

orbital of the adjacent positively charged carbon atom. Consequently, the point position of this substituent cannot be included in Figure 1 and it should be correlated with σ^+ values. However, σ^+ values have been defined for substituents on the benzene ring and not directly attached at the reaction site. Despite the fact that steric factors can simultaneously interfere with delocalization, the effect of $\text{CH}_2=\text{CH}$ substituent is polar in nature.

In conclusion, the results of the present work give additional support to Maccoll's theory on the heterolytic nature of the

transition state for alkyl halide pyrolyses in the gas phase.¹²

Acknowledgment. We are grateful to the Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICIT) for their support (Project No. 51.78.31, S1-1072) and to María L. Tasayco for NMR determinations and interpretations.

Registry No. $\text{CH}_3\text{CCl}_2\text{CH}_3$, 594-20-7; $\text{CH}_3\text{C}(\text{Cl})(\text{CH}_3)\text{CO}_2\text{Me}$, 22421-97-2; $\text{CH}_3\text{C}(\text{Cl})(\text{CH}_3)\text{CH}_2\text{Cl}$, 594-37-6.

Obtaining ΔC_p° and Its Temperature Coefficients from Equilibrium Constants: A Tested Procedure

H. Frank Halliwell

University of East Anglia, Norwich, England

and Laurence E. Strong*

Earlham College, Richmond, Indiana 47374 (Received: March 11, 1985; In Final Form: May 13, 1985)

An empirically justified pattern of the variation of ΔC_p° with temperature ($\Delta C_p^\circ = \Delta a + \Delta bT + \Delta cT^2$) is used to establish the relationship $R \ln K^\circ(\beta) = \Delta S^\circ(\beta)_{298} - \Delta H^\circ_{298}K_1 + \Delta C_p^\circ_{298}K_2 + \Delta bK_3 + \Delta cK_4$ where K_1 , K_2 , K_3 , and K_4 are temperature-dependent variables (TDV), tables of which are included, and β indicates which of the temperature-independent concentration scales is used. The equation is of general applicability. Although it has been developed for aqueous ionization reactions it has been profitably applied to high-temperature gas reactions, to the solubility product of ionic salts, and to the solution of gases in water. The number of terms in the ΔC_p° function that is justified (often a matter of dispute) can be indicated graphically by direct reference to experimental values and their confidence limits established by means of the proposed method of intervals. Values of any of the thermochemical properties at 298.15 K obtained independently (e.g., calorimetrically) can, by adoption or adaptation, be incorporated into the processing procedure during the evaluation of the remaining properties. Sets of simulated results incorporating precisely stated thermochemical values at 298.15 K and processed to have differing and known levels of uncertainty in the resulting $R \ln K^\circ(m)$ values are used to assess the reliability of the proposed procedure by noting the adequacy of the recovery of the generating values.

1. Introduction

To obtain ΔH° , $\Delta S^\circ(m)$, and ΔC_p° for a reaction from equilibrium information it is customary to fit $\ln K^\circ(m)$ to some reasonable and convenient function of T , and then to perform appropriate differentiations on the result.

We suggest that this treatment suffers from four weaknesses.

(i) The decision to use any specific equation for $\ln K^\circ(m)$ in terms of T imposes a form on the temperature dependence of ΔC_p° irrespective of any calorimetric evidence. This point is discussed in detail by Timimi¹ and by Blandamer et al.² Of course, the converse is also true, but it is true to a lesser extent as is summarized in Chart I.

(ii) The form of the equation usually employed is

$$pK = A + B/T + C \log T + DT + ET^2$$

This will be referred to as the standard equation. Its form is a weakness in that it cuts itself off from other thermochemical measurements: any immediate significance of the coefficients is sacrificed to the simplicity of the temperature-dependent variables. For recall or interpolation of smoothed values at any temperature within a specified range, it is excellent. For obtaining thermochemical information, we suggest that there is a more convenient and reliable alternative.

(iii) The above characteristic also prevents independent thermochemical work from being simultaneously taken into account during data processing.

(iv) Lastly, the question of which and how many terms of the standard equation are used is usually controlled by statistical decisions built into the evaluating programs. Thus it can well happen that it is the uncertainties in the experimental results rather than any independent thermochemical evidence which impose a pattern on ΔC_p° .

The first two of these weaknesses are removed by the Clarke and Glew³ treatment, but the last two remain. This paper attempts to alter the situation by two strategies: (a) by reversing, in two areas, the priorities on which the standard equation is based, namely, first by deciding on the form of an empirical equation for ΔC_p° and then processing it to give an equation for $R \ln K^\circ_T(m)$, and second by doing this in such a way that the coefficients are values of clearly defined thermochemical properties while it is the temperature-dependent variables (TDV) which are the part whose immediate significance is sacrificed. (b) by developing a diagnostic procedure using a method of intervals whereby a plot of a ΔC_p° function provides the basis for deciding on the number of terms to be incorporated into the formula for the temperature dependence of $R \ln K^\circ_T(m)$.

2. The Pattern of ΔC_p°

The behavior of C_p° for pure electrolytes and that of \bar{C}_p° for their dissolved species show extremely different pictures: the former always positive, showing a gently increasing value with near rectilinearity at high temperatures; the latter often markedly negative with a great rise and fall in value within the narrow range of 0–100 °C. The former, as Maier and Kelley⁴ and Kelley⁵

(1) Timimi, B. A. *Electrochim. Acta* 1974, 19, 149.

(2) Blandamer, M. J.; Burgess, J.; Robertson, R. E.; Scott, J. W. M. *Chem. Rev.* 1982, 82, 259.

(3) Clarke, E. C. W.; Glew, D. N. *Trans. Faraday Soc.* 1966, 62, 539.

CHART I

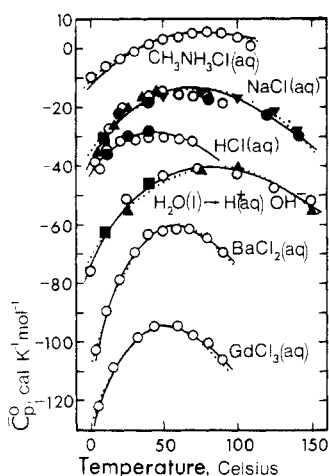
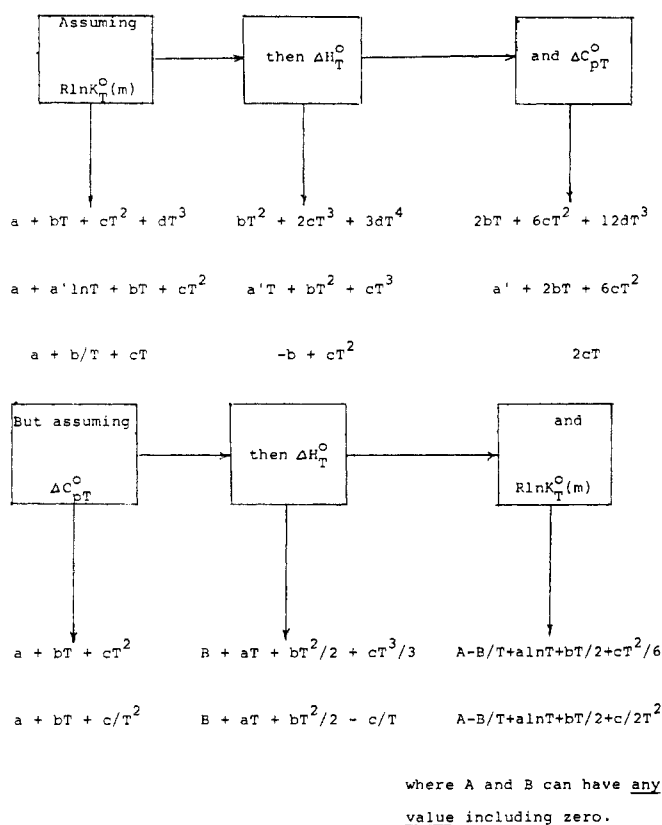


Figure 1. Variation of \bar{C}_p° (and ΔC_p°) with temperature. Experimental values fitted to $\bar{C}_p^\circ = a + bT + c/T^2$ (—) and $\bar{C}_p^\circ = a + bT + cT^2$ (---). $\text{CH}_3\text{NH}_3\text{Cl(aq)}$, ref 6; NaCl(aq) , ref 7–11; HCl(aq) , ref 9 and 12; $\text{H}_2\text{O(l)} \rightarrow \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$, ref 9, 13, and 14; $\text{BaCl}_2(\text{aq})$, ref 7; $\text{GdCl}_3(\text{aq})$, ref 11.

established, are summarized over a very wide temperature range above 0 °C by the relationship

$$\bar{C}_p^\circ = a + bT + c/T^2$$

TABLE I: Comparison of \bar{C}_p° Values for NaCl(aq) As Derived with Two Different Polynomials

$t/^\circ\text{C}$	$C_p^\circ/\text{cal K}^{-1}\text{mol}^{-1}$	ref	C_p°			
			$(T^2)^a$	calcd – obsd	$(1/T^2)^b$	calcd – obsd
0			[–33.25]		[–36.63]	
2.51	–38.3	7 ^c	–31.99	+6.31	–34.70	+3.60
5.0	–38.0	15 ^d	–30.78	+7.22	–32.89	+5.11
7.5	–31.6	7 ^c	–29.62	+1.99	–31.18	+0.42
12.5	–26.8	7 ^c	–27.39	–0.59	–28.06	–1.26
15.0	–25.2	16 ^d	–26.35	–1.15	–26.65	–1.45
17.49	–22.9	7 ^c	–25.36	–2.46	–25.33	–2.43
20.0	–23.3	16 ^d	–24.40	–1.10	–24.09	–0.79
22.49	–19.1	7 ^c	–23.49	–4.39	–22.94	–3.84
25.0	–21.1	15 ^d	–22.61	–1.51	–21.87	–0.77
25.0	–21.5	16 ^d	–22.61	–1.11	–21.87	–0.37
30.0	–17.8	7 ^c	–21.00	–3.20	–19.97	–2.17
30.0	–20.1	16 ^d	–21.00	–0.90	–19.97	+0.13
39.98	–15.2	7 ^c	–18.30	–3.10	–17.05	–1.85
45.0	–15.5	15 ^d	–17.20	–1.70	–15.99	–0.49
49.92	–14.2	7 ^c	–16.29	–2.09	–15.18	–0.98
59.85	–15.6	7 ^c	–14.97	+0.63	–14.23	+1.37
65.0	–14.3	15 ^d	–14.55	–0.25	–14.06	+0.24
69.94	–16.0	7 ^c	–14.32	+1.68	–14.09	+1.91
80.0	–16.0	7 ^c	–14.37	+1.63	–14.70	+1.30
80.0	–16.3	10 ^c	–14.37	+1.93	–14.70	+1.60
85.0	–15.4	15 ^d	–14.65	+0.75	–15.24	+0.16
90.08	–18.5	7 ^c	–15.11	+3.39	–15.96	+2.54
100	–18.00	10 ^c	–16.53	+1.47	–17.77	+0.23
120	–23.03	10 ^c	–21.46	+1.57	–22.94	+0.09
140	–29.51	10 ^c	–29.14	+0.36	–29.80	–0.29
160	–36.06	10 ^c	–39.57	–3.51	–38.05	–1.99
				$\pm 2.74^e$		$\pm 1.77^e$

^a Using $\bar{C}_p^\circ = -429.9878 + 2.3933T - 3.4445 \times 10^{-3} T^2$, maximum at $T = -b/2c = 347.41 \text{ K}$ (74.3 °C); max $\bar{C}_p^\circ = -14.25$. ^b Using $\bar{C}_p^\circ = 422.4822 - 0.85651T - 1.67994 \times 10^7/T^2$, maximum at $T = (2c/b)^{1/3} = 339.78 \text{ K}$ (66.6 °C); max $\bar{C}_p^\circ = -14.08$. ^c Unsmoothed. ^d Smoothed. ^e Standard deviation.

The possibly unexpected fact is that the latter are summarized by the same form of equation, although at higher temperature a more reliable relationship is usually

$$\bar{C}_p^\circ = a + bT + cT^2$$

Figure 1 shows for a few examples of dissolved electrolytes that within the temperature limits 10–90 °C there is often little to choose between the two equations. The standard deviations on fitting results to either are often less than the differences in the values reported by different workers. At the lowest temperatures the equation using $1/T^2$ is often a better summary. This is illustrated by the \bar{C}_p° values for NaCl(aq) given in Table I.

For use with $R \ln K^\circ(m)$ results it is desirable to restrict an expression for ΔC_{pT}° at present to three terms. Marginally, and for temperatures from 25 to 100 °C, the better summary is

$$\Delta C_{pT}^\circ = \Delta a + \Delta bT + \Delta cT^2 \quad (1)$$

In some cases, and particularly at temperatures limited to the range 0–50 °C, the equation

$$\Delta C_{pT}^\circ = \Delta a + \Delta bT + \Delta c/T^2 \quad (2)$$

may be more reliable.

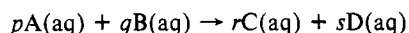
We refer to these forms as the (T^2) equation and the $(1/T^2)$ equation. It must be remembered that Δa , Δb , and Δc have no theoretical meaning. They are merely coefficients which taken together enable ΔC_{pT}° to be recalled at any temperature within the 0–100 °C range.

- (4) Maier, C. G.; Kelley, K. K. *J. Am. Chem. Soc.* **1932**, *54*, 3243.
- (5) Kelley, K. K. *U.S., Bur. Mines, Bull.* **1949**, No. 476.
- (6) Rüterjans, H.; Schreiner, F.; Sage, U.; Ackermann, Th. *J. Phys. Chem.* **1969**, *73*, 986.
- (7) Criss, C. M.; Cobble, J. W. *J. Am. Chem. Soc.* **1961**, *83*, 3223.
- (8) Perron, G.; Roux, A.; Desnoyers, J. E. *Can. J. Chem.* **1981**, *59*, 3049.
- (9) Allred, G. C.; Woolley, E. M. *J. Chem. Thermodyn.* **1981**, *13*, 147.
- (10) Likke, S.; Bromley, L. A. *J. Chem. Eng. Data* **1973**, *18*, 189.
- (11) Helgeson, H. C.; Kirkham, D. H.; Flowers, G. C. *Am. J. Sci.* **1981**, *281*, 1249.
- (12) Ahluwalia, J. C.; Cobble, J. W. *J. Am. Chem. Soc.* **1964**, *86*, 5377.
- (13) Olofsson, G.; Olofsson, J. J. *Chem. Thermodyn.* **1981**, *13*, 437.
- (14) Sweeton, F. H.; Mesmer, R. E.; Baes, C. F. *J. Solution Chem.* **1974**, *3*, 191.

- (15) Tanner, J. E.; Lamb, F. W. *J. Solution Chem.* **1978**, *7*, 303.
- (16) Parker, V. B. *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* **1965**, NSRDS-NBS 2.
- (17) Ashby, J. H.; Crook, E. M.; Datta, S. P. *Biochem. J.* **1954**, *56*, 190.
- (18) King, E. J. "Acid-Base Equilibria"; MacMillan: New York, 1965.

3. Concentration Scales

Consider the reaction



The value of ΔH° for the forward reaction with reactants in their standard states is obtained by the extrapolation of ΔH values at different concentrations along the chosen concentration scale to zero concentration—which is the same on any scale. It follows that the value of ΔH° is independent of the scale used to define the standard state. Since this is true at all temperatures, ΔC_p° and its own temperature derivatives are also independent of the concentration scale used. Both ΔH° and ΔC_p° are²⁵ dependent only on temperature (a fact that makes the latter property a convenient basis for the proposed equation). It is therefore not necessary to indicate the concentration scale used.

This independence from concentration scales, however, is not true for $R \ln K^\circ$ ($\equiv -\Delta G^\circ/T$) or ΔS° , and for these the concentration scale used must be indicated. If concentrations are expressed in molalities (m), which are temperature independent, then

$$\partial R \ln K^\circ(m)/\partial T = \Delta H^\circ/T^2$$

If concentrations are expressed in molarities—which are temperature dependent—then, as shown by Guggenheim,^{19,20}

$$\partial R \ln K^\circ(c)/\partial T = \Delta H^\circ/T^2 - nR\alpha$$

where α is the coefficient of cubical expansion of water and n is the increase in the stoichiometric number of particles ($n = r + s - p - q$) whose activities are involved in the equilibrium constant. It is worth mentioning that for the purpose of recall or interpolation the standard equation can be used for $pK(m)$ or $pK(c)$. But if the equation is used to calculate thermochemical properties, the concentration scale used must be temperature independent.^{19,21} For the proposed equation we use $R \ln K^\circ(m)$ in this report, but it is equally applicable to $R \ln K^\circ(x)$ or $R \ln K^\circ(p)$.

However, experimental values of equilibrium conditions are often measured in molarities. Then the first step in fitting to the proposed equation is to convert $R \ln K^\circ(c)$ to $R \ln K^\circ(m)$. Using the Guggenheim relationship given above and since $\alpha = -\partial \ln d_0/\partial T$, it follows that

$$R \ln K^\circ(m) = R \ln K^\circ(c) - nR \ln d_0 \quad (3)$$

Since calculations with $R \ln K^\circ(m)$ will necessarily give $\Delta S^\circ(m)$ it may be desired to convert $\Delta S^\circ(m)$ back to a molarity standard state. This can be done by

$$\Delta S^\circ(c) = \Delta S^\circ(m) + nR \ln d_0 \quad (4)$$

A table of $R \ln d_0$ is given in Table X for temperatures between 0 and 100 °C.

4. The Proposed Equation

The proposed equation is based on the Planck function

$$\begin{aligned} R \ln K^\circ(m) &= \Delta S^\circ(m)(\text{total}) \\ &= \Delta S^\circ(m)(\text{system}) + \Delta S^\circ(\text{environment}) \\ &= \Delta S^\circ(m) - \Delta H^\circ/T \end{aligned}$$

First we assume eq 1 in (T^2), so that for $T > 273.15$

$$\Delta H^\circ = h + \Delta aT + \Delta bT^2/2 + \Delta cT^3/3 \quad (5)$$

$$\Delta S^\circ(m) = s(m) + \Delta a \ln T + \Delta bT + \Delta cT^2/2 \quad (6)$$

Then these three yield

$$\begin{aligned} R \ln K^\circ(m) &= \\ &s(m) + \Delta a(\ln T - 1) - h/T + \Delta bT/2 + \Delta cT^2/6 \quad (7) \end{aligned}$$

But from eq 1, 5, and 6, writing 298 for 298.15 for convenience $s(m) =$

$$\Delta S^\circ(m)_{298} - \Delta a \ln 298.15 - \Delta b298.15 - \Delta c298.15^2/2$$

$$\Delta a = \Delta C_p^\circ_{298} - \Delta b298.15 - \Delta c298.15^2$$

$$-h = -\Delta H^\circ_{298} + \Delta a298.15 + \Delta b298.15^2/2 + \Delta c298.15^3/3$$

Substituting in eq 7 and reorganizing yields the proposed equation

$$\begin{aligned} R \ln K^\circ(m) &= \\ &\Delta S^\circ(m)_{298} - \Delta H^\circ_{298}K_1 + \Delta C_p^\circ_{298}K_2 + \Delta bK_3 + \Delta cK_4 \quad (8) \end{aligned}$$

where

$$K_1 = 1/T$$

$$K_2 = \theta/T + \ln(T/\theta) - 1$$

$$K_3 = T/2 - \theta^2/(2T) - \theta \ln(T/\theta)$$

$$K_4 = T^2/6 + \theta^2(1/2 - \ln(T/\theta)) - 2\theta^3/(3T) \quad (9)$$

and in which $\theta = 298.15$ K.

Numerical values for a set of these TDV are given in Table XI. They are functions only of T and 298.15 K, and except for K_1 , necessarily become zero at 298.15 K. If, however, we assume eq 2 in ($1/T^2$), then for $T > 273.15$ K

$$\begin{aligned} R \ln K^\circ(m) &= \\ &\Delta S^\circ(m)_{298} - \Delta H^\circ_{298}K_1 + \Delta C_p^\circ_{298}K_2 + \Delta bK_3 + \Delta cK_{4R} \quad (8a) \end{aligned}$$

where K_1 , K_2 , and K_3 have the same values as for the (T^2) equation while K_{4R} is given by

$$K_{4R} = 1/(2T^2) + (3/2 - \ln(T/\theta))/\theta^2 - 2/(\theta T) \quad (9a)$$

Should values of the thermochemical properties be desired at temperatures other than 298.15 K, they are given for eq 1 in (T^2) by

$$\Delta C_p^\circ = \Delta C_p^\circ_{298} + \Delta b(T - \theta) + \Delta c(T^2 - \theta^2)$$

$$\begin{aligned} \Delta H^\circ &= \Delta H^\circ_{298} + \Delta C_p^\circ_{298}(T - \theta) + \Delta b(T - \theta)^2/2 + \\ &\Delta c\theta^3(T^3/\theta^3 - 3T/\theta + 2)/3 \quad (10) \end{aligned}$$

$$\begin{aligned} \Delta S^\circ(m) &= \Delta S^\circ(m)_{298} + \Delta C_p^\circ_{298} \ln(T/\theta) + \\ &\Delta b\theta(T/\theta - \ln(T/\theta) - 1) + \Delta c\theta^2(T^2/\theta^2 - 2 \ln(T/\theta) - 1)/2 \end{aligned}$$

5. Use of the Proposed Equation

5.1. Incorporation of Results from Other Work. A major advantage gained from using the proposed equation is that other values of the thermochemical properties can be adopted or adapted during the processing of $R \ln K^\circ(m)$ values. For example, if ΔH°_{298} is accurately known from calorimetric sources, it can be adopted outright thus:

$$\begin{aligned} (R \ln K^\circ(m) + \Delta H^\circ_{298}K_1) &= \\ &\Delta S^\circ(m)_{298} + \Delta C_p^\circ_{298}K_2 + \Delta bK_3 + \Delta cK_4 \end{aligned}$$

The set of values for the left-hand side are then fitted to the terms on the right-hand side. Similarly for any of the other properties.

If a value (say one for $\Delta C_p^\circ_{298}$) is to be taken into account but not adopted outright, then a preliminary fitting of values of $R \ln K^\circ(m)$ yields a value of $\Delta C_p^\circ_{298}$. A weighted and acceptable value of $\Delta C_p^\circ_{298}$ is then arrived at, adopted, and incorporated as suggested above.

$$\begin{aligned} (R \ln K^\circ(m) - \Delta C_p^\circ_{298}K_2) &= \\ &\Delta S^\circ(m)_{298} - \Delta H^\circ_{298}K_1 + \Delta bK_3 + \Delta cK_4 \end{aligned}$$

5.2. The Heat Capacity Function, Z , as a Diagnostic Device. With some programs, paucity or inaccuracy of results may well result in statistical disapproval or even rejection of some of the terms. As will be seen in section 6 on Evaluation, this is most

(19) Guggenheim, E. A. *Trans. Faraday Soc.* **1937**, *33*, 607.

(20) Guggenheim, E. A. "Thermodynamics"; North-Holland: Amsterdam, 1959; p 319.

(21) Hepler, L. G. *Thermochim. Acta* **1981**, *50*, 69.

TABLE II: Abbreviated Example of Data Processing for the Method of Intervals (Temperature Interval 20 deg)

temp step	$\Delta R \ln K^a$	$\Delta R \ln K / \Delta K_1$	$\Delta(\Delta R \ln K / \Delta K_1)$	$\Delta(\Delta R \ln K / \Delta K_1) / \Delta(\Delta K_2 / \Delta K_1) = Z$
0-20	0.1766	-707.1 ± 20.8	822.7 ± 31.7	-41.10 ± 1.58
20-40	-0.0252	115.7 ± 23.9		
40-60	-0.1752	913.9 ± 27.1		
5-25	0.1208	-500.9 ± 21.6	820.1 ± 32.8	-40.97 ± 1.64
25-45	0.0673	319.2 ± 24.7		

^a All $\pm 0.0005_2$.

likely for ΔH°_{298} if that is near zero (as it is in many cases of ionization of carboxylic acids) or for Δb or Δc . The former case will be dealt with in section 5.3 below. The latter is the basis of controversy and pessimism and is discussed by Timimi¹ and King.¹⁸ We have therefore developed and tested a procedure which helps diagnose whether or not to insist, on *experimental grounds*, on the inclusion of what has met with statistical disapproval or rejection.

Our method of diagnosis is only a variation on an old theme with one major difference: instead of using gradient differences as approximations to differentials, as described by Ives and Moseley,²² they are used in a way that is always precise and is as accurate as the experimental data allow.

Subtraction of any two values of $R \ln K^\circ(m)$ gives $\Delta R \ln K^\circ(m)$ where the Δ refers here and subsequently to the process

$$\Delta X = \text{value of } X \text{ at } T_2 - \text{value of } X \text{ at } T_1 \quad (T_2 > T_1)$$

From eq 8

$$\Delta R \ln K^\circ(m) = -\Delta H^\circ_{298} \Delta K_1 + \Delta C_p^\circ_{298} \Delta K_2 + \Delta b \Delta K_3 + \Delta c \Delta K_4 \quad (11)$$

and hence

$$\Delta R \ln K^\circ(m) / \Delta K_1 = -\Delta H^\circ_{298} + \Delta C_p^\circ_{298} \Delta K_2 / \Delta K_1 + \Delta b \Delta K_3 / \Delta K_1 + \Delta c \Delta K_4 / \Delta K_1 \quad (12)$$

A second subtraction of any two values of $\Delta R \ln K^\circ(m) / \Delta K_1$ and subsequent division results in

$$Z \equiv \frac{\Delta(\Delta R \ln K^\circ(m) / \Delta K_1)}{\Delta(\Delta K_2 / \Delta K_1)} = \frac{\Delta C_p^\circ_{298} + \frac{\Delta b \Delta(\Delta K_3 / \Delta K_1)}{\Delta(\Delta K_2 / \Delta K_1)} + \frac{\Delta c \Delta(\Delta K_4 / \Delta K_1)}{\Delta(\Delta K_2 / \Delta K_1)}}{\Delta(\Delta K_2 / \Delta K_1)} \quad (13)$$

which has the form

$$Z = \Delta C_p^\circ_{298} + \Delta b x + \Delta c y \quad (14)$$

This looks cumbersome and offputting but all the terms except $\Delta R \ln K^\circ(m)$ contain only terms in T so that tables of only four derived TDV's are needed (see Tables XII–XVIII). They are

$$\Delta K_1 \quad \Delta(\Delta K_2 / \Delta K_1) \quad \frac{\Delta(\Delta K_3 / \Delta K_1)}{\Delta(\Delta K_2 / \Delta K_1)} = x \quad \frac{\Delta(\Delta K_4 / \Delta K_1)}{\Delta(\Delta K_2 / \Delta K_1)} = y$$

The above deduction holds for the subtraction of any two $R \ln K^\circ(m)$ and $R \ln K^\circ(m)$ values but the volume of tabulation of derived TDV's required could be unacceptably large for irregular intervals. We reduce that volume by (i) measuring $R \ln K^\circ(m)$ at specified temperature steps, e.g., precisely 5-deg steps from 0 to 100 °C and (ii) restricting subtractions to selected successive differences, as illustrated by the table of derived TDV in Tables XII–XVIII. The procedure is best illustrated in Table II by an abbreviated example based on the treatment of benzoic acid data.

A plot of Z against x (the latter given in the table of derived TDV in Tables XII–XVIII) for each of the temperature steps indicates whether the Z function should be considered a horizontal straight line ($\Delta b = \Delta c = 0$), a sloping straight line ($\Delta b \neq 0$; Δc

TABLE III: Approximate Uncertainties in Z Values^a

at 10° intervals	0-10° 10-20°	$\delta = 1660x$ and	40-50° 50-60°	$\delta = 2090x$
at 15° intervals	0-15° 15-30°	$\delta = 760x$ and	35-50° 50-65°	$\delta = 930x$
at 20° intervals	10-30° 30-50°	$\delta = 460x$ and	45-65° 65-86°	$\delta = 570x$
at 25° intervals	5-30° 30-55°	$\delta = 300x$ and	40-65° 65-90°	$\delta = 370x$
at 30° intervals	0-30° 30-60°	$\delta = 200x$ and	40-70° 70-100°	$\delta = 250x$
at 35° intervals	0-35° 35-70°	$\delta = 160x$ and	30-65° 65-100°	$\delta = 190x$
at 40° intervals	0-40° 40-80°	$\delta = 120x$ and	20-60° 60-100°	$\delta = 140x$

^a Intermediate values can be obtained by interpolation.

= 0), or a quadratic ($\Delta b \neq 0$; $\Delta c \neq 0$)—or whether the initial data need smoothing before a decision can be made.

Although the need to use the diagnostic step may occur only if the program for direct fitting has statistically rejected a term in Δb or Δc , there are times when confirmation is worthwhile. We have found the following points of value:

a. The size of the temperature steps used to calculate successive differences is important. It should be chosen so as to give as many first differences as possible PROVIDING that these differences are adequately large relative to their uncertainties. Z values for three temperature intervals are adequate, and for the ionization of substituted benzoic acids we have found, with data recently available, that the balance between an adequate number of points (small intervals) and small uncertainties (large intervals) is struck by using intervals of 20, 30, and 40 deg. With 21 experimental points between 0 and 100 °C this gives 13, 9, and 5 Z values, respectively, for the three intervals. If $\Delta c = 0$ then, all three plots will be approximately parallel as well as rectilinear.

b. *Uncertainties in Z values* calculated from uncertainty levels in $R \ln K$ should always be included in the Z plot. They can be a great help in deciding how far the accuracy of experimental values justifies the insistence on a term in Δb and/or Δc (see Figure 2).

c. *A superimposed plot of the Z function, back-calculated using eq 12 from values of $\Delta C_p^\circ_{298}$, Δb , and Δc obtained by direct fitting of $R \ln K^\circ(m)$ to the proposed equation, offers evidence as to how far the Z plots and the direct fitting are mutually supportive.* Figure 2 illustrates this.

d. If the Z plot is programmed on a computer, the uncertainties in Z due to the initial ones in $R \ln K(m)$ can be included in the plot of the individual points. If the plot is done by hand, a rough guide is given in Table III derived in the following way. Assuming an average uncertainty of x for the three values of $R \ln K^\circ(m)$ needed for one Z value, then the uncertainty, δ , in the resulting Z is negligibly different from $\delta = x 2^{1/2} T_2 (T_1^2 + T_3^2)^{1/2} / (\Delta T)^2$ where ΔT is the temperature interval: $\Delta T = T_2 - T_1 = T_3 - T_2$.

The value of this diagnostic procedure can be judged from Figure 2 which shows the Z plots for five substituted benzoic acids, some of which had Δb and/or Δc terms rejected on statistical grounds during a direct fitting procedure. The 30- and 40-deg interval plots are offset to make comparisons easier. The double-headed arrows show the size of a $1/5000$ uncertainty. An asterisk superscripted to the figure number indicates that for that set of data a direct fitting by one or more procedures rejected terms higher than the third. Experimental results used in Figure 2a–d

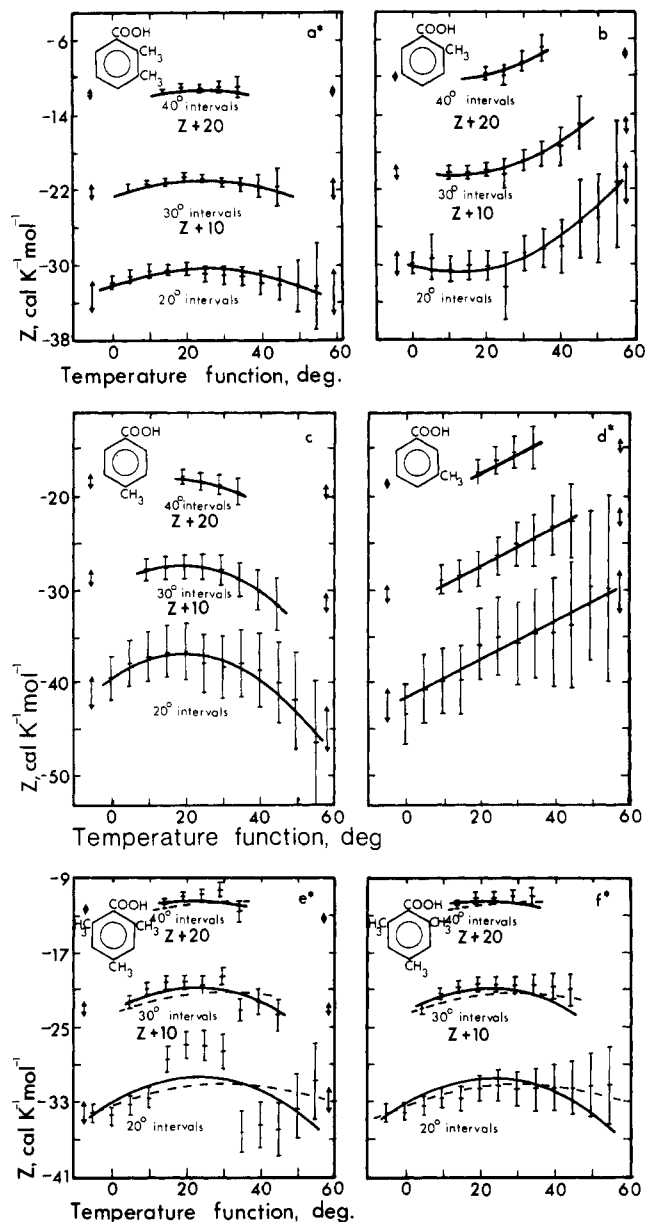


Figure 2. Plots of the heat capacity function, Z , for six substituted benzoic acids. Z values for 30- and 40-deg intervals have been displaced by 10 and 20 units, respectively, for easier inspection. * indicates that there is statistical rejection of a Δc and/or a Δb term in a direct fitting to the standard form. I, Z values and error bars by method of intervals. —, Z by back-calculation as described in text. \downarrow , $1/5000$ error in initial $R \ln K$ data.

are from Strong et al.²³ Those in Figure 2e,f are from Strong et al.²⁴

Figure 2a* is an example which shows relatively small experimental errors in $R \ln K^\circ(m)$ (less than $1/5000$) for nearly the entire temperature range and a definite curvature in Z which

(23) Strong, L. E.; Copeland, T. G.; Darragh, M.; Van Waes, C. J. *Solution Chem.* **1980**, *9*, 109.

(24) Strong, L. E.; Blubaugh, D. J.; Kallmyer, J. B.; Taylor, S. P. *J. Phys. Chem.* **1985**, *89*, 1318.

(25) This is apparently in direct contradiction to the remarks of Ashby, Crook, and Datta¹⁷ as well as King¹⁸ who stated

$$\Delta H^\circ(c) = \Delta H^\circ(m) + 2.3026RT^2 d \log d_0/dT$$

$$\Delta C_p^\circ(c) = \Delta C_p^\circ(m) + 2.3026RT(2d \log d_0/dT + T^2 d^2 \log d_0/dT^2)$$

where d_0 is the density of water. However, it is not in contradiction to their remarks if by $\Delta H^\circ(c)$ and $\Delta C_p^\circ(c)$ they meant the inappropriate and wrong value of ΔH° and ΔC_p° obtained when the procedure appropriate to molal values of K° is applied to $K^\circ(c)$ values.

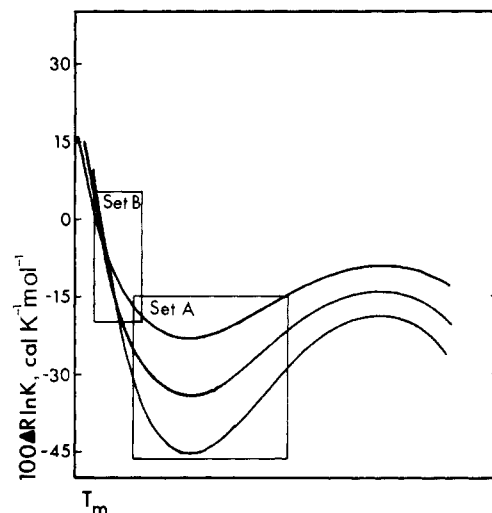


Figure 3. Generalized pattern of $\Delta R \ln K^\circ(m)$ values plotted against the midpoint temperature, T_m . The insets indicate two common smoothing plots which are similar to actual plots given by set A and set B of the simulated results used in section 6.

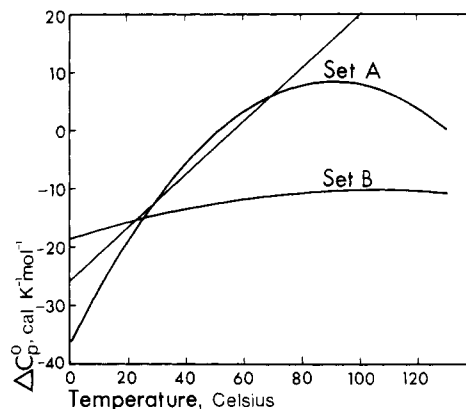


Figure 4. Variation of ΔC_p° with temperature for the two sets of simulated results as described in section 6.1. Set A: $\Delta C_p^\circ = -718.686 + 4T - 0.00557T^2$, maximum at 90.50 °C and $\Delta C_p^\circ = 0$ at 50.98 and 130.00 °C; set B: $\Delta C_p^\circ = -122/775 + 0.6T - 0.0008T^2$, maximum at 101.85 °C. The straight line indicates values of $\Delta C_p^\circ_T$ recovered from set A having a precision of $1/1500$. See section 6.2.2.

points to a five-term equation in $R \ln K$ with ΔC_p° going through a maximum as a function of temperature although a more conventional statistical analysis rejects the possibility of a Δb or Δc term. Figure 2b is an acid for which the experimental errors are higher than in Figure 2a* but where, nonetheless, curvature is clearly evident while Figure 2c is similar except that curvature is in the opposite direction so that ΔC_p° must go through a minimum within the experimental temperature range. An acid is shown in Figure 2d* for which a direct fitting of the experimental data by one of the procedures results in a statistical rejection of terms higher than the third in $R \ln K$. In this the Z plot is quite unambiguous in its indication that ΔC_p° is linearly related to the temperature and so requires a fourth term in the $R \ln K$ equation. In each of the parts a*–d of Figure 2 smooth curves are drawn which were calculated from the direct fitting of the experimental data to eq 8. No smoothing at the $\Delta R \ln K$ stage was deemed necessary.

Figure 2e* is an example of a Z plot in which the scatter is too great to be sure what the best number of terms in eq 8 should be and in which fitting by more conventional statistical means indicated only three terms to be acceptable. Following the procedure outlined in section 5.3 below for smoothing at the $\Delta R \ln K$ stage a new set of Z values was calculated and plotted in Figure 2f*. The largest adjustments to $\Delta R \ln K$ were no more than 0.1% of $R \ln K$. The continuous curves shown in parts e* and f* are as described above. In these two cases a dashed curve is also

TABLE IV: Procedural Scheme for the Use of the Proposed Equation

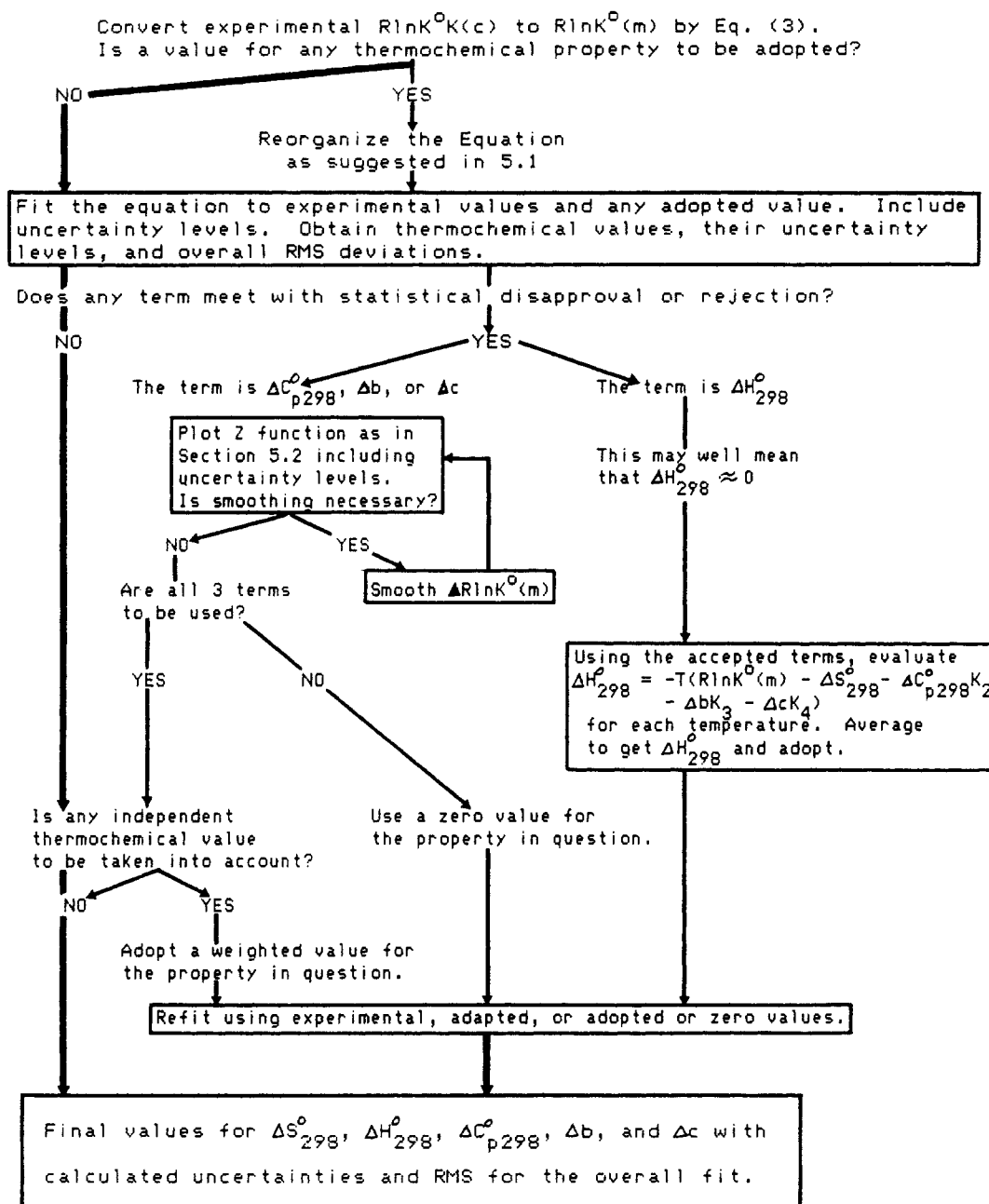


TABLE V: Selected Values for Eq 8 Used To Derive Simulated Results

	$\Delta S_{298}^{\circ}/\text{cal K}^{-1} \text{ mol}^{-1}$	$\Delta H_{298}^{\circ}/\text{cal mol}^{-1}$	$\Delta C_{p298}^{\circ}/\text{cal K}^{-1} \text{ mol}^{-1}$	$\Delta b/\text{cal K}^{-2} \text{ mol}^{-1}$	$\Delta c/\text{cal K}^{-3} \text{ mol}^{-1}$
Set A	-20.0	-1000.0	-15.0	+4.0	-0.0055
Set B	-20.0	0.0	-15.0	+0.6	-0.0008

shown. It is for Z calculated after smoothing $\Delta R \ln K$. It is clear from Figure 2f* that the $R \ln K(m)$ data for this acid are best represented by five terms of eq 8 in spite of the initial statistical rejection.

A spinoff from the Z -plot procedure is that it offers a means of fitting values of $R \ln K^{\circ}(m)$ to a five-term equation on any pocket calculator which will fit data to a three-term equation. (1) Obtain Z values as above and fit to the three-term equation

$$Z = \Delta C_{p298}^{\circ} + \Delta b x + \Delta c y$$

so getting ΔC_{p298}° , Δb , and Δc . (2) Then using

$$R \ln K^{\circ}(m) - \Delta C_{p298}^{\circ} K_2 - \Delta b K_3 - \Delta c K_4 = \Delta S^{\circ}(m)_{298} - \Delta H^{\circ}_{298} K_1 \quad (15)$$

and the basic TDV from Tables XII–XVIII obtain $\Delta S^{\circ}(m)_{298}$ and ΔH°_{298} .

5.3. Smoothing of Experimental Values. One value of a Z plot is that it can indicate whether some of the experimental values show a scatter that is greater than the expected random uncertainty level. This is illustrated in Figure 2. Even with a substantial number of data points, adjusting one or two of them can be risky if the adjustments are to be made near the end of the range. Adjustment can also be unreliable when the values go through a gentle maximum or minimum. We have found that both these risks can be reduced by doing the adjusting at the $\Delta R \ln K^{\circ}(m)$ stage of the calculations. This is due to the values of $\Delta R \ln K^{\circ}(m)$ at differing temperature intervals and for different substances being part of a common pattern as shown in Figure 3. The generality of this very useful approximate pattern has been confirmed by a first approximation equation for $\Delta R \ln K^{\circ}$ as a function of T_m .

As is seen in Figure 2, the Z plot can indicate that some of the experimental values have a greater than random uncertainty level. Smoothing at the $R \ln K^{\circ}(m)$ stage is usually somewhat ineffectual and even dangerous,²² and if values go through a maximum, is

TABLE VI: Simulated Experimental Results of Differing Confidence Levels: Sample from Set A

temp °C	$R \ln K^\circ(m)/\text{cal K}^{-1} \text{mol}^{-1}$	$1/500 (\pm 0.03)$	$1/1500 (\pm 0.01)$	$1/5000 (\pm 0.003)$	$1/15000 (\pm 0.0010)$	$1/50000 (\pm 0.0003)$
0	-16.42461	-16.43	-16.425	-16.426	-16.4237	-16.4246
5	-16.45474	-16.46	-16.456	-16.452	-16.4542	-16.4545
10	-16.49384	-16.51	-16.490	-16.496	-16.4932	-16.4940
15	-16.53989	-16.53	-16.540	-16.537	-16.5401	-16.5498
20	-16.59111	-16.56	-16.592	-16.594	-16.5904	-16.5909
25	-16.64598	-16.67	-16.635	-16.647	-16.6454	-16.6463
30	-16.70320	-16.73	-16.695	-16.702	-16.7024	-16.7033
35	-16.76166	-16.76	-16.752	-16.761	-16.7616	-16.7617
40	-16.82043	-16.82	-16.822	-16.818	-16.8209	-16.8206
45	-16.87872	-16.87	-16.876	-16.877	-16.8784	-16.8787
50	-16.93589	-16.93	-16.927	-16.934	-16.9366	-16.9357
55	-16.99142	-17.02	-17.000	-16.994	-16.9910	-16.9917
60	-17.04492	-17.03	-17.047	-17.044	-17.0460	-17.0449
65	-17.09606	-17.13	-17.097	-17.096	-17.0951	-17.0958
70	-17.14465	-17.16	-17.155	-17.146	-17.1446	-17.1448
75	-17.19053	-17.21	-17.185	-17.192	-17.1907	-17.1904
80	-17.23363	-17.20	-17.222	-17.233	-17.2337	-17.2334
85	-17.27396	-17.26	-17.278	-17.271	-17.2730	-17.2743
90	-17.31157	-17.35	-17.312	-17.310	-17.3119	-17.3118
95	-17.34655	-17.38	-17.352	-17.345	-17.3467	-17.3464
100	-17.37906	-17.35	-17.372	-17.381	-17.3796	-17.3792

TABLE VII: Effect of Limiting the Temperature Range on the Recovery of Thermochemical Properties^a

subset	temp range	no. of exptl points	ΔS°_{298}	ΔH°_{298}	$\Delta C_p^\circ_{298}$	Δb	$1000\Delta c$
"True" Values							
			-20	-1000	-15	4	-5.5
Recovered Values							
1	5°-55° at 10-deg intervals	6	-20.13 thru -19.87	-1040 thru -960	-22 thru -8	-29 thru +37	-70 thru +60
2	5°-55° at 5-deg intervals	11	-20.10 thru -19.90	-1025 thru -975	-19 thru -11	-20 thru +30	-45 thru +30
3	0°-100° at 10-deg intervals	11	-20.04 thru -19.96	-1010 thru -990	-16 thru -14	3 thru 6	-7 thru -4
4	0°-100° at 10-deg intervals ^b	21					

^a Each subset is based on SR set A at $1/50000$ precision in $R \ln K^\circ(m)$. ^b For precision see Table IX; for accuracy see Figure 5.

especially undesirable since it can impose an unreliable value on ΔH°_{298} .

The various steps of the procedure are summarized by a flow chart in Table IV.

6. Evaluation

6.1. The Use of Simulated Results as an Evaluative Tool. To compare the efficacy of different schemes for obtaining thermochemical properties from values of $R \ln K^\circ(m)$, exact values were chosen for ΔS°_{298} , ΔH°_{298} , $\Delta C_p^\circ_{298}$, Δb , and Δc not unlike those found for the ionization of some substituted benzoic acids. From these, "precise" simulated values of $R \ln K^\circ_T(m)$ were produced by means of eq 8 for 21 evenly spaced temperatures between 0 and 100 °C. Then, by feeding in random errors of decreasing size into these precise values, subsets of simulated experimental results (SR) of increasing confidence levels $1/500$, $1/1500$, $1/5000$, $1/15000$, and $1/50000$ were produced. There will be frequent reference to these confidence levels. It is important to note that they refer to values of $R \ln K^\circ(m)$. This is stressed because a target confidence level in $R \ln K^\circ(m)$ is achieved from a confidence level in $K^\circ(m)$ that varies with the size of $K^\circ(m)$. For example: if $K = 10^{-1}$ then $1/15000$ in $R \ln K^\circ(m)$ arises from $1/6500$ in K while if $K = 10^{-9}$ then $1/15000$ in $R \ln K^\circ(m)$ is produced by $1/700$ in K . Two sets of exact values were used as shown in Table V.

The pattern of ΔC_p° for the two synthetic sets is shown in Figure 4. Set A has a ΔC_p° which over a limited temperature range could be thought rectilinear in T with $\Delta c = 0$. Furthermore, if the precision of the available data is low, then a term in Δc may well be rejected on statistical grounds and a straight line obtained for ΔC_p° as shown in Figure 4. Set B has a ΔC_p° which over a moderate temperature range might even be thought constant, with $\Delta b = \Delta c = 0$. Set B, which is representative of some para- and/or meta-substituted benzoic acids, offers greater difficulties for accurate analysis than does set A which is more representative of rather different acids.

From these two sets, using eq 8, "precise" synthetic values of $R \ln K^\circ(m)$ were produced and then from these were produced

TABLE VIII: Extent of Statistical Disapproval—Simulated Results Which Lead to One or More Terms Rejected on Statistical Grounds When Being Fitted Directly to a Five-Term Equation: a List of Rejected Terms^a

precision in $R \ln K^\circ$		terms rejected							
		set A				set B			
		no.	stand.	C & G	proposed	stand.	C & G	proposed	
$1/500$	1	2	b	c	c	b	c	c	h
	2	3	b	c	p	b	c	b	c
	3	4	b	c	c	b	c	b	c
	4	5	b	c	p	b	c	b	c
	5	6	b	c	c	b	c	b	c
$1/1500$	1	1	c	c	c	c	c	c	h
	2	2	c	c	c	c	c	c	h
	3	3	c	c	c	b	c	b	c
	4	4	c	c	c	b	c	b	c
	5	5	c	c	c	c	c	c	b
$1/5000$	1	1	c	c	c	c	c	c	h
	2	2	c	c	c	c	c	c	h
	3	3	c	c	c	c	c	c	h
	4	4	c	c	c	c	c	c	h
	5	5	c	c	c	c	c	c	h
$1/15000$	1	1	c	c	c	c	c	c	h
	2	2	c	c	c	c	c	c	h
	3	3	c	c	c	c	c	c	h
	4	4	c	c	c	c	c	c	h
	5	5	c	c	c	c	c	c	h

^a $h = \Delta H^\circ$; $p = \Delta C_p^\circ$; $b = \Delta b$; $c = 1000\Delta c$. The fitting procedures used were as follows: standard multiple linear regression analysis; C & G, Taylor expansion procedure as recommended by Clarke and Glew;³ proposed, the "all possible subsets" procedure using BMD-P9R.

five levels of confidence for each set and finally five sets of randomized numbers were introduced to give a total of 50 subsets (each covering 21 temperatures) for analysis. For the sake of simplicity we have held the confidence level constant in any one subset of SR. In practice, experimental values at either end of the temperature range often have uncertainties 2 or 3 times larger than in the middle of the range. Table VI shows one of the five samples from set A.

TABLE IX: Simulated Results Sets A and B: 90% Confidence Limits for 40 Samples with Each Having 21 Data Points in the Temperature Range 0–100 °C

thermochemical quantity	recovered values			
$\Delta S^\circ_{298}/\text{cal K}^{-1} \text{ mol}^{-1}$	± 0.30	± 0.09	± 0.03	± 0.009
$\Delta H^\circ_{298}/\text{cal mol}^{-1}$	± 80	± 24	± 8	± 2.4
$\Delta C_p^\circ_{298}/\text{cal K}^{-1} \text{ mol}^{-1}$	± 5.0	± 1.5	± 0.5	± 0.15
$\Delta b/\text{cal K}^{-2} \text{ mol}^{-1}$	± 9.0	± 2.7	± 0.9	± 0.27
$1000\Delta c/\text{cal K}^{-3} \text{ mol}^{-1}$	± 13	± 4	± 1.3	± 0.4
$(-\Delta H^\circ/T)_{298}$	± 0.27	± 0.08	± 0.03	± 0.008
confidence level for $R \ln K^\circ(m)$ values	1/500	1/1500	1/5000	1/15000

TABLE X: Values of $d(\text{water})_T$ and $R \ln d(\text{water})_T^a$

t °C	$d^\circ_T/\text{g cm}^{-3}$	$-R \ln d^\circ_T/\text{cal K}^{-1} \text{ mol}^{-1}$	t °C	$d^\circ_T/\text{g cm}^{-3}$	$-R \ln d^\circ_T/\text{cal K}^{-1} \text{ mol}^{-1}$
0	0.9998 ₄	0.0003 ₂	55	0.9857 ₀	0.0286 ₃
5	0.9999 ₆	0.0000 ₇	60	0.9832 ₀	0.0336 ₇
10	0.9997 ₀	0.0006 ₀	65	0.9805 ₅	0.0390 ₂
15	0.9991 ₀	0.0017 ₉	70	0.9777 ₇	0.0446 ₇
20	0.9982 ₀	0.0035 ₇	75	0.9748 ₅	0.0506 ₂
25	0.9970 ₄	0.0058 ₈	80	0.9718 ₀	0.0568 ₅
30	0.9956 ₅	0.0086 ₇	85	0.9686 ₂	0.0633 ₆
35	0.9940 ₃	0.0119 ₀	90	0.9653 ₂	0.0701 ₄
40	0.9922 ₂	0.0155 ₃	95	0.9619 ₀	0.0771 ₉
45	0.9902 ₁	0.0195 ₄	100	0.9583 ₆	0.0845 ₁
50	0.9880 ₄	0.0239 ₂			

^a $R = 1.98717 \pm 0.00019 \text{ cal K}^{-1} \text{ mol}^{-1}$.**TABLE XI: Basic Temperature-Dependent Variables**

temp/°C	$10000K_1/\text{deg}^{-1}$	$1000K_2$	$1000K_3/\text{deg}$	K_4/deg^2
0	36.609 92	3.949 18	-33.388 72	-19.488 68
5	35.951 82	2.467 47	-16.639 71	-9.754 71
10	35.316 97	1.355 53	-6.835 87	-4.024 69
15	34.704 15	0.588 61	-1.973 17	-1.166 70
20	34.112 23	0.143 82	-0.240 38	-0.142 74
25	33.540 16	0.000 00	0.000 00	0.000 00
30	32.986 97	0.137 53	0.228 58	0.136 88
35	32.451 73	0.538 23	1.784 24	1.072 83
40	31.933 58	1.185 23	5.877 57	3.548 66
45	31.431 71	2.062 82	13.603 05	8.246 64
50	30.945 38	3.156 44	25.949 80	15.795 63
55	30.473 87	4.452 50	43.811 40	26.775 61
60	30.016 51	5.938 34	67.994 62	41.721 89
65	29.572 67	7.602 17	99.227 28	61.128 80
70	29.141 77	9.432 97	138.165 44	85.453 10
75	28.723 25	11.420 45	185.399 73	115.117 04
80	28.316 58	13.554 99	241.461 22	150.511 18
85	27.921 26	15.827 61	306.826 66	191.996 91
90	27.536 83	18.229 86	381.923 23	239.908 78
95	27.162 84	20.753 86	467.132 86	294.556 57
100	26.798 87	23.392 21	562.796 13	356.227 25

6.2. The Emergent Patterns. Since we are offering evidence that the temperature dependence of $\Delta C_p^\circ_T$ is much more accessible than is usually acknowledged, we are interested in the accuracy and the confidence level with which thermodynamic properties are deducible from $R \ln K^\circ(m)$ values. We explored this under five headings.

6.2.1. Effect of Restricting the Temperature Range of Experimental Measurements. Five samples of SR were used (with one taken from Table VI). They all had an uncertainty level of $1/5000$ in $R \ln K^\circ(m)$. The difference between the results from subset 2 and subset 3 given in Table VII is quite remarkable in its indication of the significance of the temperature range for precision in the recall of thermodynamic quantities. However, exploration of a system similar to subset 2 indicates that useful recovery of ΔC_p° , Δb , and Δc is possible even there, providing $R \ln K^\circ(m)$ values have not too small a temperature range and providing the uncertainties in $R \ln K^\circ(m)$ are $< 1/5000$.

Work with solubility products of ionic salts has confirmed advice by Timimi:¹ to get reliable values of $\Delta C_p^\circ_{298}$ at least six values

TABLE XII: Temperature-Dependent Variables (10 °C Intervals)

interval/°C	$10000\Delta K_1/\text{deg}^{-1}$	$\Delta(\Delta K_2/\Delta K_1)/\text{deg}$	x^a	y^b
0–10	-1.292 951	-10.002 08	-15.058 88	-8 736.17
10–20	-1.204 741	-10.001 94	-5.056 87	-2 973.17
20–30	-1.125 259	-10.001 81	4.945 01	2 989.83
30–40	-1.053 392	-10.001 70	14.946 76	9 152.83
40–50	-0.988 197	-10.001 60	24.948 41	15 515.83
50–60	-0.928 872	-10.001 50	34.949 96	22 078.83
60–70	-0.874 734	-10.001 42	44.951 42	28 841.83
70–80	-0.825 195	-10.001 34	54.952 80	35 804.83
80–90	-0.779 749	-10.001 26	64.954 10	42 967.83
90–100	-0.737 956			
5–15	-1.247 677	-10.002 01	-10.057 86	-5 879.67
15–25	-1.163 983	-10.001 88	-0.055 91	-16.67
25–35	-1.088 436	-10.001 76	9.945 90	6 046.33
35–45	-1.020 013	-10.001 65	19.947 60	12 309.33
45–55	-0.957 846	-10.001 55	29.949 20	18 772.33
55–65	-0.901 194	-10.001 46	39.950 70	25 435.33
65–75	-0.849 423	-10.001 38	49.952 12	32 298.33
75–85	-0.801 989	-10.001 30	59.953 46	39 361.33
85–95	-0.758 421			

^a $x = \Delta(\Delta K_3/\Delta K_1)/\Delta(\Delta K_2/\Delta K_1)$, deg. ^b $y = \Delta(\Delta K_4/\Delta K_1)/\Delta(\Delta K_2/\Delta K_1)$, deg².

TABLE XIII: Temperature-Dependent Variables (15 °C Intervals)

interval/°C	$10000\Delta K_1/\text{deg}^{-1}$	$\Delta(\Delta K_2/\Delta K_1)/\text{deg}$	x^a	y^b
0–15	-1.905 774	-15.006 78	-10.130 22	-5 900.52
15–30	-1.717 177	-15.006 13	4.876 23	2 968.98
30–45	-1.555 256	-15.005 56	19.882 07	12 288.48
45–60	-1.415 206	-15.005 07	34.887 38	22 057.98
60–75	-1.293 258	-15.004 64	49.892 24	32 277.48
75–90	-1.186 421			
5–20	-1.839 595	-15.006 55	-5.128 00	-2 994.02
20–35	-1.660 501	-15.005 93	9.878 24	6 025.48
35–50	-1.506 347	-15.005 39	24.883 90	15 494.98
50–65	-1.372 707	-15.004 92	39.889 05	25 414.48
65–80	-1.256 095	-15.004 51	54.893 77	35 783.98
80–95	-1.153 738			
10–25	-1.776 805	-15.006 33	-0.125 85	-37.52
25–40	-1.606 586	-15.005 74	14.880 18	9 131.98
40–55	-1.459 709	-15.005 23	29.885 67	18 751.48
55–70	-1.332 094	-15.004 78	44.890 67	28 820.98
70–85	-1.220 513	-15.004 39	59.895 25	39 340.48
85–100	-1.122 388			

^a $x = \Delta(\Delta K_3/\Delta K_1)/\Delta(\Delta K_2/\Delta K_1)$, deg. ^b $y = \Delta(\Delta K_4/\Delta K_1)/\Delta(\Delta K_2/\Delta K_1)$, deg².

TABLE XIV: Temperature-Dependent Variables (20 °C Intervals)

interval/°C	$10000\Delta K_1/\text{deg}^{-1}$	$\Delta(\Delta K_2/\Delta K_1)/\text{deg}$	x^a	y^b
0–20	-2.497 692	-20.015 54	-5.227 66	-3 023.24
20–40	-2.178 651	-20.013 62	14.786 91	9 102.77
40–60	-1.917 069	-20.012 03	34.799 72	22 028.78
60–80	-1.669 930	-20.010 70	54.811 08	35 754.78
80–100	-1.517 705			
5–25	-2.411 660	-20.015 03	-0.223 84	-66.74
25–45	-2.108 450	-20.013 19	19.790 26	12 259.27
45–65	-1.859 040	-20.011 68	39.802 69	25 385.28
65–85	-1.651 413			
10–30	-2.330 000	-20.014 53	4.779 86	2 939.77
30–50	-2.041 589	-20.012 79	24.793 51	15 465.77
50–70	-1.803 607	-20.011 34	44.805 57	28 791.78
70–90	-1.604 944			
15–35	-2.252 419	-20.014 07	9.783 44	5 996.27
35–55	-1.977 859	-20.012 40	29.796 66	18 722.28
55–75	-1.750 617	-20.011 01	49.808 36	32 248.28
75–95	-1.560 410			

^a $x = \Delta(\Delta K_3/\Delta K_1)/\Delta(\Delta K_2/\Delta K_1)$, deg. ^b $y = \Delta(\Delta K_4/\Delta K_1)/\Delta(\Delta K_2/\Delta K_1)$, deg².

between 0 and 50 °C are needed. To get Δb and Δc further values at higher temperatures are needed as well.

6.2.2. Results with Samples of 21 Data Points Covering 0–100

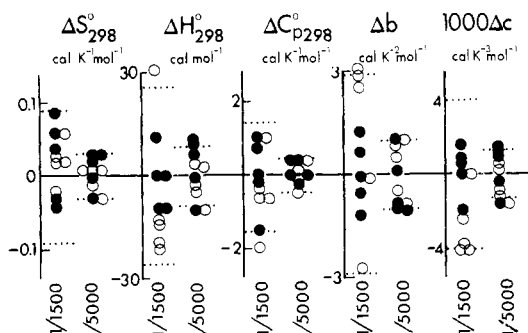


Figure 5. Simulated results (SR) ($1/1500$ and $1/5000$): accuracy of recall (calcd - "true"); five subsets of set A and five subsets of set B; each subset contained 21 temperatures. --- indicates 90% confidence level from Table IX.

TABLE XV: Temperature-Dependent Variables (25 °C Intervals)

interval/ °C	$10000\Delta K_1 / \text{deg}^{-1}$	$\Delta(\Delta K_2 / \Delta K_1) / \text{deg}$	x^a	y^b
0-25	-3.069 757	-25.029 38	-0.349 95	-104.34
25-50	-2.594 783	-25.025 00	24.677 20	15 428.19
50-75	-2.222 130	-25.021 53	49.700 44	32 210.71
75-100	-1.924 377			
5-30	-2.964 854	-25.028 41	4.655 84	2 902.17
30-55	-2.513 101	-24.024 24	29.682 13	18 684.69
55-80	-2.157 289			
10-35	-2.865 242	-25.027 50	9.661 44	5 958.67
35-60	-2.435 219	-25.023 52	34.686 92	21 991.20
60-85	-2.095 247			
15-40	-2.770 569	-25.026 62	14.666 86	9 065.18
40-65	-2.360 903	-25.022 82	39.691 56	25 347.70
65-90	-2.035 844			
20-45	-2.680 515	-25.025 79	19.672 11	12 221.68
45-70	-2.289 940	-25.022 16	44.696 06	28 754.20
70-95	-1.978 934			

^a $x = \Delta(\Delta K_3 / \Delta K_1) / \Delta(\Delta K_2 / \Delta K_1)$, deg. ^b $y = \Delta(\Delta K_4 / \Delta K_1) / \Delta(\Delta K_2 / \Delta K_1)$, deg².

TABLE XVI: Temperature-Dependent Variables (30 °C Intervals)

interval/ °C	$10000\Delta K_1 / \text{deg}^{-1}$	$\Delta(\Delta K_2 / \Delta K_1) / \text{deg}$	x^a	y^b
0-30	-3.622 951	-30.049 16	4.504 06	2 856.16
30-60	-2.970 461	-30.040 68	34.548 90	21 945.22
60-90	-2.479 679			
5-35	-3.500 097	-30.047 57	9.512 14	5 912.67
35-65	-2.879 053	-30.039 48	39.555 59	25 301.72
65-95	-2.409 834			
10-40	-3.383 392	-30.046 06	14.519 97	9 019.18
40-70	-2.791 803	-30.038 33	44.562 09	28 708.23
70-100	-2.342 900			
15-45	-3.272 433	-30.044 62	19.527 54	12 175.69
45-75	-2.708 463			
20-50	-3.166 848	-30.043 24	24.534 88	15 382.20
50-80	-2.628 802			
25-55	-3.066 296	-30.041 93	29.542 00	18 638.71
55-85	-2.552 607			

^a $x = \Delta(\Delta K_3 / \Delta K_1) / \Delta(\Delta K_2 / \Delta K_1)$, deg. ^b $y = \Delta(\Delta K_4 / \Delta K_1) / \Delta(\Delta K_2 / \Delta K_1)$, deg².

°C: *Extent of Statistical Rejection.* Table VIII summarizes our survey limited to four confidence levels. The increased uncertainty encountered if $R \ln K^\circ(m)$ goes through a maximum or minimum (refer to sections 5.2 and 6.2.3) is obvious here. All three programs rejected a Δc term unless experimental results were very precise. However, if the statistical disapproval was disregarded (*since we knew that there were Δb and Δc terms*) and five terms were calculated then the recovered thermodynamic values show characteristics which will be dealt with later.

6.2.3. Results with Samples of 21 Data Points covering 0-100 °C: Comparison of the Three Procedures.

When five terms were insisted on, *direct fitting by all three equations* (the standard

TABLE XVII: Temperature-Dependent Variables (35 °C Intervals)

interval/ °C	$10000\Delta K_1 / \text{deg}^{-1}$	$\Delta(\Delta K_2 / \Delta K_1) / \text{deg}$	x^a	y^b
0-35	-4.158 193	-35.075 64	9.335 44	5 858.22
35-70	-3.309 953			
5-40	-4.018 246	-35.073 24	14.346 11	8 964.73
40-75	-3.210 327			
10-45	-3.885 255	-35.070 94	19.356 45	12 121.25
45-80	-3.115 135			
15-50	-3.758 766	-35.068 75	24.366 46	15 327.77
50-85	-3.024 119			
20-55	-3.638 361	-35.066 66	29.376 16	18 584.29
55-90	-2.937 038			
25-60	-3.523 655	-35.064 67	34.385 58	21 890.80
60-95	-2.853 668			
30-65	-3.414 295	-35.062 76	39.394 71	25 247.32
65-100	-2.773 800			

^a $x = \Delta(\Delta K_3 / \Delta K_1) / \Delta(\Delta K_2 / \Delta K_1)$, deg. ^b $y = \Delta(\Delta K_4 / \Delta K_1) / \Delta(\Delta K_2 / \Delta K_1)$, deg².

TABLE XVIII: Temperature-Dependent Variables (40 °C Intervals)

interval/ °C	$10000\Delta K_1 / \text{deg}^{-1}$	$\Delta(\Delta K_2 / \Delta K_1) / \text{deg}$	x^a	y^b
0-40	-4.676 343	-40.109 49	14.145 17	8 901.81
40-80	-3.616 999			
5-45	-4.520 110	-40.106 05	19.158 71	12 058.34
45-85	-3.510 453			
10-50	-4.371 588	-40.102 78	24.171 82	15 264.87
50-90	-3.408 551			
15-55	-4.230 278	-40.099 65	29.184 53	18 521.40
55-95	-3.311 027			
20-60	-4.095 720	-40.096 66	34.196 85	21 827.93
60-100	-3.217 635			
25-65	-3.967 489			
30-70	-3.845 195			
35-75	-3.728 477			

^a $x = \Delta(K_3 / \Delta K_1) / \Delta(\Delta K_2 / \Delta K_1)$, deg. ^b $y = \Delta(\Delta K_4 / \Delta K_1) / \Delta(\Delta K_2 / \Delta K_1)$, deg².

equation, the Clarke and Glew procedure, and the proposed equation) gave the same values for each thermochemical property in 190 of the 250 cases, and negligibly different values in 55 others. Only in five cases was there a noticeable difference in outcome, and it was always in the Δb and Δc values when $R \ln K^\circ(m)$ went through a maximum or minimum.

This quite unexpected uniformity shows that *if five terms are demanded and 21 data points over a 100-deg temperature range are available, there is nothing to choose (as far as precision is concerned) between the three equations for direct fitting.* Whether they give *accurate* answers is a different question. How far that is the case is dealt with in section 6.2.5 and illustrated in Figure 5.

6.2.4. Results with Samples of 21 Data Points Covering 0-100 °C: Confidence Levels. Because we had arranged that each sample had the same uncertainty level at all temperatures, Cramer's Rule has a simple application: the uncertainties of a given thermochemical value derived from our SR will be proportional to $1/500$, $1/1500$, $1/5000$, and $1/15000$. A survey of 120 cases of deduced values of each of the five thermodynamic properties confirmed this. Table IX shows the outcomes of this survey.

The uncertainty in ΔH°_{298} may seem large compared to the others. However, in the Planck function equation the more significant term might well be taken as $-\Delta H^\circ_{298}/T$ which has the dimensions of entropy. Note in Table IX that the uncertainty of the latter is essentially the same as for $\Delta S^\circ(m)_{298}$.

6.2.5. Results with Samples of 21 Data Points Covering 0-100 °C: Accuracy. Accuracy can of course only be known if SR values are used. In Figure 5 a measure of the accuracy (calculated value-generating value) is shown for the thermodynamic properties

recovered from five subsets of 21 data points from both set A and set B. In view of the finding in 6.2.3, the values of thermodynamic properties presented were obtained by direct fitting to the proposed equation. To avoid congestion in the table, only those representing satisfactory ($1/1500$) to very good ($1/5000$) experimental results are given.

It is obvious that the great majority of the processed SR yield thermodynamic values which agree with the generating values to within the 90% confidence levels given in Table IX—*providing* five terms in the $R \ln K^\circ(m)$ equation are insisted on and providing

at least 16 experimental points are included in a temperature range of about 100 deg or more.

Acknowledgment. L.E.S. is indebted for support, during the preparation of this paper, by a Research Corporation Cottrell Science grant and by two grants from the National Science Foundation (PRM-7908348; R11-8305005). Acknowledgement is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Electron Spin Resonance Studies of Vanadyl Acetylacetonate in One- and Two-Component Solvents

Bruce A. Kowert,* Oh-Wol Yoon, Charles H. Klestinske, Joseph F. Schmidt, Allen D. Baudendistel, and Michael J. Palazzolo

Department of Chemistry, St. Louis University, St. Louis, Missouri 63103 (Received: April 25, 1985)

The vanadyl acetylacetonate (VOAA) radical has been studied by electron spin resonance (ESR) in several one- and two-component solvents. Analysis of the ESR line widths gave the reorientational correlation time, τ_θ , for VOAA in these liquids. The one-component solvents were a series of ethers: dimethoxyethane, tetrahydrofuran, 2-methyltetrahydrofuran, and tetrahydropyran. The τ_θ values were found to follow the modified Debye equation $\tau_\theta = (4\pi r^3 \eta \kappa) / (3kT)$; k is the Boltzmann constant, T is the absolute temperature, $4\pi r^3 / 3$ is a molecular volume, η is the solvent viscosity, and κ is the anisotropic interaction parameter. Values of κ were obtained for each of the four ethers. VOAA was also studied in naphthalene-benzene and naphthalene-toluene mixed solvents. The τ_θ for these systems, determined as a function of temperature and mixed solvent composition, also followed the modified Debye equation. Because of the near equality of the κ values for benzene, toluene, and naphthalene, the relative values of τ_θ depended primarily on the factor η/T and conclusions concerning the short-range interactions of VOAA with the solvent could not be drawn solely from the τ_θ values. Consideration of the viscosity and thermodynamic properties of the naphthalene-benzene and naphthalene-toluene solutions, which are near ideal or regular, and comparison with earlier results for liquid-liquid mixed solvents indicated that the average κ in the mixed solvents was likely to be a linear function of composition and the κ values of the components of the mixed solvents (naphthalene and either benzene or toluene); i.e., the solutions were dynamically "ideal".

I. Introduction

The free radical vanadyl acetylacetonate (VOAA) has been used as an ESR (electron spin resonance) spin probe in a wide variety of solvents.¹⁻¹³ The positions of the lines in the ESR spectra can be used to determine the isotropic hyperfine and Zeeman parameters. The line widths are determined by the anisotropic hyperfine and Zeeman parameters and the rate of the radical's reorientational motion. Analyses of the VOAA ESR spectra have been used to obtain the reorientational correlation time, τ_θ , characteristic of the reorientation about an axis perpendicular to the unique V-O bond.^{1,7} The axial symmetry of the anisotropic hyperfine and Zeeman parameters does not permit

a determination of the reorientation correlation time about the unique V-O bond. The experimental values of τ_θ have been interpreted by using the modified Stokes-Einstein-Debye formula^{1,2,7,14}

$$\tau_\theta = (4\pi r^3 \eta \kappa) / (3kT) \quad (1)$$

where k is Boltzmann's constant, T is the absolute temperature, η is the coefficient of shear viscosity, r is an effective radius determined from translational diffusion experiments, and κ is a dimensionless parameter determined by the anisotropic interactions between VOAA and the solvent molecules.

Several comments concerning the parameters r and κ are in order. (a) The discussion in ref 7 establishes the equivalence between the radius obtained from the translational diffusion experiments and the radius required in eq 1. (b) The discussion in ref 4 and 7 also shows that eq 1, which seems to be written for a sphere, holds for the nonspherical VOAA molecule as well. (c) When $\kappa = 1$, eq 1 is the well-known Debye expression. The introduction of $\kappa < 1$ by Kivelson and co-workers^{7,15} came after a careful series of studies showed that the "volume", $V = (4/3)\pi r^3$, calculated from the experimental τ_θ and eq 1 with $\kappa = 1$ was usually smaller than the value of V calculated with the value of

- (1) Wilson, R.; Kivelson, D. *J. Chem. Phys.* **1966**, *44*, 154.
- (2) Wilson, R.; Kivelson, D. *J. Chem. Phys.* **1966**, *44*, 4440.
- (3) Walker, F. A.; Carlini, R. L.; Rieger, P. M. *J. Chem. Phys.* **1966**, *45*, 4181.
- (4) Luckhurst, G. R.; Ockwell, J. N. *Mol. Phys.* **1969**, *16*, 165.
- (5) Angerman, N. S.; Jordan, R. B. *J. Chem. Phys.* **1971**, *54*, 837.
- (6) Hoel, D.; Kivelson, D. *J. Chem. Phys.* **1975**, *62*, 4535.
- (7) Hwang, J.; Kivelson, D.; Plachy, W. *J. Chem. Phys.* **1973**, *58*, 1753.
- (8) Kowert, B.; Kivelson, D. *J. Chem. Phys.* **1976**, *64*, 5206.
- (9) Bruno, G. V.; Harrington, J. K.; Eastman, M. P. *J. Phys. Chem.* **1977**, *81*, 1111.
- (10) Ahn, M.-K.; Ormond, D. E. *J. Phys. Chem.* **1978**, *82*, 1635.
- (11) Ahn, M.-K.; Derlacki, Z. J. *J. Phys. Chem.* **1978**, *82*, 1930.
- (12) Campbell, R. F.; Freed, J. H. *J. Phys. Chem.* **1980**, *84*, 2668.
- (13) Patron, M.; Kivelson, D.; Schwartz, R. N. *J. Phys. Chem.* **1982**, *86*, 518.

- (14) Kivelson, D.; Kivelson, M. G.; Oppenheim, I. *J. Chem. Phys.* **1970**, *52*, 1810.
- (15) McClung, R.; Kivelson, D. *J. Chem. Phys.* **1968**, *49*, 3380.