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,

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[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.]

in its beginnings, through a descriptive stage. The bare facts, the materials with which a science has to deal, are laboriously collected and, in so far as is possible, they are systematically arranged. Not until this patient collection of empirical facts has gathered together a comparatively extended mass of more or less thoroughly classified material does it become possible, with this material as a basis, to begin a study of the causal relations between the different classes of phenomena coming in question. In entering upon this second stage of development the Descriptive Science becomes a Rational Science, the discovery of *facts* gives place to the discovery of *relations*, isolated phenomena appear as parts of the coherent whole, and a completed network of its exact relations makes this science a known thing, brings its phenomena under the absolute control of the all-ruling principles of mathematics. A recognition of the connection between phenomena, and not the observation and description of individual facts, is the final aim of science.

Botany, for example, is in its development just emerging from the descriptive stage. The seeking and classifying of kinds of plants has furnished a broad basis of known fact, and men seek now to know the cause of the flow of sap in trees, to follow the transformations in the growing plant and fruit, to understand the chemistry and the mechanics of plant life. The science of physics has made a considerable progress into the rational stage, its investigations are mainly conducted under the guidance of known relations between the phenomena of heat and work, of work and electricity, of electricity and magnetism, and the like. Its world of phenomena is coming more and more under the unerring control of mathematics. But the most complete, the classical instance of this advanced stage of development is offered by solar astromony the relations between its elements being known with such exactness that the minute details of its stupendous phenomena are foretold by computers with nothing less than an astounding accuracy. The command of man over the phenomena of the heavens is one of the most complete as well as one of the grandest achievements of the human intellect.

Our science of chemistry is in its nature like these others; its progress has hitherto been in the main that of a descriptive science and a fearful mass of necessary chemical material has been accumulated in the course of it. And now its rapid and brilliant rationalization is attracting the attention of the scientific world.

The desultory alchemy of the middle ages had become scientific investigation when Priestley and Scheele discovered that there was such a thing as oxygen, and Lavoisier showed that matter is not to be annihilated. From this time the increase in our knowledge of descriptive chemistry has been rapid. Valuable principles of classification were furnished by the atomic hypothesis of Dalton and the molecular hypothesis of Avogadro, both appearing early in the century, and they have been employed in a systematic investigation of the properties and reactions of inorganic compounds, which has ever since been carried forward with vigor, to no slight extent under the brilliant leadership of the Swede, Berzelius. This work has been accompanied in later years by an extended study of the materials of organic chemistry, by a seeking and finding of the wonderfully simple and beautiful relations existing between the different classes of the compounds of carbon. Widespread enthusiasm and devotion in this work was kindled over a half century ago in Germany by Liebig, whose gentle memory comes down to us through the science as a charm and an inspiration. This work has enriched science with a wealth of working material, has chased back into the darkness much of the mystery of ordinary life and, in supplying the most useful of our drugs and dyes, has added greatly to the material wealth of the world.

The experimental development of descriptive chemistry, both inorganic and organic, which has made up the great bulk of chemical investigation during the present century, was necessary work and it has been rich in achievement. Yet in it and through it all there is something lacking, something which must eventually claim the supreme interest. From a descriptive science we must pass to a rational science, from the *what* of chemical phenomena we must pass to the *how* and the *why*. The observation and description of individual facts must make way for a recognition of the connection of phenomena; the primitive interest in the discovery of a new compound must vanish to make way for a greater interest in the discovery of relations, of generalizations.

The Rationalization of Chemistry.—The latest phase of chemical science studies chemical processes as such, strives to rationalize chemistry, aims to make it a science of exact relations between classes of phenomena. And since chemical phenomena involve heat and electricity, density, temperature and the like, things which are specifically treated in the science of physics, the new trend of chemical work has come to be termed the physical chemistry. It is this to which we are now to turn our attention.

To say that the sciences of physics, of mechanics, and of astronomy are more highly developed, are more completely understood than are their sister sciences, is to say that they have been brought more completely under the control of mathematics. The more complete this rule over their phenomena becomes, the more perfect becomes their development as branches of human knowledge. In this respect, as the highest of them all, stands geometry. For twenty-two centuries now the geometry of Euclid has been the encouragement and guide of that scientific progress which is one thing with the advance of man from a worse to a better state; and it is even unto this day the highest aim of every scientific student to bring his science into such a state of perfection as that which has been attained by geometry. The deepest scientific insight shines through the words of the Pythagoreans, who called mathematics the Purifier of the Reasonable Soul, and it is the desire of each one of us to bring that branch of physical science in which he is more immediately interested into such a state that it too shall be, in a similar sense, a purifier of the reasonable soul.

To develop, now, a scheme which shall place chemistry upon the basis of an exact science we must clearly comprehend with *what* we are dealing, what the subject matter of our work really is. It may be conclusively shown that the actuality with which we have to do is *energy;* from a physical point of view the manifestations of energy constitute phenomena. From the laws of energy is derivable a coherent system of natural science, made up entirely of exact relations between the various energy phenomena coming in question. This enables us to construct a wide-reaching and coherent theory of the changes of state, a chemical theory characterized by the stately march and all the relentless rigor of a strictly mathematical science.

And in this matter we must stand for conservatism. We must not countenance the wild hypotheses which have so often disfigured chemistry. Facts are the things with which we must deal, and we must deal with them rigorously. Hypotheses are are to be used with the utmost caution and discarded whenever possible. In so doing we shall find that our science will become a purer one and that we shall be far less likely to fetter and blind ourselves by *belief* in hypotheses, which in themselves may be attractive but which are essentially unprovable and therefore unworthy of belief.

Energy.—Experience has made clear that heat, work, electricity and the like are mutually convertible; they are hence the same kind of thing and this kind of thing has received the general name Energy. Besides space and time[1] this is our most general conception, for these three quantities are the only ones which are common to all branches of physical science.

It has been more or less clearly understood ever since the time of Berkeley, ever since 1710, that the world which we perceive *is* our perceptions, is not something *inferred* from our perceptions. But the only things of which we can take direct cognizance are the manifestations of energy. We cannot see material objects directly with our eyes, what we actually do see is a picture upon the retina, produced by the radiant energy entering the eye—and in all probability the impression upon the optic nerves is more immediately due to the energy of the chemical changes taking place in the retina; the eye is an organ for radiant energy. The ear, likewise, reacts upon the mechanical energy of a vibrating gas, and the organs of touch react upon those forms of mechanical energy involving pressure or force as a factor. The only thing, then, of which we can take *direct cognizance* is energy, in one form or another. Energy, furthermore, despite its transformations, never increases nor decreases in amount; for example, it is impossible to create work out of noth-

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[1] It may even be maintained that time is a derived conception, but it is difficult to see how we might dispense with it as an independent variable in treating natural phenomena.

ing and thus construct a machine which shall furnish power forever; and in any transformation of energy none is ever lost. This fact, which is based upon the widest experience of exact science, is expressed by saying that the various energy forms are mutually convertible, or, better, that the total energy of the accessible universe is constant. That which *subsists* is in its very nature a *substance*, and so, when we bear in mind that energy is the only thing of which we can directly know, we are forced to the most important conclusion that:

Energy is the only *substance* of which we *know*.

Briefly the argument is this:—

That which we perceive *is* our perceptions;

These perceptions are manifestations of energy;

Hence: That which we perceive is energy manifestations, the only thing of which we directly know is energy. Furthermore energy subsists, and is hence the only substance of which we know.

We can have no knowledge of an objective reality of matter, whether the term corresponds to anything actual we do not know and ought not to care. The notion of objective reality is inferred from the evidence of our senses; it is a derived idea, an hypothesis. The only thing of which we really know is energy, which is therefore the prime subject of human interest.

This result establishes the fundamental character of the energy idea. Any natural process is a change of one or more energy forms; the transformations of energy constitute phenomena; science, the study of phenomena, is concerned with energy alone, and its laws furnish the basis of physical theory. The rational theory of phenomena, in chemistry as well as elsewhere, is an energy theory, and its fundamental principle is the great generalization:

The Energy of the Universe is Constant.

This principle is known as the First Law of Energetics.

Energetics.—The different sciences would be wholly distinct were the several energy forms which they treat not mutually convertible. This convertibility, and this alone, unites them into a general Science of Energetics. By using space, energy and time as the units common to them all there are obtained throughout measurable relations between them. The subjects of chemistry, electricity, heat, and work are thus brought together, and the respective transformations of the energies involved furnish the subject matter for the sciences of electro-chemistry, thermo-chemistry, electro-dynamics, thermo-dynamics, and mechanics.

It is especially to be emphasized that the different energy forms are of wholly independent character, no one of them is energy *par excellence*. There is no reason for assigning to the energy of motion an especially prominent character. Neither electricity nor heat is to be treated as kinetic energy, any more than kinetic energy is to be considered as electricity. And, furthermore, no energy form may be singled out as a "potential energy." The energy of distance is no less an energy than is that of motion into which it is transformable, and each energy is "potential" with respect to every other, in that it may be transformed into that other.

The Factors of Energy.—The possibility of developing a comprehensive and exhaustive science of Energetics depends upon the fact that the analytical expression for each energy form is resolvable into a product of two factors[1], one of which has the character of an intensity of the energy form in question, and the other that of a capacity for it. They are best known as the intensity and capacity factors. The intensity factor determines whether its energy may or may not be at rest, having, by definition, the same value for two energy quantities which do not influence each other. Such is, *e. g.*, the temperature factor of heat energy; a large mass of iron and a small one may contain very different amounts of heat but no conduction will take place from one to the other if their temperatures be the same. Examples of this resolution into factors are:

		Capacity.	Intensity.	Formula.
Mechanical Energies.	Distance energy	= distance	× force	$s \cdot f$
	Surface energy	= surface	× tension	$O \cdot \gamma$
	Volume energy	= volume	× pressure	$v \cdot p$
	Motion energy	= mass	× velocity square	$\frac{1}{2} m \cdot V^2$
Other Energies.	Electricity	= quantity	× potential	$\varepsilon \cdot \pi$
	Heat	$= \left(\frac{Q}{T}\right)$ or $\frac{dQ}{dT}$	× temperature	$\frac{Q}{T} \cdot T$
	Magnetism	= mag. quan.	× mag. potential	$e \cdot \Pi$

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[1] Helmholtz, 1887; also J. W. Gibbs, 1876.

The recognition of the impossibility of an unlimited transformation of one energy form into another without intensity differences, as in obtaining work from a quantity of heat of uniform temperature, or from electricity of uniform potential, constitutes the so-called Second Law of Energetics:

Unlimited conversion of an energy, without intensity differences, is impossible.

This principle[1] is as entirely a result of experience as is the first law of energetics, formulating the observed impossibility of creating energy from nothing. They are the most fundamental laws governing natural phenomena; taken together they constitute the farthest reach of science.

Energy Equilibria.—The condition for the equilibrium of a single energy form, that its intensity shall be uniform throughout, is in its application very familiar. The heat in a bar of iron which is hot at one end will be transferred by conduction until the temperature differences shall have become equalized; a mass of gas must have uniform pressure throughout (the effect of gravitational energy supposed eliminated); electricity will not pass from one electrically charged body to another when both quantities of electricity have the same potential; two moving masses will not influence each other's motion if their velocities be the same (they must correspondingly have the same direction of motion, for the definition of a velocity includes a direction). The same rule applies to the other energy forms.

But that feature of the energy theory which is of the most especial interest at the present time is its treatment of the equilibria between several energy forms which oppose one another in the same system. Such an equilibrium is said to obtain when no transformation of one energy form into another takes place. The equilibrium eventually reached may be disturbed by a change of the intensity factor of any one of the energies involved, this causing an opposed change of the correlative energy forms. At equilibrium an infinitesimal change (virtual change) of one of the energies must be exactly balanced by the resulting virtual changes of the others.

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[1] Generalized by Ostwald, 1892.

For the sake of illustration let us consider a billiard ball suspended by an elastic cord. When the system comes to rest an equilibrium is maintained between the gravitational energy, tending to pull the ball downward, and the elastic energy of the cord, tending to pull it upward. In a virtual displacement of this equilibrium, *e. g.*, pulling the ball an infinitely small distance downward, the gravitational energy expended is exactly equal to the elastic energy gained; their *algebraic* sum is zero. This is required by the first energy law. Suppose, however, the ball to be drawn downward a foot or two and then released. In its new position the two energies are not in equilibrium and, in the initial infinitesimal displacement as the ball rises, the expenditure of elastic energy exceeds the corresponding gain of gravitational energy. Only when the oscillations have ceased do the virtual changes balance each other.

The necessary and sufficient *condition of equilibrium* then, for any material system whatsoever, is

The algebraic sum of the energy changes involved in a virtual displacement of the equilibrium must equal zero.[1]

If we represent energy, capacity and intensity by E, C, and I respectively, this condition is expressed analytically by

$$\sum \delta E = 0 \quad \text{or} \quad \sum C dI = 0,$$

the summation being taken over all the correlated energies of the system. It is known as the Principle of Virtual Energies and it represents the theory of all equilibria whatever, whether they be those of statics, of thermodynamics, of chemistry, or of any other branch of general Energetics.

A special case of this is the Principle of Virtual Work in statics, where the equilibria studied are between mechanical energies capable of doing work, W. When the work furnished by one in a virtual displacement is exactly counterbalanced by that of the others the mechanical system in question is in equilibrium, and the condition of equilibrium is

$$\sum \delta W = 0,$$

the same equation as before. Upon this relation, introduced into mechanics by Bernouilli and Lagrange, the science of statics is based.

Force.—It may be well to insist at this point upon the distinction between force and work or energy, a distinction not always kept clear in popular speech. Reference to the table of energies already given will show that a *force* is an intensity and must move a body through a *distance* in order to do *work* upon it; the work done is the product of force and distance. The force meant acts in the direction in which the body moves; if a force f have a different direction the *acting force* is its component lying in the direction of motion, or $f \cos \theta$ when θ is the angle made by the direction of the force with the direction of motion. Opposing forces may prevent motion in which case the force is balanced and does no work. The intensity factors of the space energies, force, surface tension, and pressure, are the quotients of an energy by a distance, a surface, and a volume respectively, and they are the intensities acting through a distance, a surface, and a volume respectively. They are the same kind of quantity as is a temperature or an electrical potential. *Power* is often used as synonomous with *work*, but *force* can never be.

The term *work* is sometimes used to designate in general the energy forms which are convertible without limit, and *force* to designate their intensity factors, but in the interest of a clear terminology this usage would better be dropped.

Units.—In dealing with energy quantities it is necessary to have an established unit. The one generally accepted as a basis of reference is the *erg*, the unit of work. It is the product of unit force into unit distance, the product into one centimeter of the force giving to one gram of mass an acceleration of one centimeter per second in a second:

$$\begin{array}{cccc} \text{Energy.} & & \text{Force.} & & \text{Distance.} \\ \text{Erg} & = & g \cdot \frac{\text{cm}}{\text{sec}} \cdot \frac{1}{\text{sec}} & \times & \frac{\text{cm}}{1} \end{array}$$

This erg is then $g \cdot \left(\frac{\text{cm}}{\text{sec}}\right)^2$, or mv^2, which is *twice* the motion energy (kinetic energy) contained in unit mass moving at unit velocity.

Nearly all the other energy units in common use are reached by the following proportionality factors:

The unit of electrical energy, of electricity, has been arbitrarily set equivalent to ten million ergs; *i. e.*

$$\text{volt-coulomb} = \frac{1}{10{,}000{,}000} \times \text{ergs}. \qquad (1)$$

The gram-centimeter, being the product into one centimeter of the gram of weight, the force giving to a gram of mass an acceleration of 980 centimeters per second in a second ($980 \frac{\text{cm}}{\text{sec}} \cdot \frac{1}{\text{sec}}$), is 980 times greater than the erg. So

$$\text{ergs} = 980 \times \text{gram-centimeters}. \qquad (2)$$

Careful determination of the proportionality factor converting work into heat units, the mechanical equivalent of heat, has given

$$\text{gram-centimeters} = 42{,}750 \text{ calories}. \qquad (3)$$

Outline of Chemical Theory.—The energy theory may be applied most interestingly in organizing into a concrete whole the exact relations of a rational chemical theory. A comprehensive treatment of the problems of the subject includes in the first place the immediate applications of the conservation law. Further than this, the energy equilibria with which the science of chemistry is concerned may be treated, for the purposes of classification, under three heads: First, those represented by differential equations, which are integrable because a known relation exists between the factors of the energy involved (as is the case with volume energy); second, non-integrable differential equations, furnishing a relation between the respective intensity factors; and, third, differential equations involving, in addition to the opposed energies of reacting substances, the influence of extraneous energy forms. These three grand divisions of the subject are then:

I. Volume energy integrals,
II. Simple differential equations,
III. Reaction equilibria,

and the three corresponding types of equilibrium equation are:

$$\int dW = \int C \cdot dI \qquad (1)$$

$$C' \cdot dI' = C \cdot dI \qquad (2)$$

$$\Sigma C' \cdot dI' = C \cdot dI \qquad (3)$$

where W, C, and I represent, respectively, work and the capacity and intensity factors of energy forms. The general form of the equations remains $\Sigma\delta E = 0$; in equation (3) the summation is taken over the reacting substances on the one hand and the reaction products on the other, the energy of the one decreasing and that of the other increasing in a virtual displacement of the equilibrium of a reversible reaction. The consideration, in a general way, of the results to which these equations lead will furnish at once a complete outline of our system of Chemical Theory. It will be well to glance over the outline before taking up the work in detail, in order to gain an idea of the coherence of the theory.

I. There may be calculated[1], by means of equation (1), the amount of work gained in the expansion of a dissolved substance or of a gas from a given pressure P to a lesser one p. This will be

$$\int dW = -\int_{P}^{p} vdP$$

$$= -RT\int_{P}^{p} \frac{dP}{P}$$

$$W = RT\log\frac{P}{p} \qquad (1, a)$$

This expression connects the amount of work required to concentrate a solution, with the resulting change of its vapor pressure. Furthermore, the electromotive activity of the various types of electrical cells may be shown to depend upon a transformation of volume energy into electricity, and since this equation determines the change of volume energy it yields the theory of the cell[2]. The relation is a fundamental one in the Theory of Solutions and in Electrochemistry.

II. By a general application of equation (2) there may be expressed the mutual dependence of

Electricity,
Surface energy,
Heat,
Volume energy.

[1] Van't Hoff, 1887.

[2] Nernst, 1889.

We will arrange the resulting equations, for subsequent reference.

For the equilibrium between electricity and surface energy:

$$O\,d\gamma = -\epsilon\,d\pi$$

$$\frac{d\gamma}{d\pi} = -\frac{\epsilon}{O} \qquad (2,\ a)$$

This expresses the relation between surface tension and electromotive force.

That between surface energy and heat is

$$\frac{q}{T}\cdot dT = O\cdot d\gamma$$

$$\frac{d\gamma}{dT} = \frac{q}{T\cdot O} \qquad (2,\ b)$$

an expression for the temperature coefficient of surface tension[1].

For the extremely important equilibrium between electricity and heat:

$$\epsilon\,d\pi = \frac{q}{T}\cdot dT$$

$$\frac{d\pi}{dT} = \frac{q}{T\cdot\epsilon} \qquad (2,\ c)$$

This famous equation[1] introduces the element of temperature into the theory of electrochemistry.

Another relation of great importance[1] is obtained from the equilibrium between heat and volume energy. [(v^1-v)—increase of molecular volume].

$$\frac{q}{T}\cdot dT = (v'-v)dp$$

$$\frac{dp}{dt} = \frac{q}{T(v'-v)} \qquad (2,\ d)$$

It comprehends the extremely extended theory of such changes of state as are involved in the processes of vaporization, sublimation, dissolving, melting and the transformation of allotropic forms, and is in consequence one of the most important relations in chemical theory.

All these special cases of equation (2) have the form

$$C'\cdot dI' = C\cdot dI$$

or

$$\frac{dI^1}{dI} = \frac{C}{C'}$$

[1] First derived in this way by Ostwald, 1892.

and they express the details of what is technically known as the Theory of "Complete" Equilibria.

III. The final division of this energy system, that dominated by equation (3), is concerned with the influence of extraneous energy forms upon the purely chemical volume energy equilibria of reversible reactions. When a system of reacting substances is in equilibrium, the total virtual change Σvdp of the volume energy of the reaction products is balanced by that ΣVdP of the original substances. p and v represent throughout the partial pressures and molecular volumes of the substances in question, and when the system is left to itself our fundamental equation (3) assumes the form

$$\Sigma vdp - \Sigma VdP = 0 .$$

With the aid of the general "equation of condition" of dilute matter, $pv = nRt$, whence $p = nRTv^{-1}$ and $dp = -nRT\frac{dv}{v^2}$, we can eliminate the pressure factor, obtaining

$$-RT(n\Sigma \, d \log v - N\Sigma \, d \log V) = 0,$$

whence, at constant temperature, replacing the molecular volume by its reciprocal the molecular concentration,

$$\Sigma \, d \log c^n = \Sigma \, d \log C^N.$$

The integral of this equation furnishes the concentration relations for a chemical equilibrium at constant temperature,

$$\Sigma \log c^n + \log k' = \Sigma \log C^N + \log k$$

i.e.

$$\frac{c_1^{n_1} \cdot c_2^{n_2} \cdot \cdot \cdot}{C_1^{N_1} \cdot C_2^{N_2} \cdot \cdot \cdot} = \frac{k}{k^1} = K$$

or

$$C_1^{n_1} \cdot C_2^{n_2} \cdot \cdot \cdot = K \cdot C_1^{N_1} \cdot C_2^{N_2} \ldots$$

which states the effect of each reacting substance to be proportional to its concentration. This is the great Law of Mass Action[1], or the Reaction Isotherm, expressing the conditions of chemical equilibrium at constant temperature. Its application has brought to light a system of experimentally confirmed quantitative relations more extended than has resulted from any other law of theoretical chemistry.

If pressure be applied to a system of reacting substances work is done upon it and a deformation of its chemical equilibrium

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[1] Guldberg and Waage, 1867.

results. The fundamental equation (3) represents this equilibrium between volume energy and work in the form

$$-\Delta v \cdot dp - (\Sigma\, v dp - \Sigma\, V dP) = 0\,,$$

where $-\Delta v$ is the volume decrease accompanying the reaction in question, and is a function of the specific volumes of the substances. The bracketed expression we have already found to be RTdlogK, K being at a given temperature the constant *characterizing* the equilibrium. So we have

$$\frac{d\ \log k}{d\ p} = \frac{-\Delta v}{RT} \qquad (3.\ b)$$

expressing the effect of pressure upon a chemical equilibrium[1].

One more case remains under this head, that concerned with the influence of temperature upon a movable equilibrium. On adding the heat quantity Q to our chemical system, the resulting balance between it and the volume energy change of the displaced chemical equilibrium is, by the governing equation (3),

$$\frac{Q}{T} \cdot dT - (\Sigma\, v \cdot dp - \Sigma\, V\, dP) = 0$$

$$\frac{Q}{T} \cdot dT - RT\, d\log K = 0$$

$$\frac{d\ \log K}{d\ T} = \frac{Q}{RT^2} \qquad (3, c)$$

This equation[2] connects the influence of temperature with the heat of reaction. Its applications to chemical phenomena have been extended and are brilliant in the extreme.

This general arrangement of the elements of chemical theory, which the energy idea leads us to adopt, takes up successively:

The Conservation of Energy,
The Theory of Solutions,
Electrochemistry,
"Complete Equilibria,"
Reaction Equilibria (including Reaction Velocities),

and includes under these heads a wealth of material really quite unanticipated by those who have not followed the results of recent research. A logical sequence has hitherto been markedly absent in what has passed for Theoretical Chemistry, and so the possibility of this coherent arrangement is a pleasing indication

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[1] Planck, 1887.

[2] Van't Hoff.

that this branch of knowledge is rapidly becoming an exact science.

Free Energy.—Chemical action usually effects changes in the state of aggregation or in the density of the substances concerned and so produces work (or other energy forms, *e. g.* electricity, entirely convertible into work) as well as heat. A distinction must therefore be made between that part of the available energy capable of direct conversion into work and that part producible only as heat. The first is appropriately termed the Free Energy, the second the Bound Energy of the system.

A spontaneously occurring natural process is one taking up no energy other than heat from the surrounding medium. Every such process may be made to yield a definite maximum amount of work. For, if its available work were negative it would have to take place without absorption of energy, and on being reversed by the addition of heat would transform this heat into work. The operation might be indefinitely repeated, continually converting constant-temperature heat into work, a result in conflict with the second energy law.

Since every spontaneous process must yield work, a system incapable of yielding work (one whose free energy has minimum value) is incapable of spontaneous change, is in stable equilibrium. So this condition of equilibrium[1], deduced from the second energy law, is

The Decrease of Free Energy must be a maximum.

Processes originating spontaneously and proceeding at constant temperature can take place only in such direction as to cause a diminution of free energy, a production of energy forms convertible without limit ("work"). It is therefore the decrease of free energy, and not the heat developed, which determines the direction in which chemical affinities can become active, *and which is the measure of the work-value of the chemical forces.*

Of all possible chemical changes in a material system the one involving the greatest decrease of its free energy (the maximum available work) will occur. Neither the reaction involving maximum production of heat, nor that of maximum thermal tonality

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[1] Helmholtz, 1882.

(sum of heat and work produced) will necessarily take place; there are in fact many spontaneously occurring chemical processes which absorb heat. The decrease of free energy in any given reaction is found by determining the work to be gained when the transformation is made reversible and isothermal.

The Equations of Thermodynamics.—The science of thermodynamics considers the mutual transformations of heat and work. An equilibrium between them must, in accordance with the general principle of virtual energies, be expressed by the equation

$$\frac{Q}{T} \cdot dT = dW \qquad (\alpha)$$

These energy differentials are equal. On changing by dT the temperature of the total heat quantity Q the fraction $\frac{dT}{T}$ of it may be transformed into work[1]. This work quantity dW is the maximum available, since no heat is supposed lost. The two energies being considered exactly in balance the energy displacement in question is a reversible one.

In any such change of a material system the decrease of its total energy is, according to the first energy law, the sum of the heat and work given out, so here (reckoning, as customary, positive Q as heat *added*)

$$\overset{\substack{\text{Decrease of}\\ \text{total energy.}\\ \text{(Thermal Tonality)}}}{U} = \overset{\substack{\text{Max. work}\\ \text{given out.}}}{W} + \overset{\substack{\text{Heat}\\ \text{given out.}}}{(-Q)}.$$

Substituting in (α) the value of Q thus given, we obtain

$$W - U = T\frac{dw}{dT} \qquad (\beta)$$

an equation of great importance in chemical thermodynamics, in that it connects the decrease of the free energy (maximum available work) of a system with its total energy change.[2]

The Energy Method.—A prominent and unfortunate phase of the history of the energy doctrine deserves especial mention in this place. In the years immediately following 1870 a singular idea worked its way into very general acceptance in the scientific world. The popular hypothesis of a molecular constitution of

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[1] Clausius.

[2] Helmholtz, 1882.

matter led to the conception of heat as the kinetic energy of moving molecules, and this ingenious thought gave rise to the idea that all energy forms are manifestations of kinetic energy, kinetic energy being regarded thereupon as *energy itself*. In consequence of this, each department of exact science came to be looked upon as a branch of mechanics.

This kineticism took the scientific world by storm and, by reason of the actual impossibility of adequately treating the phenomena of electricity, heat, etc., as kinetic energies, it has exerted a seriously hemming influence upon the development of rational ideas in physics and chemistry for a good twenty years. And it is lamentably true that its evil effects have not, even yet, died wholly away from among us. Nevertheless, in this day of progress it scarcely needs to be emphasized that the chief advances made in the theory of phenomena during the last half century have been made independently of this vicious assumption of discrete molecules. Physical theory and not mechanical hypothesis has been the guiding star.

The object of science is to find and classify the relations between phenomena, and to do this in such wise that their comprehension shall be unfettered by auxiliary assumptions. It cannot be too emphatically insisted upon that a distinct line of demarcation must be maintained between that which we *know* and that which is of essentially hypothetical nature. Neglect of this elemental necessity has made chemistry a strange mixture of empirical fact and wierd hypothesis. It is a necessary principle of scientific work that only a minimum employment of hypotheses is admissible—and herein lies an especially important feature of the theory of energy. In disregarding improved assumptions, such as, for example, the mechanical hypothesis of a molecular structure of matter, it deals directly with known facts and the results which it reaches are of necessity actual relations between measurable quantities. Among them are the remarkable relations which form the framework of thermodynamics, of electrochemistry, of chemical equilibrium, of the solution theory. The mutual dependence of vapor pressure and heat of vaporization, of electromotive force and heat of reaction, of reaction velocity and temperature, of the freezing point of a solution and the heat of fusion of its solvent are among the most brilliant results of exact science.

This energy method, with its fruitful principle of virtual changes, is rearing the framework of a coherent theory of chemical processes, and it is through this development of a science of exact relations that we must hope to be relieved from the thralldom of unproven, frequently unprovable and always unnecessary mechanical hypotheses. Through this appears for the first time in the history of chemistry a prospect of dealing directly with facts as such, *and only with facts.*

WORK OF THE COMMITTEES ON THE "INTERNATIONAL STANDARDS FOR THE ANALYSIS OF IRON AND STEEL."[1]

BY JOHN W. LANGLEY, CLEVELAND, OHIO.

THE history of the organization and work of these committees up to the present year is briefly as follows:

In the summer of 1888 it was the fortune of the present writer to present the subject of the desirability of establishing a set of samples of steel which should be analyzed with extreme care, in order that they might become standards to which scientific and commercial analyses of iron and steel could be subsequently referred; also, that greater uniformity in the results of analyses might be brought about, since these standards would bear towards analytical methods somewhat the position which the original units of weight and length, the gram and meter, or the pound and yard, do to the mechanical arts.

The plan met with hearty co-operation, with the result that committees were appointed in Sweden, Germany, France, England, and America to receive the material and see that the necessary analyses were executed.

These committees were constituted as follows:

In Sweden, Prof. Richard Åkerman; in Germany, by the authority of the minister of public works, the execution of the analyses has been entrusted to the Konigliche Chemisch Technischen Versuchungsanstalt, in Berlin; in France, Mons. Ferd.

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[1] Read before the World's Congress of Chemists, August 22, 1893.