

Chemical Kinetics. The Temperature Dependence of the Energy of Activation. The Entropy and Free Energy of Activation

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Citation: *The Journal of Chemical Physics* **1**, 289 (1933); doi: 10.1063/1.1749291

View online: <http://dx.doi.org/10.1063/1.1749291>

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THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 1

MAY, 1933

NUMBER 5

Chemical Kinetics. The Temperature Dependence of the Energy of Activation. The Entropy and Free Energy of Activation

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(Received March 4, 1933)

I. INTRODUCTION

ALL modern theories of reaction velocity recognize the importance of precise determinations of the energy of activation. For this purpose the temperature coefficients of the velocity of gaseous reactions and of non-ionic reactions in solution have been studied in some detail.

Comparable data for ionic reactions are exceedingly meager and the theoretical implications have been virtually neglected. The activation energies of ionic reactions are of particular interest for the following reasons.

The partial molal heat capacities of ions are large negative^{1, 2} values, which depend upon the electric charge, the total concentration, and certain specific factors arising from interaction with the solvent. Since the temperature dependence of the energy of activation involves heat capacities, it is conceivable for reactions between ions that $E_{\text{act.}}$ may not be independent of temperature. The approximation that $E_{\text{act.}}$ is constant is almost universally accepted in integrating the Arrhenius equation.

Interionic attraction modifies the rates of ionic reactions by changing the number and character of the effective collisions, a circumstance which

emphasizes the necessity for considering the orientation of the molecules at collision.^{3, 4}

The experimental evidence that activation energies of ionic reactions are dependent upon both temperature and concentration will be given in later papers of this series. The present paper will treat the simpler case of non-ionic reactions from the viewpoint of the statistical foundations of the Arrhenius equation; the derivation and limitations of the Brönsted equation; the validity of collision theories; and the experimental evidence for the temperature dependence of $E_{\text{act.}}$ in non-ionic reactions.

II. THE ARRHENIUS EQUATION AND ITS DERIVATIVES

We start with the Arrhenius equation in the form

$$\frac{d \ln k_2}{dT} = \frac{1}{2T} + \frac{\bar{\epsilon} - \bar{\epsilon}}{kT^2} = \frac{1}{2T} + \frac{E_{\text{act.}}}{RT^2}, \quad (1)$$

which R. C. Tolman⁵ has shown follows from statistical mechanics for a bimolecular reaction. To emphasize the salient features for later discussion, we give the simpler development valid for a unimolecular reaction and refer the reader

³ La Mer and Kamner, *J. Am. Chem. Soc.* **53**, 2832 (1931).

⁴ La Mer, *Chem. Rev.* **10**, 179 (1932).

⁵ R. C. Tolman, *Statistical Mechanics*, Chem. Catalog Co., pp. 259-69, 1927.

¹ La Mer and Cowperthwaite, *J. Am. Chem. Soc.* **55**, 1004 (1933).

² Randall and Rossini, *ibid.* **51**, 323 (1929).

to Tolman and Kassel's monographs⁶ for details of the origin of the term $\frac{1}{2}T$ in the bimolecular case.

Consider a system of molecules of index i , distributed in various quantum levels having the energies ϵ_i and the statistical weights p_i . The molecules in the higher reactive quantum states will be indicated by the index j , and will be assigned undetermined specific individual rate (reactivity) constants k_j . The number of molecules, n_j , in the j^{th} quantum state is

$$n_j = n p_j e^{-\epsilon_j/kT} / \sum_i p_i e^{-\epsilon_i/kT}, \quad (2)$$

where kT is the Boltzmann constant times the absolute temperature.

The overall, measurable, specific rate constant k_1 , is then

$$k_1 = -\frac{1}{n} \frac{dn}{dt} = \frac{\sum_j k_j p_j e^{-\epsilon_j/kT}}{\sum_i p_i e^{-\epsilon_i/kT}}. \quad (3)$$

Logarithmic differentiation yields

The differentiation yields:

$$\frac{d(E_{\text{act.}})}{dT} = \frac{1}{kT^2} \left\{ \left[\left(\frac{\sum_j \epsilon_j^2 k_j p_j e^{-\epsilon_j/kT}}{\sum_j k_j p_j e^{-\epsilon_j/kT}} \right) - \left(\frac{\sum_j \epsilon_j k_j p_j e^{-\epsilon_j/kT}}{\sum_j k_j p_j e^{-\epsilon_j/kT}} \right)^2 \right] - \left[\left(\frac{\sum_i \epsilon_i^2 p_i e^{-\epsilon_i/kT}}{\sum_i p_i e^{-\epsilon_i/kT}} \right) - \left(\frac{\sum_i \epsilon_i p_i e^{-\epsilon_i/kT}}{\sum_i p_i e^{-\epsilon_i/kT}} \right)^2 \right] \right\} \quad (7)$$

$$dE_{\text{act.}}/dT = (1/kT^2) \{ [\bar{\epsilon}^2 - \bar{\epsilon}^2] - [\bar{\epsilon}^2 - \bar{\epsilon}^2] \}. \quad (8)$$

$$= (\bar{C}_{j(\text{act.})} - \bar{C}_i) = C_{\text{act.}} \quad (8a)$$

In the case of heat capacities, the bar refers to the partial molal quantity, whereas with the energies ϵ it refers to the average.

The quantity $[\bar{\epsilon}^2 - \bar{\epsilon}^2]$ is the difference between the mean of the squares of the energies of all the molecules and the square of their mean energy, and consequently represents the *fluctuations*^{7, 8} in their energy. $[\bar{\epsilon}^2 - \bar{\epsilon}^2]/kT^2$ is equal to the calorimetrically measurable partial heat capacity of all the molecules, which heat capacity is indistinguishable from that of the non-reacting molecules.

By the same token $[\bar{\epsilon}^2 - \bar{\epsilon}^2]/kT^2$ represents the

⁶ L. S. Kassel, *Kinetics of Homogeneous Gas Reactions*, Chem. Catalog Co., pp. 19-26, 1932.

⁷ R. H. Fowler, *Statistical Mechanics*, Cambridge, 1929; Eq. (1435), p. 513.

⁸ J. W. Gibbs, *Statistical Mechanics*, Longmans, 1928; (Chap. VII, Eq. (205), Chap. XIV and XV).

$$\frac{d \ln k_1}{dT} = \frac{1}{kT^2} \left[\frac{\sum_j \epsilon_j k_j p_j e^{-\epsilon_j/kT}}{\sum_j k_j p_j e^{-\epsilon_j/kT}} - \frac{\sum_i \epsilon_i p_i e^{-\epsilon_i/kT}}{\sum_i p_i e^{-\epsilon_i/kT}} \right] \quad (4)$$

$$= (1/kT^2) [\bar{\epsilon} - \bar{\epsilon}] = E_{\text{act.}}/RT^2. \quad (5)$$

The last term in the bracket is the average energy $\bar{\epsilon}$ of all molecules, while the first term refers to the average energy of the molecules in j states, in which the usual weight factor p_j has been replaced by $k_j p_j$. This means that $\bar{\epsilon}$ refers to the average energy of the molecules which react. The quantity $N(\bar{\epsilon} - \bar{\epsilon})$ will be defined as the energy of activation per gram mole.

Since the reacting molecules constitute but a minute fraction of the total, no sensible error is made by identifying $\bar{\epsilon}$ as the average energy of those molecules which do not react.

To obtain an expression for the variation of the energy of activation with temperature, we differentiate Tolman's expression, Eq. (4), and obtain a quantity $C_{\text{act.}}$ which we shall call the *heat capacity of activation*.

$$d[kT^2(d \ln k_1)/dT] = d(E_{\text{act.}})/dT = C_{\text{act.}} \quad (6)$$

partial heat capacity of the molecules which react, but differs from the thermodynamic heat capacity of the molecules in activated states since each p_j has been replaced by $k_j p_j$ in the averaging process.

The integration of Eq. (1) under the assumption that $E_{\text{act.}}$ is independent of T is equivalent to setting Eq. (8) equal to zero, i.e., $\sum \bar{C}_{\text{act.}} = \bar{C}_{X(\text{act.})} - (\bar{C}_A + \bar{C}_B)$ is zero for the bimolecular reaction $A + B \rightleftharpoons X \rightarrow R$.

When heat capacities are neglected free energy and total energy become indistinguishable. This approximate treatment, corresponding in the integrated form to

$$\ln k = 2.3B - E_{\text{act.}}/RT \quad (9)$$

has met with considerable success in the treat-

ment of gaseous reactions, notably in the hands of Hinshelwood.⁹

The correction which we introduce by considering the temperature dependence of $E_{\text{act.}}$ can be understood better by pointing out the close analogy to the corresponding thermodynamic process of calculation. The integral

$$\int \frac{E_{\text{act.}}}{T^2} dT = -\frac{E_{\text{act.}}}{RT} + \int \left(\frac{\partial E_{\text{act.}}}{\partial T} \right) d \ln T.$$

The last term by definition is equal to $\int C_{\text{act.}} d \ln T$, which is in complete analogy with the thermodynamic expression for the entropy S ; namely, $S = \int (\partial E / \partial T) d \ln T$. We therefore consider it entirely justifiable to speak of the *entropy of activation*, $S_{\text{act.}}$, provided it is kept clearly in mind that $S_{\text{act.}}$ contains the kinetic factors k_j found in the first terms of Eq. (7).

It cannot be emphasized too strongly, that to neglect the entropy of activation, as is the case, (Eq. 9), when $E_{\text{act.}}$ is taken independent of T , has no more justification than would be the omission of the entropy terms involved in the calculation of a thermodynamic equilibrium.

In the case of electrolytes the assumption that $C_{\text{act.}} = 0$ is certainly not justified *a priori*. We shall accordingly integrate under the assumption that $E_{\text{act.}}$ is a function of T , even though we cannot take full advantage of the improvement produced; thus,

$$\ln k = \text{constant} + \frac{1}{2} \ln T - \frac{F_{\text{act.}}}{RT}. \quad (10)$$

The free energy of activation, $F_{\text{act.}} = E_{\text{act.}} - TS_{\text{act.}} = \bar{F}_{X(\text{act.})} - (\bar{F}_A + \bar{F}_B)$, where the bars refer to the chemical potentials. The subscript, activation, is retained for the X or critical state to emphasize that $\bar{F}_{X(\text{act.})}$ contains the k_j factors and therefore refers to the molecules which react, whereas \bar{F}_A and \bar{F}_B are free from k_j

factors. The X state is the rate determining intermediate state.

The constant in (10) is evaluated by comparison with $\ln k$ when $F_{\text{act.}} = 0$. For a process without activation, every collision will be fruitful and the *constant* $= \ln Z^0 - \frac{1}{2} \ln T$. For a dilute gas, Z^0 is the gas kinetic constant for the number of collisions per unit of time $= 2\sigma_1\sigma_2[2\pi RT(m_1+m_2)/m_1m_2]^{\frac{1}{2}}$, and has the dimensions of a frequency (time^{-1}).

III. SYSTEMS WITH INTERACTION. THE BRONSTED EQUATION

To account for changes in the medium with changes in concentration, Bronsted¹⁰ generalized the classical theory of reaction velocity by introducing the activity coefficients of the reactants and the critical complex in terms of a kinetic factor $f_A f_B / f_X$. His theory although most useful in treating ionic reactions is by no means so limited. The foundation of his equation has been the subject of much discussion^{11, 12, 13, 4} and a direct derivation is highly desirable.

The statistics, upon which Eqs. (1-7) are founded, were developed primarily for perfect gas mixtures. For such systems, the quantities ϵ_i , ϵ_j and k_j are independent of both temperature and concentration. However, when we consider more concentrated systems, and particularly the liquid state, ϵ_i , ϵ_j and presumably also k_j will depend upon the mutual energy of the molecules. These quantities may consequently depend upon the concentration and temperature, since the energy of each molecular system depends upon the configuration of all other molecular systems in the assembly.

The ensemble¹⁴ method of Gibbs, in contrast to the classical development of Boltzmann recognizes the fundamental character of the problem of interaction energy by including it in the conditional equations employed in deriving the

⁹ C. N. Hinshelwood, *Kinetics of Homogeneous Gas Reactions*, Oxford, 1929, p. 42, where the view is advanced that "if when $\log k$ is plotted against $1/T$ a straight line is not obtained, this is an almost certain indication that the observed reaction is a composite one made up of two or more concurrent reactions differently influenced by temperature." Cf. Kassel, reference 6, pp. 149-56, where the data on hydrogen iodide have been subjected to a critical reexamination and the conclusion drawn that $E_{\text{act.}}$ increases with temperature.

¹⁰ Bronsted, *Zeits. f. physik. Chemie* **102**, 169 (1922); **115**, 337 (1925).

¹¹ Bjerrum, *Zeits. f. physik. Chemie* **108**, 82 (1924); **118**, 251 (1925).

¹² Christiansen, *Zeits. f. physik. Chemie* **113**, 35 (1924).

¹³ Skrabal, *Zeits. f. physik. Chemie* **B3**, 247 (1929).

¹⁴ W. Gibbs, reference 8, pp. 36-7. Consult also Fowler, reference 7, where certain aspects of the problem are stated but not solved, pp. 164-5, 181-2, 307.

distribution laws. Unfortunately an explicit solution by the Gibbs method encounters unsurmountable mathematical difficulties, so that for the present we must abandon a rigorous statistical derivation and resort to thermodynamic analogies as our guide. In a thermodynamic procedure the correction factors due to interaction will enter as the empirically determined activity coefficients.

In this section we shall drop, temporarily, the subscript, activation, to simplify the notation, but without losing sight of the kinetic character of such quantities. In analogy with thermodynamic procedure we decompose \bar{F} into an ideal part $\bar{F}_{id.}$ and a non-ideal or excess part, \bar{F}_e , arising from interaction effects.

Thus

$$\bar{F} = \bar{F}^0(T) + RT \ln f(T, c) \quad (11)$$

$$= \bar{F}_{id.} + \bar{F}_e(T, c), \quad (11a)$$

equations which serve as definitions for the activity coefficient, f . The small c will refer to concentration, the large capital C to ideal heat capacity.

The omission of the term $RT \ln c$ for $\bar{F}_{id.}$ requires justification. In evaluating the free energy of activation, we are concerned only with the individual energy levels which are independent of concentration for the perfect gas mixture. Terms of the type $RT \ln c$ arise from the disorder which occurs when molecules of different types are mixed but not when like types are mixed (Gibbs paradox). In the present instance, the integration producing $\bar{F}_{id.}$ involves only quantities which are characteristic of the energies of each individual group of molecules, and consequently no terms of the type $RT \ln c$ can appear in the expression for \bar{F} . This may be more evident by considering the formal analogy to the previously mentioned thermodynamic integral $S = \int C d \ln T$, where C represents the ideal heat capacity, which of course cannot produce the term $R \ln c$, which arises from the Gibbs paradox.

On the other hand, the $RT \ln f$ term originates from the integration of the corresponding non-ideal heat capacity term produced by interaction effects whereby an excess entropy and a corresponding excess free energy result.

Introducing (11) and (11a) in (10) yields

$$\ln k = \ln Z^0 - \sum \bar{F}^0/RT - \sum \bar{F}_e/RT, \quad (12)$$

$$k = Z^0 \exp \left(\frac{-[\bar{F}_{X(\text{act.})} - (\bar{F}_A + \bar{F}_B)]}{RT} \right) \frac{f_A f_B}{f_X}. \quad (13)$$

As a result, we have Bronsted's Eq. (14)

$$k = k_0(f_A f_B)/f_X \quad (14)$$

which can also be written

$$k = k_0 e^{-F_e/RT}$$

when k_0 is set equal to

$$Z^0 \exp \left(\frac{-[\bar{F}_X^0 - (\bar{F}_A^0 + \bar{F}_B^0)]}{RT} \right) = Z e^{-F^0/RT}. \quad (15)$$

The choice of the constants \bar{F}_X^0 , \bar{F}_A^0 , \bar{F}_B^0 , which are independent of concentration, implies that $f_A f_B / f_X$ is normalized as unity for the reference solvent; hence any dependence upon concentration arising from a change in the medium (for example, neutral salt addition) finds expression in terms of the activity coefficients. In passing from the gaseous to new liquid states of reference, any purely kinetic factors such as viscosity, which can affect the numerical value of Z^0 will have to be taken into account.^{15, 16} k_0 thus corresponds to the specific velocity constant in the reference solvent when freed from all interactions between A , B and X *except idealized collisions*, but not from interaction with the solvent. If relative activity coefficients are normalized for each new solvent, the effect of interaction with the solvent will appear in the values of \bar{F}_X^0 , \bar{F}_A^0 , \bar{F}_B^0 required for each solvent.

We believe that in our method of approach we have given for the first time a clear meaning to the quantities f_X or \bar{F}_X^0 , by emphasizing the limitations which must be placed upon all attempts to interpret f_X as a pure thermodynamic quantity, for example, when f_X is replaced by a simple theoretical expression like the Debye limiting law which obviously cannot contain k_i factors.

Only in the special case where the k_i values are all equal or only one j level is involved, do the k_i values cancel in the averaging process, so that f_X

¹⁵ Jowett, Phil. Mag. 8, 1059 (1929).

¹⁶ Moelwyn-Hughes, J. Chem. Soc. (London) 1932, 95.

can be interpreted as a pure thermodynamic quantity. Equality of the k_i factors is unlikely. On the other hand, if the reaction proceeds through a single quantum state j , then by Eqs. (7) and (8), the heat capacity of the reacting molecules is zero and $C_{\text{act.}} \leq 0$; i.e., $E_{\text{act.}}$ must be constant or decrease with rising temperature. Consequently if $E_{\text{act.}}$ increases with T we have convincing evidence that the reaction proceeds through more than one reactive level and the X state is multiple.

As a corollary of our theory we have the proposition that whenever $E_{\text{act.}}$ rises with temperature, substitution of a thermodynamic expression (f. ex. (D.H.L.L.)) for f_X is illegitimate. Even if $C_{\text{act.}} \leq 0$, we cannot be certain that the X state is not multiple, since a finite heat capacity for the reacting molecules may be counterbalanced by the heat capacity of the non-reacting molecules.

Hinshelwood's statement⁹ that inconstancy of $E_{\text{act.}}$ indicates a composite reaction is, of course, true when considered from the standpoint of paths involving different quantum levels, but from the context his statement is obviously intended for the appearance of side reactions involving the production of new chemical species or entirely new mechanisms in the chemical sense.

IV. ENTROPY OF ACTIVATION, AND THE COLLISION THEORY

Recently Moelwyn-Hughes¹⁷ has extended the simple collision theory of gaseous reactions to solutions. He determines $E_{\text{act.}}$ from measurements of the temperature coefficient, and from the gas kinetic value of Z , using reasonable values of the molecular radii σ_1 , and σ_2 he computes a theoretical value of k .

For a large number of reactions the calculated value of k differs from the observed by a factor of only 10 to 100. Consequently Moelwyn-Hughes concludes that the simple collision theory is applicable to solutions.

There are two reasons why this is not convincing: (1) For a group of reactions (mostly

bimolecular associations), Moelwyn-Hughes finds k is 10^4 to 10^9 times smaller than that calculated, while our unpublished results for the β -bromopropionate-thiosulfate reaction yield rates which are many times greater than those calculated from his theory, in spite of the fact that the repulsive action of the electric charges might be expected to reduce the rate. (2) Moelwyn-Hughes' theory neglects completely the possibility of an entropy of activation ($S_{\text{act.}}$) resulting from a temperature dependence of $E_{\text{act.}}$.

By comparing Eqs. (9) and (10), we find

$$B = \log Z^0 + S_{\text{act.}}/2.3R, \quad (16)$$

where $S_{\text{act.}}$ is equal to

$$\int_0^T C_{\text{act.}} d \ln T.$$

The Hinshelwood-Moelwyn-Hughes theory makes the tacit assumption that the heat capacities of activation of the reacting and of the non-reacting molecules remain *identical down to absolute zero*. There is no valid theoretical reason for such an assumption, especially when one considers that for such minor differences as that of proton spin, the heat capacities of ortho and para hydrogen differ considerably at low temperatures,¹⁸ and consequently possess different entropies at room temperature.

There are six important cases connecting $E_{\text{act.}}$, $S_{\text{act.}}$, $C_{\text{act.}}$, Z^0 and B .

Case I. $C_{\text{act.}} > 0$ at all temperatures; $E_{\text{act.}}$ rises with increasing T ; $S_{\text{act.}} > 0$, and $B > \log Z^0$.

Case II. $C_{\text{act.}} > 0$ in the range of experimental measurement (high T) but $C_{\text{act.}} \ll 0$ at lower temperatures. Then $S_{\text{act.}} < 0$ and $B < \log Z^0$ in the range of investigation.

Case III. $C_{\text{act.}} < 0$ at all temperatures. $E_{\text{act.}}$ decreases; $S_{\text{act.}} < 0$; $B < \ln Z^0$.

Case IV. $C_{\text{act.}} < 0$ at high T , but $C_{\text{act.}} \gg 0$ at low T . $S_{\text{act.}} > 0$ and $B > \log Z^0$ in range of measurement.

Case V. Condition for the validity of Arrhenius assumption. $C_{\text{act.}} = 0$ within experimental error in temperature range of measurement; $S_{\text{act.}} > 0$ or

¹⁷ Moelwyn-Hughes, Chem. Rev. **10**, 241 (1932); Nature **129**, 316 (1932); J. Chem. Soc. (1932) 95; with Hinshelwood, (1932) 230; with Rolfe, (1932) 241.

¹⁸ Eucken, Hiller and Clusius, Zeits. f. physik. Chemie **B4**, 142 (1929); *Treatise on Physical Chemistry*, Van Nostrand (1931), p. 305.

$S < 0$ depending upon behavior of $C_{act.}$ at low T . $B > \log Z^0$, or $B < \log Z^0$.

Case VI. Condition for the validity of the Hinshelwood-Moelwyn-Hughes theory. $C_{act.} = 0$ at all temperatures or varies in such a way at low temperatures that $S_{act.} = 0$; then $B = \log Z^0$.

V. EXPERIMENTAL DATA

It is unfortunate that $E_{act.}$ cannot be measured at low temperatures to reveal to what extent the neglect of the entropy of activation accounts for the failure of the collision theory. However, a critical examination of the best existing data discloses that $E_{act.}$ varies with T in the range of measurement. All values of $E_{act.}$ have been recalculated from original data by using $R = 1.9885$ calories and $T = 273.13$ for the ice point. B is in minutes.

Table I refers to Wiig's results for the decomposition of acetone-dicarboxylic acid from 0 to 60°C at 10° intervals. No statement of the reproducibility of the individual measurements is given, but since with two different analytical techniques k checks to 1 percent (± 300 calories in $E_{act.}$) the probable error in a series for the same technique may be less. Dr. Wiig informs me that a reexamination of his original data shows that the average deviation from the mean at each temperature is about 1 percent.

The reversal in sign of $C_{act.}$ would be disregarded were it not uniformly exhibited by Segaller's extensive studies on the reaction between primary, iso- and secondary alkyl iodides with sodium phenoxide. Our calculations for the

TABLE I. The decomposition of acetone-dicarboxylic acid in water.*

B (1st order); time units minutes⁻¹.

$t^\circ\text{C}$	B	$E_{act.}$	$C_{act.}$
0-10°	13.58	22749	24
10-20	13.77	22993	
20-30	14.03	23340	35
30-40	14.37	23826	
40-50	14.13	23477	-35
50-60	14.00	23244	

* Wiig, J. Phys. Chem. **32**, 961 (1928); **34**, 596 (1930).

primary iodides, which cover a 50° range are given in Table II. Segaller called attention to the fact that his measurements at higher temperature did not fall on a straight line for a $\log k$, $(1/T)$ plot, and contends the discrepancy cannot be due to experimental error.

In Fig. 1 are plotted the values of $C_{act.}$ calculated from Wiig's data (J. Am. Chem. Soc. **53**, 4729 (1930) Table VI) for $k_{25^\circ}/k_{15^\circ}$ and $k_{35^\circ}/k_{25^\circ}$ for the decomposition of citric acid in concentrated sulfuric acid. With the exception of the two points at low water content, it is very interesting to note that with increasing water content, $C_{act.}$ changes quite uniformly from negative to positive values. This means that the addition of water increases the heat capacity of the reactive complex.

In Table III are given calculations from G. M. Murphy's measurements on the diacetone-alcohol reaction, considered as a bimolecular

TABLE II. The reaction of sodium phenoxide with primary alkyl iodides.*

Solvent, absolute ethanol. B (2nd order); $B = \text{min.}^{-1}$.

Alkyl iodide	$t = 30.1^{\circ} - 42.5^{\circ}$		$t = 42.5^{\circ} - 58.5^{\circ}$		$E_{50.5^{\circ}} - E_{36.3^{\circ}}$	$t = 58.5^{\circ} - 80.1^{\circ}$		$E_{69.3^{\circ}} - E_{50.5^{\circ}}$
	E	B	E	B		E	B	
Methyl	20,945	13.28	21,876	13.92	(931)	—	—	—
Ethyl	21,067	12.71	21,604	13.08	537	21,263	12.86	-341
Propyl	21,508	12.60	22,048	12.98	540	21,561	12.65	-487
Butyl	20,560	11.92	22,197	13.05	637	21,551	12.62	-646
Amyl	20,696	11.63	22,353	12.79	657	21,385	12.15	-968
Hexyl	20,622	11.94	22,175	13.01	553	21,770	12.75	-405
Heptyl	20,834	12.07	22,183	13.00	549	21,958	12.85	-225
Octyl	21,199	12.31	22,364	13.12	(1,165)	22,050	12.90	-314
Hexadecyl	21,307	12.37	22,188	12.98	(881)	22,146	12.96	-42
Average $C_{act.}$					41 cal. deg. ⁻¹			
						-2 to -51 cals. deg. ⁻¹		

* D. Segaller, J. Chem. Soc. **105**, 106 (1914).

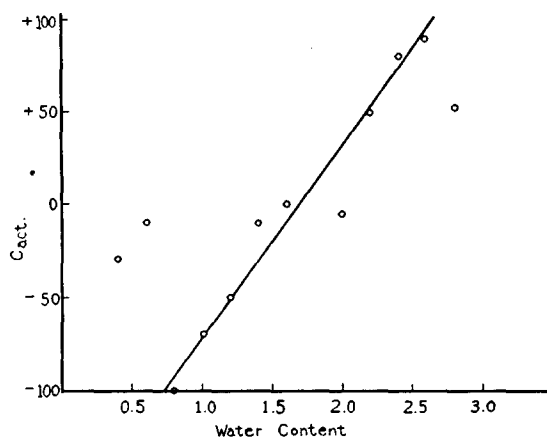


FIG. 1. Heat capacity of activation in calories/deg. mole (15–25°; 25–35°) for the water inhibited reaction. Thermal decomposition of citric acid in concentrated sulfuric acid as function of water content. Data by Wiig, J. Am. Chem. Soc. 53, 4729 (1930), Table VI.

TABLE III. The decomposition of diacetone-alcohol by 0.1M sodium hydroxide. E precise to ± 0.7 percent.*

B (mols. liter⁻¹ min.⁻¹ is computed on the basis of a bimolecular reaction between NaOH and diacetone-alcohol. B (1st order) = B (2nd order) - 1. Log Z° ($\sigma = 5A^\circ$) = 13.36 (min.⁻¹).

Solvent	E	B	E	B	$C_{act.}$
Water + 0.1M NaOH	20°–30°		25°–35°		
0% CH ₃ OH	17,040	12.19	18,098	12.94	211
10% "	17,638	12.50	18,670	13.20	206
20% "	18,311	12.85	19,481	13.70	234
30% "	18,525	12.88	19,694	13.74	234
40% "	18,852	12.99	19,822	13.71	194
50% "	19,349	13.23	20,080	13.78	146
60% "	19,776	13.42	20,578	14.03	160

* G. M. Murphy, J. Am. Chem. Soc. 53, 977 (1931).

reaction with 0.1M NaOH. A precision of 0.7 percent or 126 calories is claimed for $E_{act.}$. It will be noted that $E_{act.}$ increases over a ten degree interval by roughly 1000 calories or eight times the probable error. A calculation based upon 5° intervals indicates decreasing values of $C_{act.}$ with increasing T as in Table II. This reaction is now being investigated in this laboratory over wider ranges of temperature to verify this deduction.

VI. CONCLUDING REMARKS

After this paper was practically completed for publication the interesting papers of Scheffer¹⁹

¹⁹ Scheffer and Brandsma, Rec. Trav. Chim. 45, 522 (1926).

and Brandsma²⁰ were discovered, where the importance of considering the free energy and entropy of the intermediate state is emphasized. Their viewpoint differs from ours in at least one important respect. They consider that these pure thermodynamic properties determine the rate, whereas we consider the rate determining properties of the intermediate state to be in general kinetic quantities, since they contain k_i factors. Except for this difference, their thesis that part of the entropy of activation arises from "steric factors" and "sensitive districts" in the molecule is one which we had developed independently from our studies of the temperature dependence of ionic reactions, considered from the standpoint of the orientation theory.²¹

We can also support Scheffer and Brandsma's conclusion that the effect of a catalyst does not always result in a lowering of the energy of activation, by the following example. The velocity of the sodium bromoacetate-sodium thiosulfate reaction in highly dilute solution is increased over sixfold by the addition of small amounts of lanthanum chloride.²²

For the range 0–25°C, it has been found that $E_{act.}$ ²³ increases from $15,850 \pm 64$ to $17,700 \pm 55$ calories by the addition of 0.03M LaCl₃. An increase of 1850 calories in $E_{act.}$ should of itself decrease the velocity, were it not more than counterbalanced by an increase in the entropy of activation as exhibited by an increase in B from 11.20 to 13.40. As was anticipated quite different results, are found for the β -bromopropionate-thiosulfate reaction.

The author wishes to acknowledge the constructive criticisms which he has received in the preparation of this paper from his colleagues and from Professor Otto Halpern of the Department of Physics of New York University.

VII. CONCLUSIONS

(1) Evidence is presented that the energy of activation, measured by the temperature coefficient of the reaction velocity, varies with temper-

²⁰ Brandsma, *ibid.* 47, 94 (1928); 48, 1205 (1929).

²¹ Reference 3, p. 2850; reference 4, p. 210.

²² La Mer and Fessenden, J. Am. Chem. Soc. 54, 2351 (1932).

²³ Unpublished work of La Mer and Kamner.

ature. This necessitates a consideration of the activation quantities, heat capacity, free energy and entropy.

(2) The kinetic character of these quantities becomes evident when they are developed from R. C. Tolman's statistical formulation of the Arrhenius equation.

(3) The Brönsted equation follows readily from the concept of free energy of activation. However, the development shows that the activity coefficient of the critical complex $f_{X(\text{act.})}$ is in general a kinetic quantity which becomes equivalent to the corresponding thermodynamic quantity only when all quantum levels have the

same reactivity constant, or when only one quantum level is involved.

(4) A positive heat capacity of activation furnishes evidence that the critical state is multiple in the quantum sense and that it is illegitimate to replace $f_{X(\text{act.})}$ by a thermodynamic expression.

(5) The Hinshelwood-Moelwyn-Hughes collision theory can be valid only when the entropy of activation is zero, which is improbable from the standpoint of quantum theory, the thermodynamic requirements of equilibrium processes, or the available data for activation energies in the ranges of experimental measurement.