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The Arrhenius Equation and the Active Complex Method

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The question as to which of the forms of the Arrhenius equation should be used in calculating the activation energy and entropy of an active complex (transition state) is not yet wholly settled in the literature. Evans and Polanyi[1] maintained that the entropy of an active complex should be calculated using the quantity K_a from the equation

$$k_v = \varkappa \frac{1}{2} K_a \bar{v} \tag{1}$$

previously derived by these autors[2], but not $K^{\ddagger}$ determined by the equation of Wynne-Jones and Eyring[3]

$$k_v = \varkappa K^{\ddagger} \frac{kT}{h} \tag{2}$$

(k_v is the reaction velocity constant, K_a and $K^{\ddagger}$ are equilibrium constants for the equilibrium between the initial molecules and the active complex, defined in different ways[4]; $\bar{v}$ — the average velocity of crossing the potential barrier, k — Boltzmann's constant; T — the absolute temperature; h — Planck's constant; $\varkappa$ — the transmission coefficient).

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[1] M. G. Evans and M. Polanyi, Trans. Farad. Soc., **33**, 448 (1937).

[2] M. G. Evans and M. Polanyi, Trans. Farad. Soc., **31**, 875 (1935).

[3] W. F. K. Wynne-Jones and H. Eyring, J. Chem. Phys., **3**, 492 (1935).

[4] The relation between these quantities is as follows:

$$K_a = K^{\ddagger} \frac{(2\pi m^* kT)^{1/2}}{h},$$

where m^* is the reduced mass of the active complex.

Guggenheim[5] and Eyring[6] objected to this point of view. The Arrhenius equation is used both in the form

$$\frac{d \ln k_v}{dT} = \frac{A}{RT^2} \tag{3}$$

and in the form

$$\frac{d \ln k_v}{dT} = \frac{A'}{RT^2} + \frac{1}{2T} = \frac{A' + \frac{1}{2} RT}{RT^2}, \tag{4}$$

where A, or A', is the activation energy per mol, and R is the gas constant.

Eq. (3) is very frequently applied to unimolecular reactions, and eq. (4) to bimolecular ones in accordance with Tolman's derivation[7]. According to Polanyi and Evans, eq. (4) should be used regardless of the reaction order, since $\overline{v}$ in eq. (1) is proportional to $\sqrt{T}$. The latter opinion was shared by Guggenheim[5]. On the other hand, some authors, *e. g.*, Gershinowitz and Rice[8], maintained that eq. (4) may be applied to bimolecular reactions.

A number of other examples of such uncertainty and contradictions existing in the literature might be readily quoted. It may therefore be thought that a systematic examination of the question as to the constants in the Arrhenius equation from the standpoint of the active complex method — a task which constitutes the subject of this paper — will prove useful though it may contain nothing essentially new.

Activation Energy

Eyring's fundamental equation for homogeneous gas reactions[9] may be represented in the following form:

$$k_v = \varkappa \frac{G_i'}{G_1} \frac{kT}{h}. \tag{5}$$

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[5] E. A. Guggenheim, Trans. Farad. Soc., **33**, 607 (1937).

[6] H. Eyring, Trans. Farad. Soc., 34, 41 (1938).

[7] R. S. Tolman, "Statistical Mechanics", N. Y. Chemical Catalog Co., (1927).

[8] H. Gershinowitz and O. K. Rice, J. Chem. Phys., **2**, 273 (1934).

[9] H. Eyring, J. Chem. Phys., 3, 107 (1935).

Here $\varkappa$ is the transmission coefficient which may be considered independent of the temperature; the reaction velocity constant k_v is calculated for concentrations expressed as numbers of molecules in 1 cm^3.; G_1 is the product of complete partition functions for the initial molecules, *i. e.*, sums over the states calculated for the molecules contained in 1 cm.^{3}:

$$G=\sum_i e^{-\frac{\varepsilon_i}{kT}};\ v=1\text{ cm.}^3; \tag{6}$$

ε_i is the energy of a molecule in the state i; the summation[10] is carried out over all the possible states of a molecule in a volume of 1 cm.^{3}.

G'_t is the partition function for the active complex, calculated over all its degrees of freedom except the co-ordinate l — the "reaction path". The energies of the states are reckoned from the same initial level as for the molecules of the reagents.

It follows from eq. (6) that

$$\frac{d\ln G}{dT}=\frac{1}{kT^2}\frac{\sum_i \varepsilon_i e^{-\varepsilon_i/kT}}{\sum_i e^{-\varepsilon_i/kT}}=\frac{\bar{\varepsilon}}{kT^2}, \tag{7}$$

where $\bar{\varepsilon}$ is the average energy of a molecule. Eq. (5) therefore gives

$$\frac{d\ln k_v}{dT}=\frac{\bar{\varepsilon}'_t-\bar{\varepsilon}_1}{kT^2}+\frac{1}{T}=\frac{\bar{\varepsilon}'_t-\bar{\varepsilon}_1+kT}{kT^2}, \tag{8}$$

in which $\bar{\varepsilon}'_t$ is the average energy of the active complexes over all degrees of freedom except the reaction path, and $\bar{\varepsilon}_1$ is the average energy of the initial molecules. The "reaction path" l being considered as a translational degree of freedom, it may seem at first sight that the average energy corresponding to it equals $\frac{1}{2}kT$ and, consequently, that eq. (8) is equivalent to (4). This, however, is not the case.

In calculating the average energy one should take account of the velocity, along the co-ordinate l, of the points which represent the active complexes on the potential energy surface, and introduce a weight fac-

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[10] If the summation were carried out over the energy levels, we should write $G=\sum_i p_i e^{-\frac{\varepsilon_i}{kT}}$, where p_i is the number of states with energy ε_i. Eq. (6) is equivalent to this, since the summation is made over the states.

tor equal to the velocity along l, *i. e.*, $\frac{p_l}{m^*}$ where p_l is the momentum along the co-ordinate l and m^* is the reduced mass.

Indeed, within a time interval dt, over the top of the barrier will pass those of the points possessing some definite momentum p_l which lie at a distance $\frac{p_l}{m^*}\,dt$ or less from the plane perpendicular to the co-ordinate l and drawn through the barrier top. The number of such points per unit length along the co-ordinate l is proportional to $e^{-p^2{}_l/2m^*kT}$, and hence the number of points possessing a momentum p_l and penetrating through the barrier plane is proportional to

$$\frac{p_l}{m^*}\,e^{-p_l^2/2m^*kT}.$$

We thus have

$$\bar{\varepsilon}_l = \frac{\int\limits_0^\infty \frac{p_l^2}{2m^*}\,\frac{p_l}{m^*}\,e^{-p_l^2/2m^*kT}\,dp_l}{\int\limits_0^\infty \frac{p_l}{m^*}\,e^{-p_l^2/2m^*kT}\,dp_l} = kT, \tag{9}$$

where $\bar{\varepsilon}_l$ is the average energy of the reacting molecules associated with the co-ordinate l. The total mean energy of the reacting molecules, $\bar{\varepsilon}_l = \bar{\varepsilon}_l' + \bar{\varepsilon}_l$, is consequently equal to $\bar{\varepsilon}_l' + kT$.

Eq. (8) therefore gives

$$\frac{d\ln k_v}{dt} = \frac{\bar{\varepsilon}_l - \bar{\varepsilon}_1}{kT^2}, \tag{10}$$

which is equivalent to eq. (3).

Eq. (10) was first derived by Tolman, though only for unimolecular reactions. From the above derivation it follows that it holds for any reaction order; the quantity A calculated by eq. (3) gives in all cases the difference between the mean energies of the reacting and initial molecules.

The pre-exponential factor

Integration of eq. (10) under the assumption of constancy of $\bar{\varepsilon}_l - \bar{\varepsilon}_1$ over a narrow temperature range leads to the equation

$$k_v = Be^{-\frac{\bar{\varepsilon}_l - \bar{\varepsilon}_1}{kT}}, \tag{11}$$

where B, *i. e.*, the integration constant in the Arrhenius equation, may be evaluated by the active complex method.

Eyring[9] derived the following equation, which is equivalent to eq. (5):

$$k_v = \varkappa \frac{F_t'}{F_1} \frac{kT}{h} e^{-\frac{\varepsilon_{0t}-\varepsilon_{01}}{kT}} . \tag{12}$$

In this equation the partition functions F are defined as follows:

$$F = \sum_i e^{-\frac{\varepsilon_i-\varepsilon_0}{kT}} ; \; v = 1 \text{ cm.}^3 , \tag{13}$$

or

$$F = G e^{\varepsilon_0//kT} , \tag{13a}$$

where ε_0 is the energy of the lowest energy level of a molecule or zero-point energy. It follows that here the energy of a molecule at $T=0$ is taken as the initial energy level in contradistinction to functions G for which the initial energy level is arbitrary and equal for the reacting substances, reaction products, and active complexes.

The difference $\varepsilon_{0t}-\varepsilon_{01}$ between the zèro-point energies of the active complex and the initial molecules, *i. e.*, the height of the energy barrier, may be called the activation energy at $T=0$; it is evidently not equal to $\bar{\varepsilon}_t-\bar{\varepsilon}_1$, *i. e.*, to the activation energy at a temperature T.

Consequently, the quantity B is not equal to $\varkappa \frac{F_t'}{F_1} \frac{kT}{h}$ either.

Before examining the question as to the expression for B in eq. (11) let us consider the same point with respect to the equilibrium constant. The latter obeys the following equation

$$K = \frac{G_2}{G_1} \tag{14}$$

or

$$K = \frac{F_2}{F_1} e^{-\frac{\varepsilon_{02}-\varepsilon_{01}}{kT}} . \tag{15}$$

Here G_2 is the product of the complete partition functions for the reaction products etc. The equilibrium constant K is defined as the ratio of the product of concentrations of reaction products to the product of concentrations of initial substances, the concentrations being, as before, expressed in numbers of molecules per 1 cm.^{3}.

From eq. (14) we obtain with the aid of eq. (7):

$$\frac{d \ln K}{dT} = \frac{\bar{\varepsilon}_2 - \bar{\varepsilon}_1}{kT^2}, \tag{16}$$

i. e., the van't Hoff equation.

Let us introduce a function w defined by the equation

$$w = \sum_i e^{-\frac{\varepsilon_i - \bar{\varepsilon}}{kT}}; \quad v = 1 \text{ cm.}^3, \tag{17}$$

or

$$w = Ge^{\bar{\varepsilon}/kT}; \tag{17a}$$

w is therefore a partition function in whose calculation the energy taken as the initial energy level is the average energy of molecules at the given temperature. Such partition functions have already been considered by Rodebush[11].

Then it is evident that

$$K = \frac{w_2}{w_1} e^{-\frac{\bar{\varepsilon}_2 - \bar{\varepsilon}_1}{kT}}, \tag{18}$$

i. e., the pre-exponential factor in the van't Hoff equation (in the integral form) is equal to the ratio of the products of functions w for the reaction products and initial substances.

The function w may be readily expressed in terms of the function F. Indeed, from eqs. (17a) and (13a) it follows that

$$w = Fe^{-\frac{\bar{\varepsilon} - \varepsilon_0}{kT}}.$$

Now we have

$$\frac{d \ln F}{dT} = \frac{\bar{\varepsilon} - \varepsilon_0}{kT^2}, \tag{19}$$

and hence we obtain

$$w = Fe^{T \frac{d \ln F}{dT}} \tag{20}$$

or

$$\ln w = \ln F + T \frac{d \ln F}{dT}. \tag{21}$$

To disclose the meaning of the function w let us resort to the

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[11] W. H. Rodebush, Chem. Rev., 9, 319 (1931).

relation between the chemical potential μ of an ideal gas and the partition function F:

$$\mu = -kT \ln \frac{F}{c} + \varepsilon_0, \tag{22}$$

where the chemical potential is referred to one molecule.

Let us introduce the chemical potential of a standard state, μ^0, meaning by the latter the state corresponding to a concentration of 1 molecule per cm.^{3} ($c = 1$). Then we have

$$\mu = \mu^0 + kT \ln c. \tag{23}$$

From eq. (22) we obtain

$$\mu^0 = -kT \ln F + \varepsilon_0. \tag{24}$$

Substituting in eq. (21) the expression for $\ln F$ according to eq. (24) we shall have

$$\ln w = -\frac{1}{k} \frac{d\mu^0}{dT}.$$

Since

$$\frac{d\mu^0}{dT} = -\left(\frac{\partial S^0}{\partial N}\right)_{v,\,T},$$

where S^0 is the entropy of the substance in the standard state and N is the number of molecules, we get

$$k \ln w = \left(\frac{\partial S^0}{\partial N}\right)_{v,\,T}. \tag{25}$$

From the general relation between the entropy S and the thermodynamic probability W,

$$S = k \ln W,$$

it follows that w is the ratio in which the thermodynamic probability of the substance in the standard state as defined above increases on addition of one molecule. The function w may therefore be termed the standard probability of a molecule.

It will be noted that the quantity $\left(\frac{\partial S^0}{\partial N}\right)_{v,\,T}$ does not coincide with the entropy of one molecule in 1 cm.^{3}. In fact it is known that the entropy for monatomic gases is given by

$$S = kN \ln \left[\frac{e^{5/2} v}{h^3 N} (2\pi mkT)^{3/2} \right],$$

where m is the mass of one molecule, and hence

$$\left(\frac{\partial S}{\partial N}\right)_{v,\,T} = k \ln \left[\frac{e^{5/2} v}{h^3 N} (2\pi mkT)^{3/2} \right] - k = k \ln \left[\frac{e^{3/2} v}{h^3 N} (2\pi mkT)^{3/2} \right],$$

whence, for $c = \frac{N}{v} = 1$, we obtain

$$\left(\frac{\partial S^0}{\partial N}\right)_{v,\,T} = k \ln\left[\frac{e^{3/2}}{h^3}(2\pi mkT)^{3/2}\right],$$

whereas, for $N = 1$ and $v = 1$,

$$S = k \ln\left[\frac{e^{5/2}}{h^3}(2\pi mkT)^{3/2}\right].$$

Below we shall also obtain in another way the following relation for monatomic gases:

$$w = \frac{e^{3/2}}{h^3}(2\pi mkT)^{3/2}.$$

The partial molal quantities introduced by Lewis are defined as the derivatives of thermodynamic functions with respect to the number of mols of the component at constant pressure and temperature. For a pure substance, these derivatives are equal to the respective thermodynamic functions per one mol. This does not apply to the derivatives at constant volume and temperature.

Let us now pass to the question as to the expression for B in eq. (11). Equations (5) and (17a) give

$$k_v = \varkappa \frac{w_l'}{w_1} \frac{kT}{h} e^{-\frac{\bar{\varepsilon}_l' - \bar{\varepsilon}_1}{kT}} \tag{26}$$

or

$$k_v = \varkappa \frac{w_l'}{w_1} \frac{kTe^{-\frac{\bar{\varepsilon}_l' - \bar{\varepsilon}_1 + kT}{kT}}}{h}\,. \tag{27}$$

Taking into account that $\bar{\varepsilon}_l = \bar{\varepsilon}_l' + kT$ we obtain

$$k_v = \varkappa \frac{w_l'}{w_1} \frac{kTe}{h} e^{-\frac{\bar{\varepsilon}_l - \bar{\varepsilon}_1}{kT}}\,. \tag{28}$$

Equations (12) and (28) are equivalent to each other. Eq. (12) is convenient when a complete theoretical calculation is carried out to obtain the absolute value of the reaction rate, *i. e.*, when the potential energy surface is used to calculate both the height of the energy barrier and the distribution function of the active complex. If, however, only the pre-exponential factor is calculated theoretically, the activation energy being determined experimentally from the temperature dependence of the reaction velocity constant, eq. (28) should be used, since it directly contains the activation energy determined by the Arrhenius equation.

Calculation of standard probabilities

As is known, from the fact that the motion of the centre of gravity of a molecule is independent of the motion of its component parts, it follows that the partition function F may be represented as the product of the partition function for the translational motion $\frac{(2\pi mkT)^{3/2}}{h^3}$ (m is the mass of the molecule) and the partition function for the intra-molecular motions. The latter may be approximately expressed as the product of three factors: the electronic weight of the ground state p, the rotational partition function $\frac{8\pi^2 JkT}{\sigma h^2}$ for linear molecules, (J is the moment of inertia and σ the symmetry number), or

$$\frac{8\pi^2 (8\pi^3 J_A J_B J_C)^{1/2} (kT)^{3/2}}{\sigma h^3}$$

for non-linear molecules (J_A, J_B and J_C are the principal moments of inertia) and the product of vibrational partition functions $(1 - e^{-h\nu_i/kT})^{-1}$ according to the number of normal vibrations (ν_i is the frequency of a normal vibration).

It follows from eq. (20) that if the function F can be factored, the same may be said of the function w. Moreover, it follows from the same equation that if the function F has the form

$$F = bT^{\gamma}, \tag{29}$$

where b is independent of T, then

$$w = bT^{\gamma} e^{\gamma} = Fe^{\gamma}. \tag{30}$$

Hence, from the above expressions for F, it follows directly that for the translational motion the function w is given by

$$w_{\text{tr}} = \frac{(2\pi mkTe)^{3/2}}{h^3}, \tag{31}$$

whilst for rotational motion it equals

$$w_{\text{rot}} = \frac{8\pi^2 JkTe}{\sigma h^2}, \tag{32}$$

or

$$w_{\text{rot}} = \frac{8\pi^2 (8\pi^3 J_A J_B J_C)^{1/2} (kTe)^{3/2}}{\sigma h^3}, \tag{33}$$

in the cases of linear and non-linear molecules respectively. The electronic weight p is retained in the function w.

For harmonic vibration of frequency ν_i, the above expression for F and eq. (20) give

$$w'_{\text{vibr.}} = (1 - e^{-h\nu_i/kT})^{-1} \, e^{(h\nu_i/kT)} \, (e^{h\nu_i/kT} - 1)^{-1}. \tag{34}$$

The expressions given above render the use of standard probabilities in approximate calculations as simple as the application of partition functions.

It may be noted that the method previously applied by the present author to the computation of pre-exponential factors[12] was based on the fact that the expressions

$$k_v = Be^{-\varepsilon/kT}$$

and

$$k_v = B' \, T^{\gamma} \, e^{-\varepsilon'/kT}$$

may be held to be equivalent if $B = B' \, T_M^{\gamma} e^{\gamma}$ and $\varepsilon = \varepsilon' + \gamma kT_M$, where T_M is the mean temperature; this method fully agrees with the result obtained with the aid of functions w as may be seen from eqs. (29) and (30) and from comparison of eqs. (28) and (12).

Along with the calculation of the partition function of the active complex from the moments of inertia and frequencies either determined with the help of the potential energy surface for the given reaction or estimated in some other way, recourse is frequently had to calculation of this quantity from the experimental values of the reaction rates. In such cases Wynne Jones and Eyring's eq. (2) is ordinarily used, the constant $K^{\ddagger}$ being represented as follows:

$$K^{\ddagger} = e^{\frac{\Delta S^{\ddagger 0}}{R}} \, e^{-\frac{\Delta H^{\ddagger}}{RT}}. \tag{35}$$

The quantity $\Delta H^{\ddagger}$ is called the heat of activation and $\Delta S^{\ddagger 0}$ the entropy of activation. The latter quantity is the entropy change on formation of one mol of active complexes from the initial substances, both the former and the latter being taken at unit concentration. As active complexes, systems are taken in which the values of the "reaction path" co-ordinate lie within the interval $\frac{h}{(2\pi m^* kT)^{1/2}}$ including the top of the activation barrier.

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[12] M. Temkin, Acta Physicochimica URSS, 8, 141 (1938).

The quantity $\Delta H^{\ddagger}$ is defined by the equation

$$\frac{d \ln K^{\ddagger}}{dT} = \frac{\Delta H^{\ddagger}}{RT^2}, \tag{36}$$

and, since according to eq. (2) we may write

$$\frac{d \ln k_v}{dT} = \frac{d \ln K^{\ddagger}}{dT} + \frac{1}{T}, \tag{37}$$

it follows that

$$\Delta H^{\ddagger} = A - RT, \tag{38}$$

where A is defined by eq. (3), in accordance with eq. (10).

Since

$$k_v = \varkappa e^{\frac{\Delta S^{\ddagger 0}}{R}} e^{\frac{\Delta H^{\ddagger}}{RT}} \frac{kT}{h},$$

we have

$$k_v = \varkappa e^{\frac{\Delta S^{\ddagger 0}}{R}} \frac{kTe}{h} e^{-\frac{A}{RT}}. \tag{39}$$

Comparing the latter equation with eq. (28) we obtain in accord with the significance of the function w

$$\frac{w_i'}{w_1} = e^{\frac{\Delta S^{\ddagger 0}}{R}}. \tag{40}$$

It follows from the above that it is more expedient to introduce the constant $K^{\ddagger}$ not with the help of eq. (2) but in the following manner:

$$k_v = \varkappa K^{\ddagger} \frac{kTe}{h}. \tag{41}$$

For uniformity of notation we may introduce $\Delta E^{\ddagger} = A$. Then we have

$$K^{\ddagger} = e^{\frac{\Delta S^{\ddagger 0}}{R}} e^{-\frac{\Delta E^{\ddagger}}{RT}}. \tag{42}$$

The introduction of the quantity $\Delta H^{\ddagger}$ is superfluous.

The above refers to reactions between ideal gases. The question as to the form of the equations for solutions has been considered by Guggenheim[4]. His treatment, though faultless as a whole, requires but one correction: the constant $K^{\ddagger}$ must be determined by eq. (41) instead of eq. (2); Guggenheim has overlooked the specificity of the problem of calculation of the activation energy and therefore considers eq. (4) to be correct (see above).

Reactions at surfaces

The active complex method has been extended by the author to reactions at surfaces[12]. The application of the quasi-thermodynamic treatment, *i. e.*, calculation of the activation entropy from experimental values of the reaction velocity, requires in the first place that the standard state for the adsorbed substance should be defined. If we confine ourselves, as has been done by the author in the paper just cited, to the case of "simple adsorption", then the chemical potential of the adsorbed substance per molecule, μ_a, will be given by

$$\mu_a = -kT\ln F_a \frac{1-\theta}{\theta} + \varepsilon_{0a}, \qquad (43)$$

where θ is the fraction of the surface covered, and the quantities with the subscript *a* refer to the adsorbed substance.

Let the state for which $\theta = {}^1/_2$ be taken as the standard one. Then we have

$$\mu_a = \mu_a{}^0 + kT\ln\frac{\theta}{1-\theta}, \qquad (44)$$

μ_a being given by

$$\mu_a = -kT\ln F_a + \varepsilon_{0a}. \qquad (45)$$

As has been shown by the author, **Langmuir's** "law of surface action" which determines the reaction rate at the surface, ω, has the following general form:

$$\omega = k_v\,\theta_1^{n_1}\,\theta_2^{n_2}\ldots c_1^{r_1}\,c_2^{r_2}\ldots\theta_0^{s-(n_1+n_2+\ldots)}, \qquad (46)$$

where θ_1, $\theta_2, \ldots$ are the fractions of the surface covered by the substances entering into the reaction from the adsorbed state in the amounts of n_1, n_2 molecules, respectively; c_1, c_2 are the concentrations of the substances entering into the reaction directly from the gaseous phase in the amounts of r_1, $r_2\ldots$ molecules; θ_0 is the fraction of the surface free from adsorbed molecules; *s* is the number of sites on the surface, occupied by the active complex.

The reaction velocity constant in eq. (46) is expressed as follows:

$$k_v = \varkappa L\frac{gF_t'}{F_1}\frac{kT}{h}e^{-\frac{\varepsilon_{0t}-\varepsilon_{01}}{kT}}, \qquad (47)$$

where L denotes the number of sites on the surface, and g is the number of possible positions of the active complex when one of the sites it occupies is fixed.

On transition from functions F to functions w we shall have instead of eq. (47)

$$k_v = \varkappa L \frac{g w_t'}{w_1} \frac{kTe}{h} e^{-\frac{\bar{\varepsilon}_t - \bar{\varepsilon}_1}{kT}}. \tag{48}$$

This equation enables the standard entropy of the active complex on the surface to be determined by means of eq. (28). The definition of the standard state has been expounded above.

A calculation of the active complex entropy for the heterogeneous process of the formation of quaternary ammonium salt has been carried out by Gladischew and Syrkin[13] on the basis of experimental values of the reaction rate. This calculation, however, is lacking in rigour. Their method of calculation is equivalent to identifying the functions w and F. Since in the case considered by these authors F_1 is proportional to T^6 (neglecting, as they did, the factors corresponding to vibrational degrees of freedom), it follows that $w_1 = F_1 e^6$.

Since eq. (48), in contradistinction to eq. (47), contains the factor $\frac{kTe}{h}$, but not $\frac{kT}{h}$, the quantity w_t' is e^5 times as large as F_t' calculated by Gladischew and Syrkin. This correction changes the quantity $\Delta S^{\ddagger 0}$ by $5R$, *i. e.*. by 10 cals. per degree.

The example examined shows that the revision of concepts according to the treatment given in this paper may lead to rather considerable corrections in the numerical characteristics of active complexes.

Summary

A general derivation of the Arrhenius equation is given using the active complex method. For a reaction of any order

$$\frac{d \ln k_v}{dT} = \frac{\bar{\varepsilon}_t - \bar{\varepsilon}_1}{kT^2},$$

where k_v is the reaction velocity constant, $\bar{\varepsilon}_t$ average energy of active complexes, $\bar{\varepsilon}_1$ average energy of initial molecules. $\bar{\varepsilon}_t$ is calculated with

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[13] A. Gladischew and J. Syrkin, J. Phys. Chem. (Russ.), 11, 425 (1938).

the velocity of passing of the representative point over the potential barrier as a weight factor.

The pre-exponential factor in the Arrhenius equation is given by the equation

$$k_e = \varkappa \frac{w_t'}{w_1} \frac{kTe}{h} e^{-\frac{\bar{\varepsilon}_t - \bar{\varepsilon}_1}{kT}},$$

where functions w are related to partition functions F as follows:

$$\ln w = \ln F + T \frac{d \ln F}{dT}.$$

Formulae for calculation of w are given. The following equation holds for the standard entropy of activation defined according to Winne-Jones and Eyring, $\Delta S^{\ddagger 0}$:

$$\frac{w_t'}{w_1} = e^{\frac{\Delta S^{\ddagger 0}}{R}}.$$

The calculation of the standard entropy of active complexes from experimental data for reactions at surfaces is discussed.

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