QUARTERLY REVIEWS

DEVIATIONS FROM THE ARRHENIUS EQUATION

By J. R. HULETT

(DEPARTMENT OF CHEMICAL ENGINEERING,
HOULDSWORTH SCHOOL OF APPLIED SCIENCE, THE UNIVERSITY,
LEEDS, 2)

1. Introduction

SINCE its derivation[1] seventy-five years ago, the Arrhenius equation $k = Ae^{-E/RT}$ has been widely used in the study of chemical kinetics. k is the rate constant for a reaction at a temperature T°K. A and E are parameters which are usually assumed to be constants for a given reaction, so that when $\log_{10}k$ is plotted against $1/T$ a straight line of gradient $-E/2{\cdot}303\boldsymbol{R}$ should be obtained. This result is found for a very wide range of reactions, so that in 1929 Hinshelwood wrote "if when log k is plotted against $1/T$ a straight line is not obtained, it 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" [2]

(*a*) **Significance of the Constants.**—Arrhenius[1] considered that E represented the energy difference between the reactants and an activated species, possibly a tautomer. We now think of this activated species as having a structure intermediate between those of the reactants and products. In many ways it is a normal molecule, but has a weakness in a particular vibration leading to its decomposition.[3] E is the minimum energy difference between the reactants and the transition state, and is often spoken of as the height of the energy barrier opposing the reaction. More precise formulations take into account the zero-point energies of the reactants and the transition state without altering this general qualitative picture. Only those systems whose energy is greater than E can surmount the barrier. Application of this concept for a Boltzmann distribution of energies leads to the exponential form in which E occurs in the Arrhenius equation.

The pre-exponential factor A was originally a constant of integration. However, it was soon suggested that the rate of reaction might be the product of the number of activated molecules and their frequency of collision.[4] A would therefore be expected to be about 10^{11} litres mole^{-1} sec.$^{-1}$. This value had been obtained by Bodenstein for the reaction between hydrogen

---

[1] S. Arrhenius, *Z. Phys. Chem.*, 1889, **4**, 226.

[2] C. N. Hinshelwood, "Kinetics of Homogeneous Gas Reactions," Oxford University Press, 1929, p. 42.

[3] S. Glasstone, K. J. Laidler, and H. Eyring, "Theory of Rate Processes," McGraw-Hill, New York, 1941.

[4] W. C. McC. Lewis, *J.*, 1918, **113**, 471.

and iodine,[5] and has since been found for many other comparatively simple gas-phase reactions[6] and, perhaps surprisingly, for many reactions in solution.[7] There are, however, many reactions in which it differs from the simple collision number by many powers of ten, and so A is often divided into a true collision number Z multiplied by a "probability factor" P ranging from 10^{-8} to 10^{6}. Small values of P were thought to arise when the steric restrictions on a reaction were rather severe; large ones were less easily explained, although intuitively they might be expected for reactions between oppositely charged ions.

These general ideas accounted well for many observations, but it soon became necessary to consider their theoretical foundations more carefully.

Hinshelwood[8] showed that the simple exponential dependence on E could only be derived rigidly for systems in which the energy was distributed in two square terms, as in the motion of two bodies along their line of centres or a vibration of a particular bond. In most cases such motions are likely to be the most important. For more complex molecules, however, the fraction whose energy is greater than E distributed among n square terms is

$$[(E/RT)^{(\frac{1}{2}n-1)}/(\tfrac{1}{2}n-1)!].e^{-E/RT}$$

If n is fairly small, the term in square brackets is not very large, and the simpler expression is a good first approximation. For large values of n, however, this correction factor may be important. Thus if $n = 10$ and $E = 15$ kcal. mole^{-1}, the correction is about 10^{4}. This accounts for some of those cases where P is large.

If this equation is plotted in the Arrhenius form, the apparent activation energy becomes $E_A = E - (\frac{1}{2}n - 1)RT$. For reactions at about room temperature, if $n = 10$, $E_A \approx E - 2400$ cal. mole^{-1}. This difference clearly is significant but the *variation* in E_A over an experimental temperature range may be quite small—possibly ± 200 cal. mole^{-1} over 50°. This could well escape notice. However, Bell[9] has pointed out that a variation in E_A which might not be detectable experimentally could lead to values of E at 0°K estimated from the Arrhenius equation which are seriously in error, and wrong interpretations of the results would ensue.

The form of the collision number used in the interpretation of A implies a dependence on $T^{\frac{1}{2}}$. This would affect the apparent activation energy slightly, so that a change of about one calorie per mole per degree should be found. This deviation would be too small to be observed at all readily.

---

[5] M. Bodenstein, *Z. Phys. Chem.*, 1899, **29**, 295.

[6] See, *e.g.*, E. A. Moelwyn-Hughes, "Physical Chemistry," (2nd Edn.), Cambridge University Press, 1961.

[7] E. A. Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford University Press, 1947.

[8] C. N. Hinshelwood, *Proc. Roy. Soc.*, 1926, *A*, **113**, 230.

[9] R. P. Bell, *Trans. Faraday Soc.*, 1944, **37**, 493.

(*b*) **Types of Deviation.**—There are a number of reasons for deviations from the Arrhenius equation. They will be reviewed under the following headings (*a*) Medium effects, (*b*) Quasi-thermodynamic effects, (*c*) Quantum-mechanical effects, (*d*) Miscellaneous effects. The main interest of this Review centres on categories (*b*) and (*c*), but type (*a*) must first be mentioned to clear the ground for their discussion. Category (*d*) will be noticed briefly at the end.

2. Medium Effects

The activation energy is probably a composite function of several terms, each of which may be temperature-dependent. Likely contributions are: (*a*) a bonding term, E_b, due to stretching bonds in the reactants and forming new ones in the transition state; (*b*) E_r from repulsion forces between unbonded atoms or groups at close range; (*c*) E_e from electrostatic interactions between the reactants. In solution a term E_s will arise from the varying degrees of solvation of the reactants and transition state. These factors have long been recognised,[10,11] and their relative contributions to the total activation energies of some solution reactions have been discussed by Caldin.[12] E_b is important but not always predominant.[12] E_r is usually less important, and for simple proton-transfer reactions may be less than 15% of the whole.[9] It is unlikely to be strongly temperature-dependent, and so its contribution to dE_A/dT is probably negligible. E_e is only likely to be important in solution. Solvent dielectric constants vary with temperature and may lead to the term dE_e/dT.[6] For reactions not involving two ions this effect is only about ± 1 to 3 cal. mole^{-1} deg.$^{-1}$.[13] The forces in interionic reactions are greater and dE_e/dT may be ten or more cal. mole^{-1} deg.$^{-1}$. The experimental value of dE_A/dT for the bromoacetate–thiosulphate reaction lies between -7 and -22 cal. mole^{-1} deg.$^{-1}$,[14] in reasonable agreement with the theoretical value for dE_e/dT, about -11.5 cal. mole^{-1} deg.$^{-1}$ for ions bearing these charges.[6] For ionogenic reactions, dE_e/dT is expected to be about -13 cal. mole^{-1} deg.$^{-1}$. For most reactions, however, dE_r/dT and dE_e/dT are negligible. Studies of gas-phase reactions suggest that although E_b may account for much of E_A, dE_b/dT is usually small. Kassel[15] fits Bodenstein's[5] classical results on the decomposition of hydrogen iodide to a curve which implies that $dE_A/dT \simeq 30$ cal. mole^{-1} deg.$^{-1}$. Most other simple gas-phase reactions give smaller values, but suitable data are meagre. The smallness of dE_b/dT is not surprising, as the vibrational energy levels in most molecules are quite widely spaced, and so the effect of temperature on the energy distribution will be slight.

---

[10] R. A. Ogg and M. Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 604.

[11] M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, 1938, **34**, 11:

[12] E. F. Caldin, *J.*, 1959, 3345.

[13] Ref. 7, chap. 4.

[14] V. K. La Mer and M. E. Kamner, *J. Amer. Chem. Soc.*, 1935, **57**, 2662.

[15] L. S. Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalogue Company, New York, 1932, p. 148 *et seq.*

For reactions in solution E_s may dominate.[10] This has been shown for some complex formation and proton-transfer reactions between aromatic nitro-compounds and ethoxide ions.[11] Other evidence in support of this idea is that E_A for the solvolysis of alkyl halides is nearly equal to the heat of solvation of the halide ions,[16] and that reactions between methyl halides and hydroxide ions have activation energies approaching the energy required to remove a water molecule from the hydration shell of the hydroxide ion.[17] The interaction between solutes and solvents is relatively weak, and the vibrational levels are fairly closely spaced, so that the effect of temperature on the energy distribution is likely to be considerable. The enthalpies of the initial and transition states will be temperature-dependent, and differences in solvation could lead to large values of $\mathrm{d}E_s/\mathrm{d}T$. Many data exist in which $\mathrm{d}E_A/\mathrm{d}T$ is significant for reactions where the solvation pattern in the transition state is expected to differ markedly from that of the reactants. Values as large as -180 cal. mole^{-1} deg.$^{-1}$ are recorded[18] (see p. 233).

The temperature variation of the physical properties of the solvent are obviously likely to affect the observed rate constants, and so influence the apparent activation energies of reactions in solution. The variation of the dielectric constant with temperature has already been discussed. Other properties which may affect $\mathrm{d}E_A/\mathrm{d}T$ include the viscosity and solvent structure.

The rate at which the reactants come together is influenced by the solvent viscosity which usually decreases with increasing temperature, giving a positive $\mathrm{d}E_A/\mathrm{d}T$.[6,7] La Mer and Miller's results for the alkaline hydrolysis of diacetone alcohol,[19] which show an increase in activation energy from 15·84 to 17·24 kcal. mole^{-1} in the temperature range 5—30°C, have been analysed on this basis.[6] Almost the whole of $\mathrm{d}E_A/\mathrm{d}T$ was ascribed to the viscosity effect. However, this effect should only be significant for very fast bimolecular reactions which are effectively diffusion-controlled, and should be unimportant for reactions with "normal" A-factors whose activation energies are above about 6 kcal. mole^{-1}.[20]

Quite large deviations from the Arrhenius equation have been noted in aqueous solutions kept fluid well below 0°C by the addition of large quantities of salt. The bromination of 2-ethoxycarbonylcyclopentanone in aqueous 5·2M-sodium bromide exhibits a negative deviation below 0°C which is large enough to be clearly visible on the conventional Arrhenius plot.[21] If the structure of water becomes more ice-like or ordered at very low temperatures, a larger pre-exponential factor in the Arrhenius equation is likely to result for those reactions in which the transition state is

---

[16] J. L. Franklin, *Trans. Faraday Soc.*, 1952, **48**, 443.

[17] E. A. Moelwyn-Hughes and D. N. Glew, *Proc. Roy. Soc.*, 1952, *A*, **212**, 260.

[18] E. A. Moelwyn-Hughes, *J.*, 1961, 1517.

[19] V. K. La Mer and M. L. Miller, *J. Amer. Chem. Soc.*, 1935, **57**, 2674.

[20] R. M. Noyes, "Progress in Reaction Kinetics," Pergamon Press, 1961, p. 129.

[21] J. R. Hulett, *Proc. Roy. Soc.*, 1959, *A*, **251**, 274.

more polar than the reactants. This could lead to the deviations observed.[22]

A quite specific medium-structure effect may occur in the alkaline bromination of acetone in 6·7M-sodium perchlorate.[23] This reaction shows a deviation from the Arrhenius equation below −10°C in the direction required for proton tunnelling (see section 4), but preliminary results for the bromination of [$^2H_6$]acetone indicate a similar curvature, which would not be expected on this basis. The curvature of both plots can be explained if the more ordered structure of the solvent at low temperatures enables a hydroxide ion remote from an acetone molecule to behave as if it were in close proximity to it by the hydrogen-bond switch mechanism used to account for the high mobility of hydrogen and hydroxide[24] ions in ice. An effect of this kind is only to be expected at low temperatures with ions produced by self-ionisation of the solvent.

3. Thermodynamic Effects

(*a*) **General.**—In 1883, van't Hoff[25] suggested that the equation

$$\frac{\mathrm{d}\log K}{dT} = \frac{\Delta H}{RT^2}$$

could be divided into two parts, for the forward and reverse reactions making up the equilibrium system. The resulting equations had the form

$$\frac{\mathrm{d}\log k_1}{\mathrm{d}T} = \frac{E_1}{RT^2} + B\,;\quad \frac{\mathrm{d}\log k_2}{\mathrm{d}T} = \frac{E_2}{RT^2} + B$$

Where $k_1/k_2 = K$, $E_2 - E_1 = \Delta H$, and B is an arbitrary constant. Arrhenius suggested $B \equiv 0$, as this would fit the results of most reactions then known. Integration of these equations then leads to the usual form of the Arrhenius equation.

For most reactions ΔH varies slowly with temperature. As $E_2 - E_1 = \Delta H$, it would be expected that similar variations should be noted in E. In 1933 La Mer[26] expressed this in the form

$$\frac{\mathrm{d}E_A}{\mathrm{d}T} = \frac{1}{kT^2}\left\{[\overline{\overline{e^2}} - (\overline{\overline{e}})^2] - [\overline{e^2} - (\overline{e})^2]\right\} = \overline{C}_{j(\mathrm{act.})} - \overline{C_i} = \Delta C_p{}^{\ddagger}$$

where $\overline{e^2} - (\overline{e})^2$ is the difference between the mean squares of the energies of all the molecules and the square of their mean energies, and, divided by kT^2, is equal to the calorimetrically determinable partial heat capacity of all the molecules. As the fraction reacting at any instant is extremely small this may be closely approximated to $\overline{C_i}$, the partial heat capacity of the non-

---

[22] E. F. Caldin and E. Harbron, *J.*, 1962, 3454.

[23] J. R. Hulett, unpublished results.

[24] B. E. Conway, J.O'M Bockris, and H. Linton, *J. Chem. Phys.*, 1956, **24**, 834.

[25] J. H. van't Hoff, "Etudes de dynamique chemique," Amsterdam, 1884.

[26] V. K. La Mer, *J. Chem. Phys.*, 1933, **1**, 289.

reacting molecules. $\overline{\overline{e^2}} - (\overline{\overline{e}})^2$ is a similar function for those molecules which do react. When divided by $\boldsymbol{k}T^2$, however, the result differs from a thermodynamic heat capacity by a kinetic term which is included in the statistical averaging process. With this proviso, it becomes the partial molal heat capacity of the reacting molecules $\overline{C}_{j(\text{act.})}$.

$\Delta C_p{}^\ddagger$ then represents the change in heat capacity on activation. La Mer points out that neglect of $\Delta C_p{}^\ddagger$, as suggested by the Arrhenius equation, is thermodynamically as unjustifiable as writing for an equilibrium process $\Delta G = \Delta H$, *i.e.*, assuming that $\Delta S = \int \Delta C_p \mathrm{d} \log T$ is zero.

Robertson and Hyne[27] have taken up the idea of the variation of ΔH with temperature, writing it as a power series in T. Then, applying Arrhenius' method of derivation, they obtain an equation of the type

$$\log k = A/T + B \log T + DT + C$$

This four-parameter equation is difficult to manipulate, and so the simpler three-parameter equation, with omission of the term DT, is commonly used. Almost all the most accurate data so far obtained can be fitted within experimental error to this simpler equation.[28] The constants in the equation $\log_{10}k = A/T + B \log_{10}T + C$ have been related to the various thermodynamic functions of activation as follows:[29]

$$\begin{aligned} A &= -\Delta H_0{}^\ddagger/2{\cdot}303\boldsymbol{R} \\ B &= \Delta C_p{}^\ddagger/R + 1 \\ C &= (\Delta S_0{}^\ddagger - \Delta C_p{}^\ddagger)/2{\cdot}303\boldsymbol{R} + \log_{10}\boldsymbol{k}/\boldsymbol{h} \\ \Delta H_T{}^\ddagger &= \Delta H_0{}^\ddagger + T\Delta C_p{}^\ddagger \ ; \ \Delta S_T{}^\ddagger = \Delta S_0{}^\ddagger + 2{\cdot}303\Delta C_p{}^\ddagger.\log_{10}T \end{aligned}$$

where the subscript 0 refers to the function at 0°K and T to that at T°K. This equation implies that $\mathrm{d}E_A/\mathrm{d}T$ is linear, that is, $\Delta C_p{}^\ddagger$ is independent of temperature. In general this cannot be exactly true, but the variation of $\Delta C_p{}^\ddagger$ with temperature would probably be very difficult to detect over an experimental temperature range,[28] although it has been claimed in a few instances.[20,30]

(*b*) **Experimental Results.**—Gas-phase reactions rarely show deviations from the Arrhenius equation which can be treated this way. Kassel's calculations[15] on the decomposition of hydrogen iodide[5] have already been noted. He cites a very few other examples in which $\Delta C_p{}^\ddagger$ is much smaller. The paucity of data may be due to two causes: (*a*) Comparatively few gas reactions are simple and easily studied, and so results of sufficient accuracy to exhibit these effects are rare; (*b*) If the transition state and the reactants are not very different, their enthalpy variations with temperature are similar and so $\Delta C_p{}^\ddagger$ is small.

---

[27] R. E. Robertson and J. B. Hyne, *Canad. J. Chem.*, 1955, **33**, 1544.

[28] J. R. Fox and G. Kohnstam, *J.*, 1963, 1593.

[29] R. E. Robertson, *J. Chem. Phys.*, 1956, **25**, 375.

[30] E. A. Moelwyn-Hughes, *Proc. Roy. Soc.*, 1953, *A*, **220**, 386.

These effects are mostly found for reactions in solution. Nearly every case of variation of activation energy with temperature occurs when neutral or diffusely charged reactants (one of which is often a solvent molecule) interact to give a markedly polar transition state. In all such cases dE_A/dT is negative. A selection of the results is shown in the Table. Even when dE_A/dT is as large as −182 cal. mole^{-1} deg.$^{-1}$,[18] the deviation of the Arrhenius plot is quite small, and when dE_A/dT is much less than this, the curvature could easily escape notice. Clearly these thermodynamic effects will be detected only when the experimental work is of very high accuracy.

Reactions in which E_A varies with temperature.

Reaction	Solvent	E_A (mean) cal. mole^{-1}	Temp. range (°c)	dE_A/dT cal. mole^{-1} deg.$^{-1}$	Ref.
Hydrolysis of CH_3F	H_2O	21160	80—150	−67	*a*
Hydrolysis of CH_3Cl	H_2O	22700	50—100	−52	*b*
Hydrolysis of CH_3Br	H_2O	21425	35—100	−46·5	*b*
Hydrolysis of CH_3I	H_2O	23100	50—100	−56·5	*b*
Hydrolysis of $CH_3{\cdot}NO_3$	H_2O	25760	70—140	−42·6	*c*
Hydrolysis of CH_2Cl_2	H_2O	25590	100—150	−59	*d*
Hydrolysis of $CHCl_3$	H_2O	27940	100—150	−92	*e*
Hydrolysis of Bu^tCl	H_2O	23350	0—25	−182	*f*
Hydrolysis of $C_6H_5{\cdot}CH_2Cl$	H_2O	21450	15—65	−40	*g*
Hydrolysis of allyl chloride	H_2O	22180	35—85	−50	*g*
Hydrolysis of $(CH_3{\cdot}CO)_2O$	H_2O	11000	5—25	−80	*h*
Hydrolysis of $CH_3{\cdot}CO{\cdot}OCH_3$	H_2O	17230	15—75	−17	*c*
Hydrolysis of $C_6H_5{\cdot}SO_3{\cdot}CH_3$	H_2O	21650	10—70	−33·4	*i*
Hydrolysis of $C_6H_5{\cdot}SO_3Pr^i$	H_2O	22410	0—35	−41·2	*i*
Hydrolysis of $C_6H_5{\cdot}CCl_3$	80% Ethanol–H_2O	22430	25—65	−41	*j*
Hydrolysis of $C_6H_5{\cdot}CCl_3$	50% Ethanol–H_2O	21240	0—40	−71	*j*
Hydrolysis of $C_6H_5{\cdot}CCl_3$	50% Acetone–H_2O	19970	0—40	−44	*j*
Mutarotation of glucose	H_2O	16950	0—50	−19·6	*k*
Decarboxylation of trinitrobenzoic acid	H_2O	36410	55—100	−45	*l*
Hydrolysis of $CHCl_3$ by OH^-	H_2O	27580	15—60	−133	*e*
Dealdolisation of diacetone alcohol by OH^-	H_2O	17000	5—45	+35	*m*

[a] D. N. Glew and E. A. Moelwyn-Hughes, *Proc. Roy. Soc.*, 1952, *A*, **211**, 254. [b] R. L. Heppolette and R. E. Robertson, *Proc. Roy. Soc.*, 1959, *A*, **252**, 273. [c] J. S. McKinley McKee and E. A. Moelwyn-Hughes, *Trans. Faraday Soc.*, 1952, **48**, 247. [d] I. Fells and E. A. Moelwyn-Hughes, *J.*, 1959, 1326. [e] I. Fells and E. A. Moelwyn-Hughes, *J.*, 1959, 398. [f] E. A. Moelwyn-Hughes, *J.*, 1961, 1517. [g] R. E. Robertson and J. M. W. Scott, *J.*, 1961, 1596. [h] V. Gold, *Trans. Faraday Soc.*, 1948, **44**, 506. [i] R. E. Robertson, *Canad. J. Chem.*, 1957, **35**, 613. [j] B. Bensley and G. Kohnstam, *J.*, 1956, 287. [k] J. C. Kendrew and E. A. Moelwyn-Hughes, *Proc. Roy. Soc.*, 1956, *A*, **176**, 352. [l] P. Johnson and E. A. Moelwyn-Hughes, *Proc. Roy. Soc.*, 1940, *A*, **175**, 118. [m] V. K. La Mer and M. L. Miller, *J. Amer. Chem. Soc.*, 1935, **67**, 2674.

(*c*) **Interpretation of Results.**—Most of these deviations occur for reactions in solution, but their sign and magnitude exclude their identification with the variation of bulk solvent properties alone. There must be some more intimate effects which lead to a considerable difference in the heat capacities of the reactants and transition state.

In most instances negative values of dE_A/dT are associated with reactions in which the reactants are markedly less polar than the transition state. This polar complex is expected to orientate solvent molecules about itself, so that "freezing" of solvent molecules at the reaction centre occurs. The difference in the heat capacities of ice and water is about 9 cal. mole^{-1} deg.$^{-1}$, and dE_e/dT for ionogenic reactions is about 13 cal. mole^{-1} deg.$^{-1}$, so that $(-dE_A/dT - 13)/9$ molecules of water may be "frozen" about the transition state for reactions occurring in aqueous solution.[31] In the hydrolysis of benzenesulphonic esters, $dE_A/dT \simeq -32$ cal. mole^{-1} deg.$^{-1}$,[32] which suggests the uptake of two water molecules in the transition state. This accords with Swain's theory[33] that many reactions occur by a pull-push mechanism, demanding, in this instance, at least two water molecules. The hydrolysis of methyl halides requires a greater increase in the solvation of the transition state; $dE_A/dT \simeq -50$ cal. mole^{-1} deg.$^{-1}$ corresponds to about four water molecules[34] (earlier, somewhat less accurate, work gave $dE_A/dT \simeq -67$ cal. mole^{-1} deg.$^{-1}$, or six water molecules[31]). Probably the difference in these reactions lies in the greater solvation of the initial state for the sulphonic esters. The intermediate values of dE_A/dT obtained in the hydrolysis of nitrates may be explained similarly.[35]

This solvation of the transition state may be considered in terms of the Hinshelwood theory of the number of square terms required to express the distribution of energy in the system. The weak solvent–solute interactions are those whose oscillations will be able to take up thermal energy quite readily. The expression $E_A = E - (\frac{1}{2}n - 1)RT$ will then describe a system in which the increased number of oscillators in the transition state, $\phi = \frac{1}{2}n - 1$. For the hydrolysis of the sulphonic esters $\phi = 16$ and for the methyl halides, $\phi = 25$. However, this cannot be correct, for if the energy were distributed so widely, the proportion of activated complexes would be too small to maintain a steady state. Probably ϕ calculated in this way is too large; the whole of dE_A/dT cannot be attributed to this cause. Moelwyn Hughes[31] recognised this. In addition to the electrostatic effect already mentioned, he considered the variation with temperature of the energy required to orientate the activated solute molecules in a sheath of solvent molecules so that a position suitable for reaction was obtained. This might lead to $dE_{\text{orientation}}/dT$ of about -15 cal. mole^{-1} deg.$^{-1}$. Thus the

---

[31] E. A. Moelwyn-Hughes, *Proc. Roy. Soc.*, 1938, *A*, **164**, 295.

[32] R. E. Robertson, *Canad. J. Chem.*, 1957, **35**, 613.

[33] C. G. Swain, *J. Amer. Chem. Soc.*, 1950, **72**, 4572.

[34] R. L. Heppolette and R. E. Robertson, *Proc. Roy. Soc.*, 1959, *A*, **252**, 273.

[35] J. S. McKinley McKee and E. A. Moelwyn-Hughes, *Trans. Faraday Soc.*, 1952, **48**, 247.

overall value of ϕ would be much less, say, about 11 for the halides and 3 for the sulphonic esters. Values as small as this would enable a steady state to be attained.

The exact nature of the transition state may well influence the magnitude of dE_A/dT. Solvolysis of halides may occur by the unimolecular S_N1 mechanism, in which the rate-determining step is the stretching or breaking of the carbon–halogen bond. This will be accompanied by reorientation of the solvent molecules about the incipient ions so produced. The bimolecular or S_N2 mechanism involves a molecule of solvent directly, attacking one side of the carbon atom at the same time as the halide ion is released from the other. This process will also require reorganisation of the solvent molecules. The degree of reorientation is expected to differ in the two cases. Kohnstam[36] has used this concept to suggest that the ratio $\Delta C_p^{\ddagger}/\Delta S^{\ddagger}$ for S_N1 reactions in certain mixed aqueous organic solvents will be significantly greater than for S_N2 reactions. This criterion appears to be valid only in solvents containing less than 50% of water—possibly in more aqueous solvents the water structure itself is so well defined, that the relative changes on activation are comparable, and the distinction is no longer clear. Kohnstam suggests that deviations from the Arrhenius equation so obtained can be used as a diagnostic tool in the study of reaction mechanisms which may not be distinguished so clearly by conventional methods. It must, however, be emphasised that use of $\Delta C_p^{\ddagger}/\Delta S^{\ddagger}$ is only valid where the rate constants are known with great precision over a wide temperature range.[37] Kohnstam obtained rate constants quoted to $\pm$ 0·25% or better,[36] but for many reactions such accuracy is unattainable.

Almost every case in which significant deviations from the constancy of E_A have been observed, involves the solvolysis of a neutral compound. This may in part be due to the great accuracy with which these processes may be studied. However, the hydrolyses of many halides and esters by hydroxide ions have been examined with similar accuracy, and almost without exception have obeyed the simple Arrhenius equation.[38] Only the alkaline hydrolysis of chloroform has shown any significant deviation; $dE_A/dT = -133{\cdot}5 \pm 35$ cal. mole^{-1} deg.$^{-1}$.[38] This reaction, however, has very different characteristics from others which may be formally similar. It is thought to involve a pre-equilibrium $CHCl_3 + OH^- \rightleftharpoons CCl_3^- + H_2O$ followed by the rate-determining expulsion of a chloride ion from CCl_3^-. This pre-equilibrium will be temperature-dependent, so that the CCl_3^- concentration varies, leading to the change in E_A for the overall process. "Normal" alkaline hydrolyses which obey the Arrhenius equation are thought to be simpler than the solvolysis reactions. Probably the transition state is more like the reactants, and so the effect of temperature on their solvation is similar, leading to a nearly constant E_A. Two pieces of evidence support

---

[36] G. Kohnstam, *Chem. Soc. Special Publ.*, 1962, **16**, 179.

[37] J. R. Hulett, *Chem. Soc. Special Publ.*, 1962, **16**, 202.

[38] I. Fells and E. A. Moelwyn-Hughes, *J.*, 1959, 398.

this: reactions of the type $CH_3X + Y^- \rightarrow CH_3Y + X^-$, where X and Y are halogens, also obey the Arrhenius equation,[39] and the coefficient in the $\log_{10}T$ term in the expanded equation for solvolysis reactions is similar to that for the ionisation constants of weak acids in aqueous solution, indicating that the charge separation in the transition state is nearly complete.[18]

If the small positive residue of dE_A/dT beyond that required by the viscosity correction in the de-aldolisation of diacetone alcohol[19] is real, it may be that the rather less polar transition state is desolvated compared with the reactants. However, the effect is but marginal.[6]

These quasi-thermodynamic effects may be considered as rather special medium effects. They have been reviewed separately, because they have attracted considerable attention, and have been discussed quite widely. There can be no doubt that these deviations are real. The interpretations are many, some of which overlap. No doubt the truth lies with them all; what is observed is the complex interaction of a number of temperature dependent processes, all of which contribute to $\Delta C_p^{\ddagger}$.

4. Quantum-mechanical Effects

(*a*) **Theory.**—According to classical theories of reaction kinetics, only those systems react whose energy is sufficient to surmount the energy barrier opposing the reaction. The Arrhenius equation can be derived using this concept. However, application of the methods of quantum mechanics indicates that there is a definite probability of systems' reacting whose energy is less than the barrier height: there is said to be quantum-mechanical leakage or "tunnelling" through the barrier. Essentially the classical result appears as a good first approximation, and the correction which the more rigorous quantum-mechanical treatment requires is in most cases extremely small. Only when the barrier is narrow, or the mass of the species crossing it is small, will the difference between the classical and quantum-mechanical treatments be large.

The tunnel effect has been invoked to explain the emission of α-particles from nuclei with energies less than that calculated for the barrier surrounding the nucleus,[40] and to account for the rather high rates of certain electron-transfer processes.[41] It is only expected to be significant for orthodox chemical reactions when the species involved is the hydrogen atom.[42,43]

Wigner[42] shows that the quantum correction for the passage of a particle mass m over a col in an n-dimensional energy surface is, to a first approximation, given by

$$V_q = V_c\left\{1 - \frac{h^2}{4\pi^2}\sum_n A_i/24mk^2T^2\right\}$$

---

[39] R. H. Bathgate and E. A. Moelwyn-Hughes, *J.*, 1959, 2642.

[40] R. W. Gurney and E. U. Condon, *Nature*, 1928, **122**, 439.

[41] J. Weiss, *Proc. Roy. Soc.*, 1954, *A*, **222**, 128.

[42] R. P. Bell, *Proc. Roy. Soc.*, 1933, *A*, **139**, 466; 1935 *A*, **148**, 241; C. Eckart, *Phys. Rev.*, 1930, **35**, 1303; E. Wigner, *Z. Phys. Chem.*, 1932, *B*, **19**, 203; H. S. Johnston and D. Rapp, *J. Amer. Chem. Soc.*, 1961, **83**, 1.

[43] R. P. Bell, *Trans. Faraday Soc.*, 1959, **55**, 1.

V_q and V_c are the quantum and classical reaction rates, and A_i the curvatures of the surface in different directions. Most of the A_i are positive and correspond to zero-point energy terms in the transition state, but one, A_t, is negative, and corresponds to the tunnel effect along the reaction co-ordinate. The tunnel effect has just the same status as the zero-point energy: both arise from the operation of the uncertainty principle in the transition state,[44] and unless A_t is much smaller than the A_i, both should be of much the same importance. If resonance occurs, as in certain hydrogen *atom* transfer reactions, A_t may be smaller, *i.e.*, the barrier is flattened, but for proton transfer, or any ionic process, such flattening is unlikely, and A_t will be at least as great as the A_i.

Bell[43] has calculated the effect of quantum-mechanical leakage on the Arrhenius parameters for a one-dimensional parabolic barrier. For barriers of sizes likely to be encountered in practice his equations become

$$E^* = E + kT(\tfrac{1}{2}u.\cot \tfrac{1}{2}u - 1)$$

$$A^* = \frac{A}{2 \sin \tfrac{1}{2}u} \cdot \exp(\tfrac{1}{2}u.\cot \tfrac{1}{2}u - 1)$$

where $u = h\nu/kT = (h/kTa^2)(E/2m)^{\frac{1}{2}}$ and A is the "true" pre-exponential factor of the Arrhenius equation, E is the height of the energy barrier whose width at the base of the parabola is $2a$. ν is the imaginary frequency associated with the tunnelling correction. E^* and A^* are observed Arrhenius parameters. This simple treatment is satisfactory where the degree of tunnelling is not very large. A more exact treatment, with use of the Eckart type barrier in more than one dimension, has been developed by Johnston and Rapp,[42] but their equations are less easy to apply.

The tunnel effect should lead to experimental results as follows: (i) The Arrhenius plot should behave normally at high temperatures where E^*/E is nearly unity. At low temperatures it curves, eventually becoming nearly parallel to the $1/T$ axis as the activation energy approaches zero. The temperature at which curvature occurs is sensitive to the exact barrier dimensions, but for proton-transfer reactions it could be between −100 and +100°c.[42] The small curvature expected at more accessible temperatures is not conclusive evidence of tunnelling, as it might be confused with effects considered previously. (ii) Isotope effects may become large. The tunnelling correction is very sensitive to the mass of the particle crossing the barrier. The mass ratio 1:2 for protium and deuterium should lead to effects greater than would be expected from zero-point energy differences alone. These effects should be observed in three ways:[42] (*a*) $k_{\mathrm{H}}/k_{\mathrm{D}}$ should be large, and increase rapidly as the temperature is lowered; (*b*) $E^*_{\mathrm{D}} - E^*_{\mathrm{H}}$ should be large, and, if tunnelling is important, should be greater than the zero-point energy differences between isotopic reactants; (*c*) $A^*_{\mathrm{D}}/A^*_{\mathrm{H}}$

---

[44] R. P. Bell, J. A. Fendley, and J. R. Hulett, *Proc. Roy. Soc.*, 1956, *A*, **235**, 453.

should be much greater than unity. On classical theories this ratio should lie between $\frac{1}{2}$ and 2, the extreme values representing most unlikely conditions. Large ratios of pre-exponential factors may be found even when the curvature of the Arrhenius plot is undetectable.

(*b*) **Experimental Results.**—Following the development of these theories in the middle thirties, much experimental work was performed on proton-transfer reactions at temperatures down to -100°C,[45] but no curvature of the Arrhenius plot was detected. Some attempts were made to study isotope effects, but these were often complicated by medium effects, a change of solvent from H_2O to D_2O accompanying a change from a protium to a deuterium substrate;[46] this could be eliminated by working in aprotic solvents, but difficulty was experienced in preparing a pure deuterated substrate.[47]

The first conclusive demonstration of proton tunnelling was in the fluoride-ion catalysed bromination of 2-ethoxycarbonylcyclopentanone. This reaction was performed in deuterium oxide solution before and after complete exchange of the active hydrogen with the solvent had occurred. k_H/k_D was only 2·67, but $E^*_D - E^*_H$ was 2440 $\pm$ 100 cal. mole^{-1}, whereas the difference between the zero-point energies of C–D and C–H bonds is about 1200 cal. mole^{-1}. A^*_D/A^*_H had the unusually large value of 24 $\pm$ 4.[44] The Arrhenius plots were linear, but later work in 5·2M-sodium bromide as solvent indicated that the activation energy falls from about 20·5 kcal. mole^{-1} above -10°C to 11·5 kcal. mole^{-1} at about -18°C,[48] and k_H/k_D is certainly not less than 10 at -20°C.[49] Less striking results were obtained with other catalysts.

Bell's equations[43] were used to calculate the dimensions of the energy barriers. a was about 0·58—0·63Å, which gave a barrier width $\simeq 3a$ at the base of about 1·8 Å. This is reasonable. E^*_H/E_H for fluoride-ion catalysis was 0·81 compared with E^*_D/E_D of 0·94. The solvent and chloroacetate-ion catalysis yielded 0·90 and 0·88 for E^*_H/E_H.[48] From these figures it was calculated that $E^*_H \simeq E_H/2$ at -20°C for catalysis by fluoride ion, whereas for solvent or chloroacetate-ion catalysis this will not occur until -60°C, and at 20°C the deviation should be small. The same dimensions indicate that for fluoride-ion catalysis at -20°C, $k_H/k_D \simeq 16$, which is in fair agreement with the observed value of 10. Bell's equations can also be used to calculate barrier dimensions from the curvature of the Arrhenius plot. This has been done for the fluoride ion catalysis in 5·2M-sodium bromide,

---

[45] *E.g.*, R. P. Bell and J. K. Thomas, *J.*, 1939, 1573; R. P. Bell and A. D. Norris, *J.*, 1941, 118, 854; E. F. Caldin and J. C. Trickett, *Trans. Faraday Soc.*, 1953, **49,** 772; E. F. Caldin and G. Long, *Proc. Roy. Soc.*, 1955, *A*, **228,** 263; J. B. Ainscough and E. F. Caldin, *J.*, 1960, 2407.

[46] *E.g.*, O. Reitz, *Z. Phys. Chem.*, 1936, **176,** *A*, 363; S. Liotta and V. K. La Mer, *J. Amer. Chem. Soc.*, 1938, **60,** 1967; E. C. Baughan and R. P. Bell, *Proc. Roy. Soc.*, 1937, *A*, **158,** 646.

[47] R. P. Bell and E. F. Caldin, *Trans. Faraday Soc.*, 1951, **47,** 50.

[48] J. R. Hulett, *Proc. Roy. Soc.*, 1959, *A*, **251,** 274.

[49] J. R. Hulett, *J.*, 1960, 468.

with the result that E_H = 24.2 kcal. mole^{-1}, a = 0·71 Å.[50] The barrier dimensions appear to be affected by the change in medium. These results indicate how sensitive the degree of tunnelling is to the exact barrier shape, and the paucity of information so far available is probably due to the unfavourable shapes of the barriers in the systems investigated.

There are other reactions which show some of the experimental results expected where tunnelling is significant, but none has been investigated as fully as that cited above.

(i) The alkaline bromination of diisopropylketone has an activation energy at 0°C about half that observed above 15°C.[51] Is this due to tunnelling or to an OH$^-$ medium effect as already discussed in the case of acetone?[23] The curve fits Bell's equations[43] quite closely when a = 0·563 Å and E^* = 17·8 kcal. mole^{-1}, suggesting that the curvature is most likely due to tunnelling.

(ii) Proton transfer from acetic acid to the 2,4,6-trinitrobenzyl ion in ethanol solution has a rate at −114°C which is about 45% greater than that calculated from the Arrhenius plot between −90° and +20°C. The deviation is about 40 times the experimental error.[52] Similar results are obtained for proton transfer from *p*-nitrobenzyl cyanide to the ethoxide ion at −124°C, and from hydrogen fluoride to the 2,4,6-trinitrobenzyl ion below −60°C.[53] All these results give a fair fit to Bell's equations[43] for a parabolic barrier.

(iii) The elimination of "hydrogen" bromide from 1-bromo-2-phenylpropane and its 2-deutero-analogue by ethoxide ions gives A^*_D/A^*_H = 2·37 ± 0·35 and $E^*_D - E^*_H$ = 1·79 ± 0·35 kcal. mole^{-1}. These figures are just outside the limits prescribed by classical methods, but the discrepancy is so small that this result should not be accepted unreservedly as evidence for proton tunnelling. The Arrhenius plots are linear.[54]

(iv) When log k_H/k_D is plotted against $1/T$ for the reactions between methyl radicals and hydrocarbons, the straight line is steeper than would be expected from the difference in zero-point energies of the reactants. The plots are linear.[55]

(v) The high proton conductance in ice, and the isotope effects observed, have been interpreted in terms of proton tunnelling.[56]

(vi) The permanganate oxidation of perfluoro-alcohols exhibits the unusually large isotope effect, k_H/k_D = 16.[57] This has been interpreted in terms of proton tunnelling. The reaction is, however, somewhat complex, and the large isotope effect may be due to more than one process. No temperature-dependence datum is available.

---

[50] E. F. Caldin and M. Kasparian, personal communication.
[51] J. R. Hulett, in the press.
[52] E. F. Caldin and E. Harbron, *J.*, 1962, 3454.
[53] E. F. Caldin, personal communication.
[54] V. J. Shiner and M. L. Smith, *J. Amer. Chem. Soc.*, 1961, **83**, 593.
[55] H. S. Johnston and D. Rapp, *J. Amer. Chem. Soc.*, 1961, **83**, 1.
[56] B. E. Conway and J. O'M. Bockris, *J. Chem. Phys.*, 1958, **28**, 354.
[57] R. Stewart and R. van den Linden, *Discuss. Faraday Soc.*, 1960, **29**, 211.

If the interpretation of cases (iii)—(vi) in terms of tunnelling is correct, deviations from the Arrhenius equation should be observed if the processes can be performed at a sufficiently low temperature. This may not be easy.

No evidence has been found to suggest quantum-mechanical leakage in chemical reactions by species other than protium. The value $E^*_D/E_D \simeq 0{\cdot}95$ in the bromination of 2-ethoxycarbonylcyclopentanone[48] might be considered as some 5% tunnelling by the deuteron. However, this result is based on the assumption of a parabolic barrier, and is not to be considered as absolute. For particles larger than the deuteron, E^*/E should be about unity for all reasonable barrier dimensions, save at a very few degrees above absolute zero.

5. Miscellaneous Effects

(*a*) **Change in Mechanism.**—There are several ways in which a reaction may proceed by different mechanisms at different temperatures, leading to curvature of the Arrhenius plot.

(i) *Alternative paths.* If two processes of different activation energies are possible, the resulting Arrhenius plot will be concave upwards, in the region where the two rates are comparable. At high tempertures the plot is steeper, as the reaction with the greater activation energy dominates, but at low temperatures, the low activation energy process is the faster. Such a result is found in the homogeneous gas-phase pyrolysis of di-isopropylmercury.[58] Between 240° and 300°C the Arrhenius constants are $E_A = 40{\cdot}4$ kcal. mole^{-1}, log A (sec.$^{-1}$) $= 16{\cdot}7$, but in the range 170° to 240°C these have fallen to 27 kcal. mole^{-1} and 11·0 respectively. It is believed that the high-temperature process is $HgR_2 \rightarrow 2R\cdot + Hg$, whereas that at low temperature is $HgR_2 \rightarrow R\cdot + HgR\cdot$, the rates of the two processes becoming equal at 240°C. Similar results have been found in the thermal decomposition of nitrosyl chloride.[59] These are believed to be the first instances of such deviations noted for homogeneous gas-phase reactions, although such effects have long been known for heterogeneous and solution processes.

(ii) *Consecutive steps.* If two consecutive reactions have different activation energies, the Arrhenius plot is concave downwards in the region where the two rates are comparable, that with the low activation energy controlling at high temperature and *vice versa*. A recent example of this phenomenon is the electron-transfer reaction on the ferrous–ferric system in the presence of azide ions.[60] The first process is believed to be complex formation between the ferric monoazide ion and a ferrous ion, which has a fairly high activation energy. This is followed by the low activation energy electron transfer process between the two iron atoms. The two processes have the same rate at 13°C.

(iii) *Non-chemical control.* Many reactions, especially those involving

---

[58] B. H. M. Billinge and B. G. Gowenlock, *Proc. Chem. Soc.*, 1962, 24.
[59] P. G. Ashmore and M. G. Burnett, *Trans. Faraday Soc.*, 1962, **58**, 1801.
[60] D. Bunn, F. S. Dainton, and S. Duckworth, *Trans. Faraday Soc.*, 1961, **57**, 1131.

systems in two or more phases are limited at high temperature by the rate at which the reactants can come together. Thus diffusion, which depends approximately on $T^{3/2}$, controls rather than the exponential chemical rate process. The Arrhenius plot is similar to that obtained in case (ii), but does not become strictly linear at high temperature. A typical example is the dehydrogenation of cyclohexane to benzene over a platinum–alumina catalyst. At low temperatures the Arrhenius plot is straight, indicating $E_A = 41{\cdot}6$ kcal. mole^{-1}, but above 375°*C*, E_A falls rapidly as the rate is now limited by the diffusion of the reactants to the catalyst.[61]

(*b*) **Pre-equilibria.**—When a pre-equilibrium is involved, the rate of the overall reaction depends on the concentration of the reactant species formed in the equilibrium. If the equilibrium constant varies with temperature, a curved Arrhenius plot should result. This has already been noted for the hydrolysis of chloroform.[38] The vapour-phase photolysis of deuteroacetic acid exhibits an activation energy which decreases as the temperature is lowered.[62] This has been attributed to interference by an equilibrium process involving dimers at low temperatures.

(*c*) **Biological Reactions.**—Many biological reactions have an optimum temperature, at which the rate reaches a maximum. Typical of these are enzyme-catalysed reactions. The actual reaction rate increases steadily with temperature in an Arrhenius manner, but the thermal inactivation of the enzyme becomes more important than this at the temperature where the maximum rate is observed.[63]

(*d*) **Third-order Reactions.**—According to the absolute theory of reaction rates, the temperature dependence of third-order reactions can be expressed in the form $k = CT^{-3} \exp(-E/\boldsymbol{R}T)$.[3] If this equation is plotted as $\log_{10} k$ against $1/T$ a curve is obtained with a rather flat maximum at $T = E/3\boldsymbol{R}$.

Most simple third-order reactions are found to have zero or very small positive or negative activation energies, suggesting that most observations on these reactions are made at temperatures near that of maximum rate.

Most of these simple third-order reactions involve nitric oxide. It is thought that the processes occur by the formation of dimers $(NO)_2$ which then react with the third reactant, the equilibrium position in the dimer formation being temperature-dependent. This physical picture agrees well with the theoretical prediction.

6. Conclusion

The differential form of the Arrhenius equation, $d(\log_e k)/dT = E/\boldsymbol{R}T^2$ has a firm statistical basis. The integrated form in which it is usually ex-

---

[61] L. G. Barnett, R. E. C. Weaver, and M. M. Gilkeson, *Amer. Inst. Chem. Engineers J.*, 1961, **7**, 211.

[62] P. Ausloos and E. W. R. Steacie, *Canad. J. Chem.*, 1955, **33**, 1530.

[63] G. Tamman, *Z. Phys. Chem.*, 1895, **18**, 426; K. J. Laidler, "Chemical Kinetics and Enzyme Action," Oxford University Press, 1958, p. 194 *et seq.*

pressed, however, involves the assumption that the energy of activation does not vary with temperature. This assumption leads to the difficulties which have been the subject of this Review. The deviations occur from this integrated form. The activation energy is a thermodynamic quantity which should vary with temperature just as the heat of reaction does,[64] and so the integrated form is at best but a good approximation. The variation in E_A will be greater if different activated states exist with different probabilities of reaction.[26] One instance of this is when the transition state involves different numbers of weak interactions from the reactants. For the transfer of light nuclei across the energy barrier, we have seen that the probability of reaction is a continuous function of the energy of the systems, which is not cut off below the top of the barrier. The underlying concept again is similar.[65] La Mer[26] points out that even the effects arising from dual mechanisms, as reviewed in the last section, are but grosser manifestations of the same phenomenon.

The use of the integrated Arrhenius equation is justified because for simple reactions these deviations are usually quite small, and in only a few instances are they at all readily detectable. The concept of activation energy, as in the differential form of the equation, is still valid, but conclusions drawn from what is, in effect, extrapolation to absolute zero, should be regarded as relative rather than absolute.[9]

---

[64] R. C. Tolman, "Statistical Mechanics with Application to Physics and Chemistry," New York, 1927; F. E. C. Scheffer and W. F. Brandsma, *Rec. Trav. chim.*, 1926, **45**, 522; W. F. Brandsma, *ibid.*, 1928, **47**, 94; 1929, **48**, 1205.

[65] R. P. Bell, *Trans. Faraday Soc.*, 1938, **34**, 232, 259; R. P. Bell, *Ann. Reports Chem. Soc.*, 1939, **36**, 82; J. O. Hirschfelder and E. Wigner, *J. Chem. Phys.*, 1939, **7**, 616.