in America and then in the Tertiaries of India by Barnum Brown, has brought us to the point where we can demonstrate beyond refutation the absolute origins and continuous developments of new characters. Such observations were undreamt of by Buffon, by Lamarck or by Darwin.

THE VALUE OF THE DETERMINATION OF FREE ENERGY CHANGE FOR ORGANIC REACTIONS[1]

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IT is only within recent years that the importance of free energy determinations of organic compounds has been realized.[2]

The study of any chemical reaction resolves itself primarily into two fundamental questions: first, how nearly to completion does it go under various conditions, and second, how rapidly does it approach this limit in the presence of various catalysts. The answers to these two quesitons are to be found by means of free energy values.

The well-known formula $\Delta F.^{\circ} = -RT \ln K$ gives the relation between the equilibrium constant (K) and the change of free energy for the particular reaction under certain definite conditions. The value $\Delta F.^{\circ}$ is of more general significance than the value K and that is why this particular physical constant is usually sought. The factor R in the equation is the gas constant and T the absolute temperature

It is not necessary to determine the equilibrium constant directly under certain definite conditions in order to find $\Delta F.^{\circ}$ It is usually quite feasible to perform operations with various chemical equations in free energy terms, so that a numerical value of $\Delta F.^{\circ}$ is obtained.

It is sometimes quite expedient to use another well-known formula for the determination of $\Delta F.^{\circ}$ This is: $\Delta F^{\circ} = \Delta H - T \Delta S$.[3] In this case use is not made of the gas constant R and the equilibrium constant K, but the heat term ΔH and a change in entropy ΔS. The term ΔH is a quantitative value of the heat given off or taken up during the reaction. This heat term is usually measured while the system is at constant pressure. The reaction, however, may be from one physical state to another and not necessarily chemical.

The change in entropy ΔS is made up of a series of ΔS's from the absolute zero up to the temperature existing at equilibrium for each constituent. For example, a solid in heating up from absolute zero to some higher temperature acquires an entropy value equal to the integral of the function $\frac{Cp}{T}$ over the temperature range, where Cp is the specific heat at constant pressure. When the solid changes from the solid state to liquid state the heat of fusion divided by the absolute temperature of melting will constitute the entropy change for that change in state. From then on the specific heat of the liquid is the determining factor until the boiling point of the liquid is reached and then the latent heat of evaporation must be taken into consideration. In this way it is possible to determine from specific heats and latent heat data the S for any particular chemical compound at any definite state and condition. The ΔS for a reaction is calculated from the S values of individual compounds in exactly the same manner as ΔF. In other words, the ΔS value for the reaction is calculated by subtracting the sum of the S values of the reactants from the sum of the S values of the products.

It should be possible theoretically to measure the equilibrium constant of any chemical reaction and from this to obtain easily a $\Delta F.^{\circ}$ value. We would then have an answer to the question, what are the equilibrium conditions of the reaction, and thereby be able to determine whether or not the reaction was suitable for any particular purpose. Unfortunately, there are a great many practical difficulties that arise, especially with organic reactions.

Reactions studied by the equilibrium method have been those that, first, gave a measurable concentration of product and left a measurable concentration of reactant; second, involved relatively simple methods of analysis; third, had no complicating side reactions. With the exception of ionic reactions, as great a proportion of inorganic as organic reactions satisfy the first requirement—although that proportion is very small indeed. Analytical methods are much better developed for inorganic than for organic compounds. As for side reactions, the distinctive ability of carbon to combine with itself tends to cause much greater

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[1] Read before the Natural Academy of Sciences, University of Michigan, on November 14, 1932.

[2] See American Chemical Society Monograph No. 60, entitled "Free Energies of Some Organic Compounds," by Parks and Huffman, recently published by the Chemical Catalog Company in New York.

[3] $\Delta F = \Delta H - T \Delta S$ under any conditions. $\Delta F = \Delta F^{\circ}$ when all reactants and products are under one atmosphere pressure.

difficulty with organic compounds. The reactions studied so far, then, have been largely inorganic.

It is well known that the equilibrium constant is determined by the ratio of the activities, and the activities in turn bear definite relations to concentrations of the substances present.

It can, therefore, easily be seen why it is difficult to obtain an accurate determination of the equilibrium constant directly whenever the equilibrium is such that some of these activities and the corresponding concentrations become extremely small. Such a condition quite often occurs when organic chemical reactions are considered.

Organic chemical reactions, on the other hand, are attracting considerably more interest in the industrial world to-day than do the inorganic chemical reactions, because our industries are developing much more along organic lines than along inorganic lines. This means, however, that the determination of equilibrium constants or better yet, free energy values, is becoming more and more important from the standpoint of the applied scientist.

It is interesting to note that in any of this work it is not only desirable but sometimes essential to investigate the catalytic situation involving the particular reaction and determine roughly the rate of reaction under certain definite conditions. This means that the determination of a free energy value for a specific organic reaction usually results in not only determining how far the reaction will go under certain definite conditions, but also how fast. In other words, studies of this kind usually give a fairly complete answer to the fundamental questions concerning the chemical reaction.

We may generally assume in most organic chemical reactions that it is impractical to measure the equilibrium constant directly and thereby determine the free energy for the reaction under certain definite and practical conditions. It is usually necessary to determine the $\triangle F.^\circ$ values for a combination of reactions which, added and subtracted from one another will result in the $\triangle F.^\circ$ value required as has been shown before.

Free energy change can sometimes be determined, especially in inorganic reactions, by setting up a reversible cell. The equation then becomes $\triangle F.^\circ = -nFE^\circ$. In this equation, n is the number of equivalents, the F is a Faraday and the E° is the potential under standard conditions. In order to set up such a cell it is necessary that the electrons be mobile; that the atoms be capable of giving off and taking up electrons readily. This condition, especially of the carbon atom, is not common and therefore organic reactions do not readily lend themselves to this method of study.

The most practical methods of determining the $\triangle F.^\circ$ for organic reactions is the use of the entropy equation previously described. The reason for this is, the specific heats, latent heats, temperatures and heat change during the reaction can be measured usually with more accuracy than other physical constants.

Some preliminary results obtained by actual work of this character on certain interesting organic reactions in the industrial division of the chemistry department, University of Illinois, will be given below.

An attempt has been made to determine the $\triangle F.^\circ$ of the reaction between ethylene and water to produce ethyl alcohol. This reaction is particularly valuable because ethyl alcohol is the most important organic solvent at the present time. It is largely made by the fermentation of molasses, which involves rather large equipment cost. A study has been made of various synthetic methods during the last fourteen years, and it is believed that the action of water on ethylene has a most promising future.

The decomposition of ethyl alcohol to produce ethylene and water was first studied largely to determine what would be a satisfactory catalyst. The best catalyst found was aluminum oxide (Al_2O_3), impregnated with about 3 per cent. of phosphoric acid (H_3PO_4). Preliminary results indicated a decomposition of approximately 96 per cent. at 420–430° C. (700° K.), at a space velocity of 100. A small amount of aldehyde, ether and other by-products was found but not determined quantitatively. The $\triangle F^\circ_{700K}$, based on this 96 per cent decomposition, represented a value of $+3{,}500$ cal.

Parks and Huffman[4] indicate a value of $+17{,}900$ for $\triangle F.^\circ_{700K}$. Francis and Kleinschmidt[5] give a value for the same $\triangle F.^\circ$ of $+7{,}650$. Frost[6] indicates still another value for this physical constant of $+6{,}008$.

Our figure of 3,500 is undoubtedly low because the amount of undecomposed ethyl alcohol was probably less than the 4 per cent. indicated by the decomposition figures. There is no question, however, regarding the sign, and the probabilities are that the order of magnitude is also correct.

The difficulty with the direct determination proved to be the inaccuracy of methods of analysis pertaining to the products of the reaction.

Considerable time was spent in an attempt to improve these analyses, with unsatisfactory results. The method of attack on this problem at the present time is to divide the reaction into two steps: (1) The absorption of ethylene in concentrated sulfuric acid,

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[4] A. C. S. Monograph, "Free Energies of Some Organic Compounds," 123, 1932.

[5] "Applications of Thermodynamics," *Oil and Gas Jour.*, 25: 118, 1929.

[6] "Hydration of Olefins to Alcohols," *Zhur. Pridkladnoikhim*, 3: 1069–76, 1930.

and (2) the production of ethyl alcohol formed from the ethyl acid sulfate by further dilution. The important physical data to obtain in this case are the partial pressures of the reacting constituents.

Another reaction that is of real interest both to the scientific man and the applied scientific man is the reaction between propylene and hydrogen sulfide to produce an alkyl acid sulfide. A direct determination of the equilibrium constant at 573° K. indicated a $\triangle$ F.° of + 3,000 cal. There are no data in the literature that would indicate the accuracy of this determination.

Considerable polymerization of the propylene occurred in the presence of catalysts such as phosphoric acid on activated charcoal. A quantitative analysis of this polymer is extremely difficult.

The study at the present time is along two lines: (1) the development of a catalyst that will eliminate this and other side reactions, and (2) the determination of the $\triangle$ F.° by means of heat capacity measurements. Both methods hold out some promise.

Still another reaction which is of interest to many is the reaction between ammonia and ethylene to produce ethylamine. A study was first made of the reaction itself in order to determine directly the equilibrium constant. A silent electric discharge was used in the place of a catalyst. At 298° K., $\triangle$ F.° found from these data was approximately + 1,200 cal.

Again the difficulty was due to analytical methods, especially those involving the determination of the amount of ethylamine formed. There were indications of side reactions taking place. Unknown amines apparently were formed. Preliminary results do, however, agree with some rather qualitative work done on the reaction by Francesconi and Ciurlo.[7] It will, of course, be necessary to determine by what, if any, amount the equilibrium is displaced by the discharge.

Further work will be done in the hopes of improving the methods of analysis. If these fail, an attempt will be made to procure a catalyst that will eliminate the side reactions or the $\triangle$ F.° will be determined by heat capacity measurements.

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OBITUARY

WILLIAM JACOB HOLLAND

WITH the death of Dr. William J. Holland, which occurred on December 13, 1932, a distinguished figure in the world of science passed away. He was the dean of American entomologists, the author of innumerable publications in this field. But Dr. Holland was far more than an eminent entomologist of world-wide reputation—he was a naturalist of a universality of erudition which is but rarely found among scientific men of the present day. With a prodigious memory, a keen understanding of the diversity of scientific problems, he was at home in the manifold domains of learning. Above all, he was a man of outstanding intellectual and spiritual culture, and that is why his loss has created an irreparable void in the community with which he has been associated for nearly three scores of years and within the ranks of his fellow workers in the scientific field.

William Jacob Holland was born in Bethany, on the island of Jamaica, on August 16, 1848. His family was of Moravian extraction, residing for a long time in Salem, North Carolina. From there his father was sent as a missionary to the West Indies.

From early boyhood Holland was trained in studies of natural history. Upon graduation from the Moravian College and Theological Seminary at Bethlehem, Pennsylvania, in 1867, he received the degree of bachelor of arts from Amherst College in 1869. For a year after graduation he served as principal of a high school in Amherst, and the following year occupied the same position at Westboro, Massachusetts. Having been ordained into the Moravian ministry he entered Princeton Theological Seminary and concluded the course in 1874. Subsequently he joined the Presbytery of Monmouth and came to Pittsburgh as pastor of the Bellefield Presbyterian Church, which position he held until 1891. In the course of his pastorate Dr. Holland devoted much time to scientific studies. He went to Japan as a member of the United States Eclipse Expedition in 1887 and used this opportunity in a very profitable way for various biological investigations. In 1891 he was made chancellor of the Western University of Pennsylvania, now the University of Pittsburgh. In 1898 his friend, Andrew Carnegie, invited him to assume the responsibilities as director of the museum founded by this steel magnate. This office was held by Dr. Holland with signal success until 1922, when he became director emeritus of the Carnegie Museum. Under the administration of Dr. Holland the museum attained the rank of one of the most important scientific institutions of its kind on the continent. Dr. Holland performed the duties as vice-president of the Carnegie Hero Fund from 1904 to 1922, and upon his election as president of that body became a member of the Carnegie Corporation.

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[7] Francesconi and Ciurlo, *Gazz. chim. ital.*, 53: 598, 1923.