. Hawkes believes, when the excavations approach nearer the heart of the city. Here the king himself must have resided. In this section, the archaeologist also is prepared to find tools more serviceable than bone shovels. The town was far from being wholly primitive, he explains. Among the objects already discovered are pottery of graceful profile and metal work of amazingly high standard.

Cymbeline's capital is a site of unparalleled importance in British archaeology, Mr. Hawkes states. Not only is the native civilization of Cymbeline's subjects shown at its highest, but the archaeologist can study what happened when Roman civilization met British. The city was not abandoned for seven years after the Roman legions captured it in 43 A. D.

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