Activation Parameters for Chemical Reactions in Solution

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1 Introduction

Chemical reactions are not instantaneous; an 'energy barrier' separates reactants and products, each mole of reactant crossing this energy barrier in the process, reactants $\longrightarrow$ products. Chemical kinetics probe details of these energy barriers by examining the dependence of rates of reaction on composition, temperature, and pressure. The results are summarized using partial differentials (*e.g.* $\partial \ln k/\partial p$ at constant T; see below) which in turn characterize activation parameters. This review examines definitions and relationships between activation parameters for chemical reaction in solution.

Chemical reaction is, in thermodynamic terms, an irreversible process, the direction of spontaneous change being determined by the Second Law of Thermodynamics. Accordingly, the product of affinity for reaction A and rate of change J conforms to the condition[1], $A.J \geqslant 0$. J equals $d\xi/dt$ where $d\xi$ is the extent of chemical reaction in time dt. Intuition suggests that J is proportional to the affinity A, the driving force for reaction, such that J and A are related by a linear phenomenological equation; $J = L.A$. (L is a phenomenological coefficient.) This Ohm's Law approach[2] to chemical kinetics has merit but is rarely useful. Although J can be characterized by measuring the dependence of composition on time, the affinity cannot—no affinity meter is available commensurate with a voltmeter. Therefore the phenomenon of chemical reaction is conventionally described using the Law of Mass Action in which the ratio (J/V) {where V is the volume} is related directly to the composition at time t by the differential equation (1–1), c_j is the

$$(J/V) = k\Pi(j = 1; j = i)\,(c_j)^{\alpha(j)} \qquad (1\text{–}1)$$

concentration of substance j, α_j is the order with respect to j, and k is the phenomenological parameter called the rate constant. In this review we concentrate attention on the single reaction given in equation 1–2 where chemical substances W and Z are solutes in a solvent which is chemically inert in the sense that it is not involved in the stoicheiometric equation for the reaction; 'sln' identifies the solution state.

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[1] I. Prigogine and R. Defay, 'Chemical Thermodynamics' (trans. D. H. Everett), Longmans-Green, London, 1954.

[2] See for example, J. R. Partington, 'A History of Chemistry', MacMillan, London, 1964, volume 4, chapter 18.

$$\mathrm{W(sln)} \longrightarrow \mathrm{Z(sln)} \qquad (1\text{-}2)$$

At fixed T and p, this reaction is characterized by a first-order rate constant which is independent of time. The chemical reaction is elementary, a single energy barrier separating reactants and products. Complexities[3,4] arising from pre-equilibria, consecutive[5] and parallel[6] processes are not considered here.

Rate constant k for reaction (*cf.* equation 1–2) is an intensive dependent variable defined by the independent variables T and p for reaction in solvent l_1.

$$\ln k = \ln k[T;p] \qquad (1\text{-}3)$$

The dependences of ln k on temperature at fixed pressure and on pressure at fixed temperature define corresponding isobaric and isothermal activation parameters. We comment below on their derivation and interpretation. Also we consider isochoric (constant volume) activation parameters.

Two important themes dominate this review. First, the several conditions associated with a given activation parameter are defined using an extended symbolism. In this respect we apologize to the reader for the decoration of thermodynamic symbols. In our defence, we suggest that ambiguity may otherwise result. Possible no misunderstanding arises in the case of the familiar isobaric and isothermal activation parameters. However, for isochoric parameters we are concerned to establish the 'volume held constant'. The first theme has spilled over into a second theme in which we have been concerned to identify the standard (and reference) states associated with each activation parameter.

Interest in isochoric activation parameters stems from a seminal paper[7] by Evans and Polanyi published in 1936. These authors voiced a concern felt by all who study kinetics of chemical reactions in solution. When the dependence of rate constants on T and p is considered, one is aware that the properties of solvents and solvent–solute interactions depend on T and p. Evans and Polanyi wrote[7] (and we quote from page 893 of reference 7), 'Especial difficulty arises in solution from the interaction between solute and solvent, which depends strongly on temperature. This effect would be *to some extent* eliminated by measuring the temperature coefficients at constant volume, ...'. We have italicized three words because they indicate a compromise, prompting the calculation of isochoric activation parameters. Isochoric parameters have been calculated from data describing transport processes,[8,9] dielectric properties,[10] spectroscopic properties,[11] and chemical kinetics.[12]

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[3] B. Perlmutter-Hayman, *Progr. Inorg. Chem.*, 1976, **20**, 229.

[4] R. Koren and B. Perlmutter-Hayman, *J. Phys. Chem.*, 1971, **75**, 2372.

[5] See for example, M. J. Blandamer, J. Burgess, P. P. Duce, R. E. Robertson, and J. M. W. Scott, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 1999.

[6] J. G. Winter, J. P. Barron, and J. M. W. Scott, *Can. J. Chem.*, 1975, **53**, 1051.

[7] M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, 1936, **31**, 875.

[8] A. F. M. Barton, *Rev. Pure Appl. Chem.*, 1971, **21**, 49.

[9] S. B. Brummer and G. J. Hills, *Trans. Faraday Soc.*, 1962, **57**, 1816.

[10] G. Williams, *Trans. Faraday Soc.*, 1964, **60**, 1548.

[11] D. Griller, *J. Am. Chem. Soc.*, 1978, **100**, 5240.

[12] E. Whalley, *Adv. Phys. Org. Chem.*, 1954, **2**, 93; *Ber. Bunsenges Phys. Chem.*, 1966, **70**, 958.

2 Thermodynamics

A vital role is played in chemical kinetics by the Second Law of Thermodynamics. In this section we develop the point by considering a closed single-phase system wherein spontaneous chemical reaction 1–2 is taking place. At time t,

$$dG = -SdT + Vdp - Ad\xi \tag{2–1}$$

At fixed T and p, spontaneous chemical reaction occurs in the direction which leads to a decrease in the Gibbs Function, G. Within a microscopic volume, characteristic of the total system, local fluctuations in composition sample the dependence of G on ξ at fixed T and p. Those fluctuations are favoured which are accompanied by a decrease in G. At a given stage in the reaction (*i.e.* fixed ξ), the thermodynamic properties are related (Figure 1). As the reaction proceeds so the volume V, enthalpy H, entropy S, and isobaric heat capacity C_p change. Eventually $\{$*i.e.* limit $(t \longrightarrow \infty)\}$, the system attains chemical equilibrium, composition ξ^{eq}, where G is a minimum and ξ^{eq} is characteristic of the system, T and p. At equilibrium $J = 0, A = 0$ and $\{(\partial G/\partial\xi)_{T;p}\}^{eq} = 0$. At equilibrium all local fluctuations in composition produce an increase in G. Nevertheless the thermodynamic variables H, S, V, and C_p are not necessarily at extrema. In a particular system, V^{eq} $[= \{(\partial G/\partial p)_T\}^{eq}]$ may be a maximum; in another case it may be a minimum; in yet another case, at some intermediate value. With reference to equation 1–2, the volume of the system at limit $(t \longrightarrow \infty)$ depends on the magnitudes and signs of the partial molar volumes of solutes W and Z and the solvent.

The foregoing thermodynamic statements refer to macroscopic properties which are related to (partial) molar properties of chemical substances making up a system; Figure 2. The parent partial molar property is the chemical potential which for

$$\begin{tikzcd}
C_p(\xi) = (\partial H/\partial T)_{p;\xi} & & \alpha(\xi) = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p;\xi} & & \kappa(\xi) = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T;\xi} \\
H = -T^2\left\{\partial(G/T)/\partial T\right\}_{p;\xi} \arrow[u] & & & V = (\partial G/\partial p)_{T;\xi} \arrow[ul] \arrow[ur] & \\
& & \boxed{G} \arrow[ull] \arrow[ur] \arrow[dl] \arrow[dr] & & \\
& A = -(\partial G/\partial\xi)_{T;p} & & S = -(\partial G/\partial T)_{p;\xi} &
\end{tikzcd}$$

Figure 1 *Thermodynamic variables as a function of G at fixed composition* solute j in solution (solvent = l_1) is given by[13] equation 2–2 where m_j is the molality of j ($= n_j/n_1 M_1$) and where m_i is the molality of all other solutes in solution:

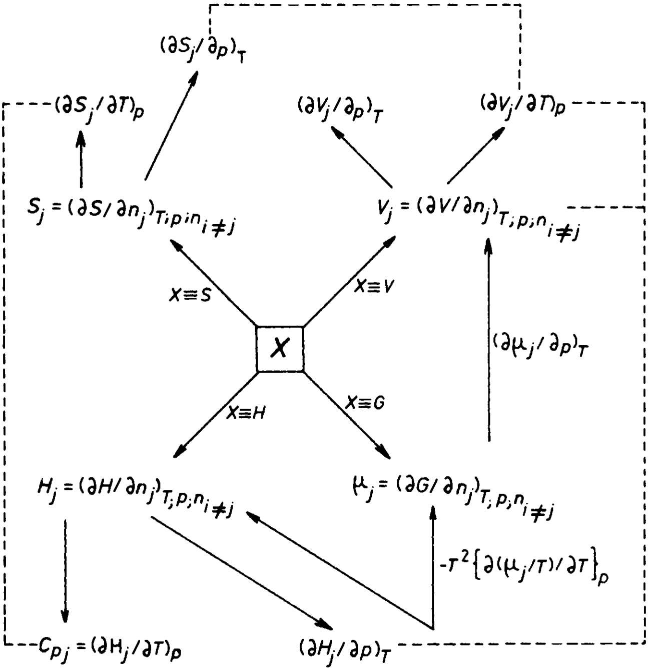

Figure 2 *Partial molar properties of substance* j *in a system containing* n_i *moles of substance* i (= 1,2,3,4 . .); *the dotted lines indicate a Maxwell relation*

$$\mu_j(\mathrm{sln};T;p) = \mu_j^{\ominus}(\mathrm{sln};T) + RT\ln(m_j\gamma_j/m^{\circ}) + \int_{p^{\circ}}^{p} V_j^{\infty}(\mathrm{sln};T;p)\,\mathrm{d}p \tag{2–2}$$

where limit ($m_j \longrightarrow 0$; $m_i \longrightarrow 0$) $\gamma_j = 1$ at all T and p. $\mu_j^{\ominus}(\mathrm{sln};T)$ is the standard chemical potential of solute j in solution at temperature T and standard pressure p°; *i.e.* an isobaric–isothermal standard state. $V_j^{\infty}(\mathrm{sln};T;p)$ is the partial molar volume of solute j at infinite dilution. From the differential of equation 2–2 with respect to pressure at constant temperature, and according to the definition of γ_j,

$$\begin{aligned} \text{limit}\,(m_j \longrightarrow 0;\, m_i \longrightarrow 0)V_j(\mathrm{sln};T;p) &= V_j^{\infty}(\mathrm{sln};T;p) \\ &= V_j(\mathrm{sln};m_j = 1;\gamma_j = 1;T;p) \end{aligned} \tag{2–3}$$

Therefore the partial molar volume of j in an ideal solution where $m_j = 1$ at temperature T and pressure p equals $V_j^{\infty}(\mathrm{sln};T;p)$, the latter being $V_j(\mathrm{sln};\,T;p)$ extrapolated to the limit of infinite dilution.[14] Similarly,[14]

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[13] M. L. McGlashan, 'Chemical Thermodynamics', Academic Press, London, 1979.

[14] J. E. Garrod and T. M. Herrington, *J. Chem. Educ.*, 1969, **46**, 165.

$$\text{limit}\,(m_j \longrightarrow 0; m_i \longrightarrow 0)\, H_j(\text{sln};T;p) = H_j^{\infty}(\text{sln};T;p) = H_j(\text{sln};m_j = 1; \gamma_j = 1;T;p) \quad (2\text{–}4)$$

and

$$\text{limit}\,(m_j \longrightarrow 0; m_i \longrightarrow 0) C_{pj}(\text{sln};T;p) = C_{pj}^{\infty}(\text{sln};T;p) = C_{pj}(\text{sln};m_j = 1; \gamma_j = 1;T;p) \quad (2\text{–}5)$$

At $p = p^{\circ}$, $V_j^{\infty}(\text{sln};T;p) = V_j^{\ominus}(\text{sln};T)$, $C_{pj}^{\infty}(\text{sln};T;p) = C_{pj}^{\ominus}(\text{sln};T)$ and $H_j^{\infty}(\text{sln};T;p) = H_j^{\ominus}(\text{sln};T)$. These equalities do not carry over to the chemical potentials and partial molar entropies of solute j because limit $(m_j \longrightarrow 0) \ln m_j = -\infty$; the standard state is not the infinitely dilute solution.

3 Chemical Kinetics

The general differential of equation 1–3 is

$$\mathrm{d}\ln k = \left[\frac{\partial \ln k}{\partial T}\right]_p \mathrm{d}T + \left[\frac{\partial \ln k}{\partial p}\right]_T \mathrm{d}p \quad (3\text{–}1)$$

Experimental data describing the dependence of composition on time are analysed to obtain an estimate of the true rate constant at given T and p. The latter two quantities are usually assumed to be error-free, *i.e.* the true temperature and true pressure. Equation 1–3 implies that a quantitative relationship exists between k, T, and p but this relationship is unknown; it is not defined by thermodynamics although the dependence can be described in thermodynamic terms. At this stage various equations are tested with the aim of describing the observed dependence.[15–21] For reactions at constant pressure, the dependence of $\ln k$ on T about $\ln k(\theta)$ at temperature θ may be expressed[15] by equation 3–2 where K is the SI unit of temperature, Kelvin.

$$\ln k = a_1 + (a_2K)[(1/T) - (1/\theta)] + a_3 \ln (T/\theta) \quad (3\text{–}2)$$

Hence,

$$(\partial \ln k/\partial T)_p = -a_2K/T^2 + a_3/T \quad (3\text{–}3)$$

Similarly the dependence of k on pressure (at fixed T) may be fitted about $k(\pi)$ at reference pressure π using equation 3–4.

$$\ln k = b_1 + (b_2/\text{Pa})(p - \pi) + (b_3/Pa^2)(p - \pi)^2 \quad (3\text{–}4)$$

Hence,

$$(\partial \ln k/\partial p)_T = (b_2/Pa) + 2\,(b_3/Pa^2)(p - \pi) \quad (3\text{–}5)$$

Statistical analysis using least squares procedures yields estimates of the

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[15] M. J. Blandamer, J. Burgess, R. E. Robertson, and J. M. W. Scott, *Chem. Rev.*, 1982, **82**, 259.
[16] T. Asano and W. J. le Noble, *Chem. Rev.*, 1978, **78**, 407.
[17] W. J. le Noble, *Rev. Phys. Chem. Jpn.*, 1980, **50**, 209.
[18] S. D. Hamann, *Rev. Phys. Chem. Jpn.*, 1980, **50**, 147.
[19] T. W. Swaddle, *Rev. Phys. Chem. Jpn.*, 1980, **50**, 231.
[20] R. van Eldik and H. Kelm, *Rev. Phys. Chem. Jpn.*, 1980, **50**, 185.
[21] B. S. El'yanov and E. M. Vasylvitskaya, *Rev. Phys. Chem. Jpn.*, 1980, **50**, 169.

dimensionless quantities a_i and b_i for $i = 1$ to 3. Various statistical advantages[15] follow if θ and π are chosen near the middle of the experimental T and p ranges. The simple polynomial in equation 3–4 can also be modified[22] by replacing p and π by T and θ respectively and used to fit the dependence of k on T at fixed p. If θ in equation 3–2 is set to 1 K, the result is the Valentiner equation.[15] If π in equation 3–4 is set to zero, the result is a simple quadratic[23] in p. However, the latter procedure has been criticized[24] on the grounds that (i) the equation predicts extrema in the dependence of ln k on p and (ii) derived parameters at low pressures depend strongly on the number of experimental points at high pressures. A more satisfactory description[24] is given by equation 3–6. (We have modified the original equation in reference 24 to express the dependence about $k(\pi)$ at pressure π.)

$$\ln\{k(p)/k(\pi)\} = (c_1/Pa)(p - \pi) + c_2 \ln\{[1 + (c_3/Pa)p]/[1 + (c_3/Pa)\pi\} \quad (3\text{–}6)$$

With reference to the dependence of ln k on T, the Clarke–Glew equation[25] for the dependence of equilibrium constants on T is readily modified to yield an equation for the dependence of ln k in terms of molar enthalpies and molar isobaric heat capacities of activation (Section 6).

A problem over dimensional analysis emerges in these fitting equations (*cf.* equations 3–2 and 3–4) concerning the units associated with rate constants. This problem is met by defining a dimensionless quantity $k^{\$}$; for a first order rate constant, $k = k^{\$}/\text{s}$ and for a second order rate constant, $k = k^{\$}/\text{s mol m}^{-3}$ where s is the SI unit of time, second.

A multitude of analytical procedures are therefore available for calculating the two partial derivatives in equation 3–1 for chemical reaction in a given solvent at temperature θ and pressure π. At θ and π, the two partial derivatives are orthogonal, no direct relationship existing between the isobaric and isothermal quantities.

4 Properties of Solvents

The volume of a closed system comprising liquid l_1 at temperature T and pressure p is an extensive property. The molar volume V_1^* ($= V/n_1$) is an intensive property defined by the intensive independent variables T and p;

$$V_1^* = V_1^*[T;p] \quad (4\text{–}1)$$

The general differential of equation 4–1 is

$$dV_1^* = (\partial V_1^*/\partial T)_p dT + (\partial V_1^*/\partial p)_T dp \quad (4\text{–}2)$$

For reversible changes (*i.e.* equilibrium conditions), thermal (isobaric) expansivity,

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[22] M. J. Blandamer, J. Burgess, P. P. Duce, R. E. Robertson, and J. M. W. Scott, *J. Chem. Soc., Perkin 2*, 1981, 1157.

[23] J. B. Hyne, H. S. Golinkin, and W. G. Laidlaw, *J. Am. Chem. Soc.*, 1966, **88**, 2104.

[24] T. Asano and T. Okada, *J. Phys. Chem.*, 1984, **88**, 238.

[25] E. C. W. Clarke and D. N. Glew, *Trans. Faraday Soc.*, 1966, **62**, 539.

$$\alpha_1{}^* = (1/V_1{}^*)(\partial V_1{}^*/\partial T)_p \tag{4–3}$$

and the (isothermal) compressibility,

$$\kappa_1{}^* = -(1/V_1{}^*)(\partial V_1{}^*/\partial p)_T \tag{4–4}$$

For stable phases, $\kappa_1{}^* > 0$ but $\alpha_1{}^*$ can be positive, zero, or negative depending on the system. The internal pressure of liquid l_1,

$$\Pi_i = T(\alpha_1{}^*/\kappa_1{}^*) - p \tag{4–5}$$

Π_i is characteristic of a liquid[26–28] at defined T and p (Table 1).

Table 1 *Internal pressures of liquids at* 298 K *and* 101 325 N m^{-2}

Liquid	$10^{-8} \cdot \Pi_i$/N m^{-2}
Methyl alcohol	2.99
Ethyl alcohol	2.91
Acetonitrile	3.89
1,4-Dioxane	4.99
Hexane	2.39
Water	1.683
Water (273 K)	−0.363
D_2O	1.228
D_2O (278 K)	−0.617

taken from references 26—29

According to equation 4–1, the molar volume of liquid l_1 at temperature θ and pressure π is defined by $V_1{}^*[\theta;\pi]$. If the temperature is changed from θ to $\theta + \delta\theta$, the molar volume is defined by $V_1{}^*[\theta + \delta\theta;\pi]$. Suppose that at temperature $\theta + \delta\theta$, the pressure is changed to $\pi + \delta\pi_1$, whereby the molar volume of liquid l_1 at $[\theta;\pi]$ and $[\theta + \delta\theta; \pi + \delta\pi_1]$ are equal. This isochoric condition can be expressed in the form,

$$V_1{}^*[\theta;\pi] = V_1{}^*[\theta + \delta\theta; \pi + \delta\pi_1] \tag{4–6}$$

$\delta\pi_1$ is characteristic of the liquid. The conditions operating either side of equation 4–6 are isobaric–isothermal but the equality is isochoric. Similar considerations may be given to a binary liquid mixture formed from n_1 and n_2 moles of liquids l_1 and l_2. The molar volume V_m $\{= V/(n_1 + n_2)\}$ is defined by the independent variables, T, p, and x_2; *i.e.* $V_m = V_m\,[T;p;x_2]$ where $x_2 = n_2/(n_1 + n_2)$ and $x_1 = 1 - x_2$. Many changes can be rung amongst the variables T, p, and x_2. If, at a given T and p, the excess molar volume of a mixture $V_m{}^E > |V_1{}^* - V_2{}^*|$, there will exist

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[26] M. R. J. Dack, *Chem. Soc. Rev.*, 1975, **4**, 211.

[27] J. Amoros, J. R. Solana, and E. Villar, *Mater. Chem. Phys.*, 1984, **10**, 557.

[28] Data for water from J. V. Leyendekkers, 'The Thermodynamics of Sea Water as a Multicomponent Electrolyte Solution', Part 1, M. Dekker, New York, 1976.

pairs of mole fractions x_2' and x_2'' where the molar volumes are equal, *i.e.* isochoric. At a given x_2, V_m is a function of T and p so that an isochoric condition analogous to equation 4–6 is,

$$V_m[\theta;\pi;x_2] = V_m[\theta + \delta\theta; \pi + \delta\pi_2;x_2] \tag{4–7}$$

where $\delta\pi_2$ is characteristic of the mole fraction composition x_2. The isochoric condition in equation 4–7 refers to a mixture having defined mole fraction composition, *i.e.* a local isochoric condition. One can also envisage a global isochoric condition where over the range $0 \leqslant x_2 \leqslant 1.0$, there exist temperatures and pressures where the molar volumes are identical.

5 Phenomenological Kinetic Parameters

According to the Arrhenius equation,[30–32] an energy of activation E characterizes the isobaric derivative in equation 3–1;

$$(\partial \ln k^{\$}/\partial T)_p = E/RT^2 \tag{5–1}$$

E is a macroscopic phenomenological property and depends on T, p, and solvent. Explanations of the factors controlling E are offered in terms of molecular processes within a system. Chemical reaction is envisaged as proceeding by the pathway (mechanism) involving the lowest activation energy of all available pathways. For reactions in solution, the solvent plays a key role in determining this pathway.

The isothermal dependence of rate constant on pressure (equation 3–1) defines an activation volume, ΔV which is also a macroscopic property of a system:

$$(\partial \ln k^{\$}/\partial p)_T = -\Delta V/RT \tag{5–2}$$

For a given chemical reaction E and ΔV characterize the orthogonal dependences of $\ln k^{\$}$ in a plot of $\ln k^{\$}$ against T and p. In another analysis we consider how $\ln k^{\$}$ depends on temperature not at constant pressure but where the pressure changes in the sense defined by equation 4–6, *i.e.* isochoric with respect to the molar volume of the solvent. The required partial derivative is,

$$\left[\frac{\partial \ln k^{\$}}{\partial T}\right]_{V_1^*}$$

Similarly we consider the dependence of $\ln k^{\$}$ on pressure not at constant temperature but where the temperature changes to hold $V_1{}^*$ constant;

$$\left[\frac{\partial \ln k^{\$}}{\partial p}\right]_{V_1^*}$$

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[30] P. D. Pacey, *J. Chem. Educ.*, 1981, **58**, 612.
[31] S. R. Logan, *J. Chem. Educ.*, 1982, **59**, 279.
[32] K. J. Laidler, *J. Chem. Educ.*, 1984, **61**, 494.

The latter two partial derivatives are related (*cf.* reference 33) to the isobaric and isothermal partial derivatives;

$$\left[\frac{\partial \ln k^{\$}}{\partial T}\right]_{V_1*} = \left[\frac{\partial \ln k^{\$}}{\partial T}\right]_p - \left[\frac{\partial V_1*}{\partial T}\right]_p \left[\frac{\partial p}{\partial V_1*}\right]_T \left[\frac{\partial \ln k^{\$}}{\partial p}\right]_T \quad (5\text{–}3)$$

$$\left[\frac{\partial \ln k^{\$}}{\partial p}\right]_{V_1*} = \left[\frac{\partial \ln k^{\$}}{\partial p}\right]_T - \left[\frac{\partial V_1*}{\partial p}\right]_T \left[\frac{\partial T}{\partial V_1*}\right]_p \left[\frac{\partial \ln k^{\$}}{\partial T}\right]_p \quad (5\text{–}4)$$

Within the plot of ln $k^{\$}$ against T and p, the two partial derivatives calculated by equations 5–3 and 5–4 are not orthogonal, being related through the properties of the solvent.

By definition,

$$\left[\frac{\partial \ln k^{\$}}{\partial T}\right]_{V_1*} = \frac{E(V_1*)}{RT^2} \quad (5\text{–}5)$$

where $E(V_1*)$ is an isochoric (V_1*) energy of activation. For solvolysis of t-butyl chloride in methyl alcohol[34] at 298 K and 101 325 N m^{-2}, $E\{V*(\mathrm{MeOH};1)\}$ = 103.76 kJ mol^{-1} and E = 94.14 kJ mol^{-1}.

The phenomenological approach to chemical kinetics has considerable merit in that no '*a priori*' assumptions are made concerning the process of chemical reaction. Nevertheless links between activation parameters and the thermodynamic properties of solutes are tenuous.

6 Transition State Theory

The wealth of data concerning the thermodynamic properties of solutes in solution offers a basis on which to build an analysis of kinetic data. Transition State Theory[35] provides a route for analysis in these terms but at the expense of adopting a particular model for the activation process.

Chemical reaction (*cf.* equation 1–2) proceeds through a transition state, symbol $\neq$. Hence for chemical reaction in solvent l_1 and at temperature T and pressure p,

$$\mathrm{W} \rightleftharpoons \neq \longrightarrow \mathrm{Z} \quad (6\text{–}1)$$

Reactant W and transition state $\neq$ are in equilibrium.[35] Hence, at time t, the thermodynamic condition is,

$$\mu_{\mathrm{w}}^{\mathrm{eq}}(\mathrm{sln};T;p) = \mu_{\neq}^{\mathrm{eq}}(\mathrm{sln};T;p) \quad (6\text{–}2)$$

If the solution is dilute, $\gamma_{\neq}^{\mathrm{eq}}/\gamma_{\mathrm{w}}^{\mathrm{eq}} = 1$ and $m_{\neq}^{\mathrm{eq}}/m_{\mathrm{w}}^{\mathrm{eq}} = c_{\neq}^{\mathrm{eq}}/c_{\mathrm{w}}^{\mathrm{eq}}$. If the

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[33] G. N. Lewis and M. Randall, 'Thermodynamics' (revised by K. S. Pitzer and L. Brewer) McGraw-Hill, New York, 1961, chapter 3.

[34] G. J. Hills and C. A. Viana in 'Hydrogen Bonded Solvent Systems', ed. A. K. Covington and P. Jones, Taylor & Francis, London, 1968, p. 261.

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

transmission coefficent[35] is unity (*cf.* references 36 and 37) at all T and p,

$$k^{\$}/T = (k_B\mathrm{s/h})\,{}^{\neq}K^{\circ}(\mathrm{sln};T)\exp\left[\int_{p^{\circ}}^{p} -\frac{\Delta^{\neq}V^{\infty}(\mathrm{sln};T;p)}{RT}\,\mathrm{d}p\right] \qquad (6\text{–}3)$$

$$\begin{aligned}\Delta^{\neq}G^{\ominus}(\mathrm{sln};T) &= RT\ln{}^{\neq}K^{\circ}(\mathrm{sln};T)\\ &= \mu_{\neq}{}^{\ominus}(\mathrm{sln};T) - \mu_{\mathrm{w}}{}^{\ominus}(\mathrm{sln};T)\end{aligned} \qquad (6\text{–}4)$$

Rate constant $k^{\$}$ is determined by the molar volume of activation $\Delta^{\neq}V^{\infty}$ and the difference between the standard chemical potentials of reactant and transition state. The standard equilibrium constant, ${}^{\neq}K^{\circ}$, depends on temperature but not on pressure. By analogy with the van't Hoff equation for the dependence of K° on T,

$$\{\partial\ln(k^{\$}/T)/\partial T\}_p = \Delta^{\neq}H^{\infty}(\mathrm{sln};T;p)/RT^2 \qquad (6\text{–}5)$$

where (*cf.* equation 2–4),

$$\Delta^{\neq}H^{\infty}(\mathrm{sln};T;p) = H_{\neq}{}^{\infty}(\mathrm{sln};T;p) - H_{\mathrm{w}}{}^{\infty}(\mathrm{sln};T;p) \qquad (6\text{–}6)$$

At $p = p^{\circ}$, the standard increase in molar enthalpy of activation,

$$\Delta^{\neq}H^{\circ}(\mathrm{sln};T) = H_{\neq}{}^{\circ}(\mathrm{sln};T) - H_{\mathrm{w}}{}^{\circ}(\mathrm{sln};T) \qquad (6\text{–}7)$$

Similarly, the reference molar volume of activation is given by,

$$\{\partial\ln k^{\$}/\partial p)_T = -\Delta^{\neq}V^{\infty}(\mathrm{sln};T;p)/RT \qquad (6\text{–}8)$$

where for the reaction in equation 1–2,

$$\Delta^{\neq}V^{\infty}(\mathrm{sln};T;p) = V_{\neq}{}^{\infty}(\mathrm{sln};T;p) - V_{\mathrm{w}}{}^{\infty}(\mathrm{sln};T;p) \qquad (6\text{–}9)$$

The reference molar enthalpy of activation, $\Delta^{\neq}H^{\infty}$ is dependent on both T and p. The reference molar isobaric heat capacity of activation,[38,39]

$$\Delta^{\neq}C_p{}^{\infty} = (\partial\Delta^{\neq}H^{\infty}/\partial T)_p \qquad (6\text{–}10)$$

Also,

$$\{\partial\Delta^{\neq}H^{\infty}/\partial p\}_T = \Delta^{\neq}V^{\infty} - T\{\partial\Delta^{\neq}V^{\infty}/\partial T\}_p \qquad (6\text{–}11)$$

$\Delta^{\neq}C_p{}^{\infty}$ may also depend on temperature but the statistical significance of a calculated dependence is often poor because it emerges from the fourth derivative of the input data, the dependence of composition on time. An important suggestion[40] concerns the measurement of relative rates at T and $T + \Delta T$ of two otherwise identical systems. Consequently, one differential operation is incorporated into the experimental procedure.

[36] H. A. Kramers, *Physica*, 1940, **7**, 284.

[37] B. Gavish and M. M. Werber, *Biochemistry*, 1979, **10**, 1209.

[38] R. E. Robertson, *Progr. Phys. Org. Chem.*, 1967, **4**, 213.

[39] M. J. Blandamer, R. E. Robertson, and J. M. W. Scott, *Progr. Phys. Org. Chem.*, in press.

[40] W. J. Albery and B. H. Robinson, *Trans. Faraday Soc.*, 1969, **65**, 980.

The molar volume of activation $\Delta^{\neq}V^{\infty}$ also depends on temperature and pressure, striking evidence for these dependences being shown by kinetic data for hydrolysis of methyl *p*-nitrobenzene sulphonate,[41] methyl bromide,[42] and methyl acetate.[43]

The quantities defined by equations 6–10 and 6–11 are related to the partial differentials in the general differential of the equation, $\Delta^{\neq}H^{\infty} = \Delta^{\neq}H^{\infty}\ [T;p]$. Activation parameters, $\Delta^{\neq}V^{\infty}$ and $\Delta^{\neq}H^{\infty}$ refer to the differences between the partial molar properties of reactants and transition states in ideal solutions under isothermal and isobaric conditions (*cf.* equations 6–6 and 6–9).

7 Isothermal and Isobaric Activation Parameters

A diagrammatic representation[44] of the activation process described by equation 6–4 is shown in Figure 3 where chemical reaction involves rupture of a chemical bond within W to form two fragments, identified collectively as product Z.

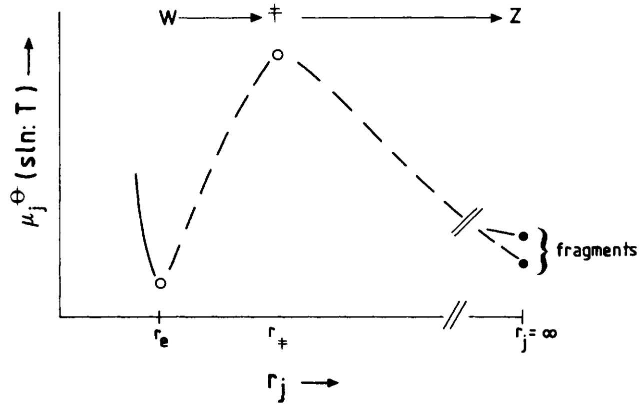

Figure 3 *Standard chemical potential as a function of bond length*

A series of solutes are envisaged where the two parts of molecule W are separated by distance r_j and the standard chemical potential is $\mu_j^{\ominus}(\text{sln};T)$. The initial and transition states are characterized by r_e and μ_w° $(\text{sln};T)$ and by $r_{\neq}$ and $\mu_{\neq}{}^{\ominus}(\text{sln};T)$ respectively. $\mu_{\neq}{}^{\ominus}(\text{sln};T)$ occurs at a maximum in the plot of $\mu_j^{\ominus}(\text{sln};T)$ against r_j. When $r_j > r_{\neq}$, $\mu_j^{\ominus}(\text{sln};T)$ decreases until, at $r_j = \infty$, there are two quantities representing the standard chemical potentials of the fragments. The maximum at $r_{\neq}$ is the key feature although we rarely know either $r_{\neq}$ or the detailed form of the plot between r_e and $r_{\neq}$ and between $r_{\neq}$ and r_{∞}. All that we calculate from experimental kinetic data is the difference, $\Delta^{\neq}G^{\ominus}(\text{sln};T)$.

Comparable plots can be constructed (at least in principle) showing the

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[41] J. L. Kurz and J. Y.-W. Lu, *J. Phys. Chem.*, 1983, **87**, 1444.

[42] B. T. Baliga and E. Whalley, *J. Phys. Chem.*, 1969, **73**, 654.

[43] B. T. Baliga, R. J. Withey, D. Poulton, and E. Whalley, *Trans. Faraday Soc.*, 1965, **61**, 517.

[44] F. R. Cruikshank, A. J. Hyde, and D. Pugh, *J. Chem. Educ.*, 1977, **54**, 288.

dependence of $X_j^{\ominus}(\text{sln};T)$ on r_j for $X = H$, C_p, V, S... There need be no similarity[17,45] between the shape of these plots and that shown in Figure 3. For a given system, $X_j^{\ominus}(\text{sln};T)$ may decrease gradually with increase in r_j. In another system, $X_j^{\ominus}(\text{sln};T)$ may pass through a minimum, but not necessarily at $r_{\neq}$.

Where $X = \text{H}$, the overall dependence of $H_j^{\ominus}(\text{sln};T)$ on r_j is likely to resemble that shown in Figure 3 on the grounds that $\Delta^{\neq}G^{\ominus}(\text{sln};T)$ and $\Delta^{\neq}H^{\ominus}(\text{sln};T)$ are, generally, of comparable magnitude. But the similarity is unlikely to extend to plots where $X = C_p$ and $X = V$. The latter point is well established, various generalizations[16–21] being reported linking molar volumes of activation with the molecularity of reaction and changes in solvent–solute interactions during the activation process.

The complexity of the dependence of X_j° on r_j is clearly indicated by systems[16,46] where $|\Delta^{\neq}V^{\infty}(\text{sln};T;p)| < |\Delta_r V^{\infty}(\text{sln};T;p)|$.

The foregoing comments go some way to explaining why interpretation of trends in $\Delta^{\neq}G^{\ominus}$ and rate constants tend to be more successful than in the case of derived parameters; the unique feature in Figure 3, the maximum, being the deciding factor. Closely related to these considerations is the observation that for a series of related substances in a given solvent or for one reaction in a range of solvents, plots of $\Delta^{\neq}H^{\ominus}$ against $\Delta^{\neq}S^{\ominus}$ (with $p = p^{\circ}$) are close to linear. The source of these isokinetic relationships[47–50] has been a matter for intense debate, although it has become clear that a proper statistical analysis of the data is mandatory before conclusions are drawn concerning the chemical significance of these relationships. Other correlations include an interdependence of molar volumes and entropies of activation.[51] The slope of the plot for reactions in aqueous solutions has been related to the number of neighbouring water molecules which break up into charged fragments, *i.e.* an ionberg–iceberg model.[52]

No actual number value can be assigned to the standard chemical potential of a solute, and so derived parameters (*i.e.* $\Delta^{\neq}G^{\ominus}$) are differences between standard chemical potentials. However, it is possible to examine trends in $\Delta^{\neq}G^{\ominus}(\text{sln};T)$ for a given reaction in a range of solvents in the light of changes in the standard chemical potentials of reactants.[53,54]

Considerable interest surrounds kinetic data for reaction in both aqueous solution and binary aqueous mixtures[55–60] because these systems provide convenient test-beds for treatments of solvent effects on rate constants for chemical reactions. At ambient pressure, $p \simeq p^{\circ}$, the integral term in equation 6–3 is ignored such that rate constant $k^{\$}$ is simply related to $\Delta^{\neq}G^{\ominus}(\text{sln};T)$. The kinetics of reaction in binary aqueous mixtures are examined by comparing the molar activation

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[45] W. J. Albery and B. H. Robinson, *Trans. Faraday Soc.*, 1969, **65**, 1623.

[46] R. A. Grieger and C. A. Eckert, *J. Am. Chem. Soc.*, 1970, **92**, 7149.

[47] J. E. Leffler and E. Grunwald, 'Rates and Equilibria of Organic Reactions', Wiley, New York, 1963.

[48] R. Lumry and S. Rajender, *Biopolymers*, 1970, **9**, 1125.

[49] O. Exner, *Coll. Czech. Chem. Commun.*, 1964, **29**, 1094; 1972, **37**, 1425.

[50] R. R. Krug, W. G. Hunter, and R. A. Grieger, *J. Phys. Chem.*, 1976, **80**, 2335, 2341.

[51] M. V. Twigg, *Inorg. Chem. Acta*, 1977, **24**, L84.

[52] J. C. Phillips, *J. Chem. Phys.*, 1984, **81**, 478.

[53] M. J. Blandamer and J. Burgess, *Chem. Soc. Rev.*, 1975, **4**, 55.

[54] M. J. Blandamer and J. Burgess, *Pure Appl. Chem.*, 1983, **55**, 55.

parameters in a mixture, mole fraction of organic cosolvent x_2, and in aqueous solution. For a second order reaction between solutes *i* and *j*,

$$\begin{aligned}\Delta(\mathrm{aq} \longrightarrow x_2)\Delta^{\ddagger}G^{\ominus}(\mathrm{sln};T) &= \Delta(\mathrm{aq} \longrightarrow x_2)\mu_{\neq}^{\ominus}(\mathrm{sln};T) \\ &\quad - \Delta(\mathrm{aq} \longrightarrow x_2)\mu_i^{\ominus}(\mathrm{sln};T) - \Delta(\mathrm{aq} \longrightarrow x_2)\mu_j^{\ominus}(\mathrm{sln};T) \qquad (7\text{–}1)\end{aligned}$$

Equation 7–1 highlights one of the major attractions of Transition State Theory.[35] Kinetic data yield the quantity on the left-hand side of this equation and equilibrium thermodynamic data (*e.g.* solubilities) are analysed to obtain the dependence of standard chemical potentials of *i* and *j* on x_2. By difference, the effect of solvent on the transition state is obtained.

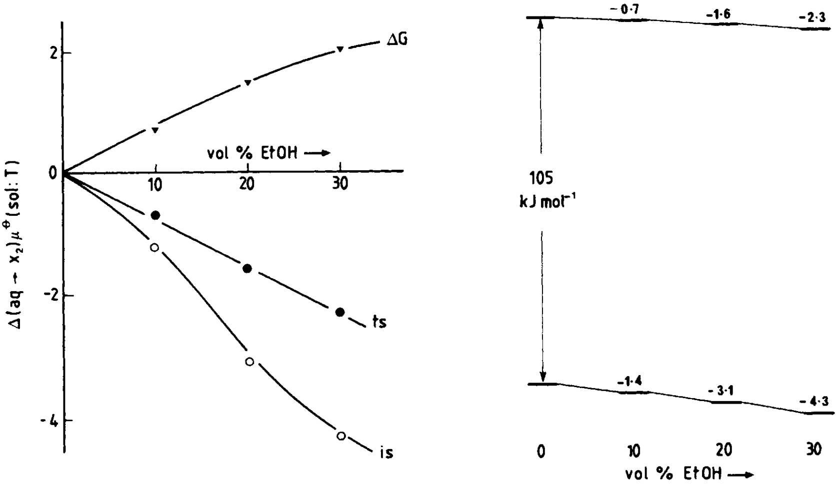

Figure 4 *Analysis of kinetic data for the dissociation of* $[\mathrm{Fe(bipy)_2(CN)_2}]$ *in water + methyl alcohol mixtures; data from reference* 61

An application of this procedure is shown in Figure 4, where the solvent effects on rate constants for dissociation of the non-electrolyte $[\mathrm{Fe(bipy)_2(CN)_2}]$ are represented in these terms.[61] The left-hand side of Figure 4 emphasizes the greater stabilizing effect of added ethyl alcohol on the initial state. The right-hand side of Figure 4 emphasizes just how small these changes in solvation effects are in relation to the activation barrier for reaction. Figure 5 illustrates the data for a simple dissociation reaction of a non-electrolyte, this time for a series of non-aqueous solvents. Again the effects of solvents on initial and transition states are in the same

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[55] M. J. Blandamer and J. Burgess, *Coord. Chem. Rev.*, 1980, **31**, 93.

[56] M. H. Abraham, *Progr. Phys. Org. Chem.*, 1974, **11**, 1.

[57] J. B. F. N. Engberts, *Pure Appl. Chem.*, 1982, **54**, 1797.

[58] J. B. F. N. Engberts in 'Water—A Comprehensive Treatise', ed. F. Franks, Plenum Press, New York, 1975, volume 6, chapter 4.

[59] M. J. Blandamer and J. Burgess, *Pure Appl. Chem.*, 1982, **54**, 2285.

[60] M. J. Blandamer, *Adv. Phys. Org. Chem.*, 1977, **14**, 203.

[61] M. J. Blandamer, J. Burgess, N. V. Reed, and P. Wellings, *J. Inorg. Nucl. Chem.*, 1981, **43**, 3245.

direction, but this time it is the solvent effect on the transition state which tends to dominate.[62] These examples from inorganic chemistry are linked to examples from organic chemistry through an interesting example from organometallic chemistry. The case concerns the bimolecular reaction (Figure 6) between tetraethyltin and mercury(II) chloride in methyl alcohol + water mixtures.[63,64] (The reference point for transfer parameters is 100% methyl alcohol in Figure 6, whereas the reference point is 100% water in Figure 4.)

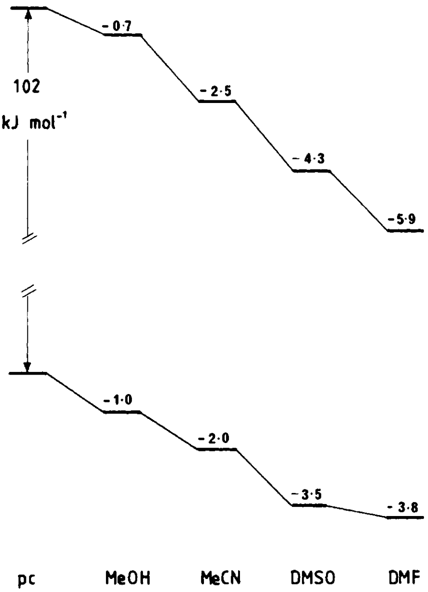

Figure 5 *Analysis of kinetic data for the dissociation of* [Mo(CO)$_4$(bipy)] *in a series of solvents; data from reference* 62. (pc ≡ propylene carbonate)

$$R_4Sn + HgCl_2 \longrightarrow RHgCl + R_3SnCl \qquad (7\text{–}2)$$

In the footsteps of the classical work by Winstein[65,66] and Arnett,[67] extensive studies of solvent effects in aqueous mixtures on activation parameters have been made of the water-catalysed hydrolysis of activated esters[68,69] and amides;[70,71] Scheme 1.

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[62] M. J. Blandamer, J. Burgess, J. G. Chambers, and A. J. Duffield, *Transition Met. Chem.*, 1981, **6**, 156.

[63] M. H. Abraham, G. F. Johnston, J. F. C. Oliver, and J. A. Richards, *J. Chem. Soc., Chem. Commun.*, 1969, 930

[64] M. H. Abraham, *J. Chem. Soc. A*, 1971, 1061.

[65] A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, 1956, **78**, 2770.

[66] S. Winstein and A. H. Fainberg, *J. Am. Chem. Soc.*, 1957, **79**, 2770.

[67] E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. McC. Duggleby, *J. Am. Chem. Soc.*, 1965, **87**, 1541.

[68] J. F. J. Engbersen and J. B. F. N. Engberts, *J. Am. Chem. Soc.*, 1975, **97**, 1563.

[69] H. A. J. Holterman and J. B. F. N. Engberts, *J. Am. Chem. Soc.*, 1980, **102**, 4256.

[70] W. Karzijn and J. B. F. N. Engberts, *Recl. Trav. Chim. Pays-Bas*, 1983, **102**, 513.

[71] J. Haak and J. B. F. N. Engberts, in press.

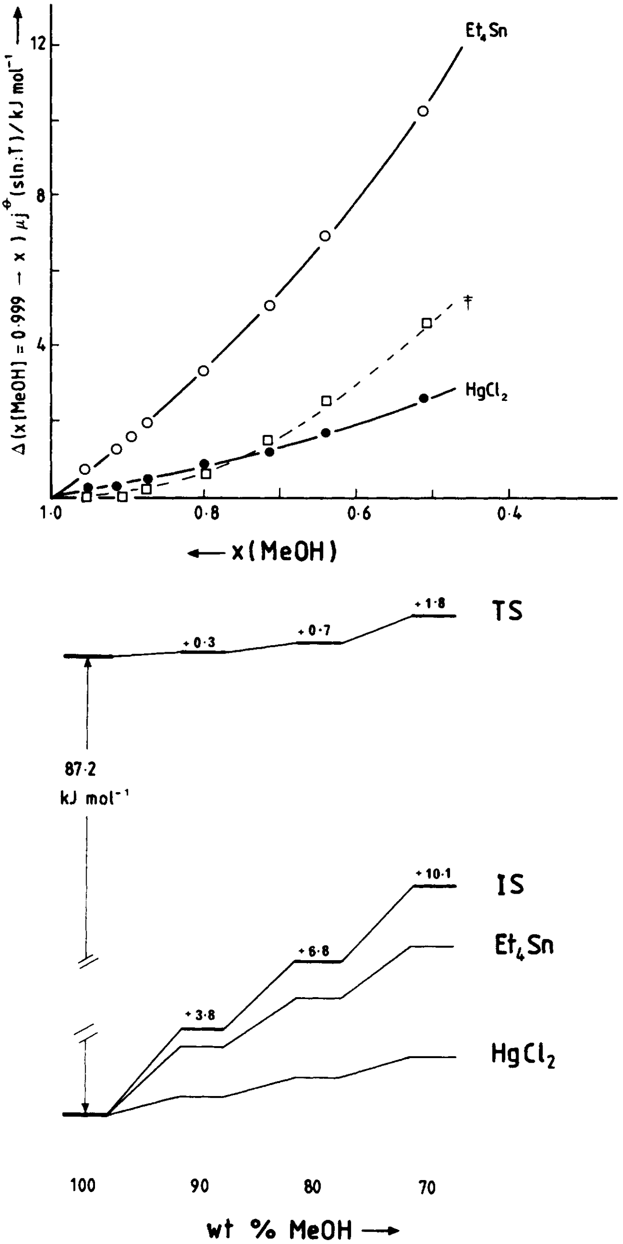
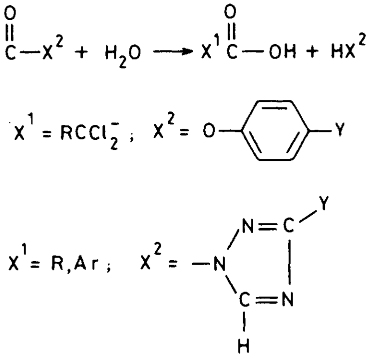


Figure 6 *Analysis of kinetic data for the reaction between* Et_4Sn *and* $HgCl_2$ *in methyl alcohol + water mixtures; reference solvent is a mixture where* x(MeOH) = 0.999; *data taken from reference* 64



Scheme 1

Different kinetic patterns[72] are observed for these reactions in water-rich typically aqueous (TA) and water-rich typically non-aqueous (TNA) mixtures.[60] In TA-mixtures (*e.g.* t-butyl alcohol + water) $\Delta^{\neq}G^{\ominus}$ usually increases (assuming $p = p^{\circ}$) continuously with increase in mole fraction of organic co-solvent. This simple pattern conceals eccentric if not capricious variation in the temperature and pressure dependences of the rate constants.[58,60] Quite generally, solvent effects on $\Delta^{\neq}H^{\circ}$ and $\Delta^{\neq}S^{\circ}$ exhibit mirror-image patterns and extrema are located around the solvent composition where the co-solvent has enhanced water–water interactions to the greatest extent. However, prerequisite for this behaviour is a marked change in the hydrophobicity of reactants in the activation process.[72] Therefore it is most likely that for reactions involving neutral substrates the changes in activation parameters with solvent composition reflect initial-state stabilization through hydrophobic interactions with the co-solvent. Interestingly, entropy changes often dominate relative rates describing changes in substituents in the substrates. Nevertheless, satisfactory correlations are obtained of substituent effects in terms of linear free-energy relationships, *e.g.* the Hammett equation.[58]

The underlying task involves establishing a link between, on the one hand, thermodynamic and kinetic data and, on the other hand, models describing the interactions at a molecular level between solutes and solvent molecules. Such an approach requires detailed insight into the roles played by dispersion, hydrogen-bonding, dipole–dipole... interactions and the contributions of these several interactions[73] to the overall solvation parameters. Despite the formidable problems involved some progress has clearly been made.

The dramatic dependence of activation parameters, particularly $\Delta^{\neq}C_p^{\infty}$, on mole fraction composition of TA mixtures may point to the importance of microheterogeneity (or, pseudo-phase separation) across a narrow range of

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[72] F. Franks, reference 58, 1973, vol. 2, chapter 1; 1975, vol. 4, chapter 1.

[73] S. Goldman, *Acc. Chem. Res.*, 1979, **12**, 409.

mixture compositions.[74,75] The marked dependence on composition of excess molar isobaric heat capacities of mixing,[76] sound absorption[77] properties, and light scattering properties[78] of these mixtures are indicative of this tendency. The close relationship between trends in the kinetic parameters for reactions in these mixtures and in microemulsions[79,80] is interesting in this respect.

In aqueous mixtures where the co-solvent is hydrophilic (*i.e.* TNA mixtures), the hydrophobic character of the substrate is important but mechanistic interpretation of solvent effects on kinetic parameters may be complicated by preferential solvation effects.[81–83] Rate limiting deprotonation of carbon acids in several water-rich TNA systems has been studied and extrema in $\Delta^{\neq} G^{\ominus}$ shown to occur in water-rich mixtures.[81,83] It has been suggested that polarization of water molecules by dipolar organic solvents is partly responsible for the observed solvent effects.[81]

If chemical reaction involves ions, the treatment is slightly less satisfactory because thermodynamic equilibrium data yield the transfer chemical potential for a salt rather than the individual ions. Consequently additional extrathermodynamic assumptions are invoked to obtain single ion quantities. In the case of a 1:1 salt ($\equiv 2$),

$$\Delta(\text{aq} \longrightarrow x_2)\mu_2^{\ominus}(\text{sln};T) = \Delta(\text{aq} \longrightarrow x_2)\mu_+^{\ominus}(\text{sln};T) + \Delta(\text{aq} \longrightarrow x_2)\mu_-^{\ominus}(\text{sln};T) \qquad (7\text{–}3)$$

Considerable progress has been made in the derivation of these single ion transfer parameters (*cf.* right-hand side of equation 7–3), the extensive set[84,85] for methyl alcohol + water mixtures being notable in this respect. Recent assignments of single ion transfer parameters are based on the assumption that $\Delta(\text{aq} \longrightarrow x_2)\mu^{\ominus}(\text{Ph}_4\text{P}^+;\text{sln};T) = \Delta(\text{aq} \longrightarrow x_2)\mu^{\ominus}(\text{Ph}_4\text{B}^-;\text{sln};T)$, *i.e.* the TPTB assumption. Figure 7 shows the transfer chemical potentials for a small selection of ions[86] in water + methyl alcohol mixtures, being derived in all cases on the TPTB assumption. The derived parameters show the expected destabilization of simple ions such as K^+, Cl^-, OH^-, and SO_4^{2-} as the proportion of methyl alcohol in the mixture increases. Again as expected, the di-negative sulphate ion is more markedly affected than the 1+ and 1− ions. Figure 7 also shows the importance of the nature of the ligand in an inorganic complex ion. Thus an increase in the methanol content

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[74] H. A. J. Holterman and J. B. F. N. Engberts, *J. Org. Chem.*, 1983, **48**, 4025.

[75] L. T. Kanerva and E. K. Euranto, *J. Am. Chem. Soc.*, 1982, **104**, 5419.

[76] C. de Visser, G. Perron, and J. E. Desnoyers, *Can. J. Chem.*, 1977, **55**, 856.

[77] M. J. Blandamer, reference 58, volume 2, chapter 9.

[78] T. Kato, N. Ito, T. Fujiyama, and Y. Udagawa, *Studies in Physical and Theoretical Chemistry*, 1982, **27**, 175.

[79] M. J. Blandamer, J. Burgess, B. Clark, P. P. Duce, and J. M. W. Scott, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 739.

[80] M. J. Blandamer, B. Clark, J. Burgess, and J. M. W. Scott, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 1651.

[81] K. Remerie and J. B. F. N. Engberts, *J. Org. Chem.*, 1981, **46**, 3543.

[82] K. Remerie and J. B. F. N. Engberts, *J. Phys. Chem.*, 1983, **87**, 5449.

[83] F. Hibbert and F. A. Long, *J. Am. Chem. Soc.*, 1972, **94**, 7637.

[84] M. A. Abraham, T. Hill, H. C. Ling, R. A. Schulz, and R. A. C. Watt, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 489.

[85] O. Popovych, *J. Phys. Chem.*, 1984, **88**, 4167.

[86] M. J. Blandamer, J. Burgess, A. Hakin, N. Gosal, S. Radulovic, P. Guardado, F. Sanchez, C. Hubbard, and E.-E. A. Abu-Gharib, submitted for publication.

of the mixture destabilizes the $[Co(NH_3)_4(CO_3)]^+$ cation but stabilizes the $[Co(phen)_2(CO_3)]^+$ ion, where hydrophilic ammonia ligands have been replaced by hydrophobic 1,10-phenanthroline ligands. The dominance of ligand hydrophobicity over ionic charge is also shown by the data for iron(II) cations included in Figure 7; the extent of stabilization by added methyl alcohol increases enormously as one goes from the very small gmi ligand through 1,10-phenanthroline to the very bulky ligand derived from 2-benzoyl pyridine and 3,4-dimethylaniline (*i.e.* $bsbMe_2$). The dominating influence of hydrophobic ligands carries through into the analysis of kinetic data in terms of solvent effects on initial and transition states, as shown in Figure 8. Here the relatively small effect of

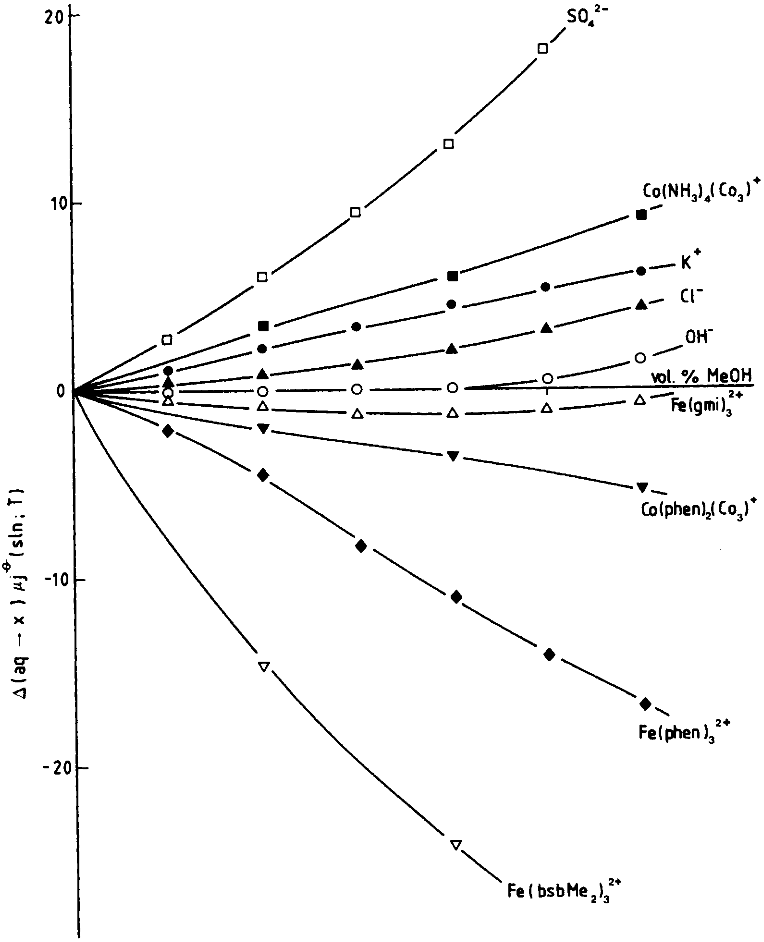


Figure 7 *Calculated dependence on solvent composition of single ion chemical potentials for various ions in methyl alcohol + water mixtures at 298 K and ambient pressure*

changes in solvent composition on the rate constant masks very large but nearly equal effects on the iron(II) complex cation and the transition state. Strong preferential solvation of hydroxide ions by water means that the transfer chemical potential of hydroxide ions does not exert a marked kinetic effect in water-rich mixtures.

The importance of solvation changes in kinetics of reaction between iron(II) diimine complex cations and hydroxide ions is dramatically demonstrated by trends in activation volumes. Despite the bimolecular nature of the rate-determining step,

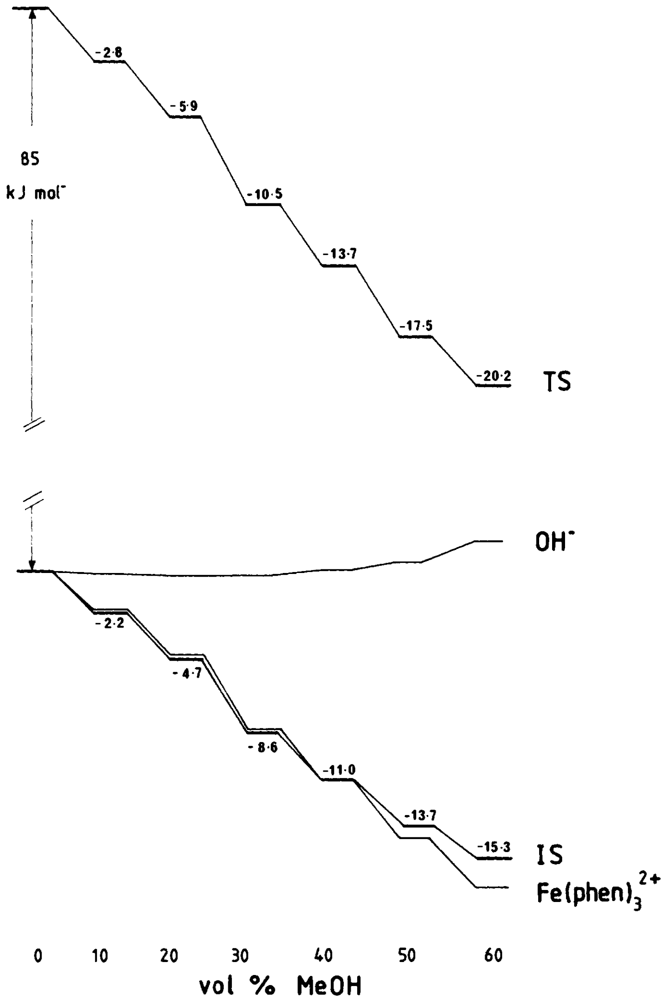
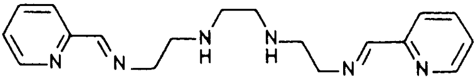
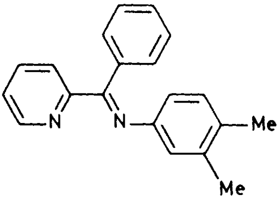


Figure 8 *Analysis of kinetic data in terms of effects of solvent composition in methyl alcohol + water mixture on* (*a*) Fe(phen)$_3^{2+}$ *ions,* (*b*) OH^- *ions, and* (*c*) *the transition state at* 298 K

$\Delta^{\neq} V^{\infty}$ is in the range $+10$ to $+20\,\mathrm{cm^3\,mol^{-1}}$ in aqueous solution.[87] These positive values may be ascribed to release of electrostricted water from hydroxide ions. The variation of $\Delta^{\neq} V^{\infty}$ with solvent composition in water + methyl alcohol mixtures shows a striking dependence on the nature of the di-imine ligand. For the complex with a relatively small and moderately hydrophobic ligand, $[\mathrm{Fe(hxsb)}]^{2+}$, $\Delta^{\neq} V^{\infty}$ decreases from 13.4 in water to $7\,\mathrm{cm^3\,mol^{-1}}$ in 85% methyl alcohol, but for the large and hydrophobic complex cation, $[\mathrm{Fe(bsbMe_2)}]^{2+}$ mentioned above, $\Delta^{\neq} V^{\infty}$ increases from $+11.1$ to $27\,\mathrm{cm^3\,mol^{-1}}$ over the same composition range.[88] Recent experiments show that the dependence of $\Delta^{\neq} V^{\infty}$ on solvent for reaction between either $[\mathrm{Fe(gmi)}]^{2+}$ or $[\mathrm{Fe(hxsb)}]^{2+}$ and hydroxide ions reflects structural effects in water + alcohol mixtures.[88,89]



hxsb



bsbMe$_2$

Returning attention to molar enthalpies of activation, absolute partial molar enthalpies cannot be determined for solutes in solution. The outlook is much brighter when we turn attention to molar volumes of activation because partial molar volumes of solutes in solution can be determined. The same situation prevails for partial molar heat capacities which can be measured using, for example, a flow calorimeter.[90,91] In the absence of volumetric and heat capacity data, group additivity schemes[92–94] lead to estimates for $C_{pj}^{\infty}(\mathrm{sln};T;p)$ and $V_j^{\infty}(\mathrm{sln};T;p)$. Analysis of kinetic data proceeds through the analogue of equation 7–1 re-expressed in terms of V- and C_p-quantities. Where one or more of the reactants are

[87] J. Burgess and C. D. Hubbard, *J. Chem. Soc., Chem. Commun.*, 1983, 1482.

[88] J. Burgess and C. D. Hubbard, *J. Am. Chem. Soc.*, 1984, **106**, 1717.

[89] M. J. Blandamer, J. Burgess, C. D. Hubbard, and S. Radulovic, unpublished work.

[90] P. Picker, P. A. Leduc, P. R. Philip, and J. E. Desnoyers, *J. Chem. Thermodyn.*, 1971, **3**, 631.

[91] J. E. Desnoyers, C. de Visser, G. Perron, and P. Picker, *J. Solution Chem.*, 1976, **5**, 605.

[92] N. Nichols, R. Skold, C. Spink, J. Suurkwesk, and I. Wadso, *J. Chem. Thermodyn.*, 1976, **8**, 1081.

[93] G. Perron and J. E. Desnoyers, *Fluid Phase Equilibria*, 1979, **2**, 239.

[94] R. N. French and C. M. Criss, *J. Solution Chem.*, 1981, **10**, 713.

ions, extrathermodynamic assumptions are again required to calculate ionic from salt properties,[95–97] *e.g.* $V_{+}^{\infty}(\text{sln};T;p)$ and $C_{p+}^{\infty}(\text{sln};T;p)$.

Analysis of kinetic data where chemical reaction involves the solvent is a little more complicated. Suppose reaction 6–1 is written,

$$\text{S} + \text{W(sln)} \Longleftrightarrow \neq \longrightarrow \text{Z} \tag{7–4}$$

In dilute solutions, $n(\text{S}) \gg n_{\text{w}}, n_{\neq}$, and n_z; the input quantity to the analysis is a first order rate constant describing a bimolecular process. But (at $p \simeq p^{\circ}$),

$$\Delta^{\neq} G^{\ominus}(\text{sln};T) = \mu_{\neq}^{\ominus}(\text{sln};T) - \mu_{\text{w}}^{\ominus}(\text{sln};T) - \mu^{\ominus}(\text{S};l;T) \tag{7–5}$$

Here $\mu^{\circ}(\text{S};l;T)$ is the standard chemical potential of the solvent. If the first-order rate constants for reaction 7–4 are compared in two solvents S1 and S2 (*e.g.* H_2O and D_2O), the ratio $k(\text{S1})/k(\text{S2})$ is related[98] to the difference between the standard chemical potentials of the liquids, S1 and S2.

If reaction 7–4 is studied in a mixed solvent formed by two liquids S1 and S3, where S3 is inert, analysis of the dependence of rate constants on solvent composition is more complicated in view of the different standard states which can be defined for solutes and solvents. The usual approach defines the chemical potentials for reactant W and transition state in terms of standard states in a solution formed by the mixture S1 and S2, using the pure liquid S1 for the standard state of S1. Therefore the dependence of rate constant on composition is accounted in part by the (non-ideal) properties of S1 in the mixture. This is a contentious subject, the arguments revolving around the extent of solvent involvement in the activation process and the amount of information which can be extracted from a first-order rate constant. The subject is complicated even further if chemical reaction is studied in a mixture of two solvents where there is a possibility of two parallel reactions involving solute W and either solvent.

8 Isochoric Activation Parameters

The molar enthalpy of activation $\Delta^{\neq} H^{\infty}(\text{sln};T;p)$ describes the dependence of rate constants for a given reaction on temperature under isobaric conditions. We can also ask how the rate constant for this reaction depends on temperature, in the event that the pressure changes to hold constant the molar volume of the solvent. This isochoric condition is indicated by equation 4–6. The required partial derivative is,

$$\left[\frac{\partial \ln (k^{\$}K/T)}{\partial T}\right]_{V_1{}^*} = \left[\frac{\partial \ln k^{\$}K/T}{\partial T}\right]_p + \frac{\alpha_1{}^*}{\kappa_{1*}}\left[\frac{\partial \ln k^{\$}}{\partial p}\right]_T \tag{8–1}$$

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[95] R. N. French and C. M. Criss, *J. Solution Chem.*, 1982, **11**, 625.

[96] F. J. Millero, *Chem. Rev.*, 1971, **71**, 147.

[97] S. Cabani, G. Conti, and E. Matteoli, *J. Chem. Soc., Faraday Trans.*, 1978, **74**, 2408.

[98] M. J. Blandamer, J. Burgess, R. E. Robertson, K. M. Koshy, E. C. F. Ko, H. S. Golinkin, and J. M. W. Scott, *J. Chem. Soc. Faraday Trans. 1*, 1984, **80**, 2287.

where, by definition,[99–101]

$$\left[\frac{\partial \ln k^{s}K/T}{\partial T}\right]_{V_1{}^*} = \frac{\Delta^{\neq}\psi(V_1{}^*)}{RT^2} \qquad (8\text{–}2)$$

$\Delta^{\neq}\psi(V_1{}^*)$ is expressed in J mol^{-1}. Rate constant k^s characterizes the change in composition under isobaric–isothermal conditions. Transition State Theory uses the isobaric–isothermal equilibrium condition in equation 6–2 where the chemical potentials of reactants and transition states are related to standard (or reference) chemical potentials under isobaric–isothermal conditions. Therefore the isochoric condition in equation 8–1 is extrinsic[99–101] to the reacting system. $\Delta^{\neq}\psi(V_1{}^*)$ is a pseudo-isochoric activation parameter where the isochoric condition refers to the molar volume of the solvent. The dependence of rate constant on pressure at constant $V_1{}^*$ is described by the partial derivative,

$$\left[\frac{\partial \ln (k^{s}K/T)}{\partial p}\right]_{V_1{}^*} = \left[\frac{\partial \ln k^{s}}{\partial p}\right]_{T} + \left[\frac{\kappa_1{}^*}{\alpha_1{}^*}\right]\left[\frac{\partial \ln (k^{s}K/T)}{\partial T}\right]_{p} \qquad (8\text{–}3)$$

By definition,[99–101]

$$\left[\frac{\partial \ln (k^{s}K/T)}{\partial p}\right]_{V_1{}^*} = -\frac{\Delta^{\neq}\varphi(V_1{}^*)}{RT} \qquad (8\text{–}4)$$

$\Delta^{\neq}\varphi(V_1{}^*)$, expressed in m^3 mol^{-1}, is an extrinsic isochoric activation parameter. Equations 8–1 and 8–3 are rewritten in terms of the molar isobaric and isothermal activation parameters,

$$\Delta^{\neq}{}_{\psi}(V_1{}^*) = \Delta^{\neq}H^{\infty}(\text{sln};T;p) - (\alpha_1{}^*/\kappa_1{}^*)T\Delta^{\neq}V^{\infty}(\text{sln};T;p) \qquad (8\text{–}5)$$

and

$$\Delta^{\neq}\varphi(V_1{}^*) = \Delta^{\neq}V^{\infty}(\text{sln};T;p) - (\kappa_1{}^*/\alpha_1{}^*)\Delta^{\neq}H^{\infty}(\text{sln};T;p)/T \qquad (8\text{–}6)$$

Equation 4–5 is incorporated into these equations to produce two further equations;

$$\Delta^{\neq}\psi(V_1{}^*) = \Delta^{\neq}H^{\infty}(\text{sln};T;p) - (\Pi_1{}^* + p)\Delta^{\neq}V^{\infty}(\text{sln};T;p) \qquad (8\text{–}7)$$

and

$$\Delta^{\neq}\varphi(V_1{}^*) = \Delta^{\neq}V^{\infty}(\text{sln};T;p) - \Delta^{\neq}H^{\infty}(\text{sln};T;p)/(\Pi_1{}^* + p) \qquad (8\text{–}8)$$

For liquids where $\Pi_1{}^* \gg p$, (*cf.* Table 1)

$$\Delta^{\neq}\psi(V_1{}^*) = \Pi_1{}^*\Delta^{\neq}\varphi(V_1{}^*) \qquad (8\text{–}9)$$

The latter equation has an interesting form,[100] resembling the classical

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[99] M. J. Blandamer, J. Burgess, B. Clark, R. E. Robertson, and J. M. W. Scott, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 11.

[100] J. R. Haak, J. B. F. N. Engberts, and M. J. Blandamer, *J. Am. Chem. Soc.*, in press.

[101] M. J. Blandamer, J. Burgess, B. Clark, and J. M. W. Scott, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 3350.

thermodynamic equation, $w = -p\mathrm{d}V$. Also $\pi_1{}^*$, $V_1{}^*$, $\Delta^{\neq}\psi(V_1{}^*)$, and $\Delta^{\neq}\varphi(V_1{}^*)$ depend on temperature and pressure. For a reaction in binary aqueous mixtures where π_1 and V_m depend on T, p, and x_2, then so must $\Delta^{\neq}\psi(V_m)$ and $\Delta^{\neq}\varphi(V_m)$ where V_m refers to the molar volume of a liquid having a particular mole fraction composition. If kinetic data in aqueous solution form the reference,

$$\Delta(\mathrm{aq} \longrightarrow x_2)\Delta^{\neq}\psi(V_m) = \Delta^{\neq}\psi[V_m(x_2)] - {}^{\neq}\psi[V_m(\mathrm{aq})] \qquad (8\text{–}10)$$

and

$$\Delta(\mathrm{aq} \longrightarrow x_2)\Delta^{\neq}\varphi(V_m) = \Delta^{\neq}\varphi[V_m(x_2)] - \Delta^{\neq}\varphi[V_m(\mathrm{aq})] \qquad (8\text{–}11)$$

The quantities on the right-hand sides of equations 8–10 and 8–11 are isochoric (V_m) parameters for a mixture and for water, *i.e.* local to each solvent system. The two derived quantities are differences between these local quantities; they do not measure differences under a global isochoric condition.

The effects of added t-butyl alcohol on activation parameters[102] for the neutral hydrolysis of *p*-methoxyphenyl 2,2-dichloropropionate are summarized in Table 2. With increase in x_2, the enthalpy of activation decreases, passes through a minimum and then increases, this being a common pattern for reactions in aqueous mixtures. The volume of activation decreases whereas $\Delta^{\neq}\psi(V_m)$ increases gradually. The contrast between the minimum in the isobaric parameter and the gradual change in the isochoric parameter prompted the suggestion that the latter are simpler[43,103] and more fundamental.[104] The issue is far from settled. In fact, the data in Table 2 identify problems in the interpretation of the dependence of activation parameters on solvent composition. $\Delta(\mathrm{aq} \longrightarrow x_2)\Delta^{\neq}H^{\infty}$ measures the dependence of an isobaric property at 298 K; $\Delta(\mathrm{aq} \longrightarrow x_2)\Delta^{\neq}V^{\infty}$ is the dependence of an isothermal quantity at ambient pressure. But as x_2 changes so does the molar volume of the binary mixture.[73] Hence $\Delta(\mathrm{aq} \longrightarrow x_2)\Delta^{\neq}\psi(V_m)$ is the dependence of local isochoric (V_m) quantities where the pressure $\delta\pi_2$ in equation 4–7 is characteristic of each mixture. These considerations indicate additional complexities in the term, $\Delta(\mathrm{aq} \longrightarrow x_2)\Delta^{\neq}\psi(V_m)$ rather than a simplification.

Table 2 *Isothermal, isobaric, and isochoric* (V_m) *activation parameters for neutral hydrolysis of* p*-methoxyphenyl* 2,2-*dichloropropionate in t-butyl alcohol + water mixtures at* 298 K *and ambient pressure*

x(t-butyl alcohol)	0	0.05	0.075
$\Delta(\mathrm{aq} \rightarrow x_2)\Delta^{\neq}H^{\infty}/\mathrm{kJ\ mol^{-1}}$	0	−10.5	−9.2
$\Delta(\mathrm{aq} \rightarrow x_2)\Delta^{\neq}V^{\infty}/\mathrm{cm^3\ mol^{-1}}$	0	−31	−37
$\Delta(\mathrm{aq} \rightarrow x_2)\Delta^{\neq}\psi(V_m)/\mathrm{kJ\ mol^{-1}}$	0	8.8	35.5

taken from ref. 102

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[102] H. A. J. Holterman and J. B. F. N. Engberts, *J. Am. Chem. Soc.*, 1982, **104**, 6382.

[103] B. T. Baliga and E. Whalley, *J. Phys. Chem.*, 1967, **71**, 1166.

[104] D. L. Gay and E. Whalley, *J. Phys. Chem.*, 1968, **72**, 4145; *Can. J. Chem.*, 1970, **48**, 2021.

The procedures leading to equations 8–1 and 8–3 can be repeated with reference to derived activation parameters. For example, using $\Delta^{\neq} V^{\infty}$,

$$\left[\frac{\partial \Delta^{\neq} V^{\infty}}{\partial T}\right]_{V_1^*} = \left[\frac{\partial \Delta^{\neq} V^{\infty}}{\partial T}\right]_p + \frac{\alpha_1^*}{\kappa_1^*} \cdot \left[\frac{\partial \Delta_r V^{\infty}}{\partial p}\right]_T \tag{8–12}$$

Here the derived quantity describes the dependence of $\Delta^{\neq} V^{\infty}$ on temperature in the event that the pressure changes to hold V_1^* constant. A similar equation describes the isochoric (V_1^*) dependence of $\Delta_r V^{\infty}$ on temperature.[92] For ethanoic acid in water,[105] both $\Delta_r V^{\infty}$ and $(\partial \Delta_r V^{\infty}/\partial T)$ at constant V_1^* are < 0. Equation 8–12 can be rewritten as a partial derivative for $\Delta^{\neq} H^{\infty}$. Slightly more contrived is the partial derivative of ln $(k^{\$}K/T)$ with respect to T at constant $\Delta^{\neq} V^{\infty}$;

$$\left[\frac{\partial \ln (k^{\$}K/T)}{\partial T}\right]_{\Delta^{\neq} V^{\infty}} = \left[\frac{\partial \ln (k^{\$}K/T)}{\partial T}\right]_p - \left[\frac{\partial \Delta^{\neq} V^{\infty}}{\partial T}\right]_p \left[\frac{\partial p}{\partial \Delta^{\neq} V^{\infty}}\right]_T \left[\frac{\partial \ln k^{\$}}{\partial p}\right]_T \tag{8–13}$$

The derived quantity[106] endeavours to account for differences in solvent densities around initial and transition states.

9 Discussion

The kinetic isochoric (V_m) and isochoric (V_1^*) quantities emerge from a drawing together of the isobaric–isothermal activation parameters for chemical reactions

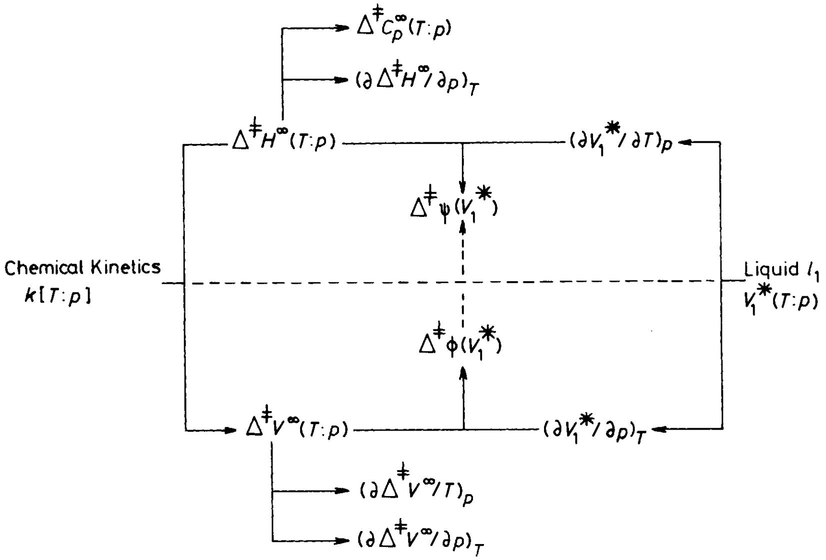

Figure 9 *Isobaric and isothermal properties; the link through isochoric conditions*

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[105] D. A. Lown, H. R. Thirsk, and Lord Wynne-Jones, *Trans. Faraday Soc.*, 1975, **66**, 57.

[106] E. F. Caldin, quoted in *ref.* 34.

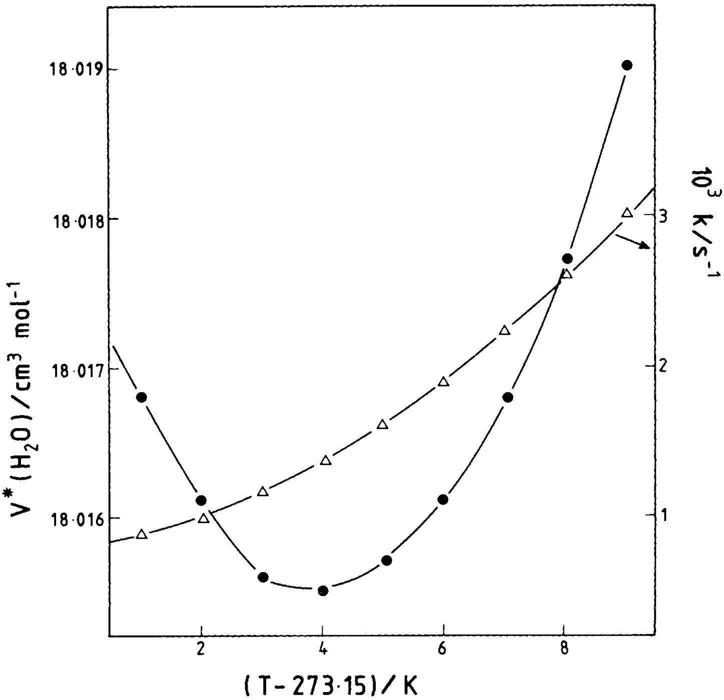

Figure 10 *Dependence on temperature at ambient pressure of molar volume for water and rate constant for solvolysis of t-butyl chloride; data from references* 107 *and* 112

and the isobaric–isothermal volumetric properties of solvents (Figure 9). A key question concerns the extent to which the isochoric activation parameters {*e.g.* $\Delta^{\neq}\psi(V_1^*)$ and $\Delta^{\neq}\varphi(V_1^*)$} satisfy the criteria described by Evans and Polanyi[7] (Introduction). We take a pessimistic view. No simple relationship exists between intermolecular separation in liquids and their molar volume. At ambient pressure, there are pairs of temperature, one above and one below the temperature of maximum density (TMD), where the molar volumes of water (and D_2O) are equal.[107] Yet *X*-ray and neutron scattering data[108] show that these equalities in molar volumes do not reflect identities in plots of pair correlation functions.[109–111] Further, rate constants for chemical reaction[112,113] in water over a temperature range spanning the TMD show no surprising features (Figure 10).

[107] G. S. Kell, reference 72, 1972, volume 1, p. 363.

[108] A. H. Narten and H. A. Levy, reference 72, volume 1, chapter 8.

[109] J. A. Polo and P. A. Egelstaff, *Phys. Rev. A*, 1983, **27**, 1508.

[110] P. A. Egelstaff and J. H. Root, *Chem. Phys.*, 1983, **76**, 405.

[111] G. A. Gabella and G. W. Nielson, *Mol. Phys.*, 1983, **50**, 97.

[112] E. A. Moelwyn-Hughes, R. E. Robertson, and S. E. Sugamori, *J. Chem. Soc.*, 1965, 1965.

[113] W. J. Albery and J. S. Curran, *J. Chem. Soc., Chem. Commun.*, 1972, 425.

In a wider context, however, interest in isochoric activation energies has revived.[100] Based on the definitions described in the previous section, interpretation of dependence on solvent composition and substrate is a topic of current research and will be the subject of future reports. The 'isochoric' condition is slightly unusual but offers a possibly new insight into chemical reactions in solution.

If the compromise suggested by Evans and Polanyi raises new problems, it might be informative to direct attention to the internal pressure of the solvent, π_i, bearing in mind that this quantity emerges in several equations reviewed above. This is not a new suggestion, many authors having commented on the role of internal pressure in kinetics of reactions in solution.[114] The analysis described in the previous sections prompts the derivation of partial derivatives at constant π_i; *e.g.*

$$\left[\frac{\partial \ln (k^s K/T)}{\partial T}\right]_{\pi_i} = \left[\frac{\partial \ln (k^s K/T)}{\partial T}\right]_p - \left[\frac{\partial \pi_i}{\partial T}\right]_p \left[\frac{\partial p}{\partial \pi_i}\right]_T \left[\frac{\partial \ln k^s}{\partial p}\right]_T \qquad (9\text{–}1)$$

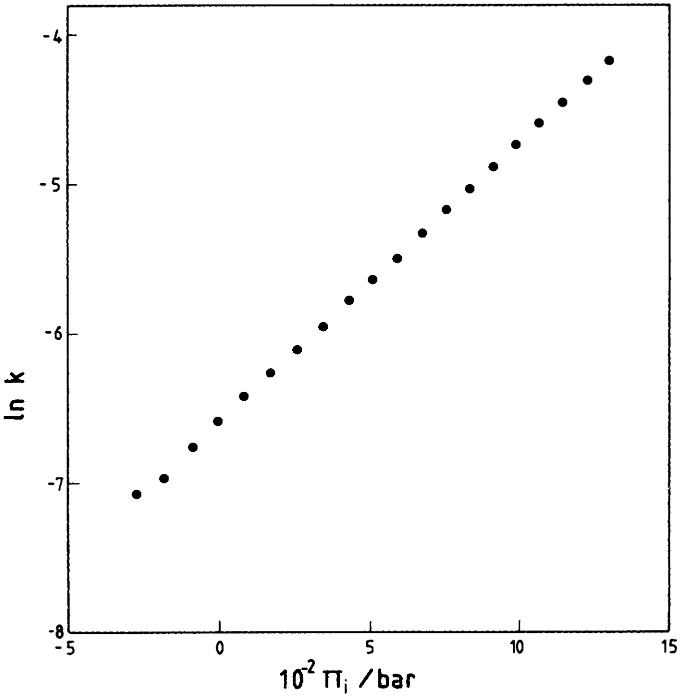

Figure 11 *Dependence on internal pressure for water at ambient pressure of rate constant for solvolysis of t-butyl chloride; data from references* 28 *and* 105

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[114] M. R. J. Dack, *J. Chem. Educ.*, 1974, **51**, 231.

Alternatively the dependence of rate constant on internal pressure can be explored[115] (Figure 11) leading to an estimate of the partial derivative, $\{\partial \ln (k^{\ddagger}/T)/\partial \pi_i\}_p$.

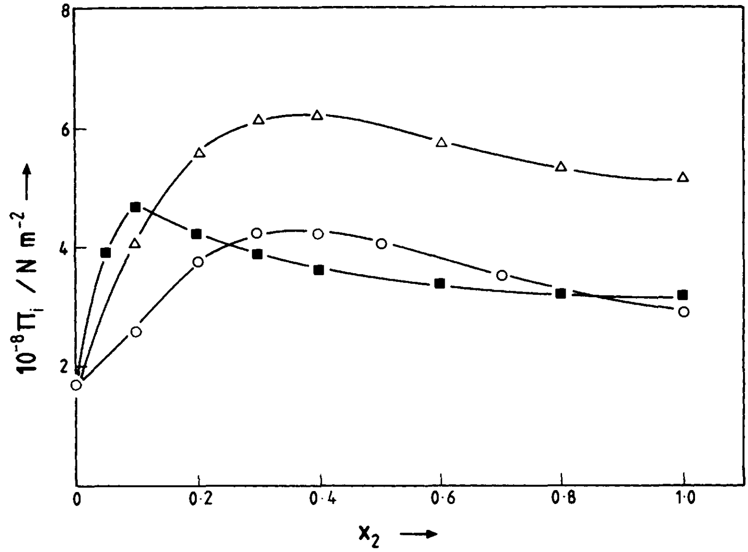

Figure 12 *Dependence of internal pressure on mole fraction for binary aqueous mixtures;* ○ = *methyl alcohol;* △ = *t-butyl alcohol; and* ■ = *DMSO; data from reference* 116

The dependences of π_i on mole fraction x_2 for several binary aqueous mixtures[116] and solutions are known (Figure 12) and there may be merit in examining the dependence of rate constants on x_2 in terms of the associated dependences of k on π_i (*cf.* reference 117). An interesting feature of aqueous solutions is the dependence of TMD on composition[118–120] which means that the composition at which Π_i is zero also depends on the nature of the co-solvent. Moreover below a TMD, the internal pressure is negative. The significance of the latter is a matter for speculation in so far as the impact on the kinetics of chemical reactions in these systems. Presumably, negative internal pressures for aqueous solutions at low temperatures are linked to the repulsive characteristics of hydrogen bonding. When a hydrogen bond forms between two near-neighbour water molecules, their centres of mass move apart. The same argument applies

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[115] M. J. Blandamer, J. Burgess, and A. Hakin, unpublished work.

[116] D. D. Macdonald and J. B. Hyne, *Can. J. Chem.*, 1971, **49**, 611, 2636.

[117] M. R. J. Dack, *Aust. J. Chem.*, 1976, **29**, 771.

[118] F. Franks and B. Watson, *Trans. Faraday Soc.*, 1967, **63**, 329.

[119] D. D. Macdonald, A. McLean, and J. B. Hyne, *J. Solution Chem.*, 1978, **7**, 63.

[120] M. V. Kaulgud, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 2246.

when a weak (distorted) hydrogen bond is strengthened within liquid water. Recent[121,122] models for liquid water emphasize the importance of fluctuations involving weak-distorted and strong-directional hydrogen bonds between water molecules. The impact of this equilibrium on the thermodynamic properties of solutes can be treated in terms of a medium-sensitive activity coefficient for a solute.[123] Interest in this development stems from applications of the model to initial and transition states, thereby estimating, for example, molar isobaric heat capacities of activation for reactions in water and aqueous mixtures.[124,125]

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[121] R. Lumry, E. Battistel, and C. Jolicoeur, *Faraday Symp. Chem. Soc.*, 1982, **17**, 93.

[122] D. Mirejovsky and E. M. Arnett, *J. Am. Chem. Soc.*, 1983, **105**, 1112.

[123] E. Grunwald, *J. Am. Chem. Soc.*, 1984, **106**, 5414.

[124] M. J. Blandamer and J. Burgess, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 1495.

[125] M. J. Blandamer, J. Burgess, and J. M. W. Scott, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 2881.