2. The specific heat-temperature curves of the various nitromethanes showed distinct irregularities, which indicate the presence of several species of molecules in the liquid.

3. Measurements of vapor pressure and density failed to show corresponding irregularities.

4. A nitromethane gel with phosphorus pentoxide and a trace of water is described.

5. The probability of an abnormal boiling point for nitromethane which has been subjected to intensive drying is discussed.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 72]

ON THE DERIVATION OF THE EQUATION FOR THE EFFECT OF TEMPERATURE ON REACTION RATE

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In order to account for the large temperature coefficient of the rate of ordinary chemical reactions, it seems impossible to escape the conclusion of Arrhenius[1] that the molecules which actually enter into the reaction must be in an activated form containing considerably more energy than the normal molecule.[2] In accordance with this view of Arrhenius, it has been customary to use the following equations to express the rates of first order unimolecular and second order bimolecular reactions, respectively, as functions of the temperature

$$-\mathrm{d}C/\mathrm{d}t = kC = k' e^{-E/RT}\, C \tag{1}$$

$$-\mathrm{d}C/\mathrm{d}t = kCC' = k'T^{1/2}\, e^{-[(E+E')/RT]}\, CC' \tag{2}$$

where E or $(E + E')$ are the energy contents per mole of the activated molecules entering into the reaction.[3]

Since the older derivations of these equations have involved special assumptions, a somewhat more elaborate analysis of the justification for the equations will not be out of place. We shall find that the magnitudes

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[1] Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889).

[2] The transition of the molecule from the normal to the activated form may be merely a change to a higher quantum state or other tautomer of high energy content or may involve dissociation or other change which is usually regarded as chemical. In the sense of the Arrhenius formulation, the "residual molecules" of Rice, Fryling and Wesolowski [THIS JOURNAL, **46**, 2405 (1924)] would often seem to be one special kind of activated molecules.

[3] The actual equation proposed by Arrhenius had for any order of reaction the form $\frac{\mathrm{d}\log k}{\mathrm{d}T} = \frac{E}{RT^2}$ where E is the total energy of activation. The introduction of the term $T^{1/2}$, however, in Equation 2 for bimolecular reactions is customary, since the number of collisions between molecules is proportional to this power of the temperature.

of the necessary energy of activation will be given, approximately at least, by Equations 1 and 2 under a wider variety of conditions than have hitherto been considered. This is of importance in connection with the difficulties that are encountered in finding mechanisms of activation that will supply fast enough the large energies calculated from these equations.[4] It would be an easy way out of these difficulties if only we could deny the validity of the Arrhenius equation, but this does not now seem possible.

Part I. Unimolecular Reactions

1. Introduction.—Derivations of Equation 1 for the rate of a unimolecular reaction have usually been based on one or the other of two possible but not inevitable assumptions as to the mechanism of activation. One class of proofs assumes a mechanism of activation so fast compared with the rate of reaction as to maintain the full Maxwell-Boltzmann quota of molecules in the activated state, and since this quota is proportional to $e^{-E/RT}$, it is easy to see why this factor then enters into the expression for reaction velocity.[5] A second class of proofs assumes that the mechanism of activation consists in the absorption of radiation of the frequency given by the quantum relation $E = Nh\nu$, and since the density of radiation of frequency ν is approximately proportional to $e^{-h\nu/kT}$, it is again easy to see why the dependence of the rate on temperature should be that given by the Arrhenius equation.[6]

In our present treatment, we shall not have to assume a velocity of activation necessarily fast enough to maintain the full Maxwell-Boltzmann quota of activated molecules, nor assume any specific mechanism for the activational process. We shall, however, assume that the *unactivated* molecules are in statistical equilibrium and that the *specific* rates at which molecules pass from one state to another are not affected by the progress

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[4] See, for example, Tolman, THIS JOURNAL, **47**, 1524 (1925).

[5] The assumption that the full quota of activated molecules is maintained is apparently present, for example, in the derivations of Marcelin [*Ann. Physik*, **3**, 120 (1915)], Rice [*Brit. Assoc. Advancement Sci. Rept.*, **1915**, 397], Rodebush [THIS JOURNAL, **45**, 606 (1923)], and Christiansen and Kramers [*Z. physik. Chem.*, **104**, 451 (1923)]; also indeed in the original quasi-thermodynamical derivation of Arrhenius.

In the derivations of Marcelin, Rice and Rodebush no hypothesis is made as to the mechanism of the activational process, there is merely the tacit assumption that it is fast enough to maintain statistical equilibrium as far as concerns the different states of the reactant. In the derivation of Christiansen and Kramers it is assumed that the full quota of activated molecules is maintained by collisions of the second kind between normal molecules of the reactant and activated molecules of the product which have not yet fallen to their normal state. In accordance with their treatment the reaction will not continue first order unless the assumed mechanism does suffice to maintain the full quota.

[6] This assumption is present in the radiation theory in its simple form as first given by Perrin and W. C. McC. Lewis and also in its later more elaborated forms. See Tolman, THIS JOURNAL, **42**, 2506 (1920); and Ref. 4 above.

of the reaction. It is further to be noted that our proof is general enough to allow for a series of different activated and unactivated states.

2. A Relation between the Velocities of Reverse Processes.—In carrying out our treatment we shall first need to obtain an important relation between the velocities of reverse processes which can be derived with the help of the *principle of microscopic reversibility*. The best formulation and precise range of validity of this principle have not yet been determined; nevertheless, the principle is one that has found increasing application in chemical kinetics, and we need not hesitate to use it in the present connection.[7] If we have a system in statistical equilibrium, the principle requires not only that the number of molecules in any given state shall remain constant, but that the number leaving that state in unit time by any particular path shall be made up by the entrance of an equal number of molecules by the reverse of that particular path.

Consider now a system in statistical equilibrium and let C_i and C_a be the concentrations of molecules in two states, S_i initial state and S_a activated state having, respectively, the energies per mole E_i and E_a. We may obviously put the rate at which molecules are passing from state S_i to S_a proportional to the concentration C_i, and the number passing in the reverse direction proportional to C_a, as given by the equations

$$\partial C_a/\partial t = \beta_{ia}C_i, \text{ and } -\partial C_a/\partial t = \alpha_{ai}C_a \tag{3}$$

where for convenience we might call β_{ia} a coefficient of activation and α_{ai} the corresponding coefficient of deactivation. Since, however, the system is in statistical equilibrium, the number of molecules in each state is a constant, and if we assume the principle of microscopic reversibility, this constancy is maintained by an exact equality in the numbers of molecules passing in the reverse directions between each pair of states, which leads to the equation

$$\beta_{ia}C_i = \alpha_{ai}C_a \tag{4}$$

The two concentrations, however, are connected in accordance with the Maxwell-Boltzmann distribution law by the equation

$$\frac{C_a}{C_i} = \frac{p_a}{p_i}\, e^{-(E_{ia}/RT)} \tag{5}$$

where p_a and p_i are the *a priori* probabilities of the two states and E_{ia} is the energy necessary to raise the molecule from state S_i to S_a. Substituting in (4) we obtain the following very important relation between the coefficients of activation and deactivation

$$\beta_{ia} = \alpha_{ai}\frac{p_a}{p_i}\, e^{-(E_{ia}/RT)} \tag{6}$$

This significant equation makes no assumption as to the mechanism of the activational and deactivational processes and the coefficients β_{ia}

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[7] For references to the history of this principle see Tolman, *Proc. Nat. Acad. Sci.*, 11, 436 (1925).

and α_{ai} may be dependent on the total concentration of molecules present if the mechanism is collisional, or on the concentration of radiant energy if this is involved, or on whatever factors may be operative. It should also be observed that the formulation of the proof and the final equation are just as valid in case the classical-theory statistical mechanics or the quantum-theory statistical mechanics is applicable to the problem at hand. In the first case, the *a priori* probabilities p_i and p_a can be taken proportional to infinitesimal phase areas of the magnitude $dq_1 \ldots . dp_n$, corresponding to different microscopic states of the molecule; in the second case they can be taken proportional to finite areas of the magnitude h^n corresponding to different quantum states.

It must further be noted that Equation 6 has been rigorously derived only for a system in statistical equilibrium. We should usually expect, however, that the *specific* rates at which molecules pass from one state to another will not be greatly affected by the deviation of the system from equilibrium, and in what follows we shall assume that Equation 6 is valid at any stage of the reaction up to complete equilibrium. It should be noted that this assumption is the less questionable, since it only necessitates the constancy of the ratio of β_{ia} and α_{ai}, rather than their individual constancy.

3. Rate of Activation and Unimolecular Reaction.—We are now ready to treat the general case of first-order unimolecular reactions in which the total process consists in the passage of molecules from the inactive to the active condition followed by reaction on the part of a certain fraction of the activated molecules. If we call states S_i unactivated and states S_a activated, we may write for the rate at which molecules are being activated

$$\mathrm{d}C_{\mathrm{act}}/\mathrm{d}t = \sum_i \sum_a \beta_{ia} C_i \tag{7}$$

A certain fraction of the molecules which arrive in any activated state S_a may react and the remainder fall back into the unactivated states. For the fraction Θ_a that reacts we may evidently write

$$\Theta_a = \frac{\sum\limits_f \alpha_{af}}{\sum\limits_f \alpha_{af} + \sum\limits_i \alpha_{ai}} \tag{8}$$

where $\sum\limits_i \alpha_{ai}$ and $\sum\limits_f \alpha_{af}$ are the total *specific* rates at which molecules pass from the activated state S_a *back* to any of the initial unactivated states S_i, or *forward* to any of the final unactivated states S_f of the products of the reaction.[8]

Introducing the fraction of the activated molecules which react into Equation 7 for the rate of activation, we obtain for the rate of a uni-

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[8] In case the reaction is an isomeric change, the final states S_f will be those of a single molecule. In cases of dissociation the designation S_f stands for a simultaneous condition of more than one molecule. In the formulation given we have felt justified in neglecting the passage of molecules from one activated state to another activated state.

molecular reaction

$$-\mathrm{d}C/\mathrm{d}t = \sum_i \sum_a \Theta_a \, \beta_{ia} \, C_i \tag{9}$$

and so far have introduced no hypothesis except our general picture as to the nature of the process.

If we now assume statistical equilibrium for the *unactivated* molecules, we may substitute for C_i the Maxwell-Boltzmann expression

$$C_i = \frac{C \, p_i \, e^{-(E_i/RT)}}{\sum\limits_i p_i \, e^{-(E_i/RT)}} \tag{10}$$

where C is the total concentration of unactivated molecules which is of course sensibly equal to the concentration of reactant. Furthermore, assuming the validity of the result obtained from the principle of microscopic reversibility, we may substitute for β_{ia} the expression given by Equation 6.

$$\beta_{ia} = \alpha_{ai} \frac{p_a}{p_i} \, e^{-(E_{ia}/RT)} \tag{11}$$

We obtain

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{\sum\limits_i \sum\limits_a \Theta_a \, \alpha_{ai} \, p_a \, e^{-(E_a/RT)}}{\sum\limits_i p_i \, e^{-(E_i/RT)}} \, C \tag{12}$$

Or for the specific reaction rate

$$k = -\frac{1}{C}\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{\sum\limits_i \sum\limits_a \Theta_a \, \alpha_{ai} \, p_a \, e^{-(E_a/RT)}}{\sum\limits_i p_i \, e^{-(E_i/RT)}} \tag{13}$$

4. Temperature Coefficient of Unimolecular Reaction Rate.—In order to obtain the final result in the desired form, we must take a logarithmic differentiation of this value of k with respect to the temperature. We obtain

$$\frac{\mathrm{d} \log k}{\mathrm{d}T} = \frac{1}{k} \, \frac{\sum\limits_i \sum\limits_a \Theta_a \, \alpha_{ai} \, p_a \, e^{-(E_a/RT)} \left\{ \frac{\mathrm{d} \log \Theta_a}{\mathrm{d}T} + \frac{\mathrm{d} \log \alpha_{ai}}{\mathrm{d}T} + \frac{E_a}{RT^2} \right\}}{\sum\limits_i p_i \, e^{-(E_i/RT)}} - \frac{\sum\limits_i p_i \, e^{-(E_i/RT)} \left\{ \frac{E_i}{RT^2} \right\}}{\sum\limits_i p_i \, e^{-(E_i/RT)}} \tag{14}$$

It is evident from the principles of averaging, however, that this may be rewritten in the form

$$\frac{\mathrm{d} \log k}{\mathrm{d}T} = \overline{\overline{\frac{\mathrm{d} \log \Theta_a}{\mathrm{d}T}}} + \overline{\overline{\frac{\mathrm{d} \log \alpha_{ai}}{\mathrm{d}T}}} + \frac{\overline{\overline{E_a}}}{RT^2} - \frac{\overline{E_i}}{RT^2} \tag{15}$$

where the double line indicates that the average is taken for the activated molecules that actually enter into the reaction, and the single line indicates the average for the unactivated molecules.

In general, however, we shall expect the first two terms on the right-hand side of Equation 15 to be small, since by referring to Equation 8 for the value of Θ_a we see that both terms in question contain merely the temperature coefficients of the specific rates at which molecules fall from states of high energy content to those of lower energy content. Such deactivations, however, can occur as far as we can see only through the loss of energy on collision with other molecules or through the emission of radiation. The first of these processes has a small temperature coefficient, since the number of collisions does not change rapidly with the temperature. The second process can be taken as occurring by a combination of spontaneous emission and induced emission as shown by Einstein's deduction of the Planck radiation law (1917). The rate of spontaneous emission is unaffected by temperature, while the rate of induced emission is dependent on the density of radiation of the particular frequency involved and the temperature coefficient for the combined process can never be large at ordinary temperatures.[9]

Assuming, then, that the first two terms are negligible, Equation 15 can be rewritten in the form

$$\frac{\mathrm{d}\log k}{\mathrm{d}T} = \frac{\overline{\overline{E}}_a - \overline{E}_i}{RT^2} = \frac{E}{RT^2} \tag{16}$$

where E is the energy of activation.

Special attention is called to the fact that the quantity $E = \overline{\overline{E}}_a - \overline{E}_i$ occurring in Equation 16 which we have called the energy of activation is the *excess* of the *average* energy of the molecules that do react over the *average* energy of the unactivated molecules. It should further be noted that if we do not try to treat the subject as generally as we have done above, but introduce the common assumption of statistical equilibrium for all molecules and specific rates of reaction for activated molecules which are independent of the temperature, the derivation of Equation 16 is then easily shown by the methods used above to be exact, provided we take E as the difference between the average energy of the molecules that react and the average energy of all the molecules. This result is in agreement with the earlier derivation of the author, which assumed, however, a special mechanism of activation.[10]

[9] For the specific rate of deactivation by emission of radiation we may write $\alpha_{ai} = A_{ai} + B_{ai}\,\rho$ where A_{ai} and B_{ai} are Einstein's coefficients of spontaneous emission and induced emission and ρ is the density of radiation of the frequency ν involved. Substituting the known relations $A_{ai} = \frac{8\,\pi\,h\nu^3}{c^3}\,B_{ai}$ and $\rho = \frac{8\,\pi\,h\nu^3}{c^3}\,\frac{1}{e^{h\nu/kT}-1}$ and taking the logarithm we obtain, $\log \alpha_{ai} = \log \frac{e^{h\nu/kT}}{e^{h\nu/kT}-1} + \text{const.}$, $\frac{\mathrm{d}\log\alpha_{ai}}{\mathrm{d}T} = \frac{h\nu}{kT^2}\,\frac{1}{e^{h\nu/kT}-1}$. The maximum value that this temperature coefficient can attain, however, is seen to be $1/T$, which is not large compared with the usual values of E/RT^2.

[10] Tolman, THIS JOURNAL, **42**, 2506 (1920).

In connection with the discussion presented in the foregoing paragraph it should be noted that we may expect the average energy of the *unactivated* molecules to be practically the same as the average energy of *all* the molecules.

It certainly seems most convenient to continue to use the term "energy of activation" or "heat of activation" in the above sense to mean the *excess* of energy which on the *average* has to be supplied to the molecules that react. Lewis and Smith,[11] however, in a recent article have proposed to re-define the heat of activation as the *minimum* internal energy which a molecule must have in order to be able to react. It is evident, however, that the quantity thus defined is not the one occurring in the Arrhenius equation, and hence it would seem unfortunate to adopt the proposed change in definition.[12]

5. Final Expression for Unimolecular Reaction Rate.—Returning now to our original problem, if we integrate Equation 16, neglecting the change of E with the temperature, we can obtain the original equation we started out to test

$$-\mathrm{d}C/\mathrm{d}T = k' e^{-(E/RT)}\, C \tag{1}$$

where k' is the constant of integration.

This completes our analysis of the justification of using the Arrhenius Equation 1 to calculate energies of activation. It seems evident from an examination of the assumptions involved in the deduction that the equation will be approximately correct under a wider variety of conditions than have hitherto been considered. The result emphasizes the necessity of finding mechanisms of activation capable of supplying the large energies calculated from Equation 1.

In this connection the treatment of the maximum rate of activation by collision recently given by Lewis and Smith[13] does not seem entirely satisfactory. They assume that the average internal energy of unactivated molecules might be available as part of the energy E occurring in the Arrhenius equation, but in accordance with the foregoing treatment, the quantity E is the *excess* in the average energy of the molecules that react *over* the *average* energy of the unactivated molecules.

It should be noted also, as already pointed out by the author,[4] that the possibility of raising the molecules from their average energy content to the activated state by a series of collisions which carry the molecules through intermediate states does not seem a probable method of obtaining the necessary rates of activation by collision, since to offset the increased specific rate of activation from an intermediate state, we have the decreased concentration of molecules in the intermediate state, as well as the possibility of loss of energy by collisions of the second kind.

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[11] Lewis and Smith, This Journal, **47**, 1515 (1925).

[12] Using the assumptions which were mentioned above as leading to an exact derivation of the Arrhenius equation, but inserting their new definition of the heat of activation, Lewis and Smith indeed discover (Ref. 11, pp. 1513–1514), as would be expected, that they do not get an exact derivation of the Arrhenius equation.

[13] Ref. 11, pp. 1513–1514.

Part II. Bimolecular Reactions

The justification for using our original equation (2) for bimolecular reactions is rather simpler. A bimolecular reaction could result either from the collision of two molecules which have previously been activated or from the collision of molecules having more than average kinetic energy, thus merging the process of activation and reaction. We shall treat the two cases separately.

1. The Molecules Have Been Previously Activated.—If reaction results from the collision of molecules which already have been activated, it is evident that the reaction can be of the second order over a range of concentrations only if the rate of activation is fast enough compared with the rate of reaction, so that the full Maxwell-Boltzmann quota of activated molecules is maintained. Hence for the concentration of molecules of kind M or M' in a given activated state S_a or S_a' we can write the expressions

$$C_a = \frac{C\,p_a\,e^{-(E_a/RT)}}{\sum\limits_i p_i\,e^{-(E_i/RT)}} \quad \text{and} \quad C_a' = \frac{C'\,p_a'\,e^{-(E_a'/RT)}}{\sum\limits_i p_i'\,e^{-(E_i'/RT)}} \tag{17}$$

where the summations are to be carried out for all possible states. Then, since the number of collisions between activated molecules is proportional to the square root of the absolute temperature, we may write for the rate of reaction

$$-\mathrm{d}C/\mathrm{d}t = T^{1/2} \sum_a \sum_{a'} k_{aa'}\,C_a\,C_a'$$

$$k = -\frac{1}{CC'}\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{T^{1/2}\sum\limits_a \sum\limits_{a'} k_{aa'}\,p_a\,p_a'\,e^{-[(E_a + E_a')/RT]}}{\left(\sum\limits_i p_i\,e^{-(E_i/RT)}\right)\left(\sum\limits_i p_i'\,e^{-(E_i'/RT)}\right)} \tag{18}$$

where $k_{aa'}$ is a constant depending on the particular pair of activated states involved, and the double summation in the numerator is to be taken over all activated states, that is, all states for which $k_{aa'}$ has an appreciable value.

Carrying out a logarithmic differentiation we obtain

$$\frac{\mathrm{d}\log k}{\mathrm{d}T} = \frac{\mathrm{d}\log T^{1/2}}{\mathrm{d}T} + \frac{1}{k}\,\frac{T^{1/2}\sum\limits_a \sum\limits_{a'} k_{aa'}\,p_a\,p_a'\,e^{-[(E_a + E_a')/RT]}\,\dfrac{E_a + E_a'}{RT^2}}{\left(\sum\limits_i p_i\,e^{-(E_i/RT)}\right)\left(\sum\limits_i p_i'\,e^{-(E_i'/RT)}\right)}$$

$$- \frac{\sum\limits_i p_i\,e^{-(E_i/RT)}\,\dfrac{E_i}{RT^2}}{\sum\limits_i p_i\,e^{-(E_i/RT)}} - \frac{\sum\limits_i p_i'\,e^{-(E_i'/RT)}\,\dfrac{E_i'}{RT^2}}{\sum\limits_i p_i\,e^{-(E_i'/RT)}} \tag{19}$$

This can evidently be rewritten in the form

$$\frac{\mathrm{d}\log k}{\mathrm{d}T} = \frac{\mathrm{d}\log T^{1/2}}{\mathrm{d}T} + \frac{\overline{\overline{E_a + E_a'}} - \overline{E_i + E_i'}}{RT^2} \tag{20}$$

where the double lines indicate an average taken for the molecules that react and the single line an average taken for all molecules. The numerator in the last term of Equation 20 is evidently the average energy of activation which we may denote as previously by $E + E'$. Integrating, neglecting the small change in the energy of activation with temperature we can evidently obtain the desired equation

$$-\mathrm{d}c/\mathrm{d}t = k'\, T^{1/2}\, e^{-\frac{E+E'}{RT}}\, CC' \qquad (2)$$

where k' is a constant of integration. Hence, under these circumstances the justification for using Equation 2 to calculate energies of activation is very satisfactory.

2. **Activation and Reaction Due to the Same Collision.**—In the case of bimolecular reactions, in addition to the possibility that reaction results from the collision of previously activated molecules, we have the special possibility that normal unactivated molecules will react providing they collide with the proper relative velocity. Such a mechanism could be regarded as merging the process of activation and reaction, and has appealed favorably to Hinshelwood.[14]

In the present state of our knowledge of molecular mechanics we can not, of course, specify the precise nature of the collisions which would lead to reaction. If, however, there are cases in which the suggested merging of activation and reaction does take place, it would seem reasonable to assume as a first approximation that reaction occurs for all collisions in which the component of velocity parallel to the line of centers of the molecules exceeds a minimum value V. Now it has been shown by Langevin and Rery[15] that $e^{-\frac{1}{2}\frac{MM'}{M+M'}\frac{V^2}{RT}}$ is the fraction of all collisions between molecules of molecular weights M and M' in which this is true. Hence we may evidently again write for the rate of reaction

$$-\mathrm{d}C/\mathrm{d}t = k'\, T^{1/2}\, e^{-[(E+E')/RT]}\, CC' \qquad (2)$$

where

$$E + E' = {}^1/_2\, \frac{MM'}{M+M'}\, V^2 \qquad (21)$$

In this case the quantity $E + E'$ would be a sort of minimum rather than average energy of activation; the minimum and average, however, are not far apart owing to the form of the Maxwell distribution law. Other plausible assumptions as to the conditions for the merging of activation and reaction lead to not very different results.

There is no way at the present time of deciding between the two proposed mechanisms of bimolecular reaction, preliminary activation or activation through the same collision that leads to reaction. The writer, however, is inclined to believe the former alternative the more probable. Both mechanisms agree with our original equation (2), the energy of activation being at least as great as the quantity $(E + E')$.

Summary

1. The familiar equation

$$-\mathrm{d}C/\mathrm{d}t = kC = k'\, e^{-(E/RT)}\, C \qquad (1)$$

connecting the rate of first-order unimolecular reactions with temperature

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[14] Hinshelwood and Burk, *Proc. Roy. Soc.*, **106A**, 284 (1924). Hinshelwood and Hughes, *J. Chem. Soc.*, **125**, 1841 (1924).

[15] Langevin and Rery, *Le Radium*, **10**, 142 (1913).

and energy of activation has usually been derived either on the assumption of a rate of activation fast enough to maintain the full Maxwell-Boltzmann quota of activated molecules, or on the assumption that the activational process consists in the absorption of radiation. In this article a derivation has been presented making *no specific assumptions either as to the rate or mechanism of activation*, which shows that Equation 1 will be at least approximately valid under a wide variety of conditions.

2. Derivations have also been presented for the familiar equation

$$-\mathrm{d}C/\mathrm{d}t = k\,CC' = k'\,T^{1/2}\,e^{-[(E + E')/RT]}\,CC' \qquad (2)$$

connecting the rate of second-order bimolecular reactions with temperature and energy of activation, both on the assumption that the reacting molecules have received their energies of activation preceding the collision which leads to reaction, and on the assumption that the processes of activation and reaction are merged in one collision having sufficient available kinetic energy.

3. These results re-emphasize the necessity of discovering mechanisms of activation which will supply fast enough the large energies of activation calculated from Equations 1 and 2.

4. Since the quantity E occurring in Equation 1 is the excess per mole in the energy of the molecules that react over the *average* energy of the unactivated molecules, it cannot be assumed that this average energy is available as part of the energy of activation.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

AN APPLICATION OF X-RAY CRYSTALLOMETRY TO THE STRUCTURE OF NICKEL CATALYSTS

BY GEORGE L. CLARK, W. C. ASBURY AND R. M. WICK

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The purpose of this investigation was to examine hydrogenation and dehydrogenation of nickel catalysts, prepared in different ways and with different activities,[1] by means of the X-ray powder-diffraction method to obtain information upon three questions: (1) whether there is a fundamental difference in the space lattice; (2) whether there is a fundamental variation in the particle size; (3) whether X-ray analysis will indicate the condition of the surface of nickel catalysts.

[1] Excellent comparative studies of activity as it depends upon the method of preparation of the catalyst have been made recently by (a) Armstrong and Hilditch, *J. Soc. Chem. Ind.*, **42**, 217 (1923); (b) **44**, 701 (1925); (c) Thomas, *ibid.*, **42**, 21T (1923); (d) Adkins and Lazier, THIS JOURNAL, **46**, 2291 (1924). This last paper states that nickel catalysts which show different hydrogenation and dehydrogenation activities are even *more widely* dissimilar in their abilities to break carbon chains.