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Dependence of Equilibrium and Rate Constants on Temperature and Pressure

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Contents

I. Introduction

This review is concerned with the analysis of the dependence on temperature and pressure of both equilibrium and rate constants in solution. Although the subject matter is not new,[1–5] it seems timely to draw together various strands in these discussions. A glance at the literature reveals that opinions are strongly held, numerous reasons being advanced why a particular method of data analysis merits general acceptance. For our part, the seeds of this review were planted during the summer of 1979 when two of the authors (M.J.B. and J.M.W.S.) were on study leave at the University of Calgary. During that summer, considerable argument revolved around methods of analysis of the kinetic data obtained over the years by the research group working under the direction of one of us (R.E.R.).[6,7] In particular we were concerned with the analysis of the dependence of rate constants on temperature. The background to the debate puts the problem in perspective.

In the late 1940s, C. K. Ingold commented to R.E.R. that a detailed understanding of the role of solvents in chemical reaction was being impeded by a lack of good kinetic data. The challenge was taken up by R.E.R. who over many years assembled a set of precise kinetic data for the solvolysis in water of relatively simple organic halides and related derivatives.[7] The solvent, water, was chosen because there was and is a considerable amount of physicochemical information concerning aqueous solutions.[8,9] In addition, the progress of chemical reaction for these solvolytic reactions can be precisely followed by measuring the electrical conductivity of the solution, a property which is extremely sensitive to the concentration of ions in solution. The rate constant, k, for these reactions can be determined with a reproducibility of better than ±1% over a range of temperatures, T, extending to ~50 K. However it was at this stage that new problems emerged.

A plot of ln k against T^{-1} is, for many reactions in solution, linear, the slope yielding the (Arrhenius) activation energy, E_A. However for these solvolytic reactions in water, this plot is clearly nonlinear.[7,10,11] These observations confirmed the generality of the results reported in the 1930s by Moelwyn-Hughes[12] for the solvolysis of methyl halides in water. Numerous reasons[13] can be advanced for the nonlinearity of plots of ln k against T^{-1}, but these experimental observations raise the problem of the analysis of such behavior. In this context, one useful analytical technique has been to use transition-state theory[14] and thereby to establish a link between kinetic and thermodynamic parameters.

If the validity of transition-state theory[14] is accepted,[15] the rate constant for chemical reaction, k, can be transformed into a pseudoequilibrium quantity, $K^{\ddagger}$, describing the equilibrium between initial and transition states. Consequently the dependence of rate constants on temperature can be analyzed in terms similar to those used in the analysis of the dependence of equilibrium constants, K, on temperature. The litera-

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ture dealing with the latter topic is more extensive.[2,3] In addition it is well established[3] that ln K often shows a nonlinear dependence on T^{-1}. Consequently many methods have been proposed[2,3] which attempt to relate ln K and T^{-1}. One of the first equations was proposed around the turn of the century by Valentiner.[16]

The Valentiner equation[16] (see section VA2) expresses the dependence of ln K on T using three linear terms characterized by three parameters a_i where i = 1, 2, and 3. The equation has been used more recently by other workers, notably by Everett and Wynne-Jones.[17,18] The analogue of the Valentiner equation where k replaces K has been used[7] to express the dependence of ln k on T. The kinetic data can be fitted to the resulting equation by using conventional linear least-squares techniques (see section IVA). Up until the 1960s, this fitting procedure was not a simple task with a typical electromechanical calculator, especially where 20 or more rate constants were available. Fortunately these arithmetical chores have disappeared with the advent of the digital computer. In addition it is now a relatively straightforward task to probe different methods of data analysis by use of appropriate computer programs. Consequently some of the less obvious implications of a given method of data analysis can be probed. This aspect of the problem prompted the writing of this review. Rather than confine our attention to kinetic data we have broadened the discussion to include a consideration of equilibrium data, together with the dependence of both equilibrium and rate constants on pressure. Indeed, in order to develop several key arguments, it is convenient to start out with some well-trodden concepts in thermodynamics. We ask the reader to bear with us.

II. Thermodynamic Background

The first and second laws of thermodynamics combine[19] to show that a closed system in equilibrium with the surroundings and at fixed temperature and fixed pressure is at a minimum in the Gibbs function G. We assume that for a closed system at a given overall composition the minimum is unique.[20,21] If the system is held at constant composition (ξ = fixed, where ξ is the extent of chemical reaction[19]), the Gibbs–Helmholtz equation relates the dependence of G on temperature to the enthalpy, H. The differential of G with respect to pressure at fixed T and ξ is related to the volume V of the system.[19] These two statements together with the definition[19] of the affinity $\mathcal{A}$ for chemical change $[=-(\partial G/\partial \xi)_{T,p}]$ constitute the foundations on which this review is based. The state functions, G, H, and V refer to the macroscopic properties of the system. However chemists stray from the certainty of these thermodynamic statements, extending their arguments from the macroscopic to the molecular level. Thus chemical analysis of an equilibrium state may point to the existence of various chemical species in chemical equilibrium. The number of chemical species and the number of chemical equilibria are obtained from this additional experimental evidence. These comments are self-evident, but they draw attention to the operational definition of a system's characteristics.

If, for example, the experimental data can be understood in terms of one chemical equilibrium, the derived parameters (e.g., the enthalpy change, $\Delta H^{\ominus}$) refer to that defined equilibrium. Another set of experimental data for the same system may be understood in terms of two chemical equilibria. Consequently a different set of parameters will be obtained from analysis of the experimental data (e.g., two enthalpy terms, $\Delta H_1^{\ominus}$ and $\Delta H_2^{\ominus}$). Hence there exists a close relationship between the chemical model (one or two equilibria) adopted for a given system and the parameters calculated on the basis of that model. It may also be that both descriptions of the system are equally valid, neither being right or wrong. Indeed different experimental techniques may prompt different models for the same system. For example, the electrical conductivity of a salt solution may be accounted for in terms of one equilibrium between free ions and contact ion pairs, but the spectroscopic properties may be accounted for in terms of equilibria involving solvent-separated ion pairs.[22] Both models serve their purpose; we are unaware of a set of equations which allows the electrical conductivity to be calculated from the spectroscopic data.

The importance of chemical information is also apparent in the treatment of kinetic data. In thermodynamic terms, chemical reaction is one method whereby a closed system (at fixed temperature and pressure) in a nonequilibrium state moves towards a minimum in G, the spontaneous chemical change being driven by the affinity for change, $\mathcal{A}$. Eventually the system reaches equilibrium, where $\mathcal{A}$ is 0. However, chemists endeavour to describe this approach to chemical equilibrium in terms of molecular processes within the system. Additional experimental evidence is used to identify the number of chemical processes and the number of chemical species so involved. If the experimental information can be accounted for in terms of one chemical reaction, then a set of activation parameters (e.g., enthalpy of activation, $\Delta H^{\ddagger}$) can be calculated. If another description of the approach to chemical equilibrium identifies two chemical reactions (e.g., a consecutive reaction), another set of parameters will be obtained. Again these comments are self-evident. Nevertheless we point them out in order to stress the importance of linking three key aspects, (i) experimental information, (ii) a chemical description of the system, and (iii) the method of calculation of the required parameters. There remains a fourth stage, comparison.

In certain circumstances, the sign and magnitude of a calculated quantity (e.g., an enthalpy) based on a certain chemical description of a system may appear unreasonable when compared with other properties of the system or with values calculated for similar chemical changes. A subjective element is now introduced into the discussion because the numerical analysis does not necessarily discriminate between the reasonableness of different chemical models for the same system. This is the area where debate is most intense.

A. Chemical Equilibria

In this section, we adopt a particular chemical description of a closed system at fixed T and p, in equilibrium with the surroundings. It is assumed that i solute species are involved in a single chemical equilibrium. The transformation from the macroscopic state function G to the properties of each chemical

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Ross E. Robertson, Professor Emeritus of Chemistry, A.O.S.T.R.A. Research Professor, University of Calgary, graduated with a Ph.D. from McGill University in 1944. For the next 25 years he was associated with the National Research Council, Ottawa. During a sabbatical year (1947–1948) at University College (London), with C. K. Ingold, he became interested in the relation between mechanism, solvation, and the temperature dependence of solvolytic reactions. With the able assistance of many associates, a unique body of kinetic data was assembled. This work was continued when he transferred to the University of Calgary in 1969. In 1976 the threatening energy crisis led to an interest in problems associated with bituminous emulsions derived from Alberta oil sands. This is the focus of his research interest at present.

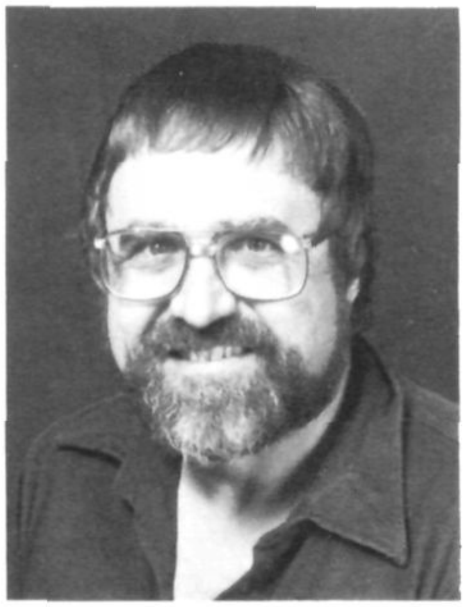

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TABLE I. Chemical Equilibria: One-Equilibrium Process

$$\Delta G^{\ominus} = \sum_{j=1}^{j=i} \nu_j \mu_j^{\ominus} = -RT \ln K \qquad (1)$$

$$\text{van't Hoff eq: } (\partial \ln K/\partial T)_p = \Delta H^{\ominus}/RT^2 \qquad (2)$$

$$\partial^n \Delta H^{\ominus}/\partial T^n)_p = \Delta^n C_p^{\ominus}, n = (1), 2, 3, \ldots \qquad (3)$$

$$(\partial \ln K/\partial p)_T = -\Delta V^{\ominus}/RT \qquad (4)$$

$$(\partial^n \Delta V^{\ominus}/\partial p)_T = \Delta^n \beta^{\ominus}; n = (1), 2, 3, \ldots . \qquad (5)$$

$$(\partial \Delta S^{\ominus}/\partial T)_p = \Delta C_p^{\ominus}/T \qquad (6)$$

species[19] is made through the chemical potential μ_j. If ν_j is the stoichiometry such that ν_j is positive for products and negative for reactants, the thermodynamic condition for equilibrium is that $\sum_{j=1}^{j=i}\nu_j\mu_j$ is 0. If m_j is the molality of the solute j and γ_j is the molal activity coefficient ($\gamma_j \rightarrow 1.0$ as $m_j \rightarrow 0.0$), the equilibrium condition can be expressed in terms of the chemical potentials of each solute j in their standard state in solution where $m_j = 1.0$ and $\gamma_j = 1.0$, i.e., $\mu_j^{\ominus}$. The latter quantities together with ν_j define $\Delta G^{\ominus}$ and the equilibrium constant K (eq 1, Table I). Thus characterization of the total system by a description in terms of a single equilibrium leads to the definition of the equilibrium constant K.

The differentials of ln K with respect to temperature (at fixed pressure) and with respect to pressure (at fixed temperature) are related to the standard enthalpy, $\Delta H^{\ominus}$, and standard volume, $\Delta V^{\ominus}$, quantities (eq 2 and 4, Table I). Here is our first encounter with a problem which dominates this review. Thus the van't Hoff equation relates the dependence of ln K on temperature *at temperature* T *to* $\Delta H^{\ominus}$ *at that temperature.* Further $\Delta H^{\ominus}$ can and probably does depend on temperature (and pressure). However thermodynamics does not define what form this dependence takes. Nevertheless thermodynamics can describe this dependence in terms of a heat capacity term, $\Delta C_p^{\ominus}$ (eq 3, Table I). The latter is the differential of $\Delta H^{\ominus}$ with respect to temperature at temperature T, yielding $\Delta C_p^{\ominus}$ at that temperature. Now differentiation is usually less hazardous than integration because the latter needs additional information if we require the definite integral. Thus it is not possible to construct a plot showing the dependence of $\Delta H^{\ominus}$ on temperature given the value of $\Delta C_p^{\ominus}$. Even if $\Delta H^{\ominus}$ is known at some temperature Θ, there remains the possibility that $\Delta C_p^{\ominus}$ is also dependent on temperature (eq 3 where $n = 2, 3 ...$, Table I). In fact the variation of $\Delta C_p^{\ominus}$ with temperature is probably more correctly handled by using statistical thermodynamics because classical thermodynamics provides no formal treatment of this dependence. Indeed a plausible aim of the work discussed here is to calculate the thermodynamic parameters for a given system by using statistical thermodynamics and to compare the values so obtained with the values of, for example, $\Delta H^{\ominus}$, $\Delta C_p^{\ominus}$, and $\Delta S^{\ominus}$ calculated from the experimental dependence of K on T.

Another important feature of this work is the comparison between thermodynamic parameters calculated from the dependence of K on temperature and those determined calorimetrically. However we do not consider this topic in this review in any great detail.

The foregoing comments are readily extended to a consideration of $\Delta V^{\ominus}$ (eq 4, Table I). The dependence of $\Delta V^{\ominus}$ on pressure at pressure p is described by the compressibility $\Delta\beta^{\ominus}$ ($n = 1$ in eq 5, Table I) at that pressure p. Consequently a continuous series of differential functions can be defined with reference to the dependence of $\Delta V^{\ominus}$ on pressure. The pressure- and temperature-dependent parameters are linked through a series of cross relations which come under the general heading Maxwell equations.[23]

The discussion given above can be extended to other equilibrium transformations. The solubility of a gas in a solvent[24] can be characterized by a $\Delta G^{\ominus}$ quantity which is related to the Henry's law coefficient L describing the equilibrium between the species in the gas phase at pressure p and in solution with molality m_j. Similar treatments can be applied to the solubility of a solid in solution and the distribution of a solute between two solvents. Perhaps the simplest chemical equilibrium describes that between two conformers in solution. In all cases, there exists a family of thermodynamic parameters $\Delta X^{\ominus}$ ($X = G, H, S, C_p, V ...$), each defined in a similar fashion to that set out in Table I.

B. Chemical Kinetics

A rate constant k, a phenomenological property of a system, describes the time dependence of the chemical composition of a system resulting from chemical reaction. If the overall system is not too far from chemical equilibrium,[25] the rate of change of composition at a given time is related by a simple differential equation to the rate constant and the chemical composition of the system at that time. The rate constant often provides no detailed information concerning the actual chemical processes involved. In many cases, the rate constant characterizes a change in a macroscopic property of the system, e.g., electrical conductivity.[7] Usually one chooses to monitor some property which shows significant changes for unit stoichiometric change. In any event, a chemical description of the kinetic processes is developed to account for the observed macroscopic change. We develop this point by reference to the changes in electrical conductivity observed when, for example, *tert*-butyl chloride solvolyzes in water.[7]

TABLE II. Chemical Kinetics

Arrhenius Treatment

model: $(\partial \ln k/\partial T)_p = E_A/RT^2$ (1)

assume: $(\partial E_A/\partial T)_p = 0$ (2)

equation: $\ln k = \ln k[T = \infty] - E_A/RT$ (3)

Transition-State Theory

$(\partial \ln [k/T]/\partial T)_p = \Delta H^{\ddagger}/RT^2$ (4)

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

As it stands, the rate constant derived from an increase in electrical conductivity characterizes a "black box" releasing ions into the system. In a chemical context, the simplest description identifies one key process, reactants → products. The next stage is to develop an analytical description to account for the observation that the rate constant depends on temperature, i.e., $k = f(T)$. The fact that it does so depend can be understood in terms of a Boltzmann distribution of molecular energies. However neither this distribution nor classical thermodynamics yields a quantitative relationship between rate constant and temperature. Arrhenius suggested a differential equation for the dependence of ln k on temperature, leading to the definition of an activation energy for reaction, E_A (eq 1, Table II). However progress is again impeded because the differential equation cannot be integrated unless some new assumption is invoked. One approach is to assume that E_A is independent of temperature and, hence, that ln k is a linear function of T^{-1} (eq 2, Table II). This model for the dependence of k on temperature can now be tested against experimental data.

For the solvolysis of many organic halides in water,[7] ln k is not a linear function of T^{-1}. We are now faced with a dilemma because the model building exercise has clearly broken down. At least two options present themselves. First, we can accept the description for the chemical reaction (i.e., a single process) but reject the model which sets E_A as independent of temperature. Second, we can argue that the description of the chemical reaction is incorrect, suggesting instead that there are at least two key processes with discrete rate constants which depend on temperature in a manner described by eq 3 (Table II). In the latter case it would be argued that each activation energy is different, thus leading to curvature in the plot of ln k_{obsd} against T^{-1}. Thermodynamics establishes no criteria in helping to decide which option is correct. Indeed if we select the first option, new problems emerge because we have no a priori indication of how E_A depends on temperature. We consider below some of the consequences of choosing either option.

The rate constant for a chemical reaction k can be related[14] to the pseudoequilibrium constant $K^{\ddagger}$ through

Planck's and Boltzmann's constants. The dependence of ln (k/T) on temperature at fixed pressure and of ln k on pressure at fixed temperature is related to the enthalpy of activation $\Delta H^{\ddagger}$ and volume of activation $\Delta V^{\ddagger}$, respectively (Table II). In exactly analogous fashion to the problems associated with analysis of equilibrium properties, $\Delta H^{\ddagger}$ is the enthalpy of activation at temperature T, although the theory does not define how it depends on temperature. A description of its dependence on temperature is possible through the heat capacity of activation $\Delta C_p^{\ddagger}$ and its dependence on temperature (cf. Table I). The theory leads to a series of differential functions but does not indicate how these functions can be used to obtain the definite integral form. Consequently we are faced with the problem of formulating different descriptions of the temperature and pressure dependence of the rate constant. Different descriptions of how k depends on T and p lead to different numerical values for the activation parameters. We can expect numerous problems associated with the interpretation and significance of these derived parameters.

So far we have identified two important stages in the overall analytical problem. First it is important to set down a chemical description of the system under investigation. Second we need to devise some quantitative description of the dependence of equilibrium (or rate) constant on temperature (or pressure). In the following section, we consider in more detail the first stage.

III. Comparison of Models for the System

In the absence of thermodynamic criteria, it is often possible to adopt different chemical descriptions to account for the macroscopic properties of a given system. There are no limits to the chemical complexity of these descriptions other than those set by our imagination. However it is interesting to explore how the parameters for different models are related. In this section we consider examples from equilibrium and kinetic properties.

A. Chemical Equilibria

TABLE III. Comparison of Models for Chemical Equilibria

Model I

$$A \underset{}{\overset{K}{\rightleftharpoons}} D$$

Model II

$$B \overset{K_1}{\rightleftharpoons} C \overset{K_2}{\rightleftharpoons} D$$

Comparison

$$K = K_2/(1 + K_1^{-1}) \tag{1}$$

$$\Delta H^{\ominus} = \Delta H_2^{\ominus} + (\Delta H_1^{\ominus}/[1 + K_1]) \tag{2}$$

$$\Delta C_p^{\ominus} = \Delta C_{p_2}^{\ominus} + \frac{\Delta C_{p_1}^{\ominus}}{(1 + K_1)} - \frac{(\Delta H_1^{\ominus})^2 K_1}{(1 + K_1)^2 RT^2} \tag{3}$$

$$\Delta V^{\ominus} = \Delta V_2^{\ominus} + \Delta V_1^{\ominus}/(1 + K_1) \tag{4}$$

$$\Delta \beta^{\ominus} = \Delta \beta_2^{\ominus} + \frac{\Delta \beta_1^{\ominus}}{(1 + K_1)} + \frac{(\Delta V_1^{\ominus})^2 K}{RT(1 + K_1)^2} \tag{5}$$

As the first example, we consider a solute (e.g., a weak monobasic carboxylic acid) in solution and assume that the experimental data describe the proportion of total solute in one particular form (e.g., ions). The closed system is held at fixed temperature and pressure. In model I (Table III), the solute exists in one of two states, A and D, such that the equilibrium is characterized by a series of thermodynamic parameters, $\Delta X^{\ominus}$, where $X = G, H, C_p, V$ ... (Table I). In model II (Table III) for the same system, the solute exists in three states, B, C, and D, involving two equilibrium constants, K_1 and K_2 (Table III). Thus each equilibrium is characterized by a set of parameters, $\Delta X_1^{\ominus}$ and $\Delta X_2^{\ominus}$. We now suppose that the experimental data characterized the equilibrium state by measuring the proportion of solute in the form D. It follows that K in model I can be related to K_1 and K_2 in model II by eq 1 of Table III. Differentiation (Table I) yields equations relating $\Delta X^{\ominus}$ with $\Delta X_1^{\ominus}$ and $\Delta X_2^{\ominus}$ (Table III). Inspection of the equations reveals some interesting details. If, for example, $K_1 > 1.0$, then as K_1 increases so $\Delta H^{\ominus} \rightarrow \Delta H_2^{\ominus}$. If $K_1 \ll 1.0$, $\Delta H^{\ominus} \approx \Delta H_1^{\ominus} + \Delta H_2^{\ominus}$. It may also arise that at a particular temperature $\Delta H^{\ominus}$, calculated by using model I, passes through a maximum at some temperature. Then at that temperature, the following condition holds:

$$\Delta H_2^{\ominus}(1 + K_1) = -\Delta H_2^{\ominus} \tag{1}$$

Further since $K_1 > 0$, then $\Delta H_1^{\ominus}$ and $\Delta H_2^{\ominus}$ must have opposite signs at the extremum. Indeed eq 1 is the condition for the plot of ln K against T, using model I, to show an extremum. In this context we recall that plots of ln K against T for several monocarboxylic acids in water show maxima.[3] If we use model I to account for this trend, $\Delta C_p^{\ominus}$ (and possibly higher temperature derivatives) is nonzero. If we use model II, the explanation of the extremum is quite different. Indeed Eigen suggests[26] that the association of H_3O^+ and carboxylate anion to form the undissociated acid, RCOOH, is correctly represented as a two-stage process where the intermediate is formed in an encounter. Turning to the heat capacity terms, $\Delta C_p^{\ominus}$ calculated by using model I is not simply the sum of $\Delta C_p^{\ominus}{}_1$ and $\Delta C_p^{\ominus}{}_2$ calculated by using model II, eq 3 of Table III. Similar comments apply to $\Delta^2 C_p^{\ominus}$, $\Delta^3 C_p^{\ominus}$ ... . There is a further interesting feature. Suppose that as a derivative of model II (Table III) both $\Delta C_p^{\ominus}{}_1$ and $\Delta C_p^{\ominus}{}_2$ are set equal to 0. It turns out that $\Delta C_p^{\ominus}$ calculated by using model I is not 0. The value calculated for $\Delta C_p^{\ominus}$, called $\Delta C_p^{\ominus}$ (diff), is given by eq 2. Because K_1 is always a positive quantity,

$$\Delta C_p^{\ominus}(\text{diff}) = -(\Delta H_1^{\ominus})^2 K_1/[(1 + K_1)^2 RT^2] \tag{2}$$

$\Delta C_p^{\ominus}$(diff) is always negative and depends on temperature by virtue of the term T^2 and the dependence of K_1 on temperature. Further differentiation of eq 2 with respect to temperature reveals that if $\Delta C_p^{\ominus}{}_1$ is 0 then $\Delta C_p^{\ominus}$(diff) has an extreme value at temperature T(ex) given by eq 3,

$$T(\text{ex}) = (\Delta H_1^{\ominus}/2R)([1 - K_1]/[1 + K_1]^2) \tag{3}$$

where

$$\Delta C_p^{\ominus}(\text{diff}; T = T(\text{ex})) = -4RK_1(1 - K_1)^2 \tag{4}$$

Since by definition T is a positive quantity, if $\Delta H_1^{\ominus} >$

TABLE IV. Solubility of a Volatile Solute in a Liquid

Model I

$$\mathrm{Y}(\text{gas}; p_y) \rightleftharpoons \mathrm{Y}(\text{solution}; m_y); K$$

$$\Delta G^\ominus(\text{gas} \rightarrow \text{solution}) = -RT \ln|K| = -RT \ln (m_y p^\ominus / p_y) \quad (1)$$

Model II

$$\mathrm{Y}(\text{gas}; p_y) \rightleftharpoons \mathrm{Y}(\text{solution}; m_y); K_1$$

$$2\mathrm{Y}(\text{solution}; m_y) \rightleftharpoons \mathrm{Q}(\text{solution}; m_q); K_2$$

$$\Delta G_1^\ominus(\text{gas} \rightarrow \text{monomer in solution}) = -RT \ln K_1 = -RT \ln (m_y p^\ominus / p_y) \quad (2)$$

$$\Delta G_2^\ominus(\text{monomer} \rightarrow \text{dimer; solution}) = -RT \ln K_2 = -RT \ln (m_q / m_y^2) \quad (3)$$

Comparison

$$m \text{ (total Y in solution)} = m_y + 2m_q \quad (4)$$

$$K(\text{obsd}) = m/(p/p^\ominus) \quad (5)$$

$$K(\text{obsd}) = K_1 + 2K_1K_2m \quad (6)$$

$$\Delta H^\ominus(\text{obsd}) = \Delta H_1^\ominus + [2K_1K_2(m\Delta H_2^\ominus + RT^2\mathrm{d}m/\mathrm{d}T)/(K_1 + 2K_1K_2m)] \quad (7)$$

0 then $K_1 < 1.0$, and if $K_1 > 1.0$ $\Delta H_1^\ominus < 0$.

Examination of volume parameters reveals similar constraints and relationships. Thus if $K_1 \gg 1$, $\Delta V^\ominus$ calculated by using model I equals $\Delta V_2^\ominus$ calculated by using model II; if $K_1 \ll 1$, $\Delta V^\ominus = \Delta V_1^\ominus + \Delta V_2^\ominus$. Similarly we can define a quantity $\Delta\beta^\ominus$(diff), eq 5. The

$$\Delta\beta^\ominus(\text{diff}) = (\Delta V_1^\ominus)^2 K_1/(RT[1 + K_1]) \quad (5)$$

possibility that the same set of data can be described by using either model I or II raises new considerations. We outline just two aspects which warrant attention.

Analysis of substituent effects on equilibrium constants is conveniently handled[27,28] by using the δ_R operator, e.g., $\delta_R\Delta G^\ominus$. From eq 1 of Table III the substituent effect in terms of model I can be related to the substituent effects on the separate equilibria in model II (eq 6). The presence of the term ln $(1 + K_1)$ means

$$\delta_R\Delta G^\ominus = \delta_R\Delta G_1^\ominus + \delta_R\Delta G_2^\ominus + RT\,\delta_R \ln (1 + K_1) \quad (6)$$

that the substituent effect on $\Delta G^\ominus$ (model I) is not simply the sum of the substituent effects on the two equilibria in model II.

The second area of note follows from eq 6 where the substituent effects in two different classes of chemical equilibria are related as in the Hammett equation.[27,28] Thus, through the two series "R" and "Q", a linear relationship between $\delta_R\Delta G^\ominus$ and $\delta_Q\Delta G^\ominus$ in terms of model I requires that a linear relationship exists between $\delta_R\Delta G_1^\ominus$ and $\delta_Q\Delta G_2^\ominus$, between $\delta_R\Delta G_2^\ominus$ and $\delta_Q\Delta G_2^\ominus$, and between δ_R ln $(1 + K_1)$ and δ_Q ln $(1 + K_1)$ in terms of model II. This analysis prompts a number of questions concerning equations relating the enthalpy and entropy terms in extensions of these treatments.[29,30]

The foregoing analysis with reference to chemical equilibria can be extended to other equilibrium situations. In Table IV we consider a situation where the solubility data for a volatile solute in a liquid are under examination. In model I (Table IV) the solute exists in one state in each phase. In model II, the solute in solution exists as monomer and dimer in equilibrium. However the composition of the solution is experimentally determined in terms of the total molality of the solute such that the data are summarized in terms of K(obsd) which is related to the total molality and the partial pressure of the volatile solute in the gas phase. Application of eq 2 in Table I yields an enthalpy term, $\Delta H^\ominus$(obsd), eq 7 of Table IV. The observed $\Delta H^\ominus$ is, therefore, a function of $\Delta H_1^\ominus$ and of K_1, K_2, $\Delta H_2^\ominus$, and m. The corresponding expression for $\Delta C_p^\ominus$(obsd) is clearly complex; $\Delta C_p^\ominus$(obsd) will be nonzero even if $\Delta C_{p}{}^\ominus{}_1$ is 0.

TABLE V. Chemical Kinetics: Comparison of Models for Chemical Reaction

Model I

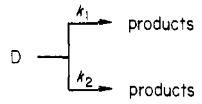
$$\mathrm{A} \xrightarrow{k} \text{products}$$

Model II

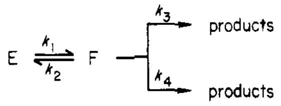
$$\mathrm{B} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{C} \xrightarrow{k_3} \text{products}$$

$$\alpha = k_2/k_3; \Delta\Delta X^\ddagger = \Delta X_3^\ddagger - \Delta X_2^\ddagger$$

Model III



Model IV



Comparison

Models I and II

$$k = k_1/(1 + \alpha) \quad (1)$$

$$\Delta H^\ddagger = \Delta H_1^\ddagger + [\alpha/(1 + \alpha)]\Delta\Delta H^\ddagger \quad (2)$$

$$\Delta C_p^\ddagger = \Delta C_{p_1}^\ddagger + [\alpha/(1 + \alpha)]\Delta\Delta C_p^\ddagger - [(\Delta\Delta H^\ddagger)^2\alpha/[RT^2(1 + \alpha)^2]] \quad (3)$$

$$\Delta V^\ddagger = \Delta V_1^\ddagger + \Delta\Delta V^\ddagger/(1 + \alpha) \quad (4)$$

$$\Delta\beta^\ddagger = \Delta\beta_1^\ddagger + [\alpha/(1 + \alpha)]\Delta\Delta\beta^\ddagger + [(\Delta\Delta V^\ddagger)^2\,\alpha/(1 + \alpha)^2RT] \quad (5)$$

Models I and III

$$k = k_1 + k_2 \quad (6)$$

$$\Delta H^\ddagger = (k_1\Delta H_1^\ddagger + k_2\Delta H_2^\ddagger)/(k_1 + k_2) \quad (7)$$

$$\Delta C_p^\ddagger = [(k_1\Delta C_{p_1} + k_2\Delta C_{p_2}^\ddagger)/(k_1 + k_2)] + [k_1k_2(\Delta H_1^\ddagger - \Delta H_2^\ddagger)^2/(k_1 - k_2)RT^2] \quad (8)$$

$$\Delta V^\ddagger = (k_1\Delta V_1^\ddagger + k_2\Delta V_2^\ddagger)/(k_1 + k_2) \quad (9)$$

The foregoing analysis can be extended to a number of phenomena. The analysis in Table IV is with minor modification applicable to the solubility of a pure liquid Y in a solvent, e.g., benzene in water. Indeed for these systems, this type of analysis can be used to account for the disagreement between van't Hoff enthalpies of solution and the values obtained from calorimetric data[31] although in the particular case, benzene in water, disagreement may have arisen from incomplete dissolution in the solubility studies.[32] Indeed it has been often implied that van't Hoff quantities (i.e., thermodynamic quantities derived from dependence of K on T) are suspect, but as the analysis in Table IV shows, the problem lies not with the equation itself but with the description of the system and the experimental techniques used to probe the properties of the system.[33] A similar state of affairs exists in the context of the kinetics of chemical reactions.

B. Chemical Kinetics

We examine some of the problems which arise in this subject by reference to various models for a chemical reaction which is experimentally characterized by a first-order rate constant. We consider a solvolytic reaction where the progress of reaction has been followed by monitoring the change in concentration of products (e.g., ions) with time[6,7] (Table V).

In model I of Table V, the reaction is an elementary single-stage process characterized by the rate constant k and a series of activation parameters, $\Delta X^\ddagger$, where X

= G, H, S, C_p, V ... . In model II the reaction is a two-stage process where the first stage is reversible and the overall reaction proceeds through a common intermediate. Consequently, each stage in the process is characterized by a rate constant k_i and a set of activation parameters $\Delta X_i^\ddagger$ where i = 1, 2, and 3. The quantity α describes the kinetic fate of the intermediate. This nomenclature was suggested by Albery and Robinson[34] in their discussion of the kinetics of solvolysis of *tert*-butyl chloride. Model III of Table V represents the kinetic process as two parallel reactions having characteristic rate constants while model IV is a composite of models II and III. This model (IV) is based upon the mechanism proposed by Winstein and coworkers[35] for solvolytic reactions.[36] We now ask what happens to the values for the activation parameters calculated on the assumption that model I is operative when in fact the reaction actually proceeds via one of the other mechanisms.

With reference to models I and II (Table V) the measured rate constant k is a function of k_1 and α (eq 1). Differentiation with respect to temperature leads to an expression relating $\Delta H^\ddagger$ (model I) with $\Delta H_1^\ddagger$ and $\Delta\Delta H^\ddagger$ (model II) (eq 2 of Table V). If at temperature T $\alpha \gg 1$, then $\Delta H^\ddagger = \Delta H_1^\ddagger + \Delta\Delta H^\ddagger$; if $\alpha \ll 1$, $\Delta H^\ddagger = \Delta H_1^\ddagger$. Further differentiation with respect to temperature shows that $\Delta C_p^\ddagger$ is not simply the sum of $\Delta C_p{}^\ddagger{}_1$ and $\Delta\Delta C_p^\ddagger$. Indeed if the latter two quantities are 0, $\Delta C_p^\ddagger$ is not necessarily 0, leading to the definition of a quantity $\Delta C_p^\ddagger$(app) (eq 7). It follows that $\Delta C_p^\ddagger$(app)

$$\Delta C_p^\ddagger(\text{app}) = -(\Delta\Delta H^\ddagger)^2\alpha/(RT^2[1 + \alpha]^2) \qquad (7)$$

is always negative,[36] irrespective of the sign of $\Delta\Delta H^\ddagger$. In addition $\Delta C_p^\ddagger$(app) exhibits a complex dependence on temperature because α is temperature dependent. At the temperature where $\alpha = 1$, $\Delta C_p^\ddagger(\text{app}) = -(\Delta\Delta H^\ddagger)^2/4RT^2$ although further differentiation of eq 7 with respect to temperature shows that the extreme value of $\Delta C_p^\ddagger$(app) occurs at a different temperature from that at which $\alpha = 1$. A similar complex pattern emerges from analysis of the dependence of rate constants on pressure. Thus it follows from eq 5 of Table V that even if $\Delta\beta_1^\ddagger$ and $\Delta\Delta\beta^\ddagger$ are 0, $\Delta\beta^\ddagger$ is not necessarily 0. In this case we can define a quantity $\Delta\beta^\ddagger$(app) (eq 8). Thus, $\Delta\beta^\ddagger$(app) is a positive quantity, independent of the sign of $\Delta\Delta V^\ddagger$. Moreover $\Delta\beta^\ddagger$(app) is dependent on pressure because α is also dependent on pressure. The equations given in Table V are also relevant to analysis of solvent effects on rate constants and derived activation parameters. The solvent effect on k is, according to model II, equal to the combined effects of solvent on k_1 and α. Similarly the solvent effect on $\Delta H^\ddagger$ expressed in terms of the medium operator[28] δ_m, is related in model II to the effect of solvent on $\Delta H_1^\ddagger$, $\Delta\Delta H^\ddagger$, and α in eq 9. A similar expression relates $\delta_\text{m}\Delta C_p^\ddagger$ to $\delta_\text{m}\Delta C_p{}^\ddagger{}_1$, $\delta_\text{m}\Delta\Delta C_p^\ddagger$, and $\delta_\text{m}\alpha$.

$$\Delta\beta^\ddagger(\text{app}) = \alpha(\Delta\Delta V^\ddagger)^2/(RT[1 + \alpha]^2) \qquad (8)$$

$$\delta_\text{m}\Delta H^\ddagger = \delta_\text{m}\Delta H_1^\ddagger + \frac{\alpha}{1 + \alpha}\delta_\text{m}\Delta\Delta H^\ddagger + \frac{\Delta\Delta H^\ddagger}{(1 + \alpha)^2}\delta_\text{m}\alpha \qquad (9)$$

Comparison of models I and III (Table V) shows that even if $\Delta C_p{}^\ddagger{}_1$ and $\Delta C_p{}^\ddagger{}_2$ are both 0, $\Delta C_p^\ddagger$ (i.e., $\Delta C_p^\ddagger$(app)) is nonzero and always positive (eq 10). Differentiation with respect to temperature reveals that $\Delta C_p^\ddagger$(app) has a positive extreme value when the temperature equals $(k_2\Delta H_1^\ddagger + k_1\Delta H^\ddagger)/2R$.

$$\Delta C_p^\ddagger(\text{app}) = k_1k_2(\Delta H_1^\ddagger - \Delta H_2^\ddagger)^2/(RT^2[k_1 + k_2]) \qquad (10)$$

The type of analysis outlined in Table V can be repeated for the remaining kinetic models. Underlying the material presented in the foregoing is the aim of accounting for the trends in measured equilibrium and kinetic parameters. It is to the problems of handling the experimental data which we now direct our attention.

C. Estimated and True Values—Practical Considerations

It is assumed that in a closed system at fixed temperature and pressure, there exists a single-stage chemical equilibrium, e.g., model I in Table III. Thermodynamic arguments (Table I) lead to the conclusion that there exists a single true value for the equilibrium constant. We represent this true value by K^*. In real life, analysis of experimental data leads to an estimate K of this true value. Similarly the measured values of temperature T and pressure p are estimates of the true values T^* and p^*. However it is usual practice to assume that the measured values of T and p are the true values and thus free from error. Consequently experimental data comprise estimated values of the dependent variable K^* as a function of the independent variables T and p. It is conventionally assumed that with improvement in experimental technique so the estimate K will approach K^* and that the error δ will fall (eq 11). As a result of a series of experiments at different temperatures T_i where i = 1, 2, 3 ... n, but at fixed pressure p, there will be n equations of the form

$$K = K^* + \delta \qquad (11)$$

$$K(T_i,p) = K^*(T_i,p) + \delta(T_i,p) \qquad (12)$$

It is further assumed that there are no systematic errors in the estimates $K(T_i,p)$ and that the errors $\delta(T_i,p)$ are not correlated. In other words, the sign and magnitude of $\delta(T_1,p)$ are not, for example, related to $\delta(T_2,p)$. However practical considerations limit the number of equations n of the form given in eq 12. Simple limitations of time and patience mean that the values of T_i will be at intervals of, e.g., 5 K rather than 0.1 K. In addition the range of T_i values is limited by the properties of the system. Thus for dilute aqueous solutions at ambient pressure, this range is $273 < T_i < 373$ K. In this sense, the physical properties of the solvent define a "window" across which we can, but outside of which we cannot, measure the properties of the system. Consequently the range of values for $K(T_i,p)$ for a given system is limited by this window.

In the context of chemical kinetics for a reaction involving a single-stage process (e.g., model I of Table V) we assume that there exists a true value k^* for the rate constant at fixed T and p. The experimental data yield an estimate k of the true value, and hence we can write analogues of eq 11 and 12. In similar fashion, the properties of the system define the limits of the window.

Practically, the window is often fairly small because at low temperatures the rate of reaction may be very slow and too time consuming to measure. Alternately at high temperatures, the reaction may be too fast to follow by using currently available techniques. This means, for example, that in kinetic data measurements for the solvolysis of organic halides in water[6,7] the temperature range rarely exceeds 50 K. Similar comments apply to the measurement of the dependence of rate constants and equilibrium constants on pressure, although here the window is determined by the extent of technical expertise in handling high pressures. However there is another important consideration.

In both equilibrium and kinetic studies, neither the equilibrium nor the rate constant is directly determined. Thus for the kinetics of solvolytic reactions,[6,7] the measured property is the electrical conductivity at time t. Each individual measurement of conductance is subject to experimental error. The dependence of conductance on time is fitted by using a least-squares technique (see section IVA) to a first-order rate equation such that the calculated rate constant is the outcome of many experimental observations.[6,7] Similarly the acid dissociation constant for a weak carboxylic acid is obtained, for example, by analyzing the dependence of the emf of an electrolytic cell on composition.[3] Each measurement of the emf is subject to experimental error. In the following sections we do not consider the consequences of these errors but assume that the data at hand comprise values (i.e., estimates) of K (or k) as a function of temperature and pressure.

IV. Analytical Descriptions of the Dependence on Temperature

Let us assume we have a set of n values of K_i at temperatures T_i, these values being estimates of the true values K_i^*. We also assume that there exists a set of true thermodynamic values $\Delta X^\ominus$ ($X = G, H, S, C_p, V$ ...). The aim is to examine the dependence of K_i on T_i in order to obtain estimates $\Delta \hat{X}^\ominus$ of the true values $\Delta X^\ominus$. There is another assumption implicit in this argument. Thus it is assumed that there exists a quantitative relationship between K_i and T_i. However thermodynamics does not define this quantitative relationship. Consequently we formulate an equation for the dependence of K_i^* on T_i and test its adequacy by examining the dependence of K_i on T_i. Initially there is no thermodynamic restriction on how we choose to relate K_i^* and T_i. It may, for example, be that we express this dependence with a trigonometric equation, along the lines indicated by Hine[37] for the dependence of heat capacity terms on temperature (eq 13).

$$K_i^* = a_1 \sin (a_2 T_i) \tag{13}$$

Equation 13 introduces two new parameters, a_1 and a_2, which are assumed to be independent of temperature. Estimates $\hat{a}_1$ and $\hat{a}_2$ of a_1 and a_2 are required which satisfy the measured values, K_i. The criteria on which these estimates are based are discussed below. For the moment, however, it could be argued that eq 13 looks wrong. This intuitive feeling is generated by the equations set out in Table I which describe derivatives of ln K rather than K.

If the thermodynamic hint is accepted, it seems advisable to express the dependence of K_i^* on T_i as shown in eq 14. Moreover chemists have taken advantage of

$$\ln K_i^* = f(T_i) \tag{14}$$

the extensive literature describing the linear least-squares method[38,39] of obtaining estimates of fitting parameters. In order to use this method, it is necessary that the equation expressing the dependence of ln K^* on T should be linear in the unknown parameters. A simple two-term equation for the dependence of ln K^* [or ln k^*] on T which satisfies this requirement is shown in Table VI. Thus the differential of ln K^* with respect to a_1 at fixed T, and a_2 is not dependent on either a_1 or a_2. Further the second differentials [e.g., $\partial^2 \ln K^*/\partial a_1^2$] are 0. A similar test of eq 13 shows that this description of the dependence of K^* on T does not meet the requirement, and so the conventional least-squares method cannot be used to obtain estimates of a_1 and a_2 in eq 13.

Granted that we can use the least-squares method to fit the dependence of ln K^* on T to eq 1 of Table VI, the analysis is set a number of tasks. First from the estimates K_i at T_i we require estimates $\hat{a}_1$ and $\hat{a}_2$ of a_1 and a_2. Second we need to test the adequacy of the equation in fitting the observed dependence. If the description of the dependence proves inadequate, other equations are tested which attempt to describe the observations. In this sense the testing of equations is a continuation of the experiment.[38] We anticipate considerable debate concerning the acceptability of the various equations. In principle we seek a description of the dependence of K on T which satisfies as many objective criteria as possible. Then it can be concluded that we have the link which thermodynamics does not provide. If, for example, the first equation in Table VI is the final choice of the description, then from the estimate $\hat{a}_1$, the enthalpy parameter is calculated. If, however, we had used eq 13, then from the associated estimates of a_1 and a_2, the estimate of $\Delta H^\ominus$ is obtained, i.e., $\hat{a}_2 R T^2 \cot (\hat{a}_2 T)$. It is possible that the most satisfactory equation for one set of data is not necessarily that for another.

Analogous arguments accompany the analysis of the dependence of K on p, k on T, and k on p. Thus in Table VI, a two-term equation is shown which relates ln k and T^{-1}. Here again this dependence is not a requirement of transition-state theory. It is attractive because the equation has the correct form for analysis using a linear least-squares method. Clearly, the latter has had a profound influence in this subject. Consequently we examine some important aspects of this analytical technique.[36,37]

A. Linear Least-Squares Analysis

The input to the analysis is a set of values for a dependent variable y_i (e.g., ln K_i) and independent variables x_i (e.g., T_i). It is assumed that the unknown linearly dependent variables β_j (e.g., a_1 and a_2 in Table VI) are given by eq 15. Here $\mathbf{y}$ is a column vector of the

$$\mathbf{y} = \mathbf{X}\beta + \epsilon \tag{15}$$

dependent variables, $\mathbf{X}$ is a matrix comprising functions of the independent variable, β is a column vector of the unknown parameters, and ϵ is a column vector of the unknown errors associated with the measured dependent variables.

For example, suppose we have n values of K_i at temperatures T_i and the first equation given in Table VI is to be examined; then X is a $2 \times n$ matrix. The linear least-squares method leads to estimates $\hat{\beta}$ which minimizes the sum of squares of differences between $\hat{\mathbf{y}}$ and $\mathbf{y}$ (e.g., between measured value ln K_i and the estimated value, ln K_i over all n values). The key stage is given in eq 16 where X^{T} denotes the transpose of X. Thus

$$\hat{\beta} = (\mathbf{X}^{\mathrm{T}}\mathbf{X})^{-1}\mathbf{X}^{\mathrm{T}}\mathbf{y} \tag{16}$$

from the estimates $\hat{\beta}$, we can calculate the estimated values $\hat{\mathbf{y}}$, eq 17 (e.g., values of ln K_i from $\hat{a}_1$ and $\hat{a}_2$ in Table VI). The values of $\hat{\beta}$ are the most precise unbiased estimates of β. Consequently, if the whole experiment were repeated q times (i.e., q sets of n values for K_i and T_i), the individual q estimates of each β_j parameter would be distributed about the true value of β_j with minimum variance, e.g., eq 18 for β_1. Returning to the single set of n values for x_i and y_i, the least-squares estimate $\hat{\beta}$ can be used to estimate the variance associated with the errors, $\hat{\sigma}^2$. If for example the values of m linear coefficients are estimated, $\hat{\sigma}^2$ is given by eq 19. The quantity $n - m$ is called the number of degrees of freedom. If we repeat the whole experiment q times, analysis will provide q values for $\hat{\sigma}^2$. Each estimate $\hat{\sigma}^2$ is an unbiased estimate of the variance s^2, and the q values of $\hat{\sigma}^2$ will be distributed about s^2.

$$\hat{\mathbf{y}} = \mathbf{X}\cdot\hat{\beta} \tag{17}$$

$$s_j^{\,2} = \sum_{j=1}^{j=q} (\hat{\beta}_1(j) - \beta_1)/(q - 1) \tag{18}$$

$$\hat{\sigma}^2 = (\mathbf{y} - \mathbf{X}\hat{\beta})^{\mathrm{T}}(\mathbf{y} - \mathbf{X}\hat{\beta})/(n - m) \tag{19}$$

For a single set of data, the estimate $\hat{\sigma}^2$ provides a guide to the quality of the data and the success of the equation in accounting for the dependence of K on T. The square root $\hat{\sigma}$ of $\hat{\sigma}^2$ is the standard deviation on the fitted quantity, e.g., $\hat{\sigma}$(ln K). In this context it is often helpful to plot values of $\Delta_i = (\hat{y}_i - y_i)$ against the independent variable x_i [e.g., (ln $\hat{K}_i$ − ln K_i) against T_i]. A satisfactory description of the dependence of y_i on x_i results in a scatter of Δ values greater than and less than 0. A systematic trend in Δ may indicate that the equation under test is unsatisfactory and a new description of the dependence is called for. In addition $\hat{\sigma}$(ln K) should be compared with the estimated accuracy of the experimental values, based on a realistic assessment and experience.

If the selected dependence generates a scatter plot for Δ, further details concerning the estimates $\hat{\beta}_j$ are provided by the symmetric variance–covariance matrix, eq 20. If the analysis is designed to yield m linear coefficients, $\hat{\theta}$ is an $m \times m$ matrix. The diagonal elements $\hat{\theta}_{kk}$ (where $k = 1, 2, \ldots m$) are estimates of the variance of $\hat{\beta}_k$. The smaller the value of $\hat{\theta}_{kk}$ (it is always positive), then the closer $\hat{\beta}_k$ is to the true value for β_k. The square root of $\hat{\theta}_{kk}$ is the standard error associated with $\hat{\beta}_k$. Two factors[38] contribute to the magnitude of $\hat{\theta}_{kk}$: (1) the precision of the input data and (2) the structure of the system. Under the latter heading we identify the structure of the data and the structure of the equation describing the dependence of y_i on x_i. We have commented above on the limitations set by the practical problems, the window, and these impinge on the structure of the data. The structure of the equation refers to the defined relationship between dependent and independent variables (cf. Table VI). This aspect will attract our attention in subsequent sections because part of the task is to identify for each set of data the most satisfactory description of the dependence of K_i (or k_i) on T. In this context it is informative to examine the normalized variance–covariance matrix c (eq 21):

$$\hat{\theta} = \hat{\sigma}^2(\tilde{\mathbf{X}}\mathbf{X})^{-1} \tag{20}$$

$$c_{ij} = \theta_{ij}/(\theta_{ii}\theta_{jj})^{1/2} \tag{21}$$

If, for example, the analysis results in m values of $\hat{\beta}_j$, then c is an $m \times m$ matrix when the diagonal elements are unity. The off-diagonal elements are between −1 and +1. The magnitude of c_{ij} measures the extent of the dependence of $\hat{\beta}_i$ on $\hat{\beta}_j$. If c_{ij} is approximately ±1, the interdependence is marked but decreases as $|c_{ij}|$ tends to 0, although c_{ij} is rarely 0. The values of c_{ij} are not estimates[38] and hence provide a sound basis for comments on the structure of the data and the equation used to describe the dependence of y_i on x_i.

The least-squares analysis yields, for a given set of data and a given equation, an estimate $\hat{\beta}_j$ and the standard error, $(\theta_{jj})^{1/2}$. It is possible to estimate with a specified degree of confidence that the true value of β_j lies within a band centered on $\hat{\beta}_j$. Thus we can calculate the limits within which we are p% confident (p = 90, 95, 99; usually 95) that the true value exists. If p = 95, there is a 5% chance that the true value exists outside these limits. A Student t factor[39] is obtained from published tables for a required confidence limit and the number of degrees of freedom. The band within which the true value exists is given by $\hat{\beta}_j \pm t\,(\hat{\theta}_{jj})^{1/2}$. If the values so calculated include 0, then the term in β_j is unimportant at the p level of confidence in describing, for example, the dependence of ln K on temperature. A further statistical test is discussed in a later section. However there are various aspects of the least-squares analysis which are noteworthy.

Suppose a dependent variable q is related to two independent variables w and v by eq 22. We assume

$$q = \beta_1 w + \beta_2 v \tag{22}$$

that eq 22 is essentially the true model for the system. When experimental values of q are used, the least-squares analysis yields the estimates $\hat{\beta}_1$ and $\hat{\beta}_2$. It is also possible to rewrite eq 22 in two algebraically equivalent forms:

$$q/w = \beta_1 + \beta_2(v/w) \tag{23}$$

$$q/v = \beta_1(w/v) + \beta_2 \tag{24}$$

The data can be fitted to eq 23 and 24 to obtain two more sets of estimates, $\hat{\beta}_1$ and $\hat{\beta}_2$. Comparison reveals that the three sets of estimates are rarely identical. This is a consequence of the experimental error in the dependent variable q and of the fact that the minimizations have considered three different quantities, q, q/w, and q/v.

There is a related problem which is relevant to several equations discussed in subsequent sections. Suppose that we identify a set of independent variables, v_0 and w_0, as reference values where the dependent variable is q_0. Equation 22 can be written as follows:

TABLE VI. Equations Expressing the Dependence of Rate and Equilibrium Constants on Temperature

phenomenon	equation	enthalpy term	heat capacity term
1. Two-Term Equation			
E	$\ln K = a_1T^{-1} + a_2$	$\Delta H^{\ominus} = -a_1R$	$\Delta C_p^{\ominus} = 0.0$
K	$\ln k = a_1T^{-1} + a_2$	$\Delta H^{\ddagger} = -(a_1 + T)R$	
2. Two-Term Nonlinear Dependence			
E	$K = \exp(a_1T) + a_2T$		
3. Polynomial for K as Function of T			
E	$K = a_1 + a_2T + a_3T^2$	$\Delta H^{\ominus} = (a_2 + 2a_3T)RT^2/(a_1 + a_2T + a_3T^2)$	
4. Two-Term Equation with Reference Temperature θ			
E	$\ln K = a_1(T^{-1} - \theta^{-1}) + a_2$	$\Delta H^{\ominus} = -a_1R$	
5. Linear Dependence on T			
E	$\ln K = a_1T + a_2$	$\Delta H^{\ominus} = a_1RT^2$	$\Delta C_p^{\ominus} = 2a_1RT$
K	$\ln k = a_1T + a_2$	$\Delta H^{\ddagger} = RT(a_1T - 1)$	$\Delta C_p^{\ddagger} = R(2a_1T - 1)$
6. Valentiner Equation			
E	$\ln K = a_1T^{-1} + a_2 + a_3 \ln T$	$\Delta H^{\ominus} = R(a_3T - a_1)$	$\Delta C_p^{\ominus} = a_3R$
at $\ln K =$ extremum;	$T = a_1/a_3$; $\ln K = a_2 + a_3[1 + \ln(a_1/a_3)]$		
K	$\ln k = a_1T^{-1} + a_2 + a_3 \ln T$	$\Delta H^{\ddagger} = R(a_3T - a_1 - T)$	$\Delta C_p^{\ddagger} = R(a_3 - 1)$
7. Robinson Equation			
E	$\ln K = a_1T^{-1} + a_2 + a_3T$	$\Delta H^{\ominus} = -a_1R + a_3RT^2$	$\Delta C_p^{\ominus} = 2a_3RT$
at $\ln K =$ extremum;	$T = (a_1/a_3)^{1/2}$; $\ln K = a_2 - 2(a_1/a_3)^{1/2}$		
K	$\ln k = a_1T^{-1} + a_2 + a_3T$	$\Delta H^{\ddagger} = -R(a_1 + T - a_3T^2)$	$\Delta C_p^{\ddagger} = R(2a_3T - 1)$
8. Ives and Pryor			
E	$\ln K = a_1 + a_2T + a_3T^2$	$\Delta H^{\ominus} = (a_2T^2 + 2a_3T^3)$	$\Delta C_p^{\ominus} = (2a_2T + 6a_3T^2)R$
at $\ln K =$ extremum;	$T = -a_2/2a_3$ where $\ln K = a_1 - (a_2^2/4a_3)$		
9. Polynomial in T^{-1}			
E	$\ln K = a_1 + a_2T^{-1} + a_3T^{-2}$	$\Delta H^{\ominus} = -R(a_2 + 2a_3T^{-1})$	$\Delta C_p^{\ominus} = -2Ra_3T^{-2}$
10. Harned and Embree equation			
E	$\ln K = \ln K(\theta) + a_1(T - \theta)^2$	$\Delta H^{\ominus} = 2a_1RT^2(T - \theta)$ $\Delta H^{\ominus}(\theta) = 0$	$\Delta C_p^{\ominus} = 2a_1RT(3T - 2\theta)$ $\Delta C_p^{\ominus}(\theta) = 2a_1R\theta^2$
11. Wold Equation			
E	$\ln K = \ln K(\theta) + a_1(T^{-1} - \theta^{-1}) + a_2(T^{-1} - \theta^{-1})^2$	$\Delta H^{\ominus} = -a_1R - 2a_2R(T^{-1} - \theta^{-1})$ $\Delta H^{\ominus}(\theta) = -a_1R$	$\Delta C_p^{\ominus} = 2a_2RT^{-2}$
K	$\ln k = \ln k(\theta) + a_1(T^{-1} - \theta^{-1}) + a_2(T^{-1} - \theta^{-1})^2$	$\Delta H^{\ddagger} = -RT - a_1R - 2a_2R(T^{-1} - \theta^{-1})$	$\Delta C_p^{\ddagger} = -R + 2a_2R/T^2$
12. Polynomial in $(T - \theta)$			
E	$\ln K = \ln K(\theta) + a_2(T - \theta) + a_3(T - \theta)^2 + a_4(T - \theta)^3$	$\Delta H^{\ominus} = R(a_2T^2 + 2a_3T^2[T - \theta] + 3a_4T^2[T - \theta]^2)$ $\Delta H^{\ominus}(\theta) = a_2\theta^2R$	$\Delta C_p^{\ominus}(\theta) = R(2a_2\theta + 2a_3\theta^2)$
K	$\ln k = \ln k(\theta) + a_2(T - \theta) + a_3(T - \theta)^2 + a_4(T - \theta)^3$	$\Delta H^{\ddagger}(\theta) = (a_2\theta^2 - \theta)R$	$\Delta C_p^{\ddagger}(\theta) = R(2a_2\theta - 1 + 2a_3\theta^2)$

	13. Polynominal in $(T-\theta)$		
E	$\ln K = \ln K(\theta) + \frac{\Delta H^\ominus(\theta)}{R\theta^2}(T-\theta) + \left[\frac{\Delta C_p^\ominus(\theta)}{2\theta^2 R} - \frac{\Delta H^\ominus(\theta)}{R\theta^3}\right](T-\theta)^2 +$ $\left(\frac{1}{R\theta^3}\right)\left[\frac{\theta}{6}\Delta^2 C_p^\ominus + \frac{\Delta H^\ominus(\theta)}{\theta} - \frac{2}{3}\Delta C_p^\ominus(\theta)(T-\theta)^3\right]$		
if $\ln K = (\ln K)_{\max}$ at θ	$\ln K = \ln K(\theta) + \left[\frac{\Delta C_p^\ominus(\theta)}{2\theta^2 R}\right](T-\theta)^2 + \left[\frac{\Delta^2 C_p^\ominus}{6} - \frac{2}{3}\Delta C_p^\ominus(\theta)\right]\frac{(T-\theta)^3}{R\theta^3}$		
	14. Orthogonal Polynomial ($h = 5$ K)		
E	$\ln K = a_0 + a_1\gamma_1 + a_2\gamma_2 + a_3\gamma_3 + \ldots\ldots$ $\phi = (T - T_m)/5.0$ $\gamma_1 = \phi; \gamma_2 = 3\phi^2 - 20$ $\gamma_3 = (5\phi^3 - 59\phi)/6$ $\gamma_4 = [(7\phi^2/12) - (115\phi^2/2) + 18]$	$\Delta H^\ominus = \frac{RT^2}{5}\left[a_1 + 6a_2\phi + a_3\left(\frac{15\phi - 59}{6}\right)\right]$	$\Delta C_p^\ominus = -\frac{2RT}{5}\left[a_1 + a_2\left(6\phi + \frac{3T}{5}\right) + a_3\left(\frac{15\phi^2 - 59}{6} + \frac{\phi T}{2}\right)\right]$
	15. Adams Equation[103]		
K	$\ln k = a_1 + a_2 T^{a_3}$	$\Delta H^\ddagger = R(a_3 a_2 T^{(a_3+1)} - T)$	$\Delta C_p^\ddagger = R[(a_3 + 1)a_3 a_2 T^{a_3} - 1]$

$$(q - q_0) = \beta_1(w - w_0) + \beta_2(v - v_0) \qquad (25)$$

The latter equation describes the variation of q about q^0 in terms of $(w - w_0)$ and $(v - v_0)$. Equation 25 can be written in the following algebraically equivalent form:

$$q = q^0 + \beta_1(w - w_0) + \beta_2(v - v_0) \qquad (26)$$

If q is the dependent variable subject to experimental error and if q_0 is the true value at v_0 and w_0, being free from experimental error, eq 25 can be used to estimate $\hat\beta_1$ and $\hat\beta_2$. If, however, q_0 is an experimental value subject to random error, then it is only statistically meaningful to use eq 26. In this case the dependence of q on $(w - w_0)$ and $(v - v_0)$ is analyzed to obtain the estimates $\hat q_0$, $\hat\beta_1$, and $\hat\beta_2$. The estimate $\hat q_0$ can, if the data are available, be compared with the experimental value for q_0. Indeed this approach is used in subsequent sections where we examine the dependence of ln K on T about a reference temperature θ and hence calculate the estimate ln $\hat K$ when $T = \theta$.

There is one further technique in the least-squares analysis which has attracted attention.[2] Suppose, for example, that we are testing a description of the dependence of some quantity P on temperature T which expresses P as a polynomial in T, i.e., $P = \sum_{i=1}^{i=n} a_1 T_1^{i-1}$. If we set $n = 2$, then the least-squares analysis leads to the estimates $\hat a_1$ and $\hat a_2$. If the analysis is repeated with $n = 3$, then we obtain $\hat a_1$, $\hat a_2$, and $\hat a_3$. It happens, however, that the values of $\hat a_1$ and $\hat a_2$ also change. A technique which avoids this transposes the polynomial in T_i to a polynomial in another set of independent variables such that each successive coefficient is independent of the preceding coefficients. This is the method of orthogonal polynomials. However there is a limitation in that the independent variables (e.g., T) must be equally spaced over the experimental range. We consider an application of this analysis below.

B. Nonlinear Least-Squares Analysis

In an examination of the dependence of an equilibrium constant on temperature, a particular description of this dependence might prompt the examination of an equation which does not satisfy the criteria for a linear least-squares analysis. However this is not a sound basis for rejecting this and related nonlinear equations. Clearly some alternate method is required in order to fit the data to the new equation. We may decide to retain the same overall criterion for fitting the data, namely that $\sum_{i=1}^{i=n} [y_i(\text{obsd}) - y_i(\text{calcd})]^2$ is a minimum. A method is required for hunting among all possible values of, say, $\hat\beta$ for those values which correspond to this minimum. This is a specialized and growing branch of statistics usually linked to computer-based calculations under the general heading optimization techniques.[40]

Suppose that we wish to examine eq 2 of Table VI as a possible description of the dependence of K on temperature. Although $(\mathrm{d}K/\mathrm{d}a_2)_{Ta_1}$ is independent of both a_1 and a_2, a similar differential with respect to a_1 is dependent on a_1. Thus the linear least-squares method is inappropriate. Nevertheless, given a value of K at temperature T, values of a_1 and a_2 are sought which minimize ϵ (=ln K − exp($\hat a_1 T$) − $\hat a_2 T$). The two unknowns a_1 and a_2 are the system parameters and can be expressed as the column vector **a**, such that ϵ can be expressed as follows:

$$\epsilon = \mathrm{f}(\mathbf{a}) \tag{27}$$

The quantity f(**a**) is the objective function, and if we guess the values of the components of the vector (e.g., a_1 and a_2 in eq 2 of Table VI) ϵ can be calculated. The initial guess $\mathbf{a}_0$ is likely to be a poor estimate of $a_{\min}$ which minimizes ϵ. Optimization techniques provide a number of iterative routines (algorithms) such that at each iteration values for Δa are calculated which move **a** toward $\mathbf{a}_{\min}$ where $\epsilon = \epsilon_{\min}$.

In general terms there may be m system parameters rather than just two, and without the aid of a computer the calculation would be a formidable task. Thus at the outset we do not know whether, for example, a_1 should be increased or decreased (the direction of change) or by how much. There is another important problem which is encountered by even computer-based calculations. We have implied that the vector $\mathbf{a}_{\min}$ which yields $\epsilon_{\min}$ is the global minimum. However through the whole domain of **a**, there may exist numerous local minima in ϵ. Consequently the value of $\mathbf{a}_{\min}$ obtained from a given calculation is the local minimum evolved from the seed value $\mathbf{a}_0$. It is generally assumed that there is a unique local minimum, but it is good practice to repeat the calculation with a new seed value to confirm that $\mathbf{a}_{\min}$ is unique over a reasonably large range of **a**.

An obvious practical requirement is that the calculation locates $\mathbf{a}_{\min}$ in a reasonably small number of iterations and steps between $\mathbf{a}_0$ and $\mathbf{a}_{\min}$. Indeed there are numerous optimization routines currently available, but the majority have a common approach to the problem as we now indicate.

The convergence process and hence the calculation of $\Delta\mathbf{a}$ uses the gradients of the objective function with reference to the system parameters. The Jacobian gradient vector **g** is the first derivative, and the Hessian matrix **H** is the second derivative. When these derivatives are used, $\Delta\mathbf{a}$ can be calculated by using the Newton–Raphson (or Newton) method to yield the second-order solution, $\Delta\mathbf{a} = -(\mathbf{H})^{-1}\mathbf{g}$. The calculation requires the inverse of the Hessian matrix. However this often leads to problems because away from $a_{\min}$, **H** is not always positive and finite. In such cases, various techniques, i.e., quasi-Newton or modified Newton, are used to overcome these problems.[40]

The foregoing summary of optimization techniques concerned the fitting of a single value of, for example, K at temperature T to the nonlinear equation. However the techniques are readily extended to consider n values of K_i and T_i such that the routine yields a set of parameters which minimize the sum of squares of the residuals, e.g., $\sum_{i=1}^{n}[y(\text{obsd}) - y(\text{calcd})]^2$. More detailed aspects of these calculations are described elsewhere[38] and in the manuals for computer-based libraries of programs. A satisfactory routine is one which indicates the degree of confidence that $\mathbf{a}_{\min}$ is a realistic minimum. However one should not rule out the possibility that for a given equation and set of data, no minimum exists.

A rather different technique for solving nonlinear differential equations is to transpose the equations in such a way that a linear least-squares technique can be used. As above, the procedure is to start from a guessed value of the vector **a**, i.e., $\mathbf{a}_0$, and calculate by using the linear least-squares technique the values of $\Delta\mathbf{a}$ that move toward a vector **a** where the residual sum of squares is either a minimum or of comparable magnitude to that estimated from the experimental precision. The details of this method of analysis are described by Wentworth.[41] Moore[42,43] uses a similar technique to calculate rate constants from kinetic data. The general features of the technique can be illustrated as follows.

Suppose we have a dependent variable P which is related to the independent variable T by a nonlinear equation in three parameters a_1, a_2, and a_3. Thus at fixed T, P is a function of a_1, a_2, and a_3:

$$P_T = P_T\,(a_1,a_2,a_3) \tag{28}$$

Then

$$\Delta P_T = \left(\frac{\partial P}{\partial a_1}\right)_{a_2a_3T}\Delta a_1 + \left(\frac{\partial P}{\partial a_2}\right)_{a_2a_3T}\Delta a_2 + \left(\frac{\partial P}{\partial a_3}\right)_{a_1a_2T}\Delta a_3 \tag{29}$$

Given initial estimates of a_1, a_2, and a_3 we can calculate (eq 28) a value of P at each measured value of T and hence, with the measured value, the value of ΔP. In addition at each value of T, we can calculate the three differentials in eq 29. Thus for n data points there are n equations in the three unknowns, Δa_1, Δa_2, and Δa_3. The corresponding estimates may be calculated by using the linear least-squares technique and the original estimates of the parameters corrected and used as input to a new calculation. The iteration continues until ΔP is, as described above, satisfactorily small. The assumption is made that the iterative calculation converges on a global minimum. Wentworth[41] comments on procedures to be used if the analysis is failing to converge.

V. Descriptions of the Dependence on Temperature of Equilibrium and Rate Constants

We start out with the assumption that the chemical composition of a closed system at fixed temperature and pressure can be characterized by the true equilibrium constant K^*. The aim is to describe how K^* depends on temperature given that we have measured values K at a series of temperatures T. The first task is to formulate an equation to describe the observed dependence. Three approaches to the problem have been suggested. In the first method, an equation is proposed which relates K and T so that differentiation with respect to temperature leads to an equation for $\Delta H^\ominus$ (Table I). A further differentiation yields an equation for $\Delta C_p{}^\ominus$. Unfortunately differentiation results in a loss of precision such that, for example, $\Delta C_p{}^\ominus$ is less precisely established than $\Delta H^\ominus$. Similarly the standard error in both $\Delta C_p{}^\ominus$ and $\Delta H^\ominus$ is a function of the standard error in K. King claims[2] that even for the most precise data it is not possible to attach significance to changes of less than approximately 80 J mol^{-1} in $\Delta H^\ominus$ and 8 J mol^{-1} K^{-1} in $\Delta C_p{}^\ominus$. The majority of equations in this first class are formulated such that the linear least-squares analysis can be used. In addition, there is a strong prejudice in favor of equations expressing $\ln K$ as a function of T which can be readily differentiated to yield the thermodynamic parameters (cf. Table II). Thus in principle we might choose to express K in terms of a simple three-term polynomial in T: eq 3 in

Table VI. While the equation for K is readily differentiated to yield the equation for $\Delta H^\ominus$ (e.g., $d \ln K \equiv K^{-1}\,dK$), the resulting expression for $\Delta C_p^\ominus$ is unattractive. Further, calculation of the standard error on $\Delta H^\ominus$ and $\Delta C_p^\ominus$ from the standard errors on a_1, a_2, and a_3 is not straightforward because $\Delta H^\ominus$ is not a linear function of these parameters.

There is an even stronger prejudice for equations for $\ln K$ which contain a term linear in T^{-1}. It is often implied that in a well-behaved system $\ln K$ is a linear function of T^{-1} and that additional terms dependent on T account for deviations from this linearity. Although we have argued against this view, it is often the case that in a preliminary perusal of the data $\ln K$ is plotted against T^{-1}.

The second approach to the problem of relating K and T is to formulate an equation expressing the dependence on temperature of the enthalpy term, $\Delta H^\ominus$. The resulting equation is integrated to obtain an equation for the dependence of $\ln K$ on T. The simplest example is to treat $\Delta H^\ominus$ as independent of temperature so that integration (Table I) yields an equation which relates $\ln K$ and T^{-1}: eq 1 of Table VI.

The third approach is to express the dependence of $\Delta C_p^\ominus$ on T in a convenient form where one integration yields an equation for $\Delta H^\ominus$ and another integration yields an equation for $\ln K$, Table I. In some instances, all three approaches may lead to an equation for $\ln K$ having the same form, but the starting hypotheses are quite different.

An important point concerns the technique of fitting $\ln K$ to an equation in temperature rather than K itself. Suppose that the true value for K is 1.0×10^{-5} and that the estimated value is 1.01×10^{-5}, a difference of 1%. In terms of logarithmic functions, the true value of $\ln K$ is -11.51293 and the estimated value is -11.50298, a difference of 0.086%. Clearly the latter figure looks more attractive, although one should not generalize because $\ln x$ is not a linear function of x. Nevertheless, we should be wary of presenting the goodness of fit in a way which yields an overoptimistic picture. A further advantage of the linear least-squares analysis based on the dependence of $\ln K$ on T is that the errors on the derived thermodynamic parameters are linear functions of the calculated coefficients. Thus the estimated error on $\Delta H^\ominus$ in eq 1 of Table VI is related to standard error on $\hat{a}_1$.

When the analysis is completed, it is often possible to compare, for example, van't Hoff based enthalpy parameters and those obtained from calorimetric data. In such comparisons the definition of the standard states for solutes in solution is important. Thus if the standard state for the solute is defined as the hypothetical solution where m_2 and γ_2 are both unity, the derived equilibrium constant refers therefore to the molality scale, i.e., $K(m)$.

$$\Delta G^\ominus(m) = -RT \ln K(m) \qquad (30)$$

However it may be that the concentration scale has been adopted where the standard state for the solute is the hypothetical solution where $c_2 = 1.0$ and $y_2 = 1.0$, to yield the equilibrium constant $K(c)$. Similarly on the mole fraction scale, the standard state for the solute is the hypothetical solution where $x_2 = 1.0$ and the asymmetric activity coefficient $f_2 = 1.0$, to yield the equilibrium constant $K(x)$.

It is a matter, at least initially, of convenience which scale is chosen in a particular study because these methods reflect different ways of expressing the same chemical potential of a solute in a given solution. However various arguments have been advanced over the merits of each scale. For example, Gurney[44] appears to favor the mole fraction scale. Quantities on this scale are called[44] unitary; quantities on other scales contain an additional cratic contribution. Ben-Naim has presented[45] arguments in favor of parameters calculated on the concentration scale. The molality scale is often preferred to the concentration scale because the molality of a solute in solution is independent of temperature and pressure. In contrast, kinetic parameters are generally expressed in terms of the concentration scale such that second-order rate constants are given in, for example, $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ rather than $\mathrm{kg\ mol^{-1}\ s^{-1}}$. This plethora of units[46] often presents problems,[47] but conversion from one scale to the next is relatively straightforward.[48]

A. Analysis Using Linear Least-Squares Techniques

In this section we confine attention to those equations which have attracted attention in the chemical literature. Where appropriate we examine application of the equation to experimental data and comment on the estimates of derived parameters. However because our interest also concerns the adequacy of the model, values of the correlation functions (eq 21), standard deviations on the fitted quantity, and errors on the derived parameters are examined.

1. Two-Term Equation: Linear Dependence of ln K on T^{-1}

This treatment has been commented on in previous paragraphs (eq 1 of Table VI). The equation requires that $\Delta H^\ominus$ is independent of temperature, $\Delta C_p^\ominus$ being 0. Consequently $\Delta S^\ominus$ is independent of temperature (eq 6 of Table I), and so $\Delta G^\ominus$ is a simple linear function of temperature. In the formally empirical equation (eq 1 of Table VI), a_2 is the value of $\ln K$ when T^{-1} is 0, i.e., when $T = \infty$. When T is 0, $\ln K$ is indeterminate, but when $T = 1$ K, $\ln K = a_1 + a_2$. Thus the two temperature values $T = 1$ and $T = \infty$ constitute the boundary values of the empirical equation for $\ln K$ and exist some way removed from the window over which the values of K are measured.

For many systems, e.g., acetic acid,[49] formic acid,[50] and propionic acid[51] in water, simple inspection of the data rules out analysis of the data in terms of eq 1, Table VI. However for other systems it is often conventional to examine the observed dependence using this empirical equation. To illustrate the point we consider the data for cyanoacetic acid[52] in water. The outcome of the analysis is summarized in Table VII for a set of data at 5 K intervals over the range $278.15 \leq T \leq 318.15$ K where K (in $\mathrm{dm^3\ mol^{-1}}$) for the acid dissociation constant decreases with increase in temperature. The standard deviation, $\hat{\sigma}(\ln K)$, is larger than that anticipated from the accuracy claimed by the investigators.[52] The difference Δ between observed and calculated values of $\ln K$ shows a smooth dependence on temperature, Figure 1, rather than a scatter of points. Thus it might be concluded that the equation used to fit the dependence is inadequate and that the

TABLE VII. Cyanoacetic Acid[52] in Water[a]

analysis[b]	θ/K	$\hat{\sigma}(\ln K)$	$\hat{a}_1$	$\hat{a}_2$	$\hat{a}_3$	$\Delta H^\ominus$ (298.15 K)/kJ mol^{-1}	$\Delta C_p^\ominus$ (298.15 K)/J mol^{-1} K^{-1}	comments
eq 1 (Table VI)		1.84×10^{-2}	426.9 (42.2)	−7.137 (0.142)		−3.55 (0.35)		$c_{12} = -0.9991$
eq 4	298.15	1.84×10^{-2}						$c_{12} = -0.043$
eq 5		1.57×10^{-2}	-4.867×10^{-3} (0.407×10^{-3})	−4.252 (0.121)		−3.60 (0.30)	−24.1 (2.0)	
eq 6		6.08×10^{-4}	-5.432×10^{3} (73.0)	124.8 (1.6)	−19.71 (0.25)	−3.696 (0.002)	−163.9 (2.0)	$c_{12} = -0.999$; $c_{13} = 0.998$; $c_{23} = -1.000$
eq 14		1.7×10^{-4}				−3.728	−150.6	
eq 1 (Table XII)	298.15	6.079×10^{-4}				−3.693 (0.011)	−163.9 (2.0)	
eq 3 (Table XII)	298.15	6.07×10^{-4}				−3.693 (0.012)	−163.9 (2.0)	$c_{12} = 0.0865$; $c_{13} = -0.7501$; $c_{23} = 0.153$

[a] Number of data points = 9; range, $278.15 \leqslant T \leqslant 318.15$. [b] Standard errors given in parentheses; equations refer to Table VI.

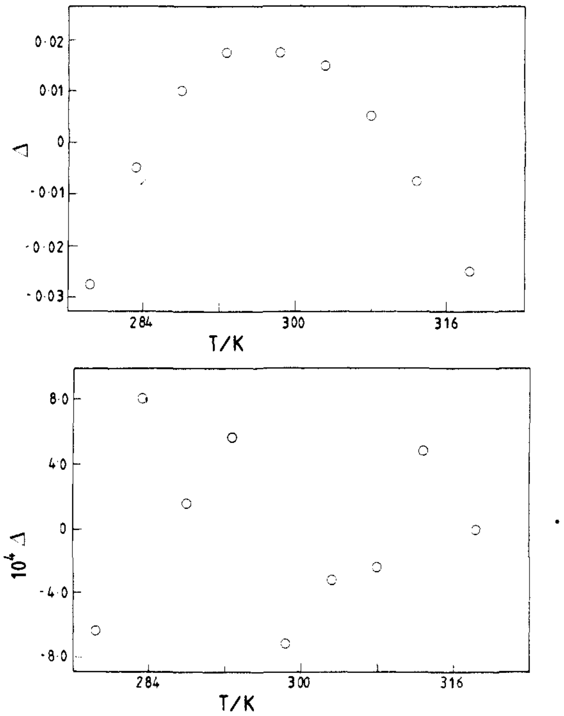


Figure 1. Dependence on temperature of the difference, Δ, between observed and calculated values of ln K for cyanoacetic acid in water[52] following analysis using (a) eq 1 and (b) eq 6 of Table VI.

derived thermodynamic parameters are unsatisfactory.

The high value for the magnitude of the correlation coefficient c_{12} between the estimates $\hat{a}_1$ and $\hat{a}_2$ indicates the following features of the fit. If the analysis were repeated but with, for example, a value of a_1 fixed at some value away from $\hat{a}_1$ obtained above, then the best fitted line would require a value of $\hat{a}_2$ proportionately lower, c_{12} being negative. The goodness of fit would be less satisfactory, but the data could be fitted in this way. The magnitude of c_{12} can be lowered by adopting a slightly different approach. We noted above that when $T = 1$, eq 1 of Table VI requires that ln K equals $a_1 + a_2$. It is possible to rewrite this equation, using the technique first suggested by Harned and Embree,[53] to express the dependence of ln K on temperature about a reference temperature θ (eq 4 of Table VI). In the application of eq 4 (Table VI), θ is defined at the outset, and the least-squares analysis yields estimates $\hat{a}_1$ and $\hat{a}_2$. Here the latter quantity equals the value of ln K at θ, and if the value of K has been measured at θ, then the calculated and observed values can be compared. Equation 4 of Table VI is equivalent to eq 1 of Table VI when $\theta = \infty$. If the analysis is repeated with $\theta = 1$, values of the independent variable $T^{-1} - \theta^{-1}$ are negative and c_{12} becomes positive, i.e., ~+1.0. However when $\theta = 298.15$, values of $T^{-1} - \theta^{-1}$ are less than and greater than 0 for the cyanoacetic acid data. The value of c_{12} now drops to −0.043 (Table VII). In other words it is not now possible to fix, for example, a_2 and at the same time fit the data with a proportionately different value of a_1. It is noteworthy that the standard deviation, the estimates $\hat{a}_1$ and $\hat{a}_2$, and their standard errors are not altered by switching from eq 1 to eq 4 of Table VI.

TABLE VIII. *tert*-Butyldimethylsulfonium Ion in Water[46]

analysis: eq 1 of Table VI

$\hat{a}_1 = -1.626 \times 10^4$; SE on $\hat{a}_1 = 5.8$

$\hat{a}_2 = 38.31$, SE on $\hat{a}_2 = 0.02$

$c_{12} = -0.9992$

$\Delta H^\ddagger(318.159\ \text{K}) = 137.84 \pm 0.05^a$ kJ mol^{-1}

$\Delta H^\ddagger(363.157\ \text{K}) = 138.21 \pm 0.05^a$ kJ mol^{-1}

$\hat{\sigma}(\ln k) = 2.357 \times 10^{-3}$

[a] Standard errors.

A similar trend is observed in correlation functions when the kinetic data for the solvolysis of *tert*-butyldimethylsulfonium ion[54] in water are analyzed by using eq 1 of Table VI (Table VIII). The dependence of the residuals on temperature, Figure 2, shows that the fit is poor, as is also confirmed by the standard deviation, $\hat{\sigma}(\ln k)$.

A consequence of the restrictions placed by the window is that the numerical range of T is relatively small. It is therefore interesting to note that, for example, in the case of cyanoacetic acid, a plot over the measured range of T^{-1} against T is reasonably linear. A least-squares fit of the trend yields the following equation and associated standard errors.

$$T^{-1} = -[(1.129 \pm 0.016) \times 10^{-5}]T + [(6.726 \pm 0.048) \times 10^{-3}] \quad (31)$$

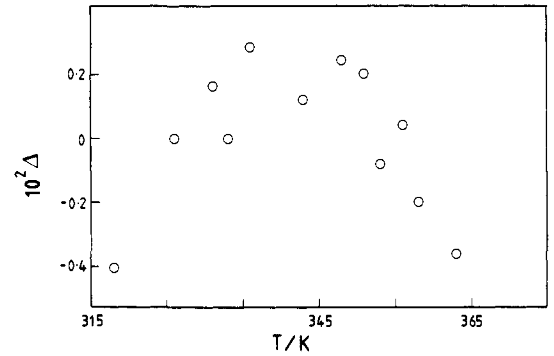


Figure 2. Dependence on temperature of the difference, Δ, between observed and calculated values of ln k for solvolysis in water of *tert*-butyldimethylsulfonium ion[54] as calculated by using eq 1 of Table VI.

This observation prompts the testing of the following model for the dependence of ln K on temperature.

2. *Two-Term Equation: Linear Dependence of In K on T*

Perhaps the simplest equation, prompted by eq 31, expresses ln K as a linear function of T (eq 5 of Table VI). It is now interesting to observe that differentiation of this equation yields an expression for $\Delta H^{\ominus}$ where $\Delta H^{\ominus}$ is dependent on temperature. Formally the new equation yields an expression for $\Delta C_p^{\ominus}$. Analysis of the dependence on temperature of the acid dissociation constant for cyanoacetic acid[52] leads to the parameters given in Table VII. Equation 5 (Table VI) fits the data slightly better than eq 1 of Table VI, but the overall goodness of fit remains poor. However it seems, at first sight, odd that the amount of information obtained from the same set of data depends on whether ln K is expressed as a function of either T or T^{-1}. The problem is resolved if one plots the dependence of $\Delta H^{\ominus}$ on temperature together with the standard errors and on the same plot includes the values of $\Delta H^{\ominus}$ and the standard errors from eq 1 of Table VI (Figure 3). It follows from eq 5 (Table VI) that the error on the estimate for $\Delta H^{\ominus}$ increases with increase in T^2 whereas from eq 1 (Table VI) this error is independent of T. Further the values encompassed between the standard errors from eq 1 also encompass most of the range covered by $\Delta H^{\ominus}$ calculated from eq 5. The overlap is complete if the plot is redrawn with confidence factors calculated from the Student t values at the 95% confidence level. Thus the two analytical equations are not in conflict in the extent to which they provide information about the system. However eq 5 (Table VI) is unsatisfactory because it starts out with the requirement that $\Delta H^{\ominus}$, $\Delta C_p^{\ominus}$, and $\Delta^2 C_p^{\ominus}$ have the same sign. This condition is, however, not demanded by thermodynamics. Clearly, in order to avoid this requirement of the analysis, information concerning heat capacity terms requires another term in the equation for ln K. This observation prompts therefore the development of equations which contain three terms, two of which are dependent on temperature.

3. *Three-Term Equations for Dependence of In K on T*

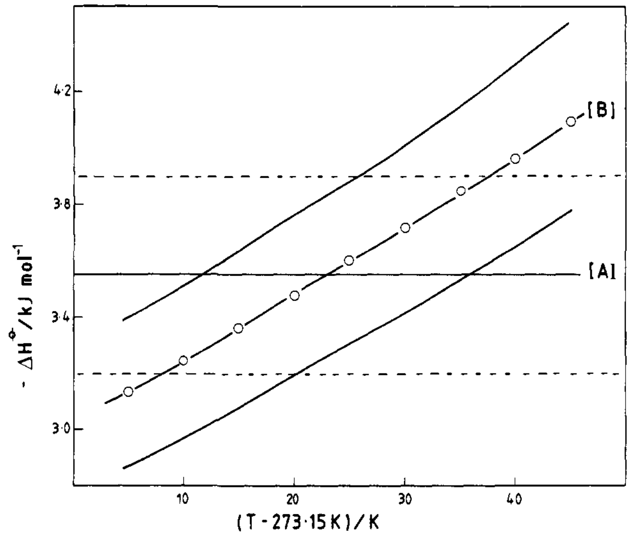


Figure 3. Enthalpy terms and standard errors for cyanoacetic acid[52] in water calculated following analysis of data using (a) eq 1 and (b) eq 5 of Table VI.

Many equations used to analyze the dependence of ln K on temperature take as their basis eq 1 of Table VI but include an additional term dependent on temperature. The implied aim is, as noted above, to account for deviations from the anticipated linear dependence of ln K on T^{-1}. The new class of equations can be written in the following general form:

$$\ln K = a_1 + \sum f(T) \tag{32}$$

Some general features can now be identified bearing in mind the form of the van't Hoff equation, Table I. If f(T) contains a term linear in T^{-1}, the equation for $\Delta H^{\ominus}$ contains a term independent of temperature. If f(T) contains a term linear in ln T, the equation for $\Delta H^{\ominus}$ contains a term linear in T. If f(T) contains a power series in T, then with each additional term (eq 33), an equation is obtained for a further differential of $\Delta C_p^{\ominus}$ with respect to temperature.

$$f(T) = \sum_{i=1}^{i=q} a_i T^i \tag{33}$$

If f(T) contains a power series in T^{-1} (eq 34), expressions for all differentials of $\Delta C_p^{\ominus}$ with respect to temperature are recovered. Here again we encounter

$$f(T) = \sum_{i=1}^{i=q} a_i T^{-i} \tag{34}$$

the conclusion that the amount of information extracted from the same set of data depends on the form of the equation used to express the dependence of ln K on temperature. Thus to obtain equations for all temperature differentials of $\Delta C_p^{\ominus}$ it is apparently only necessary to add one term proportional to T^{-2} in eq 1 of Table VI. This highlights the necessity of examining with utmost rigor the statistical significance of the derived parameters and their associated errors.

(a) Valentiner Equation. One of the first methods for analyzing the dependence of ln K on T was proposed by Valentiner[16] who suggested that f(T) in eq 32 should include two terms, one proportional to T^{-1} and another proportional to ln T (eq 6 of Table VI). In contrast to the equations given above, the Valentiner equation can accommodate situations where the plot of ln K against T passes through a maximum or minimum. At this temperature $\Delta H^{\ominus}$ is 0. The equation leads to indeterminate values of K when T is either zero or infinity. At

TABLE IX. Acetic Acid in Water; Analysis Using Equations in Table VI

analysis	θ/K	σ ln K	$\Delta H^\ominus$ (298.15 K)/ kJ mol^{-1}	$\Delta C_p^\ominus$ (298.15 K)/ J mol^{-1} K^{-1}	T(ln K = max)/K	$10^5K_{\max}$/ kg mol^{-1}
eq 6[a]		1.14×10^{-3}	−436.5 (5.1)	−155.1 (1.5)	295.3	1.756
eq 7[b]		1.16×10^{-3}	−391.5 (5.8)	−153.0 (1.6)	298.58	1.756
eq 8		2.45×10^{-3}	−250 (1.95×10^3)		296.38	1.754
eq 12	298.15	1.18×10^{-3}	−411 (31)	−155.7 (2.3)		

[a] $c_{12} = -0.9997$; $c_{23} = -1.000$; $c_{13} = 0.9996$. [b] $c_{12} = -0.9996$; $c_{23} = -0.9996$; $c_{13} = 0.9985$.

$T = 1$ K, ln K equals $a_1 + a_2$ and $\Delta H^\ominus$ equals $R(a_3 - a_1)$. The major requirement of the Valentiner equation is that $\Delta C_p^\ominus$ is independent of temperature, being equal to a_3R. Using these derived thermodynamic parameters at $T = 1$, it is possible to replace the three a parameters to obtain the following equivalent form.

$$\ln K = \left[\frac{\Delta C_p^\ominus}{R} - \frac{\Delta H^\ominus(T=1)}{R}\right]T^{-1} + \left[\ln [K(T = 1)] - \frac{\Delta C_p^\ominus}{R} + \frac{\Delta H^\ominus(T = 1)}{R}\right] + (\Delta C_p^\ominus/R)\ln T \quad (35)$$

In fitting the data to the Valentiner equation, King[2] first estimates a_3 by using pairs of values (e.g., K_1/T_1 and K_2/T_2) in conjunction with eq 36 which is an equation for a straight line, slope a_3. This procedure

$$\left[\frac{T_1 \ln K_1 - T_2 \ln K_2}{T_1 - T_2}\right] = a_3\left[\frac{T_1 \ln T_1 - T_2 \ln T_2}{T_1 - T_2}\right] + a_2 \quad (36)$$

is a convenient method for assessing whether a given set of data is consistent with a nonzero $\Delta C_p^\ominus$.

The results of fitting the dependence on temperature of K_A for cyanoacetic acid in water[52] to the Valentiner equation are summarized in Table VII. The standard variation $\tilde{\sigma}$(ln K) is significantly less than that obtained using eq 1 of Table VI and is in line with the probable errors estimated on the measured dissociation constants.[52] The differences Δ (ln K(obsd) − ln K(calcd)) show a scatter when plotted against temperature (Figure 4). The calculated value of $\Delta H^\ominus$ at 298 K is negative, becoming more negative with increase in temperature. A similar good fit is obtained for the data describing the acid dissociation constants for acetic acid in water[49] (Table IX), the derived parameters predicting that K is a maximum at 295.33 K. The value of $\Delta C_p^\ominus$ is slightly lower than that obtained from calorimetric experiments.[18,55,56]

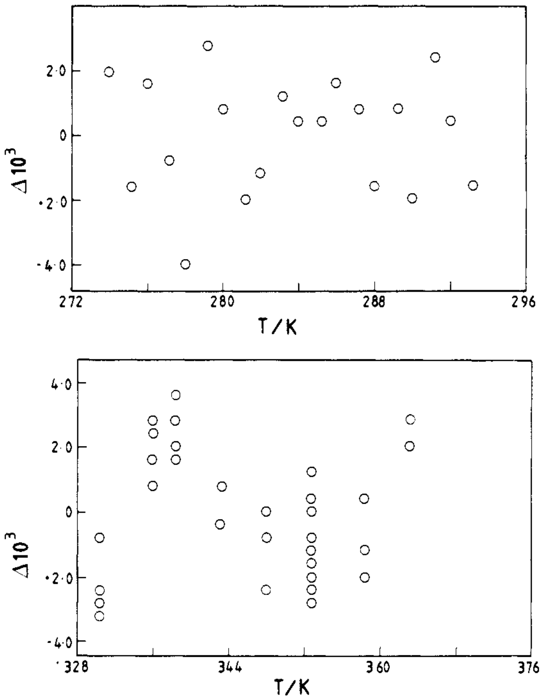


Figure 4. Dependence on temperature of the difference, Δ, between observed and calculated values of ln k following analysis using eq 6 of Table VI for solvolysis in water of (a) *tert*-butyl chloride[57] and (b) ethyl bromide.[58]

As commented in the introduction, the Valentiner equation has been extensively used by Robertson to analyze kinetic data for solvolytic reactions in water.[7] The results of the analysis for 2 sets of data are summarized in Table X and Figure 4, i.e., solvolysis in water of *tert*-butyl chloride[57] and ethyl bromide.[58] The data are satisfactorily fitted by using this approach although there is some indication that the residuals Δ for ethyl bromide (Figure 4) follow a pattern rather than generating a scatter when plotted against temperature. It would appear that there is some feature of the data which is not accounted for by the Valentiner equation. The original point of interest[7] in these data was the much smaller value for $\Delta C_p^{\ddagger}$ shown by *tert*-butyl chloride than by ethyl bromide. If the reaction is indeed a simple one-stage reaction (i.e., model I of Table V), then it was suggested that a significant amount of solvent reorganization accompanied the activation process for *tert*-butyl chloride.[7,57] We do not pursue the discussion of these points.

Despite the apparent success in fitting a wide range of both equilibrium and kinetic data with the Valentiner equation, there are several worrying features. For both equilibrium and kinetic data, the correlation coefficients are very close to unity. Indeed, examination of the data for numerous carboxylic acids,[59] the self-dissociation constants of water[60] and deuterium oxide,[61] and the kinetic data for many solvolytic reactions[62] reveals this to be a common feature of the Valentiner equation. There is another feature. A plot of a_3 against a_1 (Figure 5) for ten carboxylic acids in water shows that these quantities are not only related for one acid but, within a group of related acids, a close link appears to exist. A similar pattern is generated[66] by the parameters obtained when kinetic data for solvolytic reactions are fitted to the Valentiner equation. Indeed for the equilibrium data at the 95% level of confidence, the line passes through the origin with slope equal to (30 ± 7) × 10^{-3}. Two characteristics of the analysis indicate that this unexpected correlation is an artifact of the Valentiner equation. The correlation coefficient c_{13} is close to unity because over a restricted range of temperature ln T is close to a linear function of T^{-1}. For the range $278 \le T \le 318$ K quoted in the data for cyanoacetic

TABLE X. Analysis of Kinetic Data for Solvolytic Reactions

analysis	θ/K	$\hat{\sigma}$ ln k	$\hat{a}_1$	$\hat{a}_2$	$\hat{a}_3$	$\hat{a}_4$	$\hat{a}_5$	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta C_p^{\ddagger}$/J mol^{-1} K^{-1}	at T/K	comments
ethyl bromide[a]											
eq 6 (Table VI)		1.99×10^{-3}	-2.029×10^5 (3.2×10^2)	189.1 (6.4)	-23.8 (0.9)			96.828 (16)	-198.2 (7.7)	347.99	
eq 12 (Table VI)	347.99	1.11×10^{-3}	-8.7097 (4.1×10^{-4})	9.882×10^{-3} (5.2×10^{-5})	-3.594×10^{-3} (8.6×10^{-6})	2.760×10^{-6} (2.7×10^{-7})	-7.1×10^{-8} (3.1×10^{-8})	96.606 (52)	-160 (17)	347.99	five terms
eq 3	347.99	1.16×10^{-3b}						96.571 (46)	-193 (1.3)		four terms[f]
tert-butyl chloride[c]											
eq 6 (Table VI)		1.90×10^{-3}	-2.3813×10^5 (6.5×10^2)	308.8 (15.4)	-40.8 (2.3)			99.579 (5×10^{-3})	-348 (19)	283.173	
eq 11 (Table VI)	283.173	1.93×10^{-3}	-1.225×10^4 (6)	-1.638×10^6 (9.4×10^4)				99.551 (5×10^{-3})	-348 (10)	283.173	$c_{12} = -0.023$; $c_{13} = 0.089$; $c_{23} = -0.746$
eq 12 (Table VI)	283.173	1.85×10^{-3}	-5.637 (6×10^{-4})	0.15307 (7.3×10^{-5})	-7.91×10^{-4} (1.4×10^{-5})			99.68 (0.12)	-342 (20)	283.173	
eq 3 (Table XII)	283.173	1.90×10^{-3b}						99.57 (0.05)	-347 (19)	283.173	three terms; $c_{12} = 0.04$; $c_{13} = -0.75$; $c_{23} = -0.116$
isopropyl benzenesulfonate[d]											
eq 1 (Table XII)[e]	293.141	3.89×10^{-3b}						92.201 (0.055)	-156 (8)	293.141	

[a] 33 data points. [b] σ ln (k/T). [c] 20 data points. [d] 45 data points. [e] Three terms. [f] $\Delta^2 C_p^{\ddagger} = 10 \pm 1.3$ J mol^{-1} K^{-2}.

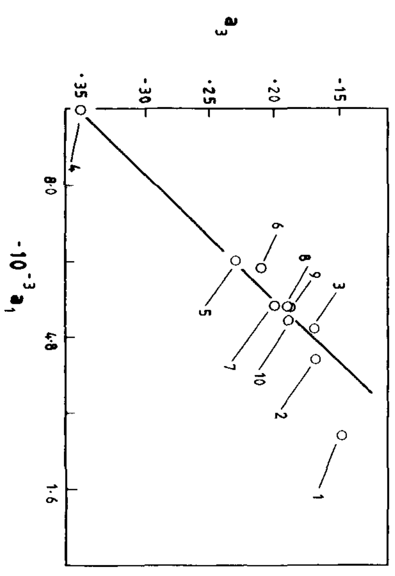


Figure 5. Dependence of $\hat{a}_3$ on $\hat{a}_1$ following analysis using the Valentiner equation (eq 6 of Table VI) of the acid dissociation constants in water for (1) diisopropylcyanoacetic acid,[63] (2) iodoacetic acid,[64] (3) acetic-d_3 acid,[65] (4) fluoroacetic acid,[64] (5) chloroacetic acid,[64] (6) formic acid,[50] (7) cyanoacetic acid,[52] (8) bromoacetic acid,[64] (9) acetic acid,[49] and (10) propionic acid.[51]

acid, a least-squares fit of ln T against T yields the following parameters:

$$\ln T = [(3.38 \pm 0.02) \times 10^{-3}]T + 4.696 \pm 0.007 \qquad (37)$$

In other words the terms in T^{-1} and ln T in eq 6 of Table VI can be replaced[67] by a single term in either T^{-1} or ln T with only a modest change in the goodness of fit. Thus the quantities a_1 and a_3 cannot be independently estimated. This observation is borne out by eq 35. Inspection reveals that each parameter, a_1, a_2, and a_3, contains a contribution from $\Delta C_p^{\ominus}$ and two contain the enthalpy quantity $\Delta H^{\ominus}(T = 1)$. It follows through a series of related compounds the dependence of a_1 on a_3 can be represented by eq 38. Moreover,

$$\delta_R a_1 = \delta_R a_3 - R^{-1}\,\delta_R \Delta H^{\ominus}\,(T = 1) \qquad (38)$$

$\delta_R \Delta H^{\ominus}$ $(T = 1)$ is 0 for monocarboxylic acids in water although the significance of this plot is not clear. Nevertheless these additional features of the Valentiner equation throw some doubt on the advisability of its use to analyze kinetic and thermodynamic data.

(b) Robinson Equation. This equation[46,68] is similar to the Valentiner equation except that f(T) in eq 32 contains a term proportional to T rather than ln T (Table VI). For equilibrium parameters, $\Delta H^{\ominus}$ is a function of T^2 the equation for $\Delta H^{\ominus}$ containing no term linear in T. The heat capacity quantity $\Delta C_p^{\ominus}$ is a linear function of T, being zero when $T = 0$. The Robinson equation can accommodate situations where ln K shows an extremum when plotted against temperature, the condition being that a_1 and a_3 have the same sign. At $T = 1$, ln K is equal to $a_1 + a_2 + a_3$. Substitution for the three a coefficients by the thermodynamic parameters yields the analogue of eq 35.

$$\ln K = \left[-\frac{\Delta H^{\ominus}(T = 1)}{R} + \frac{\Delta C_p^{\ominus}(T = 1)}{2R}\right]\frac{1}{T} + \left[\ln K(T = 1) + \frac{\Delta H^{\ominus}(T = 1)}{R} - \frac{\Delta C_p^{\ominus}(T = 1)}{R}\right] + \left[\frac{\Delta C_p^{\ominus}}{2R}\right]T \qquad (39)$$

We note how, for example, $\Delta H^{\ominus}(T = 1)$ appears in two of the terms. Moreover, we have shown that over a restricted temperature range, T^{-1} is close to a linear function of T. It is anticipated, therefore, that the correlation coefficients will be close to unity. Indeed this is the case, as shown, for example, in the analysis of the data for acetic acid (Table IX). The equation fits the data with a standard deviation similar to that for the Valentiner equation, as are the derived quantities, e.g., the temperature at which ln K is a maximum. The overall prediction of the Robinson equation is that $\Delta G^{\ominus}$ is a quadratic function of temperature. However, the requirement that $\Delta C_p{}^{\ominus}$ is a linear function of temperature is restrictive. The error on the estimate of $\Delta C_p{}^{\ominus}$ increases with increase in temperature. The equation for the error in $\Delta H^{\ominus}$ includes a term linear in T^2.

(c) **Ives and Pryor Equation.** This equation was originally proposed[64] in order to overcome the restrictions imposed by the Valentiner equation. In particular it was argued that $\Delta C_p{}^{\ominus}$ is likely to be dependent on temperature. The outcome is an equation which expresses $\Delta C_p{}^{\ominus}$ as the sum of two terms, one dependent on T and the other dependent on T^2 (Table IV). The equation is essentially the first three terms of a polynomial in T and is the first example here of an equation for the dependence of ln K on temperature having no term in T^{-1} (eq 40; cf. eq 32). The data describing the

$$\ln K = \sum_{i=1}^{i=3} a_i T^{i-1} \tag{40}$$

dependence of dissociation constants for acetic acid can be fitted to this equation, the derived parameters being summarized in Table IX. The standard deviation $\hat{\sigma}$(ln K) is slightly larger than in the case of the Valentiner equation, and a plot of the residuals against temperature shows some evidence of a sinusoidal dependence. The correlation coefficients are again close to ±1. Part of this behavior can be attributed to the fact that over the range $273 \leq T \leq 333$ K, T^2 is close to a linear function of T, the equation being

$$T^2 = (606.3;\ \mathrm{SE} = 5.0)T - (9.155 \times 10^4;\ \mathrm{SE} = 1.52 \times 10^3) \tag{41}$$

Consequently the closeness of the correlation coefficients to ±1 is an unhappy feature, again a consequence of the form of the equation. We also note that $\Delta H^{\ominus}$ and the estimated error on $\Delta H^{\ominus}$ are dependent on T^2. Hence at 273.15 K, $\Delta H^{\ominus}$ is 2.817 kJ mol^{-1} with standard error 1.57 kJ mol^{-1}, and at 333.15 K, $\Delta H^{\ominus}$ is -6.63 kJ mol^{-1} with standard error 2.58 kJ mol^{-1}. Similarly the standard error in $\Delta C_p{}^{\ominus}$ is proportional to T. At 298.15 K, $\Delta H^{\ominus}$ is -250 J mol^{-1} with standard error 1.95 kJ mol^{-1} and hence is statistically indistinguishable from 0. Although formally the equation for ln K results in an estimate of $\Delta^3 C_p{}^{\ominus}$ (i.e., -9.75×10^{-3} [SE = 2.19×10^{-4}] J mol^{-1} K^{-3}), this is at the expense of being able to estimate $\Delta H^{\ominus}$ within reasonable limits.

In a later publication, Feates and Ives[52] comment that the dependence of $\Delta C_p{}^{\ominus}$ on temperature required by eq 8 of Table VI is too restrictive, and they set down a number of equations which express the dependence of ln K on T. Some of these equations contain a product term in T ln T. One of the examples listed by Feates and Ives[52] is the following three-term equation.

$$\ln K = a_1 + a_2 T + a_3 T \ln T \tag{42}$$

However application of the van't Hoff equation (Table I) shows that here also $\Delta H^{\ominus}$ is proportional to T^2, which means that the errors on the estimate of $\Delta H^{\ominus}$ must also increase in T^2. An equation for ln K which avoids these problems was proposed by Wold[69] although the particular application was to kinetic data and incorporated a fitting procedure using spline functions. This technique fits the dependence of ln k on T piecewise to the eq 9 of Table VI, the pieces being joined at knot points where the first and second derivatives are continuous. In addition to the parameters in the equation for ln k, the number of knots is also a variable.

4. *Four-Term Equations for Dependence of ln K on T*

The equations in this section were proposed on the grounds that the dependence of ln K on temperature could not be accounted for by expressions which contain one term in T^{-1} and one other term in temperature. In principle, the floodgates are now open, and all manner of combinations of temperature terms can be employed. The Harned equation[49,70] can be considered as an extension of the Valentiner equation with the addition of a term linear in temperature (eq 43). In view of the

$$\ln K = a_1 T^{-1} + a_2 + a_3 \ln T + a_4 T \tag{43}$$

observation above that both T^{-1} and ln T are close to linear functions of T, this equation does not seem satisfactory. Indeed efforts to fit the dependence of ln K on T for acetic acid in water were unsuccessful because one of the three terms in temperature is redundant once the other two were calculated. Under these conditions, the coefficients a_1, a_3, and a_4 are said to be aliased.

A similar difficulty was experienced with the Jenkins equation[71] which expresses ln K as a function of T in an equation which contains the first three terms of a series in ln T (eq 44).

$$\ln K = a_1 + a_2 T^{-1} + a_3 T^{-1} \ln T + a_4 T^{-1} (\ln T)^2 \tag{44}$$

5. *Linear Equations Using a Reference Temperature θ for Dependence of ln K on T*

These equations describe the dependence of ln K on temperature about a reference temperature θ, such that in the limit $T \rightarrow \theta$, so $\ln K \rightarrow \ln K(\theta)$. A number of equations have been proposed which use this general procedure.

(a) **Harned and Embree Equation.** This equation[53] represents the first application of this technique. Originally the equation was developed in order to account for the observation that ln K showed a maximum at a certain temperature in the case of various carboxylic acids in water. As proposed, the temperature θ is the temperature at which ln K is a maximum such that $\Delta H^{\ominus}(\theta)$ is 0 (Table VI). As written, a linear least-squares analysis cannot be used to obtain estimates of ln $K(\theta)$, a_1, and θ. Therefore it is necessary to estimate θ from a plot of ln K against T and hence use the analysis to obtain estimates of ln $K(\theta)$ and a_1. This is rather unsatisfactory. The importance[72] of the Harned and Embree equation arises from the concept of defining a reference temperature. Thus, it is possible to select any convenient temperature as the reference and to fit the data to the proposed equation using the linear least-squares technique. Thus, Feates and Ives in an extension of the equations described in the previous section used 298.16 K as their reference temperature.

It is therefore possible to rewrite the equations described above in terms of the reference temperature θ. Thus the Valentiner equation can be rewritten as follows:

$$\ln K = \ln K(\theta) + a_1(T^{-1} - \theta^{-1}) + a_2 \ln (T/\theta) \qquad (45)$$

In the following section we examine several methods of analyzing experimental data which have used the concept of the reference temperature in the development of treatments which are not simple derivatives of previous equations.

(b) **Wold Equation.** In the Wold equation,[69] the third term in eq 45 is replaced by a term proportional to the square of $(T^{-1} - \theta^{-1})$ (Table VI). An example of the application of this equation is summarized in Table X for *tert*-butyl chloride in water. The standard deviation is comparable to that obtained by using the Valentiner equation, but the correlation coefficients between the estimates have fallen appreciably. The reference temperature θ corresponds to a data point so that comparison between observed and calculated values at θ is possible; e.g., if $\theta = 283.173$, $k(\text{calcd}, \theta) = 3.565 \times 10^{-3}\ \text{s}^{-1}$ and $k(\text{obsd}, \theta) = 3.569 \times 10^{-3}\ \text{s}^{-1}$, representing a difference of 0.11%.

(c) **Polynomial Equation.** Several of the equations discussed above contain terms in T which correspond to the first few terms in a polynomial. Recognition of this feature prompts the idea that the goodness of fit might be improved if the series were extended to include higher terms in the polynomial. The problem of deciding where the polynomial should be terminated is resolved by testing the statistical significance of each new term. If these ideas are coupled with the concept of fitting the data about a reference temperature, the following polynomial is proposed.

$$\ln K = \sum_{i=1}^{i=n} a_i(T - \theta)^{i-1} \qquad (46)$$

If the polynomial is truncated when $n = 4$, the equations given in Table VI are obtained.

The data[58] for the solvolysis of ethyl bromide in water have been fitted to eq 12 of Table VI. The improvement in the goodness of fit as measured by the difference Δ ($\ln k(\text{obsd}) - \ln k(\text{calcd})$ is shown in Figure 6 as the number of terms in the polynomial is increased. A scatter of values does not emerge until five terms are used. The cut-off point in the polynomial can be judged by using either the Student t test or an F test of the variance. If, for example, six terms are used in the polynomial with reference to the 33 data points for ethyl bromide, the mean of the square of the residuals on 27 degrees of freedom is 1.190×10^{-6}. The sum of squares accounted for by introducing the sixth term is 2.28×10^{-6}, and so the variance ratio equals 1.19. However since $F(1,27,0.05)$ equals 4.2, we conclude that there is less than a 5% chance that inclusion of the sixth term is significant. A similar test shows that the variance ratio for inclusion of the fifth term is 5.3 and there is less than a 5% chance that the fifth term is insignificant. The derived parameters are summarized in Table IX. In contrast to the Valentiner equation, the polynomial equation indicates that $\Delta C_p^{\ddagger}$ is dependent on temperature, becoming less negative with increase in temperature (Figure 7). The parameters also indicate that $\Delta C_p^{\ddagger}$ passes through an extremum around 298 K. The **c** matrix for this analysis is shown in Table XI. With 5 coefficients, the result is a 5×5 matrix of coefficients. The coefficients c_{24} and c_{35} are close to ± 1. This can be understood by examining plots of $(T - \theta)$ against $(T - \theta)^3$ and of $(T - \theta)^2$ against $(T - \theta)^4$; the curves show a rough proportionality between these quantities. The same pattern is not formed by plots of, for example, $(T - \theta)$ against $(T - \theta)^2$.

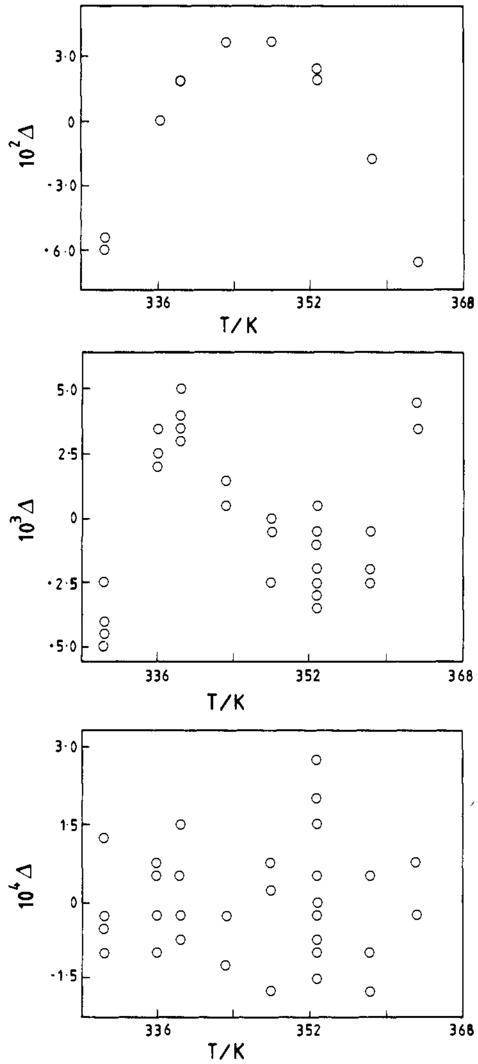


Figure 6. Dependence on temperature of the difference, Δ, between observed and calculated values for $\ln k$ for the solvolysis of ethyl bromide in water[58] as calculated by using eq 12 of Table VI with (a) two terms, (b) three terms, and (c) five terms in the polynomial equation.

TABLE XI. Correlation Matrix for Analysis of Dependence of Rate Constant on Temperature for Ethyl Bromide in Water[a]

	Correlations of Estimates				
1	1.0000				
2	−0.4066	1.0000			
3	−0.8199	0.4866	1.0000		
4	0.4226	−0.9187	−0.5380	1.0000	
5	0.7153	−0.5192	−0.9670	0.6109	1.0000
	1	2	3	4	5

[a] Data analyzed by using five terms in the polynomial equation (eq 7, Table X).

The outcome of the analysis for the kinetics of solvolysis in water of *tert*-butyl chloride[57] is summarized in Table X. The dependence of $\Delta C_p^{\ddagger}$ on temperature is shown in Figure 7b where $\Delta C_p^{\ddagger}$ becomes more neg-

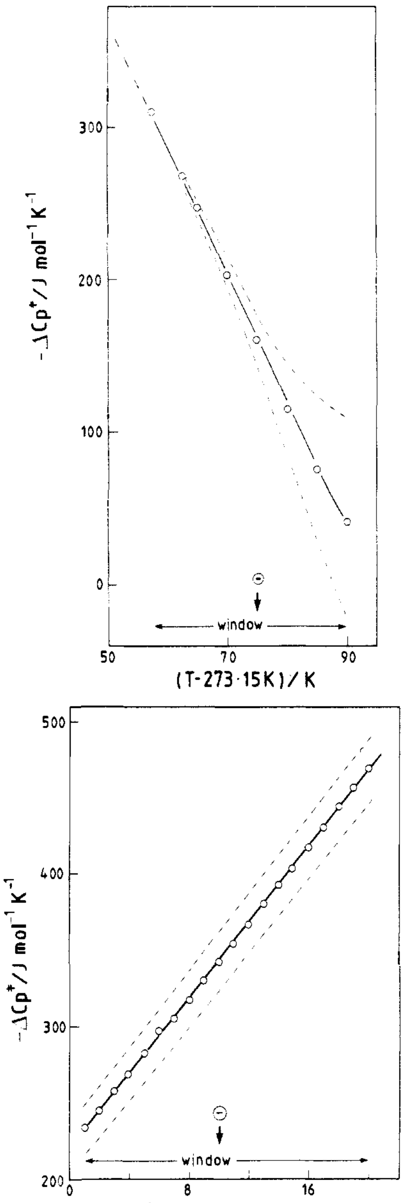


Figure 7. Dependence of the heat capacity of activation on temperature calculated from the kinetic data by using eq 12 of Table VI for (a) ethyl bromide[58] and (b) *tert*-butyl chloride.[57]

ative with increasing temperature. Application of the polynomial equation to the acid dissociation constant for acetic acid leads to the parameters summarized in Table IX. The calculated dependence of $\Delta C_p^\ominus$ on temperature is shown in Figure 8. In the last two examples the correlation matrices have characteristics similar to those shown in Table XII. The corresponding plots of the residuals are similar to those shown in Figure 6.

The resulting dependence of $\Delta C_p^\ominus$ on temperature for acetic acid in water is in qualitative agreement with the trend calculated from calorimetric data.[73] However the latter predict a more dramatic dependence with a minimum around 293 K where $\Delta C_p^\ominus$ is approximately -172 J mol^{-1} K^{-1}.

A comparison of the standard deviations between different methods of fitting the same data (cf. Tables IX and X) shows that the polynomial equations provide a reasonable fit to both equilibrium and rate data. The amount of information extracted from the data increases as the number of terms increases. A five-term polynomial allows an estimate to be made of the fourth derivative of $\Delta C_p^\ominus$ with respect to temperature. If two terms are used in the polynomial, only $\Delta H^\ominus$ can be estimated. Nonetheless in all cases the error on the estimate of $\Delta H^\ominus$ is proportional to T^2.

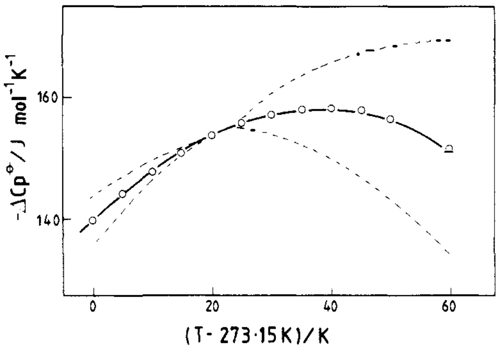


Figure 8. Dependence on temperature of the heat capacity quantity $\Delta C_p^\ominus$ for acetic acid in water[49] as calculated by using eq 12 of Table VI.

(d) Orthogonal Polynomials. We illustrate the application of this method of analysis to the data for cyanoacetic acid[52,74] in water where the data comprise values of the dissociation constants at nine temperatures at 5 K intervals over the range 278.15–318.15 K.

The orthogonal polynomial expresses the dependence of ln K on a new set of variables, γ_i (Table VI), which are functions of a quantity ϕ; ϕ is defined as $(T - T_m)/5.0$ where T_m is the mean temperature and the denominator is the temperature interval for this data set.[52] In this example, it is statistically justified to include the cubic term in the polynomial. A consequence of the orthogonal polynomials is that the standard errors on the estimates of a parameters are independent. However the enthalpy and heat capacity quantities (Table VI) depend on more than one a quantity, and hence their standard errors are dependent on the standard errors in each a term (Table VII).

6. Equations Using a Reference Temperature θ for the Dependence on Temperature of Enthalpy Parameters

Rather than starting out with an equation for the dependence of ln K on temperature, we noted above that it is possible to formulate an expression for the dependence of, say, $\Delta H^\ominus$ on temperature. Integration of this equation yields (Table I) an expression for the dependence of ln K on temperature. A definite integral is obtained if the limits, $\Delta H^\ominus$ at T and $\Delta H^\ominus(\theta)$ at θ, are used. Moreover if the equation expresses $\Delta H^\ominus$ as a linear function of the fitting parameters, the final equation for ln K will be amenable to analysis by using the linear least-squares technique. Here we consider three models of varying complexity which start out with an expression for the dependence of $\Delta H^\ominus$ on T.

(a) Scott Equation. The simplest model[75] expresses $\Delta H^\ominus$ as a linear function of $T - \theta$ such that $\Delta C_p^\ominus$ is independent of temperature (Table XII). Integration leads to an equation for ln K where the unknown parameters are ln $K(\theta)$, $\Delta H^\ominus(\theta)/R$, and $\Delta C_p^\ominus/R$. A similar treatment based on a linear dependence of $\Delta H^{\ddagger}$ on $T - \theta$ leads to an equation for the dependence of ln k on temperature. The results of applying this method of analysis are summarized in Table VII for cyanoacetic acid in water[52] and Table X for the solvolysis of isopropyl benzenesulfonate.[76] In the case of cyanoacetic

TABLE XII. Equations for the Dependence of Enthalpy Parameters on Temperature

analysis	equation	ln K	$\Delta C_p^{\ominus}$
		1. Scott Equation	
E	$\Delta H^{\ominus} = \Delta H^{\ominus}(\theta) + \Delta C_p^{\ominus}(T-\theta)$	$\ln K = \ln K(\theta) + \frac{\Delta H^{\ominus}}{R}\left[\frac{1}{\theta} - \frac{1}{T}\right] + \frac{\Delta C_p^{\ominus}(\theta)}{R}\left[\frac{\theta}{T} - 1 + \ln\left(\frac{T}{\vartheta}\right)\right]$	
K	$\Delta H^{\ddagger} = \Delta H^{\ddagger}(\theta) + \Delta C_p^{\ddagger}(T-\theta)$	$\ln k = \ln\frac{k(\theta)T}{\theta} + \frac{\Delta H^{\ddagger}}{R}\left[\frac{1}{\theta} - \frac{1}{T}\right] + \frac{\Delta C_p^{\ddagger}(\theta)}{R}\left[\frac{\vartheta}{T} - 1 + \ln\left(\frac{T}{\theta}\right)\right]$	
		2. Three-Term Polynomial in $T-\theta$	
E	$\Delta H^{\ominus} = \Delta H^{\ominus}(\theta) + \Delta C_p^{\ominus}(\theta) + \Delta^2 C_p^{\ominus}(T-\theta)^2/2$	$\ln K = \ln K(\theta) + \frac{\Delta H^{\ominus}(\theta)}{R}\left[\frac{1}{\vartheta} - \frac{1}{T}\right] + \frac{\Delta C_p^{\ominus}(\theta)}{R}\left[\frac{\theta}{T} - 1 + \ln\left(\frac{T}{\theta}\right)\right] + \frac{\Delta^2 C_p^{\ominus}}{R}\left(\frac{\theta}{2}\right)\left[\frac{T}{\theta} - \frac{\theta}{T} - \frac{1}{2}\ln\left(\frac{T}{\vartheta}\right)\right]$	$\Delta C_p^{\ominus} = \Delta C_p^{\ominus}(\theta) + \Delta^2 C_p^{\ominus}(T-\theta)$
		3. Clarke–Glew	
E	$\Delta H^{\ominus} = \Delta H^{\ominus}(\theta) + \Delta C_p^{\ominus}(T-\theta) + \frac{\Delta^2 C_p^{\ominus}(\theta)}{2}(T-\theta)^2 + \frac{\Delta^3 C_p^{\ominus}(\theta)}{6}(T-\theta)^3 + \frac{\Delta^4 C_p^{\ominus}}{24}(T-\theta)^4$	$\ln K = \ln K(\theta) + \frac{\Delta H^{\ominus}(\theta)}{R}\left[\frac{1}{\theta} - \frac{1}{T}\right] + \frac{\Delta C_p^{\ominus}(\theta)}{R}\left[\frac{\theta}{T} - 1 + \ln\left(\frac{T}{\theta}\right)\right] + \frac{\Delta^2 C_p^{\ominus}(\theta)}{R}\left(\frac{\vartheta}{2}\right)\left[\frac{T}{\theta} - \frac{\theta}{T} - 2\ln\left(\frac{T}{\theta}\right)\right] + \frac{\Delta^3 C_p^{\ominus}(\theta)}{R}\left(\frac{\theta^2}{12}\right)\left[\left(\frac{T}{\theta}\right)^2 - 6\left(\frac{T}{\theta}\right) + 3 + 2\left(\frac{\theta}{T}\right) + 6\ln\left(\frac{T}{\theta}\right)\right] + \frac{\Delta^4 C_p^{\ominus}}{R}\left(\frac{\theta^3}{72}\right)\left[\left(\frac{T}{\theta}\right)^3 - 6\left(\frac{T}{\theta}\right)^2 + 18\left(\frac{T}{\theta}\right) - 10 - 3\left(\frac{\theta}{T}\right) - 12\ln\left(\frac{T}{\theta}\right)\right]$	$\Delta C_p^{\ominus} = \Delta C_p^{\ominus}(\theta) + \Delta^2 C_p^{\ominus}(\theta) \times (T-\theta) + (\Delta^3 C_p^{\ominus}/2)(T-\theta)^2 + (\Delta^4 C_p^{\ominus}/3)(T-\theta)^3$
K		$\ln k = \ln k(\theta)T/\theta + \ldots\ldots$	

acid the fit is as good as that obtained by the Valentiner equation, but the correlation coefficient between the estimates of the second and third terms, c_{23}, is much lower, 0.153. Indeed we have commented that the Valentiner equation uses as one boundary value the temperature $T = 1$. If the Scott equation is rewritten in terms of the reference temperature $\theta = 1$, eq 35 is recovered. Similarly if $\Delta C_p^{\ominus}$ is set equal to 0 and $\theta = 1$, we recover eq 1 of Table VI. If θ corresponds to the temperature at which ln K is a maximum, the Scott equation simplifies to the following.

$$\ln K = \ln K_m(\theta) + \frac{\Delta C_p^{\ominus}}{R}\left[\frac{\theta}{T} - 1 + \ln\left(\frac{T}{\theta}\right)\right] \quad (47)$$

A link between eq 47 and eq 10 of Table VI can be established if $\Delta C_p^{\ominus}$ is set equal[77] to -40 cal mol^{-1} K^{-1}. Therefore eq 47 can be rewritten as follows.

$$\ln (K/K_m) = 8.74\left[\frac{\theta}{T} - 1 + \ln\left(\frac{T}{\theta}\right)\right] \quad (48)$$

If eq 48 and eq 10 of Table VI are equivalent, the two temperature functions should be linearly related. Indeed over the range $273.15 \leq T \leq 373.15$ this turns out to be the case, the ratio of the term in eq 48 to $(T-\theta)^2$ being, for acetic acid, 5.76×10^{-5}.

(b) Three-Term Polynomial Equation. The equation discussed above prompts the extension of the polynomial for $\Delta H^{\ominus}$ to three terms[78] on the basis of a Taylor expansion about the temperature θ (Table XII). We recall that proof of the Taylor expansion starts with a polynomial for the function, f(x). Differentiation with respect to temperature leads to an equation showing a linear dependence of $\Delta C_p^{\ominus}$ on T and integration leads to the required linear equation for ln K, in terms of the four parameters, ln $K(\theta)$, $\Delta H^{\ominus}(\theta)/R$, $\Delta C_p^{\ominus}(\theta)/R$, and $\Delta^2 C_p^{\ominus}/R$. Although the equation can be used to fit the data for both acetic (cf. Table IX) and cyanoacetic acid (cf. Table VII), the standard deviation on the estimate for $(\Delta^2 C_p^{\ominus}/R)$ is such that incorporation of this term is not significant at the 95% level of confidence.

Equation 2 for ln K given in Table XII resembles that given by Eyring and co-workers.[78] Another derivation is to start with a four-term polynomial ($n = 4$ in eq 46) in $T - \theta$. The equation for $\Delta H^{\ominus}(\theta)$ [cf. eq 12 of Table VI] can be used to obtain an expression for a_2. Combination with the equation for $\Delta C_p^{\ominus}(\theta)$ leads to an expression for a_3 in terms of $\Delta H^{\ominus}(\theta)$ and $\Delta C_p^{\ominus}(\theta)$. Differentiation of the equation for ΔC_p^{θ} yields an expression for $\Delta^2 C_p^{\ominus}(\theta)$. Because it is assumed that $\Delta^2 C_p^{\ominus}$ is independent of temperature, all terms in this equation containing $T - \theta$ are 0 so that a_4 can be related to $\Delta H^{\ominus}(\theta)$, $\Delta C_p^{\ominus}(\theta)$, and $\Delta^2 C_p^{\ominus}$. The final equation is given as eq 13 in Table VI.

The difference in sign on the enthalpy parameters in the third and fourth terms between eq 13 (Table VI) and that given by Eyring[78] is a consequence of the binomial expansion used by Eyring for T^{-1}. If θ corresponds to the temperature where ln K is a minimum and if $\Delta^2 C_p^{\ominus}$ is 0 we recover the Harned and Embree equation[53] (eq 10 of Table VI). If in eq 2 of Table XII we set $\Delta^2 C_p^{\ominus}(\theta)$ equal to 0, we recover eq 1 of Table XII for the dependence of ln K on temperature. It is also noteworthy that in eq 13 of Table VI there is no term in ln T. This feature does not bear out the claim that

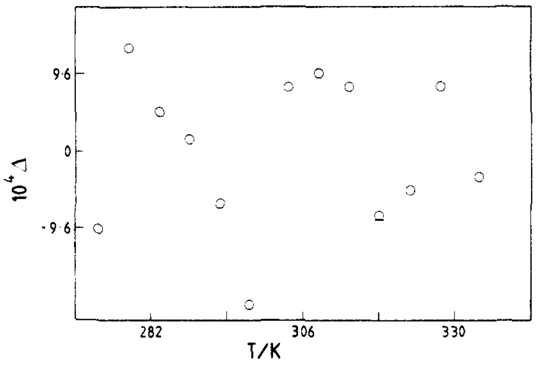


Figure 9. Dependence on temperature of the difference, Δ, between calculated and observed values of $\ln K$ for the self-dissociation constant of water[60] following analysis using eq 3 of Table XII.

TABLE XIII. Self-Dissociation Constant for Water[49]

analysis: eq 3 of Table XII

$\theta = 298.15$ K; $\hat{\sigma} \ln K = 1.069 \times 10^{-3}$

$\Delta H^\ominus(\theta) = 56.196$ kJ mol^{-1}; SE = 29 J mol^{-1}

$\Delta C_p^\ominus(\theta) = -216.8$ J mol^{-1} K^{-1}; SE = 1.8 J mol^{-1} K^{-1}

$\Delta^2 C_p^\ominus = 1.54$ J mol^{-1} K^{-2}; SE = 0.27 J mol^{-1} K^{-2}

equations which omit such a term are purely empirical, a comment we take to imply a criticism.

(c) Clarke and Glew Equation. The treatment outlined above prompts the development of an equation which extends the Taylor expansion for the dependence of $\Delta H^\ominus$ on temperature about $\Delta H^\ominus(\theta)$ at θ. This treatment forms the basis of the Clarke–Glew equation[79] for the dependence of $\ln K$ on temperature. The equation (3 of Table XII) for $\Delta H^\ominus$ is differentiated with respect to temperature, yielding a series for the heat capacity, $\Delta C_p^\ominus$ in terms of $\Delta C_p^\ominus(\theta)$; integration yields the equation for $\ln K$. As in the case of the polynomial equation for $\ln K$ (eq 46) it is necessary to test the significance of adding each new term in the expression. The Taylor expansion requires[79] that we cannot set one of the terms (e.g., the second) to zero and use higher terms (e.g., the third) in the analysis. This means that if, for example, $\Delta C_p^\ominus(\theta)$ or $\Delta C_p^\ominus(\theta)$ is 0, the analysis will not lead to satisfactory values for $\Delta^2 C_p^\ominus(\theta)$ or $\Delta^2 C_p^\ddagger(\theta)$. Two examples of the application of Clarke–Glew equation to equilibrium data show that the analysis yields a satisfactory fit of the data. The derived parameters are summarized in Table VII for cyanoacetic in water.[52] In the case of the self-dissociation constant for water,[60] a four-term equation is statistically significant (Table XIII and Figure 9). The small but significant disagreement between values of $\Delta H^\ominus$ (298.15 K) for the self-dissociation obtained by emf. and calorimetric methods has prompted comment and considerable efforts to resolve the disagreement.[60] The calorimetric value, 55.815 J mol^{-1}, is slightly lower.[80-82] The current best value[60] for the pK_w of water at 298.15 K is 14.004. The value of $\Delta C_p^\ominus$ at 298.15 (Table XIII) is in good agreement with the value, -215 ± 4 J mol^{-1} K^{-1}, obtained from measurement of heat capacities of solutions using a flow microcalorimeter.[83]

The Clarke–Glew equation can also be used to analyze kinetic data. Thus for the solvolysis in water of ethyl bromide,[58] it is significant to calculate the dependence of $\Delta C_p^\ddagger$ on temperature in terms of its first derivative (Table X). It is interesting to observe that the equation predicts that $\Delta C_p^\ddagger$ becomes less negative with increase in temperature (cf. Figure 7a). However for the solvolysis in water of *tert*-butyl chloride[57] and isopropyl benzenesulfonate,[76] only the estimate for $\Delta C_p^\ddagger$ is statistically significant.

In their application of the analysis, Clarke and Glew[79] were particularly concerned with the numerical precision in the calculation because $T - \theta$ is smaller than θ. The equations were recast by defining a new variable, x $[(T - \theta)/\theta]$. This procedure is probably not so important if the calculations are carried out on a main frame computer employing a large number of bits per word. However this procedure should be followed if the calculations are performed using a small desk-top calculator.

If only four terms are used in the Clarke–Glew expression, we recover eq 2 in Table XII, and if only three terms are used, we recover[84] eq 1 in Table XII. The Clarke–Glew equation has attracted considerable attention. Bolton[85] strongly recommends this analytical procedure on the grounds that it is simple to use, nonempirical, and exact. The latter two descriptive terms seem rather sweeping. Clarke and Glew[79] claim that the analysis provides a unique, thermodynamically meaningful, and completely general representation of the data. For our part, we would claim the use of the word "unique" in this context is slightly overoptimistic. We do not agree with the statement by Wold[86] that the Clarke–Glew analysis uses an orthogonalization procedure. One important feature of the Clarke–Glew and related polynomial equation is that each thermodynamic parameter at temperature θ is related to one parameter obtained from the least-squares analysis. A further consequence is that if θ is near the middle of the experimental range, the standard errors on these quantities are less than those based on, say, the Valentiner equation where the effective reference is at $T = 1$. As θ moves away from the mean temperature, the standard errors increase. The correlation coefficients between estimates show a marked and complex dependence on θ.

Comparison between thermodynamic parameters derived from the above analytical techniques and those from calorimetric data raises a number of issues. In particular there is the question as to the precision necessary in the experimental determination of equilibrium constants which will lead to reliable estimates of the dependence of $\Delta C_p^\ominus$ on temperature. Timini[87] used the Clarke–Glew equation to show that reliable values of this dependence require data covering a temperature range not less than 60 K and preferably 100 K with measurements at intervals of 5 K. The comparisons[87] drawn between values of $\Delta C_p^\ominus$ calculated from equilibrium constants and from calorimetric data[88] point to a pessimistic conclusion and, at the same time, present a challenge to the experimentalist. Ramette[89] introduces a cautionary note in warning about attempts to derive more information about $\Delta C_p^\ominus$ terms from the dependence of equilibrium constants on temperature than the data can possibly contain.

7. Linear Equations Describing the Dependence on Temperature of Heat Capacity Quantities

These equations start out with a description of the dependence of, say, $\Delta C_p^\ominus$ on temperature. Integration in conjunction with a defined $\Delta H^\ominus(\theta)$ at reference tem-

TABLE XIV. Equations Describing the Dependence on Temperature of Heat Capacity Parameters

equation	$\Delta H^\ominus$	$\ln K$
1. Lewis and Randall		
$\Delta C_p^\ominus = a_1 + a_2T + a_3T^{-2}$	$\Delta H^\ominus = \Delta H^\ominus(\theta) + a_1(T-\theta) + (a_2/2)(T-\theta)^2 - a_3(T^{-1} - \theta^{-1})$	$\ln K = \ln K(\theta) + \frac{\Delta H^\ominus(\theta)}{R}\left[\frac{1}{\theta} - \frac{1}{T}\right] + \frac{a_1}{R}\left[\frac{\theta}{T} - 1 + \ln\left(\frac{T}{\theta}\right)\right] + \frac{a_2}{2R}\left[T - 2\theta + \frac{\theta^2}{T}\right] + \frac{a_3}{R}\left[\frac{1}{2T^2} + \frac{1}{2\theta^2} - \frac{1}{T\theta}\right]$
2. Clever		
$\Delta C_p^\ominus = a_1 + a_2T + a_3T^2$	$\Delta H^\ominus = \Delta H^\ominus(\theta) + a_1(T-\theta) + (a_2/2)(T^2 - \theta^2) + (a_3/3)(T^3 - \theta^3)$	$\ln K = \ln K(\theta) + \frac{\Delta H^\ominus(\theta)}{\mathrm{R}}\left[\frac{1}{\theta} - \frac{1}{T}\right] + a_1\left[\frac{\theta}{T} - 1 + \ln\left(\frac{T}{\theta}\right)\right] + \frac{a_2}{2R}\left[T - 2\theta + \frac{\theta^2}{T}\right] + \frac{a_3}{6R}\left[T^2 - 3\theta^2 + \frac{2\theta^3}{T}\right]$

perature θ leads to an equation for the dependence of $\Delta H^\ominus$ on temperature. A second integration leads to an equation for the dependence of ln K on temperature.

(a) **Lewis and Randall Equation.** This equation[90] describes the dependence of $\Delta C_p^\ominus$ on T (Table XIV) interms of a three-term expression. The resulting equation for ln K contains five parameters: ln $K(\theta)$, $\Delta H^\ominus(\theta)$, a_1, a_2, and a_3. The first three terms are identical with those found in the Clarke–Glew equation[79] (Table XII).

(b) **Clever Equation.** This equation[91] expresses the dependence of $\Delta C_p^\ominus$ on T in terms of the first three terms of a polynomial in T (Table XIV). The resulting equation for ln K contains five unknowns: ln $K(\theta)$, $\Delta H^\ominus(\theta)$, a_1, a_2, and a_3.

B. Analysis Using Nonlinear Least-Squares Techniques

In this section we turn our attention to those equations which describe the dependence of equilibrium or rate constant on temperature but which cannot be analyzed by using conventional linear least-squares techniques. The equations under this general heading differ in an important fashion from those described in the previous section. There we endeavored to fit the data to an equation, the criterion being in many instances simply the goodness of fit. In this section the equations have often been derived bearing in mind some particular explanation for the dependence of K (or k) on temperature. However, this means that the equations in this section are not necessarily related to each other in the manner shown by those discussed in section A. One exception is described in Table VI (eq 15) which expresses ln k as a linear function of T^{a_3} where a_3 is a variable depending on solute and solvent but not on temperature. Kinetic data can be fitted to this equation by using a linear least-squares analysis for estimates $\hat{a}_1$ and $\hat{a}_2$ at a preselected value for $\hat{a}_3$. The analysis is repeated for various values of $\hat{a}_3$ to obtain the set $\hat{a}_1$, $\hat{a}_2$, and $\hat{a}_3$ which minimizes the variance. This is most readily achieved by using a loop instruction within a computer program.

1. Gurney Equation

This equation[44] was developed in order to account for the dependence on temperature of ln K for carboxylic acids in water. In particular, Gurney attempted to account for the observation that ln K often shows a maximum value at some temperature within the window. Indeed we noted that the Harned and Embree equation could not be analyzed with linear least-squares methods for both a_1 and θ, where θ is the temperature at which ln K is a maximum. The Gurney equation (Table XV) has the same property although here the temperature θ has a different meaning. Gurney argued[4] that if the acid dissociation constant is determined solely by the electrical interaction between solute and solvent, the acid dissociation constant would show a maximum at θ. Contributions from the nonelectrical forces shift the maximum, although these forces are not dependent on θ but are dependent on T. Indeed Gurney argued that θ can be calculated from the dielectric properties of the solvent, being equal to 219 K for water. Gurney[44] expressed the dependence of ln K on temperature using eq 1 of Table XV. We have rewritten it in the form shown in eq 2 (Table XV), and hence the temperature T_m at which ln K is a maximum is given by the following.

TABLE XV. Gurney Equation

$$\ln K = -\frac{C}{T}[a + \exp(T/\theta)] \tag{1}$$

$$\ln K = a_1T^{-1} + (a_2/T)\exp(T/\theta) \tag{2}$$

$$\Delta H^\ominus = \mathrm{R}[-a_1 - a_2\exp(T/\theta) + (a_2T/\theta)\exp(T/\theta)] \tag{3}$$

$$\Delta C_p^\ominus = (a_2T\mathrm{R}/\theta^2)\exp(T/\theta) \tag{4}$$

$$T_m = \theta[1 + a_1/(a_2 \exp[T_m/\theta])] \tag{49}$$

Equation 2 (Table XV) is readily differentiated to yield the required matrices for a nonlinear least-squares analysis (section IVB).

In the case of acetic acid in water,[49] the Gurney equation fits the data reasonably satisfactorily,[92] the residual sum of squares being 3.19×10^{-5}. A plot of the residuals against temperature produces a reasonable scatter of points greater than and less than 0. The calculated value for θ, 184 K, is some way removed from that suggested by Gurney. The significance of this finding and the θ values for other acids will be discussed elsewhere[92] except to note that for eq 1 in Table XV, $c = 4.066 \times 10^2$ and $a = 3.0008$ for acetic acid. A plot of a_1T^{-1} and a_2T^{-1} exp (T/θ) against temperature (Figure 10) shows how the first term shifts the maximum in ln K from θ to around 298 K.

2. Equilibrium Constants—Model II

The Gurney equation[4] provides an example of an equation based on a particular explanation for the form adopted by the dependence of K on T. However in terms of the underlying chemical explanation of the observed dependence the approach is based on model I (Table III) for the chemical equilibrium, as indeed are

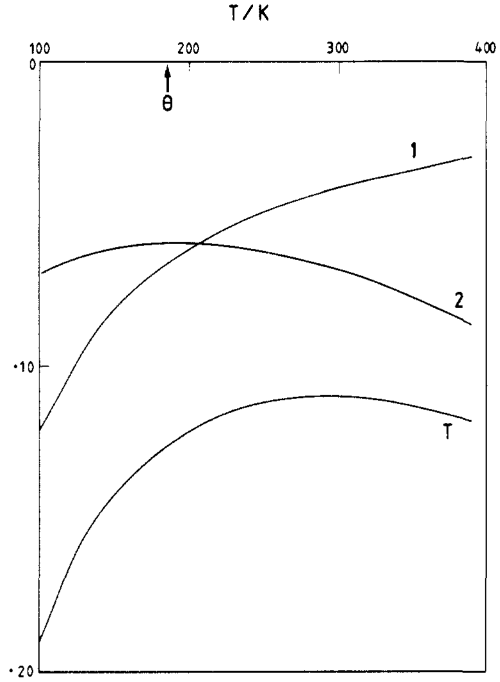


Figure 10. Dependence on temperature of a_1T^{-1} (curve 1), $a_2T^{-1}\exp(T/\theta)$ (curve 2), and their sum (curve T) for acetic acid in water[49] following analysis using eq 2 of Table XV.

TABLE XVI. Dependence on Temperature—Model II

Equilibria

$$K_1 = a_3 \exp(a_4/T) \tag{1}$$

$$K_2 = a_1 \exp(a_2/T) \tag{2}$$

$$K = \frac{a_1 \exp(a_2/T)}{1 + a_3^{-1}\exp(-a_4/T)} \tag{3}$$

Kinetics

$$k_1 = a_1 \exp(a_2/T) \tag{4}$$

$$\alpha = a_3 \exp(a_4/T) \tag{5}$$

$$k = \frac{a_1 \exp(a_2/T)}{1 + a_3 \exp(a_4/T)} \tag{6}$$

the descriptions underlying the equations described in the previous section. If, for example, model II is taken as the description of the chemical equilibrium, the dependence of the measured equilibrium constant on temperature is accounted for in terms of the dependence of K_1 and K_2 on temperature. The horrendous possibility emerges that the dependence of both $\ln K_1$ and $\ln K_2$ on temperature can be described by any one of the equations discussed in section A. However a compromise is now sought. Because we have adopted a more complicated description of the chemical equilibrium (i.e., model II rather than model I in Table III), we choose to adopt a simple equation for the dependence of $\ln K_1$ and $\ln K_2$ on T, i.e., eq 1 of Table VI. In section A we adopted a simple model for the equilibrium and complicated equations for the temperature dependence. A derivative of model II assumes that $\Delta C_p^\ominus(1)$ and $\Delta C_p^\ominus(2)$ and higher derivatives are 0. The final equation for the dependence of K on T (eq 3 of Table XVI) is differentiated to obtain the matrices for a nonlinear least-squares analysis. In practice we need to guess some initial values for these unknown parameters. Further it is advisable to incorporate into the equation appropriate powers of ten such that the derived quantities are close to unity. However, in common with nonlinear least-squares analysis, some "a priori" restrictions can be placed on the derived parameters.

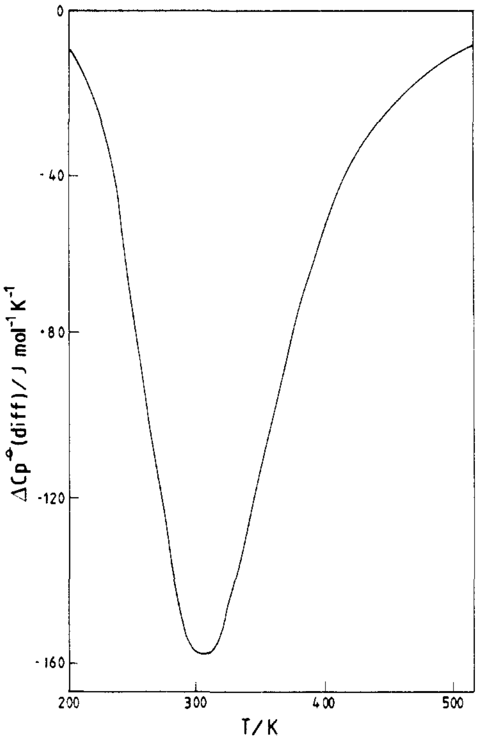


Figure 11. Dependence on temperature of $\Delta C_p^\ominus$(diff) as defined in eq 2 for acetic acid in water.[49]

In the present example, a_1 and a_3 must be positive, negative equilibrium constants being disallowed.

The data for acetic acid in water have been fitted[92] to eq 3 of Table XVI to yield $\Delta H_1^\ominus = -22.7$ kJ mol^{-1} and $\Delta H_2^\ominus = 7.33$ kJ mol^{-1}. At 298.15 K, $K_1 = 1.940$ and $K_2 = 2.660 \times 10^{-5}$ mol^{-1} kg. The calculated dependence on temperature $\Delta C_p^\ominus$(diff) as defined in eq 2 is shown in Figure 11, the graph showing a minimum near 305 K where $\Delta C_p^\ominus(\text{diff}) = -159$ J mol^{-1} K^{-1}. Thus in terms of model II (Table III) the maximum in $\ln K$ arises from two contributing equilibria having different dependences on temperature.

3. *Kinetic Data*

In this section we consider the description of the dependence of rate constant on temperature in terms of the separate dependences of k_1 and α on temperature as described in model II of Table V. As a derivative of model II, we assume that $\Delta C_p{}^{\ddagger}{}_1$ and $\Delta\Delta Cp^{\ddagger}$ are 0 on the grounds that the complexity in the chemical model is combined with a simple description of the dependence on temperature of both k_1 and α (cf. eq 1 of Table VI). If this is accepted, then the dependence of k on temperature is described by eq 6 of Table XVI, which can be fitted to the data by using a nonlinear least-squares technique.

This analysis has been applied[92] to the data for the solvolysis of *tert*-butyl chloride in water.[57] The residuals Δ scatter about 0, the sum of squares of the residuals on 20 data points being 1.984×10^{-9}. The resulting values at 298.15 K for $\Delta H_1^{\ddagger}$ and $\Delta\Delta H^{\ddagger}$ are 104.6 and −49.636 kJ mol^{-1}, respectively. Thus both k_1 and α increase with increase in temperature, α being unity at 316.7 K. The value of $\Delta C_p^{\ddagger}$(app) predicted by this description of the kinetic process (eq 7) is negative, being a minimum near 320 K (Figure 12). Thus the explanation in terms of model II of the negative $\Delta C_p^{\ddagger}$ values obtained from model I (Table V) is in terms of

TABLE XVII. Dependence of Equilibrium and Rate Constants on Pressure

analysis	equation	volume parameter
	Phenomenon: 1. Linear	
E	$\ln K = a_1 + a_2p$	$\Delta V^{\ominus} = -a_2RT$
K	$\ln k = a_1 + a_2p$	$\Delta V^{\ddagger} = -a_2RT$
	2. Laidler	
K	$\ln k = \ln k(\pi) + a_1(p - \pi)$	$\Delta V^{\ddagger} = -a_1RT$
	3. Polynomial in Pressure	
E	$\ln K = a_1 + a_2p + a_3p^2 + a_4p^3$	$\Delta V^{\ominus} = -RT(a_2 + 2a_3p + 3a_4p)$
K	$\ln k = a_1 + a_2p + a_3p^2 + a_4p^3$	$\Delta V^{\ddagger} = -RT(a_2 + 2a_3p + 3a_4p)$
	4. Polynomial with Reference	
K	$\ln k = \ln k(\pi) + a_2(p - \pi) + a_3(p - \pi)^2 + a_4(p - \pi)^3$	

a different description of the chemical process. Purely on the basis of the dependence of rate constant on temperature, it is not possible to state which description of the chemical process is correct. However model II might be deemed more satisfactory because if we use model I it is necessary to explain quite large values for $-\Delta C_p^{\ddagger}$. This is not the place to become involved in these arguments. Nevertheless the point is made concerning the element of choice in terms of the model for the chemical process, but the choice determines what parameters must be accounted for in each case. (We are currently exploring the application of the above analysis to the kinetic data for reactions in mixed solvents.[92])

The problems of interpretation and analysis may of course diminish as data covering a wider temperature range become available, i.e., the window is expanded. A recent example is to be found in the examination of the kinetics of solvent exchange at metal cations. The notorious unreliability[93,94] of NMR-derived data for certain metal ions, e.g., Ni^{2+}, has led to the establishing of exchange rates over as wide a range of temperatures as possible in certain systems. Thus by combining results from NMR line-shape analysis with results from recently developed[95] stopped-flow Fourier transform NMR experiments, it has proved possible to assemble rates of exchange of dimethyl sulfoxide at, e.g., Ga^{3+} over a temperature range of 112 K.[96] These results indicate that the plot of ln k against T^{-1} for this reaction is very close to linearity; the aforementioned doubts about the accuracy of the line-shape results preclude a meaningful analysis of this type of reaction by the methods described above for, e.g., solvolysis of *tert*-butyl chloride.

VI. Description of the Dependence on Pressure of Equilibrium and Rate Constants

We now turn our attention to analysis of data where the variation of rate and equilibrium constants with pressure is under consideration.[4,5] The problems encountered here are very similar to those discussed in section V. We have commented that thermodynamics does not define how ln k or ln K depends on pressure, but often the aim is to analyze this dependence to extract further information. The usual practice is to adopt a simple description for the chemical process (e.g., model I of Tables III and V) and hence estimate $\Delta V^{\ominus}$ or $\Delta V^{\ddagger}$ and related pressure parameters. The dependence of ln k or ln K on pressure is usually written in a manner amenable to an analysis using linear least-square techniques. We consider various methods under this heading in the next section. A problem in this subject is the many units used to measure pressure. For our part we have used the SI unit, N m^{-2}. An advantage is that the volume quantities are obtained directly from the analysis in m^3, avoiding the necessity of working with complicated conversion factors.

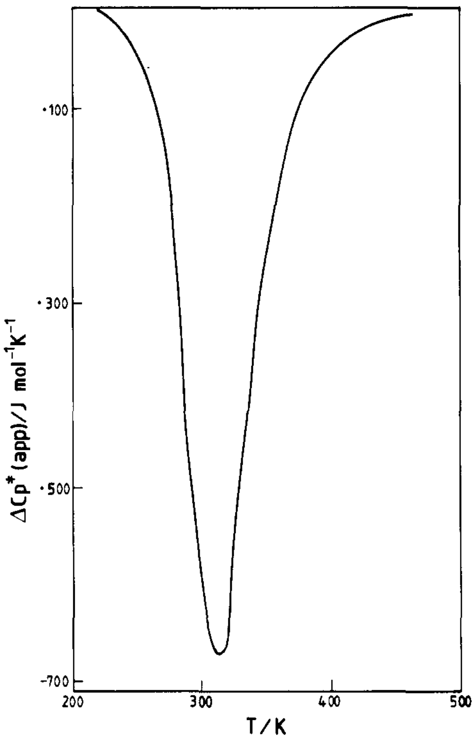


Figure 12. Dependence on temperature of $\Delta C_p^{\ddagger}$(app) as defined by eq 7 for *tert*-butyl chloride in water.[57]

A. Analysis Using Linear Least-Squares Techniques

1. Linear Dependence on Pressure

The simplest equation takes note of the thermodynamic hint (Table I) and expresses ln k or ln K as a linear function of pressure (Table XVII). As a result, $\Delta V^{\ddagger}$ is, for example, independent of pressure, and a_1 (eq 3 of Table XVII) is the value of ln k when $p = 0$.

The data[5] describing the dependence of rate constant on pressure for the solvolysis of benzyl chloride in water at 333.65 K produce the parameters summarized in Table XVIII. The fit is adequate, indicating that $\Delta V^{\ddagger}$

TABLE XVIII. Dependence of Rate Constant on Pressure

equation	$\hat{\sigma}$ ln k	$\Delta V^{\ddagger}$/cm^3 mol^{-1} [a]	$10^{14}\Delta\beta^{\ddagger}$/m^3 mol^{-1} (N m^{-2})$^{-1}$ [a]	comments
eq 1[b] (Table XVII)	0.926×10^{-3}	−10.77 (0.12)		$c_{12} = -0.8472$
eq 3[c] (Table XVII)	1.41×10^{-2}	−25.04 (0.73)	3.14 (0.42)	

[a] At 101325 N m^{-2}. [b] *tert*-Butyl chloride in water. [c] *tert*-Butyl chloride in water + *tert*-butyl alcohol ($x_2 = 0.1$).

is essentially independent of pressure. (The data[5] for the same system but in a mixture containing mole fraction $x_2 = 0.1$ of *tert*-butyl alcohol are not satisfactorily accounted for, a plot of the residuals showing a smooth dependence on pressure.) The correlation function c_{12} is −0.8472 for the same reasons discussed in section VA. As before, this coefficient decreases if the dependence of ln k on pressure is analyzed by using the Laidler[97] equation (Table XVIII). This equation fits the dependence about a reference pressure π. If this approach is adopted, then the correlation function drops to −0.144 for the same set of data.

2. Polynomial Dependence on Pressure

In this analysis, the dependence of ln K or ln k on pressure is expressed as function of a polynomial in p (Table XVII). For kinetic data,[74] it is rarely significant to go beyond the quadratic form. An example is given in Table XVIII for the solvolysis of benzyl chloride in an aqueous mixture[98] where it is statistically significant to consider the cubic term. In this case $\Delta V^{\ddagger}$ is not adequately represented as a linear function of pressure. A plot of the residuals Δ show a scatter about 0 and no clear dependence on pressure. The calculation of a compressibility term has attracted considerable interest over many years because it has been used as an indicator of mechanistic details, e.g., contrasting associative and dissociative reactions. However the use of the compressibility term in this context seems to have been discounted recently.

The representation of the dependence using the equations set down in Table XVII raises two issues. In analogous fashion to the arguments given previously, it is dangerous to imply that given a "well-behaved" system then ln k or ln K will be linear functions of pressure. The latter is not a thermodynamic requirement. The second issue concerns the significance of the term a_1 (Table XVII). As it stands, a_1 is related to ln k or ln K when $p = 0$. This is not a real situation. In some cases it is implied that the intercept is the value of, say, ln k at zero applied pressure. This is not correct. It may be advantageous in terms of avoiding these conceptual problems if the equation were recast to express the dependence of ln k on pressure about some reference pressure π as shown in eq 4 of Table XVII along the lines suggested by Burris and Laidler.[97]

3. Benson–Berson Equation

This treatment[99] of the dependence of rate constant on temperature is rather more sophisticated than the analyses discussed above. Although restricted to nonionic reactions (e.g., Diels–Alder reactions), an attempt is made to describe quantitatively the compressibility characteristics of the system using the Tait equation (see ref 3). As a result if the reference pressure π is 101325 N m^{-2}, a plot of (π/p) ln $(k/k[\pi])$ against $(p-\pi)^{0.523}$ is constructed to yield $\Delta V^{\ddagger}(\pi)$ from the intercept and information concerning the partial molar volume of the initial state from the slope.

B. Analysis Using Nonlinear Least-Squares Techniques

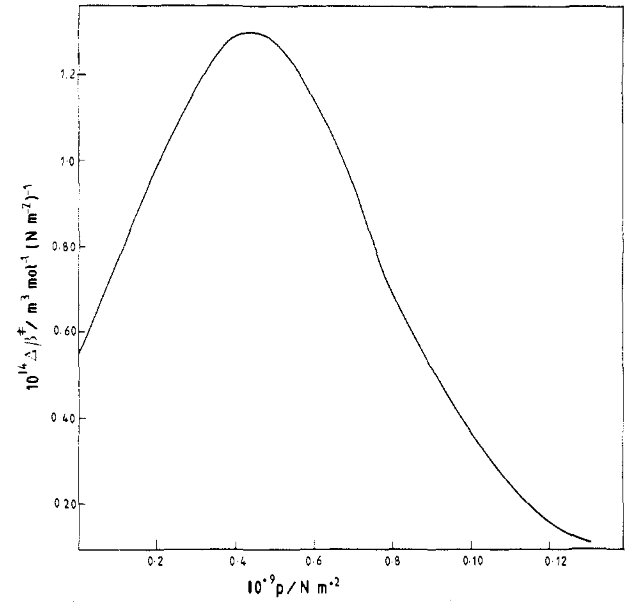


Figure 13. Dependence on pressure of $\Delta\beta^{\ddagger}$(app) as defined by eq 8 for the aquation of nitritopentaamminecobalt(III) in water[101] at 298 K.

As in the discussion of rate and equilibrium constants on temperature, the equations in this section have been developed bearing in mind particular models for the chemical process. Those equations outlined in the previous section take as the starting hypothesis model I (Table V) for the chemical reaction. If other models (e.g., model II, Table V) are used, the final equation for the dependence of rate constant on pressure cannot be analyzed with a linear least-squares analysis. By the same token, different models may be proposed for individual systems. Similarly the same set of kinetic data can be analyzed in different ways. We illustrate this point by reference to the data[100] describing the dependence on pressure of the first-order rate constant for the aquation of nitritopentaamminecobalt(III) in water at 298 K. The data were originally analyzed[100] in terms of model I (Table V) and eq 3 of Table XVII (with 3 terms). However it is also possible to reanalyze the data[101] according to model II (Table V). It is assumed that both ln k and ln α are linear functions of pressure (eq 1, Table XVII). Hence the dependence of k(obsd) on pressure about a mean reference pressure π can be written

$$k(\text{obsd}) = k(\pi)\exp[a_1(p-\pi)]\frac{1 + a_2\exp(-a_3\pi)}{1 + a_2\exp(-a_3 p)} \quad (50)$$

Consequently when $p = (\ln a_2)/a_3$, α is 1.0, a_1 being related to $\Delta V_1^{\ddagger}$ and a_3 to $\Delta V_3^{\ddagger} - \Delta V_2^{\ddagger}$ ($\Delta\Delta V^{\ddagger}$). The data were fitted to eq 48 by use of a nonlinear least-squares technique. The fit was satisfactory, with a residual sum of squares equal to 9.30×10^{-12}, yielding $\Delta V_1^{\ddagger} = 4.5$ cm^3 mol^{-1} and $\Delta\Delta V^{\ddagger} = -11.1$ cm^3 mol^{-1}. Although with increase in pressure k(obsd) increases, the calculated values of k_1 and α decrease the latter, being equal to 1 when $p = 4.397 \times 10^8$ N m^{-2}, which is just above the experimental range. If it is assumed that $\Delta\beta_1^{\ddagger}$ and $\Delta\Delta\beta^{\ddagger}$ (Table V) are 0, the plot of $\Delta\beta^{\ddagger}$ (eq 5) is always positive and shows a maximum when p is approximately 4.353×10^8 N m^{-2} (Figure 13). A similar analysis[102] of the kinetic data[98] for solvolysis of benzyl chloride at 333 K in water containing 0.1 mole fraction *tert*-butyl alcohol shows that in terms of the same kinetic model $\alpha = 1.0$ at $p = 1.736 \times 10^8$ N m^{-2}, which is within the measured pressure range, $\Delta\beta^{\ddagger}$ being a maximum at 3.939×10^{-14} m^3 mol^{-1} (N m^{-2})$^{-1}$ when $p = 1.718 \times 10^8$ N m^{-2}.

VII. Conclusions

At the outset, we suggested that it seemed timely to review this subject. In part this feeling was generated by the development of more sophisticated measurement and control devices, of data-logging equipment, and of computer-based analytical routines. There seems a widespread increase in the precision of experimental results, although the dependence of K or k on pressure seems to lag in precision the dependence on temperature. These developments can be thwarted by poor analysis of the good data, leading to an unsatisfactory discussion of the factors influencing the chemical processes under investigation. One conclusion which emerges from this review is that there is no universally correct method of analyzing equilibrium and kinetic data. Each method has its own limitations and constraints which may not be immediately apparent. Any conclusions reached about the chemistry depend on the model adopted and the method of analysis—"as you sow, so shall you reap".

The problems which we have stressed can be illustrated as follows. Suppose that we are presented with a set of rate constants for a given reaction over a range of temperatures, the window. The first exercise undertaken might be to assume a simple model for the reaction (model I, Table V) and a simple equation relating ln k and T (e.g., eq 1 of Table VI). If this proves inadequate, two options are available. We can adopt the same model for the reaction and accept varying degrees of complexity in the dependence of $\Delta H^{\ddagger}$ on temperature. Alternately we can adopt a more complicated model for the reaction (Table V) and a simple equation for the dependence of each contributing rate constant on temperature. Finally we might decide to adopt a complex model for the reaction and a more complicated model for the dependence of thermodynamic activation parameters on temperature. Running through this line of argument with respect to both equilibrium and kinetic data is an element of optimism. This arises because it is assumed at the outset that by measuring the dependence of, say, one dependent variable K on one independent variable T it is possible to extract a range of parameters characterizing changes in thermodynamic functions of state, e.g., $\Delta H^{\ominus}$, $\Delta S^{\ominus}$, $\Delta C_p^{\ominus}$ .... . Almost certainly, therefore, thermodynamics and the relationships obtained therefrom provide the basis of the analysis. We have attempted to show how from that point on all aspects of the analysis require critical evaluation.

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