Analysis of the Dependence of Acid Dissociation Constants on Temperature

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Analysis of the dependence on temperature of acid dissociation constants of weak acids in aqueous solution is considered from two standpoints. First, methods which assume a single-step reversible dissociation characterised by an acid dissociation constant K are examined with particular reference to the least-squares technique for deriving the required parameters. The importance is stressed of examining the structure of the model especially where high correlation factors are obtained between derived parameters. A method of analysis is proposed based on a polynomial in $(T - \theta)$ where θ is a reference temperature. The results of applying this technique to several sets of data are discussed with comparison, where possible, with thermochemical data. Second, the data are examined using a two-stage equilibrium process for the dissociation. The temperature dependence of K can be satisfactorily described by the final equation which contains two enthalpy terms, characterising the two reversible stages. The derived parameters indicate that the dissociation proceeds through an ion-pair intermediate.

FOR a single-stage chemical equilibrium in a closed system at fixed pressure, the van't Hoff equation relates the differential of the equilibrium constant, K with respect to temperature to the enthalpy change $\Delta H^{\ominus}$ [equation (1)].

$$\mathrm{d}\ln K/\mathrm{d}T = \Delta H^{\ominus}/RT^2 \qquad (1)$$

Here R is the gas constant. However, application of equation (1) to the analysis of experimental data comprising values of K at different temperatures is not straightforward. If it is assumed that $\Delta H^{\ominus}$ is independent of temperature, integration of equation (1) results in the familiar equation which requires that ln K is a linear function of T^{-1}, $\Delta H^{\ominus}$ being obtained from the slope. In many cases, this assumption is obviously unacceptable.[1] It follows therefore that either $\Delta H^{\ominus}$ is dependent on temperature or the measured equilibrium constant describes more than a single-stage reversible process. If the latter possibility is ruled out, the analysis is still complicated by the fact that there is often no '*a priori*' indication of the form taken by the dependence of $\Delta H^{\ominus}$ on temperature. A considerable literature [2] describes how further progress can be made. Some methods presuppose a particular form for the dependence of $\Delta H^{\ominus}$ on temperature; a linear dependence requires that the heat capacity term, $\Delta C_p^{\ominus}$, is independent of temperature. Other methods fit the dependence of ln K on temperature to an empirical equation, differentiation yielding $\Delta H^{\ominus}$ [equation (1)]. However, in both cases, the numerical analysis usually relies on the linear least-squares technique to obtain estimates of the required parameters. The present paper is concerned with the structure of the equations upon which the linear least-squares analysis is based and the impact that this structure has on estimates of the parameters. The outcome of our analysis prompted the development of two new methods for analysing the dependence on temperature of equilibrium constants.

The first method assumes that $\Delta H^{\ominus}$ is dependent on temperature and uses a polynomial dependence of ln K on $(T - \theta)$ where θ is a reference temperature near the middle of the experimental range. The second method takes the view that the non-linear dependence of ln K on T^{-1} is observed because K is a function of equilibrium constants K_1 and K_2 describing two equilibria having a common intermediate. The separate dependencies of K_1 and K_2 on temperature are described by equation (1) using the related enthalpy terms, $\Delta H_1^{\ominus}$ and $\Delta H_2^{\ominus}$.

The comments in this paper concerning the analysis of the dependence of K on T were prompted by our interest in the analysis of the dependence of rate constants on temperature for solvolytic reactions in water.[3-5] Granted therefore that we have established a basis for analysing the dependence of K on T, the same techniques can be used to analyse the dependence on temperature of $K^{\ddagger}$, the pseudo-equilibrium quantity calculated from the rate constant using transition-state theory.[6]

Linear Least-squares Analysis.—The linear least-squares method [7,8] yields values for specified parameters which minimise the sum of squares of the deviations between calculated and observed quantities. The standard error $\hat{\sigma}$ provides an indication of the quality of the data. The symmetric variance–covariance matrix θ is calculated from $\hat{\sigma}^2$ and the dispersion matrix. Normalising the matrix θ yields the correlation matrix C. The diagonal elements of C are unity and the off-diagonal elements are between -1 and $+1$. These coefficients C_{ij} (with $i \neq j$) indicate the extent to which the estimates of the β-parameters are dependent. The interdependence between $\hat{\beta}_i$ and $\hat{\beta}_j$ increases as C_{ij} tends to ± 1. The variation in the C matrix with model can be used therefore as a basis for comment on the models themselves.

Valentiner Equation.—The Valentiner equation (1) [9,10] expresses the dependence of ln K on T using three parameters a_i, where $i = 1$—3. A closely related

$$\ln K = (a_1/T) + a_2 \ln T + a_3 \qquad (2)$$

equation is that used by Harned and Robinson [11,12] and by Robinson and Stokes,[13] who replace the term ln T by T to yield the Harned–Robinson equation. Equation (2) requires that $\Delta H^\ominus$ is a linear function of temperature, $\Delta C_p^\ominus$ being equal to a_2R.

The experimental data for 16 systems have been fitted to equation (2). The systems include the dissociation constants for a range of carboxylic acids together with the self-dissociation constants for water [14] and deuterium oxide.[15] For example, the data for acetic acid [1] comprise 13 values of K_A over the range $273.15 \leqslant T \leqslant 333.15$ K. Equation (2) fits the data with a standard error in ln K of 1.988×10^{-8}. The estimates of the coefficients are summarised in Table 1 together with derived values of $\Delta H^\ominus$ and $\Delta C_p^\ominus$ at 298 K. The details for the self-dissociation constants of water and deuterium oxide (molality scale) are also given in Table 1. The coefficients for a further 13 systems are summarised in Table 2. The optimism generated by the excellence of the fit afforded by equation (2) is soon dispelled when the correlation coefficients are examined. In the three examples quoted in Table 1, these coefficients are very close to ±1. The same pattern emerges for all systems listed in Table 2 and indicates that the estimates of the a_i parameters are perfectly correlated. Indeed these high coefficients throw doubts on the validity of equation (2) in describing the dependence of ln K on T. The situation is even more serious because the analysis can produce patterns of behaviour which are completely misleading. We are led to this conclusion by the patterns generated by the linear plots of a_1 and of a_3 against a_2 for the organic carboxylic acids listed in Table 2. Thus not only are the parameters in equation (2) closely correlated between themselves for a given system (see Table 1), they are closely related within a series of chemically similar systems. Rather than indicating some underlying common feature, there is cause for concern that these patterns are artefacts of the analysis. A similar pattern of high correlation factors between derived coefficients is found when the equilibrium data are fitted to the Harned–Robinson equation.[11,12]

TABLE 1

Least squares analysis using Valentiner equation

	Acetic acid	Water	D_2O
$-10^{-3}a_1$/K	5.507	14.337	15.566
Standard error	0.056	0.011	0.015
$-a_2$	18.65	25.36	28.07
Standard error	0.19	0.35	0.51
a_3	113.8	160.3	177.7
Standard error	1.3	2.4	3.4
c_{12}	0.9996	0.9996	0.9998
c_{23}	−0.9999	−0.9999	−1.0000
c_{13}	−0.9997	−0.9997	−0.9998
$\Delta H^\ominus$(298 K)/kcal mol^{-1}	0.698	12.87	13.71
	±0.250 [a]	±0.47	±0.71
$\Delta C_p^\ominus$/cal K^{-1} mol^{-1}	−39.05	−52.37	−57.77
	±0.82	±1.57	±2.38

[a] Limits on thermodynamic parameters calculated at the 95% confidence level. 1 cal = 4.184 J.

TABLE 2

Valentiner parameters for various acids in aqueous solution

	Reference	$-10^{-4}a_1$	$-a_2$	a_3
1 Water	14	1.434	23.35	160.3
2 Cyanoacetic	17	0.5431	19.71	124.82
3 Acetic	1	0.5507	18.65	113.8
4 [$^2H_4$]Acetic–D_2O	18	0.5803	18.99	115.4
5 Deuterium oxide	15	1.557	28.07	177.7
6 Formic	19	0.6215	20.91	131.3
7 Di-isopropylcyanoacetic	20	0.2722	14.86	87.92
8 [$^2H_3$]Acetic	16	0.5020	10.96	102.49
9 Bromoacetic	21	0.5132	19.32	120.60
10 Iodoacetic	21	0.4244	16.63	101.69
11 Chloroacetic	21	0.6404	23.39	148.12
12 Propionic	22	0.5434	18.54	112.62
13 Butyric	23	0.4998	17.96	108.03
14 Dimethylcyanoacetic	24	0.4545	18.43	114.67
15 Isopropylcyanoacetic	24	0.3641	15.92	97.39
16 Acetic–D_2O	25	0.5933	19.45	118.49

A correlation between the estimates of two parameters approaches unity when these parameters attempt to account for the same underlying trend. At ambient pressure, the properties of aqueous solutions can be measured within the ' window ' given by $273.15 \leqslant T \leqslant 373.15$ K but the dependence of ln T and T^{-1} on T over this window is close to linear. This indicates that in equation (2) the two terms, one in T^{-1} and one in ln T, can be replaced by a single term expressing a linear dependence of ln K on T.[26] Moreover as ln T increases over the window, T^{-1} decreases and the third term a_3 [equation (2)] affords a balance between the two contributions. Taken together, it is not unexpected that c_{12} is close to unity and that c_{23} and c_{13} are large. It seems clear that the Valentiner equation is not a good starting point for the analysis of the dependence of ln K on T, despite recent claims for its adequacy.[27]

Scott Equation.—This treatment [28] assumes that $\Delta C_p^\ominus$ is independent of temperature, $\Delta H^\ominus$ being a linear function of temperature. The analysis adopts a technique first introduced by Harned and Embree.[29] These authors related the dependence of K on temperature with reference to the maximum value, $K_{\text{max.}}$ at temperature $T_{\text{max.}}$ [equation (3)].

$$\log (K/K_{\text{max.}}) = -p\,(T - T_{\text{max.}})^2 \qquad (3)$$

Here we use this approach in a slightly different context. We compare values of ln K at two temperatures and assume that $\Delta H^\ominus(T)$ is a linear function of $(T - \theta)$.

Consequently equation (1) can be integrated between temperatures T and θ where the equilibrium constants are $K(T)$ and $K(\theta)$, respectively [equation (4)].

$$R \ln K\,(T) = R \ln K(\theta) + \Delta H^\ominus(\theta)[\tfrac{1}{\theta} - \tfrac{1}{T}] + \Delta C_p^\ominus[\tfrac{\theta}{T} - 1 + \ln(^{T})] \qquad (4)$$

A link between equations (3) and (4) is readily established. If θ is the temperature at which K is a maximum, then $\Delta H^\ominus$ (θ) is zero and equation (4) simplifies to (5) where we have set $\Delta C_p^\ominus$ equal to -40 cal mol^{-1} K^{-1}.[29]

$$\log (K/K_{\text{max.}}) = 8.74\,[\tfrac{T}{T}^{\text{max.}} - 1 + \ln(\tfrac{T}{T\text{max.}})] \qquad (5)$$

Thus if equations (3) and (15) are equivalent, the two temperature functions should be linearly related. Indeed over the window, $273.15 \leqslant T \leqslant 373.15$ K, this is the case, yielding a value for p, 5.04×10^{-5}, which agrees with the value suggested by Harned and Owen,[12] *i.e.* 5×10^{-5}.

Clarke–Glew Equation.—Clarke and Glew[30] expressed the dependence of $\Delta H^{\ominus}$ on temperature in terms of $\Delta H^{\ominus}(\theta)$ at the reference temperature θ using a Taylor series expansion. If it is assumed that derivatives of $\Delta C_p^{\ominus}$ with respect to temperature including $\mathrm{d}^4\Delta C_p^{\ominus}/\mathrm{d}T^4$ and higher are zero and that all other derivatives are finite, the final expression for the dependence of K on T is equation (6). The first three terms on the right hand

$$R \ln K = R \ln K(\theta) + \Delta H^{\ominus}(\theta)\left[\frac{1}{\theta} - \frac{1}{T}\right] + \Delta C_p^{\ominus}\left[\frac{\theta}{T} - 1 + \ln\left(\frac{T}{\theta}\right)\right] + \frac{\mathrm{d}\Delta C_p^{\ominus}(\theta)}{\mathrm{d}T}\left[T - \theta - \frac{(T-\theta)^2}{2T} - \theta \ln\left(\frac{T}{\theta}\right)\right] + \frac{\mathrm{d}^2\Delta C_p^{\ominus}(\theta)}{\mathrm{d}T^2}\left[\left(\frac{T^2-\theta^2}{4}\right) - \frac{(T-\theta)^3}{6T} - (T-\theta) + \frac{\theta^2}{2}\ln\left(\frac{T}{\theta}\right)\right] + \frac{\mathrm{d}^3\Delta C_p^{\ominus}}{\mathrm{d}T^3}\left[\frac{T^3}{18} - \frac{(T-\theta)^4}{24T} - \frac{\theta T^2}{4} + \frac{\theta^2 T}{2} - \frac{11\theta^2}{36} - \frac{\theta^3}{6}\ln\left(\frac{T}{\theta}\right)\right] \quad (6)]$$

side of equation (6) are identical with the first three terms of the Scott equation (4). In the limit $T \longrightarrow \theta$, both sides tend to $R \ln K(\theta)$. The boundary condition is well defined, thereby contrasting the Clarke–Glew equation with, for example, the Valentiner equation. We disagree with the conclusions that these two equations are similar[30] or equivalent.[27] As written equation (6) contains six unknowns. If only the first two terms are used, there is just one correlation coefficient to consider but as more terms are brought into the analysis, the number of coefficients increases rapidly, three coefficients with three parameters, six coefficients with four parameters, and ten coefficients with five parameters.

In an analysis of the data for the self dissociation of water, at the 95% confidence level, an F-test of the variance showed that an equation in four parameters is significant (Table 3). Accordingly at the 95% level of confidence (t-distribution), the enthalpy of dissociation at 298 K lies in the range 13.416—13.446 kcal mol^{-1} and the heat capacity term in the range -52.7 to -50.9 cal mol^{-1} K^{-1}. The correlation coefficients between these parameters, c_{23}, is rather high, 0.4. Even more striking is the correlation coefficient between $\Delta H^{\ominus}$ and $\mathrm{d}\Delta C_p^{\ominus}/\mathrm{d}T$ terms where c_{24} is -0.9.

A similar pattern is observed in the correlation coefficients for propionic acid, four terms being used in equation (6). For the data reported for formic[19] and acetic acids,[1] only three terms in equation (6) were statistically acceptable (Table 3) but in both cases the correlation coefficients between enthalpy and heat capacity terms are high, being *ca.* 0.73.

The magnitude of the correlation function, c_{23}, between enthalpy and heat capacity terms is disappointing in view of the importance of these quantities in treatments of acid dissociation. However the source of this high correlation is clear. Plots of the temperature functions for both terms against temperature, with θ 298.15 over the range $273.15 \leqslant T \leqslant 333.15$, are essentially linear indicating that these terms are attempting to account for the same trend in the dependence of $\ln K$ on T. Indeed, these two terms in equation (6) could be replaced by a single term, linear in temperature. These observations prompted development of the model now described.

TABLE 3

Clarke–Glew equation. Calculated quantities at 298 K

Solute Parameter	Water	Formic acid	Acetic acid	Propionic acid
$-\ln K$	32.2445	8.6394	10.9502	11.2234
Standard error	0.0005	0.0008	0.0005	0.0005
$\Delta H^{\ominus}$/cal mol^{-1}	13.431	-38.7	-105.4	-200.8
Standard error	7	5.6	3.3	7.2
$\Delta C_p^{\ominus}$/cal mol^{-1} K^{-1}	-51.8	-41.6	-37.06	-37.76
Standard error	0.4	0.6	0.37	0.44
$(\mathrm{d}\Delta C_p^{\ominus}/\mathrm{d}T)$/ cal mol^{-1} K^{-2}	0.368			0.242
Standard error	0.065			0.067
$(\mathrm{d}^2\Delta C_p^{\ominus}/\mathrm{d}T^2)$/ cal mol^{-1} K^{-3}				
Standard error				
$(\mathrm{d}^3\Delta C_p^{\ominus}/\mathrm{d}T^3)$/ cal mol^{-1} K^{-4}				
Standard error				
c_{12}	-0.204	0.132	0.132	0.145
c_{13}	-0.751	0.357	0.357	-0.381
c_{14}	0.290			-0.225
c_{23}	0.398	-0.732	-0.732	0.727
c_{24}	-0.898			-0.911
c_{34}	-0.584			0.534

Polynomial Equation.—We express $\ln K$ as a polynomial function in $(T - \theta)$ [equation (7)]. In the limit,

$$\ln K = \sum_{i=1}^{i=k} b_i (T - \theta)^{i-1} \qquad (7)$$

$T \longrightarrow \theta$, $\ln K$ tends to b_1. When $\theta = 298.15$ K, there are clear similarities between the dependence of $T - \theta$ and $(T - \theta)^3$ on T and so we anticipate that c_{23} will be large. Indeed correlation coefficients between terms involving every other power of $T - \theta$ are expected to be significant. Equations (1) and (6) can be combined to yield expressions for the thermodynamic quantities. Thus for all terms up to the fifth power of $T - \theta$, equations (8) and (9) are obtained for the enthalpy term. Further differentiation of equation (6) leads to expressions for $\Delta C_p^{\ominus}$ and higher derivatives.

$$\Delta H^{\ominus}(T)/R = b_2T^2 + 2b_3T^2(T - \theta) + 3b_4T^2(T - \theta)^2 + 4b_5(T - \theta)^3T^2 + 5b_6(T - \theta)^4T^2 \qquad (8)$$

$$\Delta H^{\ominus}(\theta)/R = b_2\theta^2 \qquad (9)$$

The data for the systems given in Table 2 have been analysed satisfactorily using the polynomial method (Table 6). In each case the series was terminated when each parameter was significant at the 95% level of confidence according to the F-test of the variance ratio. In Figure 1 we show the change in the goodness of fit, $\Delta = [\ln K\ (\text{obs}) - \ln K\ (\text{calc})]$ for the self dissociation constant of water[14] as each new term in the polynomial is added. With only two terms ($k = 2$), a plot of Δ against $T - \theta$ generates a parabola; when $k = 3$ the same plot shows a sinusoidal dependence. A scatter of Δ values both greater than and less than zero does not emerge until $k = 5$. The correlation coefficients (Table 5) vary considerably; c_{12} is small at 0.16 but, as anticipated, c_{24} and c_{35} are close to 0.9. The calculated dependence of $\Delta C_p^{\ominus}$ on temperature (Figure 3) shows an increase with increase in temperature. At the 95% confidence level, $\Delta H^{\ominus}$ (298 K) lies in the range 13 447—13 405 cal mol^{-1}, and $\Delta C_p^{\ominus}$ in the range −53.89 to −48.38 cal mol^{-1} K^{-1}. These values agree with those obtained by using the Clarke–Glew equation. The value of $\Delta C_p^{\ominus}$ (298.15 K) agrees with the thermochemical values[31,32] as does the increase in $\Delta C_p^{\ominus}$ with increase in temperature.[31-33] Nonetheless, there is a small but significant difference (*ca.* 90 cal mol^{-1}) in $\Delta H^{\ominus}$ (298.15 K) calculated from the dependence of pK_w on temperature and from thermochemical data.[14,34]

TABLE 4

Polynomial expression for dependence of ln K on $(T - \theta)$

	Water pK_w	Propionic acid pK_a
θ	298.15	298.15
b_1	−32.24472	−11.2232
10^3 (Standard error)	0.561	4.83
$10^2 b_2$	7.6006	1.153
10^5 (Standard error)	5.12 × 10	38.54
$10^4 b_3$	−3.9967	−1.0512
10^6 (Standard error)	3.213	1.340
$10^7 b_4$	19.38	6.509
10^7 (Standard error)	1.008	0.6102
$10^9 b_5$	−9.683	
10^9 (Standard error)	3.976	
$\Delta H^{\ominus}(\theta)$/cal mol^{-1}	13.426	−203.7
Standard error	9	6.8
$\Delta C_p^{\ominus}(\theta)$/cal mol^{-1} K^{-1}	−51.14	−38.5
Standard error	1.20	0.5
$[\mathrm{d}\Delta C_p^{\ominus}(\theta)/\mathrm{d}T]$/cal mol^{-1} K^{-2}	4.168×10^{-1}	1.87×10^{-1}
Standard error	1.22×10^{-1}	0.71×10^{-1}
$[\mathrm{d}^2\Delta C_p^{\ominus}(\theta)/\mathrm{d}T^2)$/cal mol^{-1} K^{-3}	-9.246×10^{-3}	1.14×10^{-2}
Standard error	1.908×10^{-2}	0.13×10^{-2}
$[\mathrm{d}^3\Delta C_p^{\ominus}(\theta)/\mathrm{d}T^3)$/cal mol^{-1} K^{-4}	-8.242×10^{-4}	9.31×10^{-5}
Standard error	4.66×10^{-4}	8.73×10^{-6}
$[\mathrm{d}^4\Delta C_p^{\ominus}(\theta)/\mathrm{d}T^4]$/cal mol^{-1} K^{-5}	-9.236×10^{-6}	
Standard error	3.79×10^{-6}	

The data for propionic acid[22] were fitted to the polynomial equation using four terms, the difference Δ showing reasonable scatter when plotted against $T - \theta$. The derived parameters are summarised in Table 4.

TABLE 5

Correlation matrix using polynomial expression for dependence of ln K on $T - \theta$

(a) Self-dissociation constant for water; 5 terms

1	1.0000				
2	0.1577	1.0000			
3	−0.7138	−0.4525	1.0000		
4	−0.1796	−0.9180	0.5368	1.0000	
5	0.4858	0.6456	−0.9059	−0.7888	1.0000

(b) Acid dissociation constant for propionic acid; 4 terms

1	1.0000			
2	−0.2336	1.0000		
3	−0.7396	0.4095	1.0000	
4	0.3789	−0.8780	−0.6831	1.0000

The correlation coefficient c_{24} (Table 5) is again high. The enthalpy of dissociation calculated at 298.15 K from thermochemical data is −140 ± 50 cal mol^{-1} with $\Delta C_p^{\ominus}$ −38 cal mol^{-1} K^{-1}. The agreement between these values and the estimates in Table 4 is noteworthy. Harned and Ehlers originally reported[22] $\Delta C_p^{\ominus}$ −37.7 cal mol^{-1} K^{-1} with $\Delta H^{\ominus}$ −168 cal mol^{-1}.

The results of a similar analysis for other dissociation constants are summarised in Table 6. The dependence of $\Delta C_p^{\ominus}$ on temperature for three acids is shown in Figure 3 which includes a comparison with thermochemical data.[35,36]

TABLE 6

Derived parameters for dependence of ln K on T − 298.15 polynomial equation

Acid	b_1	b_2	b_3	b_4
Cyanoacetic[17]	−5.6869	-5.045×10^{-3}	-9.470×10^{-5}	6.040×10^{-7}
Standard error	3.03×10^{-4}	4.061×10^{-5}	1.369×10^{-6}	1.272×10^{-7}
Acetic[1]	−10.9502	-5.561×10^{-4}	-1.035×10^{-4}	3.853×10^{-7}
Standard error	5.206×10^{-3}	4.153×10^{-5}	1.444×10^{-6}	6.576×10^{-8}
[$^2H_4$]Acetic–D_2O[18]	−12.26	1.742×10^{-2}	-1.095×10^{-4}	
Standard error	5.72×10^{-4}	2.883×10^{-5}	2.120×10^{-6}	
D_2O (self dissoc.)[15]	−34.4353	8.0812×10^{-2}	-4.352×10^{-4}	2.018×10^{-6}
Standard error	6.084×10^{-4}	6.858×10^{-5}	2.539×10^{-6}	1.784×10^{-7}
Formic[19]	−8.6391	-2.280×10^{-4}	-1.189×10^{-4}	5.337×10^{-7}
Standard error	9.094×10^{-4}	7.255×10^{-5}	2.522×10^{-6}	1.149×10^{-7}
Di-isopropylcyanoacetic[20]	−5.8852	-1.926×10^{-2}	-1.934×10^{-5}	3.206×10^{-7}
Standard error	1.915×10^{-4}	2.562×10^{-5}	8.635×10^{-7}	8.027×10^{-8}
[$^2H_3$]Acetic[16]	−10.9862	-2.303×10^{-4}	-9.500×10^{-5}	
Standard error	1.194×10^{-2}	5.001×10^{-5}	3.581×10^{-6}	
Dimethylcyanoacetic[24]	−5.5768	-1.0587×10^{-2}	-6.8411×10^{-5}	
Standard error	4.2×10^{-4}	2.157×10^{-5}	1.904×10^{-6}	
Isopropylcyanoacetic[24]	−5.5177	-1.235×10^{-2}	-4.727×10^{-5}	
Standard error	3.88×10^{-3}	1.982×10^{-4}	1.750×10^{-5}	
Acetic–D_2O[25]	−12.2316	1.687×10^{-3}	-1.120×10^{-4}	
Standard error	5.579×10^{-4}	2.789×10^{-4}	2.051×10^{-6}	

The close agreement between the results obtained using the Clarke–Glew equation and the polynomia equation contradicts the claim[30] that an analysis based on a power series in temperature has little to commend it. In particular, we find that such a series can provide a realistic representation of the dependence of $\Delta H^\ominus$ and $\Delta C_p^\ominus$ on temperature. Neither do we agree that suppression of a term in ln T is in any sense arbitrary. As noted above, the near linear dependence of ln T on T is significant.

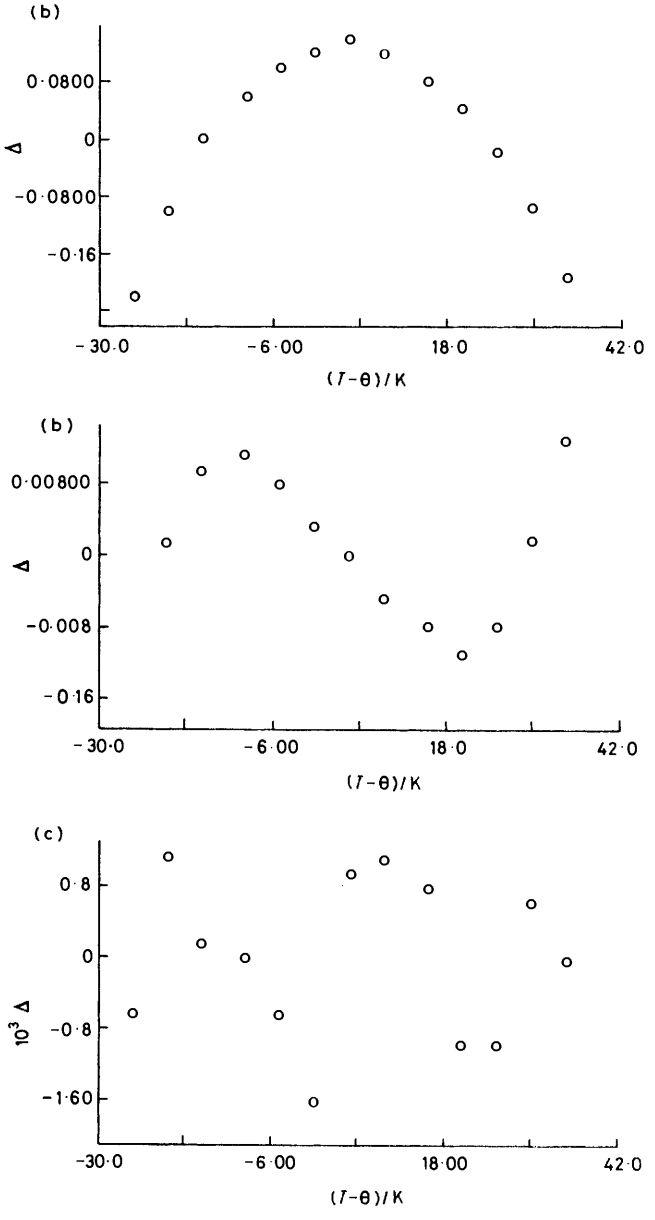

FIGURE 1 Polynomial equation: dependence of ln K(obs.) − ln K(calc.) on $(T - \theta)$ for the self-dissociation constant of water using an equation with (a) two, (b) three, and (c) five terms

Two-stage Model.—In the analyses discussed above, it is assumed that the equilibrium constant describes a single-step reversible transformation. A different approach is to assume that the measured equilibrium constant describes a two-stage process. Thus for the dissociation of a weak acid, the overall process is represented as shown in equation (10). At this stage, the

$$\mathrm{RCOOH} \overset{K_1}{\rightleftharpoons} (\mathrm{RCOOH})_{\mathrm{int}} \overset{K_2}{\rightleftharpoons} \mathrm{RCOO^-} + \mathrm{H^+} \quad (10)$$

nature of the intermediate is left unspecified but we require that it is sufficiently long-lived to be characterised by a set of thermodynamic parameters, *e.g.* partial molar enthalpy. Equation (10) defines two equilibrium constants; K_1 describes the equilibrium between the undissociated acid RCOOH and the intermediate whereas K_2 describes the equilibrium between intermediate and free ions. We now assume that the observed equilibrium constant measures the proportion of acid in the form of free ions relative to that in the form of intermediate and undissociated acid.

$$K = K_2/(1 + K_1^{-1}) \quad (11)$$

Therefore, K is related to K_1 and K_2 by equation (11). In the limit $K_1 \gg 1.0$, $K = K_2$ and in the limit $K_1 \ll 1.0$, $K = K_1K_2$. Thus at both extremes, it will not be possible to calculate the separate values of K_1 and K_2. Between the two extremes, the dependence of K on temperature can be used to calculate K_1 and K_2. This

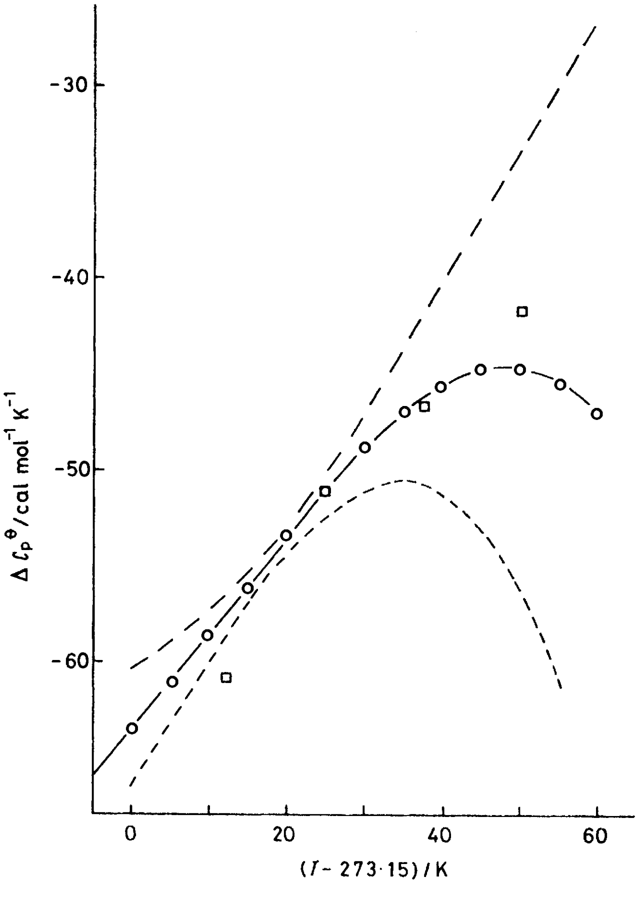

FIGURE 2 Polynomial equation: dependence of $\Delta C_p^\ominus$ on temperature for the self-dissociation constant of water calculated using parameters in Table 4; comparison with calorimetric data[31,32] (□)

assumes that the associated enthalpy terms $\Delta H_1^{\ominus}$ and $\Delta H_2^{\ominus}$ are such that the dependence of K on temperature is determined by the separate dependences of K_1 and K_2 on temperature. We will further assume that $\Delta H_1^{\ominus}$ and $\Delta H_2^{\ominus}$ are independent of temperature. If equations (12) and (13) apply, then equation (14) obtains. If at the reference temperature θ, the observed equilibrium constant is $K(\theta)$ then the ratio $K/K(\theta)$ is given by equation (15). Equation (15) describes, therefore, the dependence of K on T about a reference $K(\theta)$ at θ in terms of three parameters x_1—x_3, where x_3 is related to $\Delta H_1^{\ominus}$ and x_1 to $\Delta H_2^{\ominus}$. This is the form used in the analysis reported here, but because the dependence of the variable K on the dependent variable T is non-linear in the x_i parameters, the least squares technique is inappropriate. Consequently we used a method [37,38] of seeking those coefficients which yield a minimum in the function $[K(\text{obs}) - K(\text{calc})]^2$ using estimates of the coefficients and gradients of the functions. It was found advantageous to identify one value of K as $K(\theta)$ where θ is near the middle of the experimental range. The analysis required initial estimates of the x_i parameters and some trial and error was required in each case (Table 7). Agreement between observed and calculated equilibrium constants was usually better than 0.2%. This is shown in Figure 4 where we have plotted $\Delta\ \{= 100 \times [K(\text{obs}) - K(\text{calc})/K(\text{obs})]\}$ against temperature for formic, acetic, and propionic acids. According to equation (15), the equilibrium constant $K_{\text{max.}}$ is at a maximum when $T = T_{\text{max.}}$, the latter being related to the x_i parameters [equation (16)]. The calculated values are 297.21, 295.64, and 292.93 K for formic, acetic, and propionic acids respectively. The agreement between these values and the observed $T_{\text{max.}}$ values provides a useful cross-check on the derived parameters. From the latter, the enthalpy quantities $\Delta H_1^{\ominus}$ and $\Delta H_2^{\ominus}$ are calculated together with K_1 and K_2 at each temperature (Table 7). It is now possible to compare the separate dependences of K, K_1, and K_2 on temperature (Figure 5). For example, the maximum in K for acetic acid is a consequence of the way in which K_1 and K_2 change regularly with temperature.

$$K_1 = A_1 \exp\,(-\Delta H_1^{\ominus}/RT) \qquad (12)$$

$$K_2 = A_2 \exp\,(-\Delta H_2^{\ominus}/RT) \qquad (13)$$

$$K = \frac{A_2 \exp\,(-\Delta H_2^{\ominus}/RT)}{1 + A^{-1} \exp\,(\Delta H_1^{\ominus}/RT)} \qquad (14)$$

$$K = K(\theta) \exp\,[x_1\,(T^{-1} - \theta^{-1})] \left[\frac{1 + x_2 \exp\,(x_3/\theta)}{1 + x_2 \exp\,(x_3/T)}\right] \qquad (15)$$

$$T_{\text{max.}} = x_3/\ln\{x_1/[x_2(x_3 - x_1)]\} \qquad (16)$$

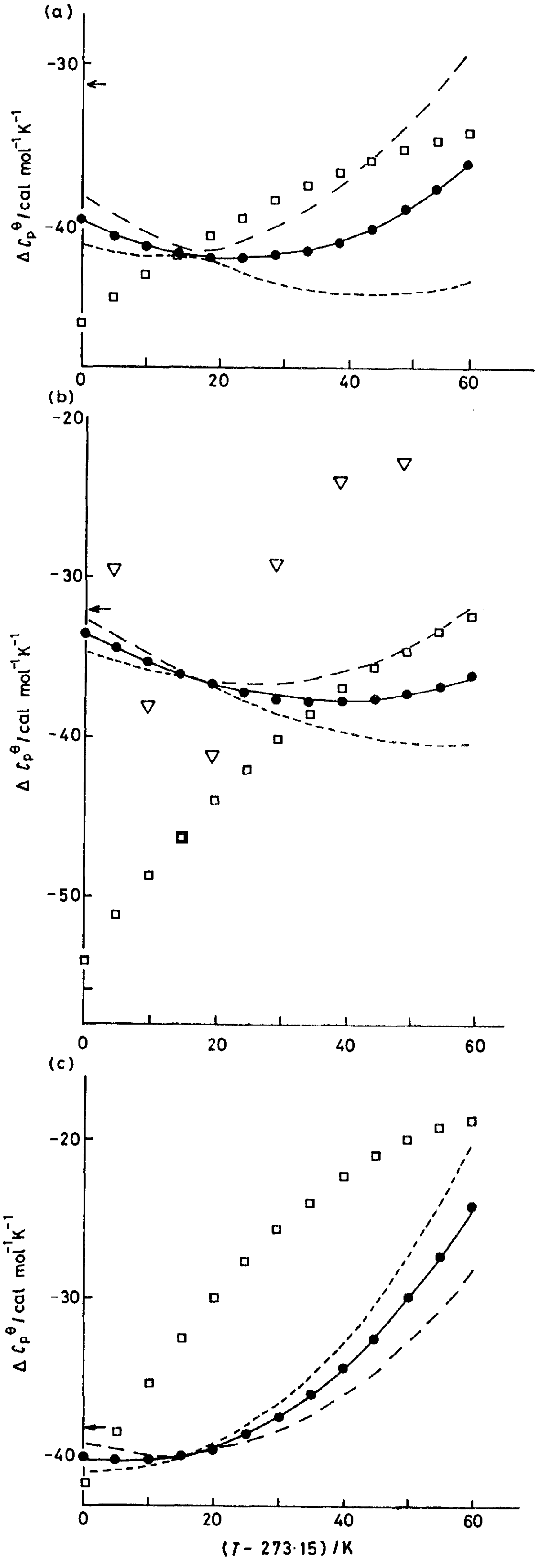

FIGURE 3 Polynomial equation: dependence of $\Delta C_p^{\ominus}$ and standard errors on temperature for (a) formic, (b) acetic, and (c) propionic acids; comparison with thermochemical data (□) [36] and (▽);[33] thermochemical data calculated [35] assuming $\Delta C_p^{\ominus}$ is independent of temperature indicated by arrow

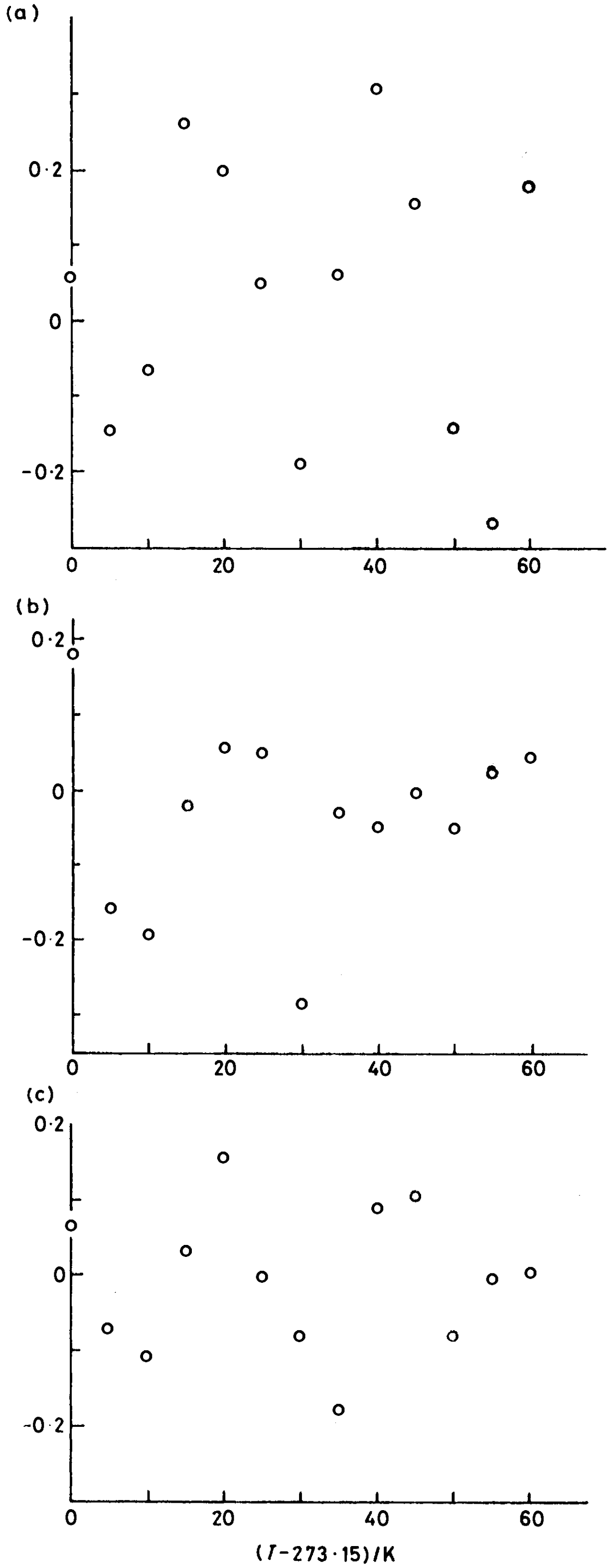

FIGURE 4 Two-stage equilibrium: dependence of Δ {$= 100 \times [K(\text{obs.}) - K(\text{calc.})]/K(\text{obs.})$} on temperature for (a) formic, (b) acetic, and (c) propionic acids

For all the systems shown in Table 7, the thermodynamic parameters show very similar behaviour. For the first stage in the dissociation, $\Delta G^{\ominus}$ is small being generally $< \pm 1.0$ kcal mol^{-1}. However, the process is exothermic with $\Delta H^{\ominus}$ at *ca.* -5.0 kcal mol^{-1} and, correspondingly, $\Delta S^{\ominus}$ is also negative. The changes in enthalpy and entropy quantities can be understood if the process involves charge separation with the production of H_3O^+ ion in close proximity to the carboxylate ion. Thus the contribution of a more intense interaction of the solute species with solvent would result in an exothermic process. Subsequent separation of these ions would not involve significant changes in these interactions and indeed $\Delta H^{\ominus}$ for the second process is for most systems much smaller. Thus strong ion–ion interactions within this intermediate will be replaced by strong ion–solvent interactions for the individual ions. However, the second stage will be characterised by considerable re-organisation within the local solvent producing a negative $\Delta S^{\ominus}$ which, in turn, results in a positive value for $\Delta G^{\ominus}$.

Discussions.—The underlying problem in the analysis described above is that the data comprise a dependent variable K and one independent variable, temperature. By analysing the dependence of K on this single variable we endeavour to calculate a number of quantities, *e.g.* $\Delta H^{\ominus}$, $\Delta C_p^{\ominus}$, and $d\Delta C_p^{\ominus}/dT$. It is not unexpected, therefore, that such a structure for the input data produces estimates of parameters with high correlation coefficients. The latter will assume even greater significance if the structure of the model is poor, as in the case of the Valentiner equations. The numerical analysis is not helped by equation (1) which, in turn, prompts the fitting of ln K rather than K on temperature. Consequently, the percentage change in ln K is significantly less than in K.

Another aspect to the analysis is the meaning of K itself, which is first and foremost an experimentally based quantity. The most precise methods for determining K are based on methods for measuring the proportion of total solute present in solution as ions. Thus in the case of conductivity, it is assumed that the mobilities of these ions can be described using the same equations describing mobilities of ions when the total solute is present as ions. By inference, we characterise the state of the non-conducting fraction of solute. In the analysis reported here we have used two approaches. For the most part we have assumed that the non-conducting fraction comprises one state, the undissociated acid, and that the system can be characterised by a single equilibrium constant. Consequently, there is assumed to exist a set of thermodynamic parameters which characterise the equilibrium.

If the model adopted assumes a single-stage reversible process, there remains the question of the reliability of the thermodynamic parameters calculated using the various methods. We have endeavoured to show that of these the polynomial expression is satisfactory. It does not, for example, assume a particular form for the dependence of $\Delta H^{\ominus}$ on temperature as is the case for the Scott and Clarke–Glew equations. Indeed the derived quantities are in agreement although the calculations in the case of the polynomial expression are more amenable to programming for a computer. Nonetheless, the derived thermodynamic parameters should be compared, where possible, with the same values from thermochemical data. Timini[39] has stressed this point although his conclusions seem pessimistic. He suggests that analysis of dissociation constant–temperature trends is not capable of yielding reliable $\Delta C_p^{\ominus}$ values. His conclusions are based on the comparison of thermochemical data[38] and the application of the Clarke–Glew equation. We are less pessimistic (*cf.* Figure 3) in view of the disagreement between values for $\Delta C_p^{\ominus}$ and its temperature dependence reported in different calorimetric studies. In addition, we have shown that the model adopted for the dependence of K on T is equally

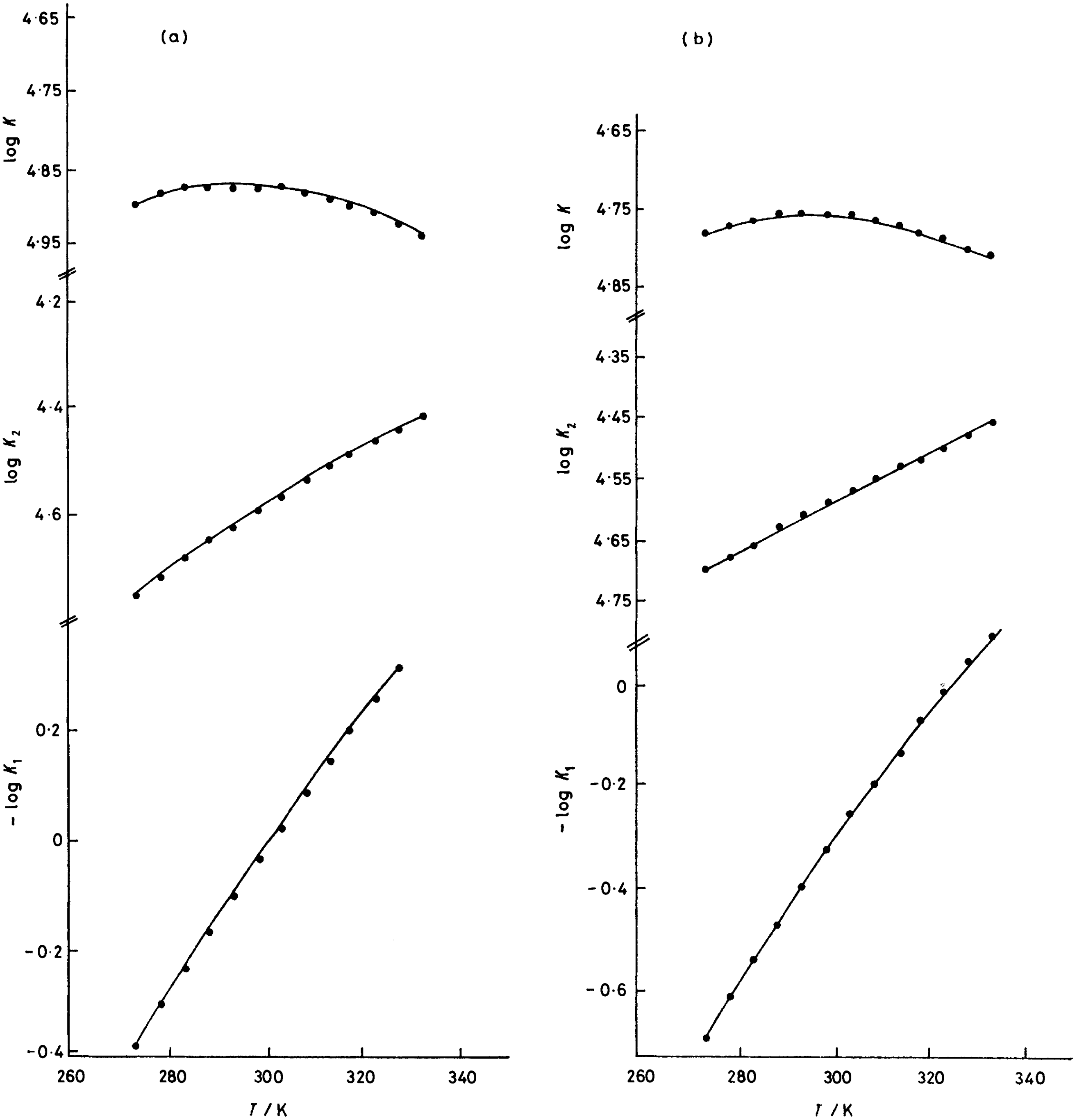

FIGURE 5 Two-stage equilibrium: comparison of the dependence on temperature of K, K_1, and K_2 for (a) acetic and (b) propionic acids

TABLE 7

Derived quantities characterising acid dissociation constants in water at 298.15 K; calculations based on two-stage equilibrium, A $\rightleftharpoons$ B $\rightleftharpoons$ C where C describes the ions, $RCOO^-$ and H_3O^+

	$A \rightleftharpoons B$			$B \rightleftharpoons C$		
Acid	K_1	$\Delta G_1^\ominus$/ cal mol^{-1}	$-\Delta H_1^\ominus$/ kcal mol^{-1}	10^6K_2/ dm^3 mol^{-1}	$\Delta G_2^\ominus$/ kcal mol^{-1}	$\Delta H_2^\ominus$/ kcal mol^{-1}
Cyanoacetic [17]	0.965	21.38	5.300	6 906	2.948	1.800
Acetic [1]	2.119	−444.9	5.492	25.8	6.259	1.668
[$^2H_4$]Acetic–D_2O [18]	2.232	−475.9	5.722	6.85	7.045	2.061
Formic [19]	1.498	−239.3	5.662	295.5	4.815	2.226
Di-isopropylcyanoacetic [20]	0.7479	172.0	4.593	6 496	2.984	−0.781
[$^2H_3$]Acetic [16]	1.291	−151.4	4.998	30.07	6.169	2.098
Bromoacetic [21]	1.845	−262.6	5.022	2 058	3.665	0.712
Iodoacetic [21]	1.388	−194.4	4.956	1 150	4.010	0.648
Chloroacetic [21]	2.754	−600.2	6.186	1 846	3.729	0.535
Propionic [22]	1.089	−50.84	5.229	25.62	6.264	2.298
Dimethylcyanoacetic [24]	2.284	−489.3	5.538	5 439	3.089	−0.190
Isopropylcyanoacetic [24]	0.2802	753.9	6.746	18 537	2.363	2.978
Acetic–D_2O [25]	0.6090	−1 070.4	7.190	5.663	7.158	1.325

critical in view of the correlation coefficients between the estimates of their thermodynamic properties.

Perhaps the most striking feature of the dependence of K on T for several carboxylic acids is the maximum in K. It is not immediately obvious what factors combine to produce this maximum. Heat capacity quantities in aqueous solutions are generally large and thus $\Delta H^\ominus$ is strongly temperature dependent. However, there seems relatively few explanations of why, for example, $\Delta H^\ominus$ at 298 K for acetic acid is zero. Gurney [40] suggested that a maximum in K was required by the electrostatic interactions but that the temperature at which K is maximum is determined by the non-electrostatic interactions, the latter being insensitive to the environment and independent of temperature. However, Ives and Marsden [20] in their discussion of the role of the solvent medium, discussed the impact of differences in the thermodynamic properties of the water in the solute-cospheres. Leung and Grunwald [33] used a two-state model for the solvation of a solute in water to account for the magnitudes of $\Delta C_p^\ominus$ in aqueous solution. There is a short step from the latter treatment to the model which treats the dissociation as a two-stage process. The intermediate is identified as an ion-pair. Thus as suggested by Eigen,[41] the first stage of the association process is an encounter as a preliminary step to the combination of the ions to form undissociated acid [42] [*cf.* equation (1) of reference 41]. The suggestion is that the large $\Delta C_p^\ominus$ values are artefacts of a two-stage process. A clear link is established here with the suggestion by Albery [43] concerning the heat capacities of activation for solvolytic reactions in water which are artefacts of a two-stage process involving an intermediate ion-pair species. Indeed, the analysis reported here using the two-stage scheme prompts a reconsideration of the kinetic data for this class of reactions.[3,44] The outcome will form the basis of a further communication.

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