Section 122.2 provides that the Secretary may issue at his discretion a permit when proper safeguards have been set up to protect the public. Application for such a permit *shall be made in advance of shipment,* and each permit shall specify the name and address of the consignee, the true name and character of each of the organisms or vectors involved, and the use to which each will be put.

All persons engaged in research involving the use of organisms or vectors as defined above should become familiar with the contents of this notice. Further information and applications for permits may be obtained by writing to the Chief, Bureau of Animal Industry, U. S. Department of Agriculture, Washington 25, D. C.

Parameters for the Description of Transition States

Of all the properties of the transition state, the free energy is the most valuable. From it may be calculated reaction rates and, consequently, the product composition of competitive reactions. In principle the free energy of the transition state may be calculated in two ways: (*a*) by statistical mechanics, and (*b*) by equations relating it to other measurable free energies. The former approach demands data as yet unavailable, and so it is the latter that is the more useful at present. The relationships with known free energies are rational but semiempirical.

Let F_r be the free energy of the reagents, F_p that of the products, and $F_{\ddagger}$ that of the transition state. Let ΔF_r, ΔF_p, and $\Delta F_{\ddagger}$ be the decrease in free energy (stabilization) of the reagents, products, and transition state for a change in a given independent variable, such as solvent or structure. A change from benzene to chlorobenzene as solvent or the introduction of a new substituent anywhere but directly at the site of reaction will serve as typical variations.

One rational first approximation is that

$$\Delta F_{\ddagger} = \alpha\,\Delta F_p + (1-\alpha)\,\Delta F_r \qquad (1)$$
$$0 \leqq \alpha \leqq 1.$$

This is chosen for the following reasons. We can expect the transition state to be intermediate between the reagent and product with respect to its free energy's sensitivity to changes in the independent variable, just as we expect it to be intermediate with respect to geometry and topology. If we assume that the transition state is *intermediate* in all its properties, including free energy changes except the absolute magnitude of the free energy itself, it is appropriate to use a linear combination of ΔF_r and ΔF_p as an approximation to $\Delta F_{\ddagger}$. We can also say that, if the transition state is intermediate, it will resemble the product less when it resembles the reagent more. This is expressed by Eq. (1) in which the parameter α measures the resemblance to the product and has 0 and 1 as limits, whereas $(1-\alpha)$ measures the resemblance to the reagent. We approximate the transition state by regarding it as a hybrid between the reagent and product states.

Since the quantity $\Delta F_{\ddagger}$ is not immediately accessible experimentally, it is desirable to rearrange Eq. (1). Let the superscripts 1 and 2 refer to two values of the independent variable (structure or solvent). Then

$$\Delta F_{\ddagger} = F_{\ddagger}{}^1 - F_{\ddagger}{}^2,\ \Delta F_p = F_p{}^1 - F_p{}^2,\ \Delta F_r = F_r{}^1 - F_r{}^2.$$

Eq. (1) then becomes

$$F_{\ddagger}{}^1 - F_{\ddagger}{}^2 = \alpha F_p{}^1 - \alpha F_p{}^2 + F_r{}^1 - F_r{}^2 - \alpha F_r{}^1 + \alpha F_r{}^2.$$

On rearrangement of terms, and introduction of the conventional symbols

$$\Delta F_1{}^{\ddagger} \equiv F_{\ddagger}{}^1 - F_r{}^1 \text{ and } \Delta F_1 \equiv F_p{}^1 - F_r{}^1$$

we have:

$$\Delta F_1{}^{\ddagger} - \Delta F_2{}^{\ddagger} = \alpha(\Delta F_1 - \Delta F_2).$$

If we now introduce an integration constant,

$$\Delta F^{\ddagger} = \alpha \Delta F + C. \qquad (2)$$

Eq. (2) deals with quantities $\Delta F^{\ddagger}$ and ΔF that are derivable from rate and equilibrium constants. It is equivalent to $\ln k = \alpha \ln K + C'$.

Whenever a plot of the logarithm of the rate constant of a reaction against the equilibrium constant for the same reaction gives a straight line, assumption (1) is justified. Furthermore, the slope of such a line is identifiable as a parameter that measures the degree of resemblance of the transition state to the products, as compared to its resemblance to the reagents.

Fairly precise relationships of the form (2) have been noted in a number of instances. For example, in the dissociation of hexaphenyl ethane, such a relationship obtains between the rates and equilibrium constants for the dissociation in a series of solvents (*1*). The value of α in this case is only about 0.2, indicating that the transition state resembles the ethane four times as much as it resembles the radical. The resemblance is probably at least partly geometric, the ethane and transition state both being sterically unable to interact strongly with the solvent. If so, it is likely that in the transition state the incipient radicals have not flattened out enough to acquire much resonance energy.

Better examples of relationship (1) are provided by Brønsted catalyses. Hammett has shown (*2*) for one case of the Brønsted relationship between the rate constant and the ionization constant of the catalyzing acid that there is derivable a linear relationship between the log of the rate constant and the log of the *equilibrium constant of the same reaction* (not just the acid ionization). The same appears to be true for most Brønsted relationships. From the slope of the Brønsted relationship it is therefore possible to calculate α. The variable in these relationships is the structure of the catalyzing acid.

There are several possible applications for α once it has been obtained. The value observed may be incompatible with one of several otherwise possible reaction mechanisms, thereby eliminating that mechanism. For example, consider a reaction thought to involve proton transfer $A^- + HB \rightleftarrows AH + B^-$, a fairly usual rate-determining step. A rough estimate of α can be obtained from the following consideration: A transition state differs from ordinary molecules in that with respect to one of its coordinates (the reaction coordinate) it has a *maximum* rather than a *minimum* free energy. If the reaction coordinate measures proton transfer, we can therefore say that in the transition state the weaker base will be more nearly neutralized than the stronger base; that is, if, in the reaction above, A^- is a weak base like a carboxylate ion, and B^- is a strong base like a carbanion, the value of α will be high (0.6 to 1.0), since the transition state must resemble the product in such a case. If the observed value of α is outside this range, the mechanism should be discarded. A proper value of α is one more criterion for an acceptable mechanism. In the base-catalyzed mutarotation of glucose we may discard the hypothesis that the nonconcerted formation of the glucose negative ion is rate-determining. The value of α is so low that the transition state would have to resemble un-ionized glucose. But this will not do, since the glucose ion must be a stronger base than carboxylate ions. The necessity for dependence of α on base strength means that, for extremely large changes in ionization constant, the Brønsted relationship will depart from linearity. This sort of restriction is typical of most linear free energy relationships.

There are several other possible applications of α not yet tested because of insufficient data. It should be possible to apply an α chosen for best fit to the relationship under changes in structure to the relationship under changes in solvent, and vice versa. Structural data should help in predicting the effect of solvent changes, and solvent data should help in predicting the effect of structural changes. This is not surprising, because the effect of solvent on reactions is very much like the effect of a substituent and can sometimes be explained by electronic interpretations similar to those applied to substituents. A still more conjectural application is to the absolute prediction of reaction rates largely from nonrate data. We may shortly expect a solution to the problem of predicting the free energy of stable molecules in mixed solvents. It should then be possible to predict the free energy of the transition state by a linear combination of the predictions made for the reagents and for the products.

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Book Reviews

Seismic Prospecting for Oil. Charles Hewitt Dix. New York: Harper, 1952. 414 pp. Illus. $7.50.

For some 30 years, applied seismology has occupied a position of supreme importance in the search for oil deposits. A textbook specifically devoted to present-day seismic prospecting and, more particularly, to the techniques of converting the field data into terms of geological significance on maps, is therefore to be welcomed. This book, in fact, treats all phases of the interpretation procedures, from the reading of "raw" seismograms to the compilation of the finished maps and reports. It does not deal with instrumentation.

The book consists of five parts, containing some 15 chapters. Each chapter is preceded by a paragraph or so introducing its material and stating for whom it is specifically intended. Consequently, the field man on a seismic crew and the exploration geologist will find the book good reading and of considerable value, even though it is strictly functional—that is to say, it is primarily a manual of procedures, rather than a continuous development of its subject matter.

The author has been engaged in seismic prospecting for oil for almost 20 years. This practical experience, coupled with his scholarly background, serves to make him an outstanding authority. Aware of these facts, the reviewer is disappointed to find the looseness of language and presentation which pervades the book. Presumably in the interest of economy of printing, practically all the mathematical developments are arranged as parts of the figures, with results that are most unfortunate insofar as clarity of expression is concerned. A more conscientious editing of the text, and a more orthodox arrangement of the mathematical arguments would have enhanced the value of the book for both the professional seismologist and the student.

For the student, in fact, the functional aspect of the book is at times disturbing. The economics of seismic operations, the personnel components of a crew—such matters are all discussed. Elasticity, wave propagation, and seismic recording are sketchily, although perhaps adequately, presented. There is, however, no historical background of seismology, applied or otherwise, which one might expect to be treated at least briefly in a book of this type. The refraction technique of seismology is only lightly touched upon—a fact presumably in keeping with its present-day low economic importance.

As a textbook, it presents little challenge to the ingenuity or the initiative of the student. It is for that reason that it will find its greatest use as a reference book for men already working as seismologists in the oil industry, and in those many college courses of the "spoon-feeding" type.

M. M. SLOTNICK

Humble Oil & Refining Company, Houston, Texas