mol,[20] while reaction 2 forming CH_4D^+ is estimated to be exoergic by 23 kcal/mol.[26] Therefore it is highly likely that internal rearrangement would occur during the initial formation of the methanium ion. Neither our results nor those of previous workers[23,24] can definitely establish the structure of the methanium ion. However, we feel that our results show a discernible isotope effect for CD_4H^+ which may reflect the uniqueness of this structure.

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References and Notes

(1) D. R. Stull and H. Prophet et al., *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 37** (1971).
(2) D. Rapp and P. Englander-Golden, *J. Chem. Phys.*, **43**, 1464 (1965).
(3) Y. Okuno, K. Okuno, Y. Kaneko, and I. Kanomata, *J. Phys. Soc. Jpn.*, **29**, 164 (1970).
(4) R. C. Pierce and R. F. Porter, *J. Phys. Chem.*, **78**, 93 (1974).
(5) A. Fiaux, D. L. Smith, and J. H. Futrell, *Int. J. Mass Spectrom. Ion Phys.*, **15**, 9 (1974).
(6) P. Sthapitanonda and J. L. Margrave, *J. Phys. Chem.*, **60**, 1628 (1956).
(7) P. L. Altick, *J. Chem. Phys.*, **40**, 238 (1964).
(8) W. C. Stwalley, *J. Chem. Phys.*, **54**, 5417 (1971).
(9) P. F. Fennelly, R. S. Hamsworth, H. I. Schiff, and D. K. Bohme, *J. Chem. Phys.*, **59**, 6405 (1973).
(10) W. A. Chupka and J. Berkowitz, *J. Chem. Phys.*, **54**, 4256 (1971).
(11) W. Tsang, *J. Phys. Chem.*, **76**, 143 (1972); F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970).
(12) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 1320 (1976).
(13) G. Herzberg, "Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules", 2nd ed, Van Nostrand, Princeton, N.J., 1955.
(14) W. J. Balfour, *Can. J. Phys.*, **50**, 1082 (1972).
(15) C. E. Moore, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 35** (1971).
(16) D. L. Smith and J. H. Futrell, *Chem. Phys. Lett.*, **40**, 229 (1976).
(17) Calculations based on proton affinity of CH_5^+ obtained from ref 7 and heats of formation from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 26** (1969).
(18) A. Gambo, G. Morosi, and M. Simonetta, *Chem. Phys. Lett.*, **3**, 20 (1969).
(19) Calculations using standard CNDO/2 computer program, see J. A. Pople and D. L. Beveridge. "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970.
(20) O. V. Dyczmons, V. Staemmler, and W. Kutzelnigg, *Chem. Phys. Lett.*, **5**, 361 (1970).
(21) Calculations based on heat of formation data, see ref 17.
(22) Calculations based on proton affinities of H_2 and NH_3, see ref 9 and 12.
(23) M. D. Sefcik, J. M. S. Henis, and P. P. Gasper, *J. Chem. Phys.*, **61**, 4321 (1974).
(24) R. D. Smith and J. H. Futrell, *Chem. Phys. Lett.*, **36**, 545 (1975).
(25) S. Ehrenson, *Chem. Phys. Lett.*, **3**, 585 (1969).
(26) Calculations based on proton affinities of H_2 and CH_4, see ref 9 and 10.

Thermodynamics of Electrolytes. 7. Sulfuric Acid

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Abstract: Although the thermodynamic properties of sulfuric acid above 0.1 M and near 25 °C are well established numerically, they have not been represented accurately by equations which are based upon the ionic species present, H^+, HSO_4^-, and SO_4^{2-}. We have developed and fitted such equations over the range from 0 to 6 M in a system compatible with those for fully dissociated, strong electrolytes. The enthalpy is treated as well as the activity and osmotic coefficients. These equations also establish the solute standard state and the relationship between the properties of sulfuric acid in that state with those for the pure acid. Among the results obtained (for 25 °C) are the dissociation constant 0.0105 and the heat of dissociation −5.61 kcal mol^{-1} for HSO_4^- and the entropy of SO_4^{2-}, 4.2 ± 0.2, and of HSO_4^-, 32.1 ± 0.3 cal K^{-1} mol^{-1}. Also for the reaction $H_2SO_4(l) = 2H^+(aq) + SO_4^{2-}(aq)$, $\Delta H° = -22844$, $\Delta G° = -12871$ cal mol^{-1}.

In view of the great practical importance of sulfuric acid, it is desirable to have the most accurate and convenient expression of its thermodynamic properties. Above 0.1 M these properties are now well established,[1-6] but there is still considerable uncertainty about the properties of very dilute solutions and the related solute standard state. In this research we have the dual purposes first to establish as accurately as possible the thermodynamic properties of dilute sulfuric acid and second to provide a convenient yet accurate analytical representation of the properties of this acid in a form compatible with that used for other electrolytes[7-9] and over as wide a range of concentration as is feasible.

The thermodynamic treatment of sulfuric acid has been unusually difficult because the dissociation constant of HSO_4^- lies in the most troublesome region where methods fail that were successful for weaker acids.[10,11] The preceding paper of this series[12] considered this general problem with phosphoric acid as an example. Sulfuric acid is even more troublesome in view of the higher charge on the sulfate ion and the correspondingly larger changes in its activity coefficient.

General Equations

The statistical mechanical basis for the form of equation for a complex electrolyte was given in the first paper of this series.[7] The general framework is that of the McMillan-Mayer theory of solutions and the equation relating intermolecular forces and distributions to the osmotic pressure.[13] Our basic equation is

$$\frac{G^{ex}}{RT} = n_w f(I) + \frac{1}{n_w}\sum_{ij} \lambda_{ij}(I) n_i n_j + \frac{1}{n_w^2}\sum_{ijk} \mu_{ijk} n_i n_j n_k \quad (1)$$

where G^{ex} is the excess Gibbs energy for a solution containing n_w kg of solvent and n_i, n_j, etc., moles of solute species i, j, etc. Here $f(I)$ is a function of ionic strength (and temperature and solvent properties) expressing the effect of long-range electrostatic forces between ions and including, of course, the Debye-Hückel limiting law. Short-range interactions of solute species lead to the terms $\lambda_{ij}(I)$ for binary interactions and μ_{ijk} for ternary interactions; the theoretical basis for expecting an ionic-strength dependence for λ_{ij} was given earlier[7] and this has been fully confirmed empirically. The λ and μ matrices are symmetric, i.e., $\lambda_{ij} = \lambda_{ji}$, etc.

Equations for Sulfuric Acid

The intermediate thermodynamic derivations of activity and osmotic coefficients and the definitions of experimentally measurable parameters and convenient empirical forms have been given previously.[9] For example, for univalent ions a measurable combination of λ's is $B_{MX} = \lambda_{MX} + \frac{1}{2}\lambda_{MM} + \frac{1}{2}\lambda_{XX}$. We shall move directly to the results appropriate for a solution of sulfuric acid with stoichiometric molality m and molality m_H of H^+, $m_1 = 2m - m_H$ of HSO_4^- and $m_2 = m - m_1$ of SO_4^{2-}. With two different anions this is a mixed electrolyte for our equations even though the second anion arises from a dissociation equilibrium of the first. For the osmotic coefficient ϕ' on a mixed electrolyte basis one finds

$$\phi' - 1 = (\Sigma m_i)^{-1}\{2If^\phi + 2m_H[m_1(B_{H1}^\phi + m_H C_{H1}^\phi) + m_2(B_{H2}^\phi + m_H C_{H2}^\phi/2^{1/2})] + m_1 m_2(\theta_{12} + m_H \psi_{H12})\} \quad (2)$$

$$f^\phi = -A_\phi[I^{1/2}/(1 + 1.2I^{1/2})] \quad (3)$$

$$B_{MX}^\phi = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} \exp(-\alpha I^{1/2}) \quad (4)$$

where the ionic strength $I = m + 2m_2$, A_ϕ is the Debye-Hückel limiting law parameter for the osmotic coefficient (see Appendix for numerical values), α is a general empirical parameter equal to 2 throughout this work, while $\beta_{MX}^{(0)}$ and $\beta_{MX}^{(1)}$ are specific parameters for the appropriate sum of λ_{ij} for binary interactions M-X, M-M, and X-X where the cation M is always H and the anion X is either $HSO_4^- = 1$ or $SO_4^{2-} = 2$. Also C_{MX}^ϕ is the corresponding third virial coefficient for triple interactions μ_{ijk} for MMX and MXX; θ_{12} is the difference in binary interaction λ_{ij} of HSO_4^- with SO_4^{2-} from the appropriate average of HSO_4^--HSO_4^- and SO_4^{2-}-SO_4^{2-} interactions; while ψ_{H12} is the corresponding difference in triple interactions μ_{ijk} involving a hydrogen ion together with two anions.

In addition we have the dissociation equilibrium

$$HSO_4^- = H^+ + SO_4^{2-} \quad (5)$$

$$K_2 = \left(\frac{m_H m_2}{m_1}\right)\left(\frac{\gamma_H \gamma_2}{\gamma_1}\right) \quad (6)$$

with the familiar dissociation constant K_2 and the activity coefficients of the various ions. These activity coefficients can be expressed in terms of the same parameters as appear in eq 1 to 4.

These equations contain two different expressions for the short-range interaction of H^+ with SO_4^{2-}: one is the association to HSO_4^- represented by $1/K_2$, the other the second virial coefficient B_{H2} containing $\beta_{H2}^{(0)}$ and $\beta_{H2}^{(1)}$. If this series of equations is expanded in powers of $m^{1/2}$, the coefficient of the term in m involves a sum with terms in $1/K_2$ and $(\beta_{H2}^{(0)} + \beta_{H2}^{(1)})$ indicating a redundancy at this order. Higher order terms, however, do not maintain this redundancy, and it is possible to include $\beta_{H2}^{(0)}$ or $\beta_{H2}^{(1)}$ or both, if desired.

In sulfuric acid above 0.1 M the more abundant anion is HSO_4^- and the osmotic coefficient has been observed to behave very much like that of HCl or a similar acid. Thus we may expect that the parameters most important for this concentration range will be $\beta_{H1}^{(0)}$ and $\beta_{H1}^{(1)}$ which relate to the short-range interaction of H^+ with HSO_4^-. Thus we expect K_2 to be most important for the very dilute range with $\beta_{H1}^{(0)}$ and $\beta_{H1}^{(1)}$ becoming important at higher concentrations.

There remain in eq 2 through 4 six additional parameters which might have significant effect at least at very high concentration. In exploratory calculations it was soon discovered that $\beta_{H2}^{(1)}$ was so nearly redundant to $1/K_2$ and $\beta_{H2}^{(0)}$ that it was best omitted. Also it was found that θ_{12} and ψ_{H12} were not needed. Good results were obtained with either the combination $\beta_{H2}^{(0)}$ and C_{H2}^ϕ or with C_{H1}^ϕ and C_{H2}^ϕ but the former proved to be slightly superior and was adopted. The equations then reduce to

$$\phi' - 1 = (\Sigma m_i)^{-1}\{2If^\phi + 2m_H[m_1 B_{H1}^\phi + m_2(\beta_{H2}^{(0)} + m_H C_{H2}^\phi/2^{1/2})]\} \quad (7)$$

with B_{H1}^ϕ still represented by the two-term expression

$$B_{H1} = \beta_{H1}^{(0)} + \beta_{H1}^{(1)} \exp(-2I^{1/2}) \quad (4a)$$

The corresponding equations for the two combinations of activity coefficients of interest are

$$\ln(\gamma_H^2\gamma_{SO_4}) = 6f^\gamma + 4m_1 B_{H1} + (4m_2 + 2m_H)\beta_{H2}^{(0)} + (8m_2 + 2m_H)m_H C_{H2} + 6m_H m_1 B_{H1}' \quad (8)$$

$$\ln(\gamma_H\gamma_{SO_4}/\gamma_{HSO_4}) = 4f^\gamma + 2(m_1 - m_H)B_{H1} + 2(m_2 + m_H)\beta_{H2}^{(0)} + 2m_H(2m_2 + m_H)C_{H2} + 4m_1 m_H B_{H1}' \quad (9)$$

$$f^\gamma = -A_\phi[I^{1/2}/(1 + 1.2I^{1/2}) + (2/1.2)\ln(1 + 1.2I^{1/2})] \quad (10)$$

$$B_{H1} = \beta_{H1}^{(0)} + (\beta_{H1}^{(1)}/2I)[1 - (1 + 2I^{1/2})\exp(-2I^{1/2})] \quad (11a)$$

$$B_{H1}' = (\beta_{H1}^{(1)}/2I^2)[-1 + (1 + 2I^{1/2} + 2I)\exp(-2I^{1/2})] \quad (11b)$$

$$C_{H2} = C_{H2}^\phi/2^{3/2} \quad (12)$$

The stoichiometric activity and osmotic coefficients for sulfuric acid (on the basis of complete dissociation) are

$$\gamma_\pm^3 = (\gamma_H^2\gamma_{SO_4})(m_H^2 m_2/4m^3) \quad (13)$$

$$\phi = \phi'(\Sigma m_i)/3m \quad (14)$$

The total excess Gibbs energy per mole of solute is given by the thermodynamic relationship

$$G^{ex}/n_2 = 3RT(\ln\gamma_\pm + 1 - \phi) \quad (15)$$

Equations for the various molal enthalpy functions can be derived from the temperature derivatives of the Gibbs energy functions. For example

$$\bar{L}_1 = (M_w m/1000)(3RT^2)\,\partial\phi/\partial T \quad (16)$$

$$\bar{L}_2 = -3RT^2\,\partial\ln\gamma_\pm/\partial T \quad (17)$$

$$^\phi L = 3RT^2(\partial\phi/\partial T - \partial\ln\gamma_\pm/\partial T) \quad (18)$$

where M_w is the molecular weight of the solvent.

In taking the temperature derivative of eq 7, 8, 13, and 14 one must recognize that I, m_H, m_1, and m_2 are temperature dependent through the change in dissociation of HSO_4^-. Any one can be chosen to express this effect and the others related thereto; we used $\partial m_1/\partial T$ but indicate derivatives at constant composition with the subscript I. One then obtains

$$\bar{L}_1 = \left(\frac{M_w RT^2}{1000}\right)\Bigg\{2i\left(\frac{\partial f^\phi}{\partial T}\right)_I + 2m_H\left[m_1\left(\frac{\partial B_{H1}^\phi}{\partial T}\right)_I + m_2\left(\frac{\partial\beta_{H2}^{(0)}}{\partial T}\right)_I + \frac{m_2 m_H}{2^{1/2}}\left(\frac{\partial C_{H2}^\phi}{\partial T}\right)_I\right] - \left(\frac{\partial m_1}{\partial T}\right)\Bigg[1 + 4f^\phi + 4I\left(\frac{\partial f^\phi}{\partial I}\right)_T - 4m_2 B_{H1}^\phi - 4m_H m_1\left(\frac{\partial B_{H1}^\phi}{\partial I}\right)_T + 2I\beta_{H2}^{(0)} + 2^{1/2}m_H(m_H + 2m_2)C_{H2}^\phi\Bigg]\Bigg\} \quad (19)$$

$$\bar{L}_2 = -RT^2\Bigg\{6\left(\frac{\partial f^\gamma}{\partial T}\right)_I + 4m_1\left(\frac{\partial B_{H1}}{\partial T}\right)_I + (4m_2 + 2m_H)\left(\frac{\partial\beta_{H2}^{(0)}}{\partial T}\right)_I + m_H(8m_2 + 2m_H)\left(\frac{\partial C_{H2}}{\partial T}\right)_I$$

$$+ 6m_{\mathrm{H}}m_1 \left(\frac{\partial B_{\mathrm{H1}}'}{\partial T}\right)_I - \left(\frac{\partial m_1}{\partial T}\right)\left[\frac{2}{m_{\mathrm{H}}} + \frac{1}{m_2} + 12\left(\frac{\partial f^\gamma}{\partial I}\right)_T - 4B_{\mathrm{H1}} - (8m + 4m_2)B_{\mathrm{H1}}' + 6\beta_{\mathrm{H2}}^{(0)} + (8m_2 + 12m_{\mathrm{H}})C_{\mathrm{H2}} - 6m_{\mathrm{H}}m_1 B_{\mathrm{H1}}''\right]\Bigg\} \quad (20)$$

with

$$B_{\mathrm{H1}}'' = (\beta_{\mathrm{H1}}^{(1)}/I^3)[1 - (1 + 2I^{1/2} + 2I + I^{3/2})e^{-2I^{1/2}}] \quad (21)$$

The change of dissociation with temperature is obtained from eq 6 and 9. After several steps one finds

$$\frac{\partial m_1}{\partial T} = \left[\frac{\partial \ln K_2}{\partial T} - 4\left(\frac{\partial f^\gamma}{\partial T}\right)_I - 2(m_1 - m_{\mathrm{H}})\left(\frac{\partial B_{\mathrm{H1}}}{\partial T}\right)_I + 4m_1m_{\mathrm{H}}\left(\frac{\partial B_{\mathrm{H1}}'}{\partial T}\right)_I + 2(m_{\mathrm{H}} + m_2)\frac{\partial \beta_{\mathrm{H2}}^{(0)}}{\partial T} + 2m_{\mathrm{H}}(2m_2 + m_{\mathrm{H}})\frac{\partial C_{\mathrm{H2}}}{\partial T}\right] \times \left[-\frac{1}{m_{\mathrm{H}}} - \frac{1}{m_2} - \frac{1}{m_1} - 8\left(\frac{\partial f^\gamma}{\partial I}\right)_T + 4B_{\mathrm{H1}} + 16m_2B_{\mathrm{H1}}' + 4m_1m_{\mathrm{H}}B_{\mathrm{H1}}'' - 4\beta_{\mathrm{H2}}^{(0)} - (8m_{\mathrm{H}} + 4m_2)C_{\mathrm{H2}}\right]^{-1} \quad (22)$$

The heat of dissociation is contained in the above, since

$$\partial \ln K_2/\partial T = \Delta H_2/RT^2 \quad (23)$$

Even with all parameters known or assumed it is not feasible to solve these equations directly; an iterative solution, however, converges quickly and easily. We found it convenient to use m_1 as the variable and to use the quadratic solution of eq 6. After each cycle the improved m_1 is used to recalculate the ionic strength, which appears throughout the equations, for the next cycle. Thus the solution for known parameters is relatively easy.

The problem of finding the best parameters to fit an array of various types of experimental data is much more difficult, since this is not only a nonlinear problem, but there is also the nonlinear auxiliary condition of eq 6. The nonlinear least-squares equations were used with the derivatives with respect to the various parameters including the indirect dependence through eq 6. While simultaneous optimization of 19 parameters was possible, we found it preferable to use a series of fixed values for K_2 at 25 °C with least-squares optimization of the remaining 18 parameters.

Experimental Data

There are three cells each of which yields the thermodynamic properties of sulfuric acid:

$$\mathrm{Pt, H_2|H_2SO_4}(m)\mathrm{|PbSO_4, Pb, Hg} \quad \text{(A)}$$

$$\mathrm{Pt, H_2|H_2SO_4}(m)\mathrm{|Hg_2SO_4, Hg} \quad \text{(B)}$$

$$\mathrm{Pt, H_2|H_2SO_4}(m)\mathrm{|PbO_2, PbSO_4, Pt} \quad \text{(C)}$$

For cells A and B the equation for the emf is

$$E = E° - (RT/2F)\ln(4m^3\gamma_\pm{}^3) \quad (24)$$

while for cell C the corresponding equation is

$$E = E° + (RT/2F)\ln(4m^3\gamma_\pm{}^3/a_{\mathrm{w}}{}^2) \quad (25)$$

where a_{w} is the activity of the water which is given by

$$\ln a_{\mathrm{w}} = -3m\phi/55.5 \quad (26)$$

For cells B and C there are extensive investigations of Wynne-Jones and collaborators[3,4] over a series of temperatures and from 0.1 to over 7 M. In addition at 25 °C there are measurements of Covington, Dobson, and Wynne-Jones[14] for dilute solutions from 0.007 to 0.1 M. These data have been shown to be consistent to high accuracy as between cells B and C and, in the range above 0.1 M, also with the osmotic data of Shankman and Gordon[1] and of Stokes.[2] Furthermore, Giauque and associates[5,6] have measured the entropies of various sulfuric acid hydrates by third law methods and combined these results with other entropy and enthalpy data to check accurately the temperature coefficient of cell C.

Cell A was measured over a range of temperatures and from 0.001 to 0.02 M by Shrawder and Cowperthwaite[15] in 1934. This work has been ignored by many more recent workers but was recently shown by Lilley and Briggs[16] to be consistent with the results of cells B and C in the region of overlap at 25 °C and has been discussed recently by one of us.[17] The early work of Hamer[18] and Harned and Hamer[19] on cells C and B, respectively, has been shown by various workers[1-4,6,14] to be less accurate than the more recent data here considered.

At the very lowest concentrations the solubility of $\mathrm{PbSO_4}$[15] or $\mathrm{Hg_2SO_4}$[20] becomes significant and corrections were made for the primary effect of the dissolved solid.

Information about the enthalpy of sulfuric acid comes primarily from heat of dilution measurements. These include the measurements of Lange, Monheim, and Robinson[21] in the very dilute range, of Kunzler and Giauque[22] for concentrated solutions, and of Groenier[23] and Wu[24] (both students of T. F. Young) for differential dilutions at intermediate concentrations. The heat of ionization of $\mathrm{HSO_4^-}$ has been measured calorimetrically[25,26] with the results −5.2 ± 0.5 and −5.74 ± 0.2 kcal/mol. These approximate values were not used directly but provided a check on values of ΔH_2 obtained from analysis of heat of dilution data.

In addition to the cell measurements on pure sulfuric acid, we considered the results of Nair and Nancollas[27] on the cell

$$\mathrm{Pt, H_2|H_2SO_4}(m)\ \mathrm{HCl}(m_3)\mathrm{|AgCl, Ag} \quad \text{(D)}$$

which yields directly the activity of HCl. Dunsmore and Nancollas[28] made further calculations on these data. Application of our equations for mixed electrolytes to these solutions yields equations with additional terms which are given in the Appendix. It suffices to note here that the additional terms which are important are those for the interaction of $\mathrm{H^+}$ with $\mathrm{Cl^-}$ which are known from the properties of pure HCl. Interaction terms for $\mathrm{Cl^-}$ with $\mathrm{SO_4^{2-}}$ are known to be small, and one can estimate that the corresponding terms for $\mathrm{Cl^-}$ interaction with $\mathrm{HSO_4^-}$ may also be neglected in good approximation at the low concentrations measured for cell D.

In contrast to the situation just described, most of the other thermodynamic data which have been used in calculating the dissociation constant for bisulfate ion involve complex mixed solutions where unknown interactions would now be estimated to be significant and where elimination of these terms by extrapolation is uncertain. The most favorable of these cases, that for mixed solutions of $\mathrm{Na_2SO_4}$ and $\mathrm{NaHSO_4}$ in cell B,[29] is discussed in the Appendix. Here the serious uncertainty is the interaction of $\mathrm{Na^+}$ with $\mathrm{HSO_4^-}$ which is not known accurately from another source.

Evaluation of Parameters

Our first calculations dealt only with the data on cells A, B, and C for pure sulfuric acid and the osmotic coefficients at 25 °C. It soon became apparent that the osmotic data were less precise than the cell data; consequently, only the smoothed values of Robinson and Stokes[30] and of Rard et al.[31] were retained for ϕ. Excellent fits were obtained for all of these cell potentials, but it was noted that K_2 was being given a value near 0.0120 which is much larger than that found in most recent work. This implied a real conflict with the data on cell D which were interpreted by Nair and Nancollas[28] to yield K_2 = 0.0110 and by Dunsmore and Nancollas[29] to yield K_2 = 0.0105. Further investigation indicated that all data for cells B and C and those for cell A at 0.005 M and above could be fitted with smaller values of K_2, including the value K_2 = 0.0105 which yielded the best agreement with the data on cell D when our more detailed equations were used with specific parameters for HCl (see Appendix).

Table I. Parameters for Equations for $H_2SO_4(aq)$

	Values for 25 °C			Values for 25 °C	
	Adopted set	Alternate set		Adopted set	Alternate set
K_2	0.0105	0.0120	C_{H2}^{ϕ}	0.0416	0.0384
$\beta_{H1}^{(0)}$	0.2103	0.2110	$E_0(A)$	-0.3528_0	-0.3517_5
$\beta_{H1}^{(1)}$	0.4711	0.4096	$E_0(B)$	0.6124_2	0.6135_4
$\beta_{H2}^{(0)}$	0.0027	0.0153	$E_0(C)$	1.6903_8	1.6892_7

Temperature Dependent Equations (Adopted Set)

$$\ln K_2 = -14.0321 + 2825.2/T$$

$$\beta_{H1}^{(0)} = 0.05584 + 46.040/T$$

$$\beta_{H1}^{(1)} = -0.65758 + 336.514/T$$

$$\beta_{H2}^{(0)} = -0.32806 + 98.607/T$$

$$C_{H2}^{\phi} = 0.25333 - 63.124/T$$

$$E_0(A) = 0.00589733T - 0.361098 - 0.00103017T \ln T$$

$$E_0(B) = 0.00487142T + 0.608163 - 0.00085249T \ln T$$

$$E_0(C) = -0.00691441T + 1.910511 + 0.00108398T \ln T$$

The results at this point yielded two sets of parameters fitting most data equally well. Further calculations indicated the heat of dilution data were better fitted by the set of parameters including $K_2 = 0.0105$ together with appropriate temperature derivative parameters. Thus we favor these parameters ($K_2 = 0.0105$) as more probably representing the true properties of sulfuric acid below 0.005 M, but we cannot assert that this choice is absolutely certain.

In further comment on the choice of the last paragraph we note that other work in the same laboratory as that for cell A with cells also involving the $PbSO_4$, Pb electrode has been found[32] to be reliable down to 0.005 M but in significant error below that concentration. Also a very simple interpretation[17] of the data for cell A cast some doubt on the results for the most dilute solutions at the higher temperatures. In contrast, however, the concentration of sulfate ion as measured by Raman spectra by Young, Maranville, and Smith[33] is better fitted by our calculations with the higher $K_2 = 0.0120$. These concentration measurements are not very precise and the difference is not very large; hence we do not believe this is a serious objection to the smaller K_2. Conductance data on sulfuric acid have been interpreted by Kerker[34] to yield $K_2 = 0.0102$ and by Dunsmore and Nancollas[28] to yield $K_2 = 0.0105$ at 25 °C and therefore favor the smaller value of K_2.

Table I gives the adopted parameters both in the form for 25 °C and that for temperature-dependent functions; also given are the alternate parameters for 25 °C as discussed above.

Of the ion-interaction parameters in Table I only $\beta_{H1}^{(0)}$ for the H^+-HSO_4^- interaction is sufficiently free from ambiguity to make comparison meaningful. The value for H^+-HSO_4^-, 0.2103, is similar to the $\beta^{(0)}$ values for other strong acids with large anions, for example, 0.236 for HI and 0.175 for $HClO_4$. For H^+-HSO_4^-, $\beta_{H1}^{(1)}$ (0.47) is higher than that found for the simple acids but not very different. Since we have arbitrarily suppressed some parameters and have the redundancy of $\beta_{H2}^{(0)}$, $\beta_{H2}^{(1)}$, and $1/K_2$, great caution should be used in interpreting these other quantities. None are so large as to be unreasonable, however.

The alternate set of parameters shifts each of the E_0 values by 1.1 mV which corresponds to a 3% increase in activity coefficients.

Table II shows the agreement with experimental cell potentials for values calculated with the adopted set in the range 0.005 to 0.1 M. Table III gives a similar comparison for the range 0.1 to 6 M but in terms of the activity coefficient; also included is the osmotic coefficient.

Table II. Comparison of Calculated and Experimental Properties below 0.1 M

m	a	$\gamma_\pm$	ΔE, mV (cell)
0.005	0.67	0.615	−0.18 (A)
0.0728	0.61	0.560	0.06 (B), 0.22 (C)
0.01	0.56	0.515	−0.04 (A)
0.0103	0.55	0.510	−0.16 (B), 0.01 (C)
0.0171			−0.15 (B)
0.02	0.45	0.419	0.11 (A)
0.0215			0.12 (B)
0.0401			0.36 (B)
0.0571	0.32	0.296	0.32 (B), −0.01 (C)
0.0840			0.31 (B)
0.095	0.27	0.247_7	0.19 (B), 0.15 (C)
0.096			0.27 (B)
0.1	0.27	0.243_8	−0.05 (B), 0.03 (C)

[a] Fraction of HSO_4^- dissociated.

Tables II and III also give the fraction of sulfate dissociated from HSO_4^- to SO_4^{2-}. This quantity is sensitive to small changes in parameters which do not seriously affect the thermodynamic properties and in particular to the choice between C_{H1} or $\beta_{H2}^{(0)}$ as a parameter to be included. Hence only two significant figures are given and these results should be used with caution.

It is clear from Tables II and III that the agreement for cell potentials (or activity coefficients) at 25 °C is within or near to experimental accuracy. Similarly, the calculated osmotic coefficients are probably within experimental uncertainty up to 5 M. At other temperatures the agreement is almost as good with standard deviations of 0.13, 0.28, and 0.16 mV for the potential values for cell A (at and above 0.005 M) and for cells B and C (up to 6.1 M), respectively.

All of the heat of dilution data were fitted directly except for the most dilute point of Lange et al. with a final concentration 0.00005 M, which is necessarily least accurate, and the large ratio dilutions of Groenier for which his calorimeter was much less accurate than Lange's. The standard deviations were: for 24 differential dilutions of Wu,[24] 3.1 cal mol^{-1}; for the earlier but similar work of Groenier,[23] with 42 points, 6.8 cal mol^{-1}; for 10 large ratio dilutions of dilute solutions by Lange et al.,[21] 35 cal mol^{-1}; and for 6 dilutions of concentrated solutions by Kunzler and Giauque,[22] 8.0 cal mol^{-1}. Although σ is largest for Lange's values, it is clearly within experimental error for these dilutions yielding final concentrations in the range 0.00009 to 0.002 M. The accurate, differential dilution data of Wu are well fitted with the adopted parameters, but for the alternate set with $K_2 = 0.0120$ there is a serious discrepancy in the range 0.1 to 0.6 M where all deviations are of the same sign for 11 measurements with $\sigma = 8.4$ cal mol^{-1}.

Thermodynamic Properties of Sulfuric Acid

The thermodynamic properties for cells A, B, and C at 25 °C are compared in Table IV with literature values. The standard potentials for cells B and C are the same within 0.1 and 0.3 mV, respectively, as those chosen by Covington et al.[14] For cell A our present value is very close to the value −0.3526 favored by Lilley and Briggs[16] but differs by 1.5 mV from the value one of us[17] obtained from the data for cell A alone, without reference to the other data considered here. This difference of 1.5 mV is essentially that of the choice between $K_2 = 0.0105$ or 0.0120 where the latter value fits cell A results down to 0.001 M but disagrees with some other results.

A more independent check is possible for the temperature coefficient of the cell potential which yields ΔS for the cell reaction. Here one has entropy values from statistical calculations or third-law methods for all of the substances involved,

Table III. Comparison of Calculated and Experimental Properties above 0.1 M

		$\gamma_\pm$		ϕ		
m	a[a]	PRS	CDW[b]	PRS	RS[30]	RHS[31]
0.1	0.27	0.243_6	0.244	0.676	0.680	0.680
0.2	0.23	0.191_8	0.192	0.666	0.668	0.665
0.3	0.21	0.167_6	0.168	0.667	0.668	0.665
0.4	0.21	0.153_2	0.153	0.672		0.669
0.5	0.21	0.143_4	0.143	0.678	0.676	0.675
0.7	0.21	0.131_1	0.130	0.694	0.689	0.691
1.0	0.22	0.121_5	0.121	0.723	0.721	0.719
1.5	0.24	0.116_0	0.116	0.778	0.780	0.777
2.0	0.25	0.117_1	0.118	0.843	0.846	0.843
2.5	0.25	0.122_4	0.124	0.915	0.916	0.916
3.0	0.24	0.131_1	0.132	0.992	0.991	0.992
3.5	0.23	0.142_5	0.143	1.071	1.071	1.070
4.0	0.20	0.156_3	0.157	1.149	1.150	1.148
4.5	0.18	0.172_4	0.172	1.225	1.226	1.225
5.0	0.15	0.190_7	0.190	1.299	1.303	1.301
5.5	0.13	0.211_3		1.369	1.376	1.374
6.0	0.11	0.234_3	0.234	1.437	1.445	1.444

[a] Fraction of HSO_4^- dissociated. [b] Reference 14 gives three sets of values differing only slightly; this is the set for cell B with $E_0 = 612.5$ mV.

Table IV. Thermodynamic Properties for Cell Reactions at 25 °C

	E_0, V		ΔS, cal K^{-1} mol^{-1}		
Cell	PRS	CDW	PRS	Lit.[a]	$S°(SO_4^{2-})$
A	−0.3528		-46.2_3	-45.7_7	4.0_4
B	0.6124_2	0.6125	-38.6_6	-38.3_3	4.1_7
C	1.6903_8	1.6901	15.9_4	16.0_7	4.3_7

[a] From literature values, see text, including $S°(SO_4^{2-}) = 4.50$.

in particular 31.208 for $H_2(g)$, 16.71 for $H_2O(l)$, 35.51 for $PbSO_4(s)$, 18.17 for Hg(l), and 47.96 for $Hg_2SO_4(s)$, all in cal K^{-1} mol^{-1} from the NBS Tables.[35] Also Duisman and Giauque[6] give 17.156 for $PbO_2(s)$, Gallagher et al.[36] give 35.509 for $PbSO_4(s)$, Meads et al.[37] give 15.514 for Pb(s), and CODATA-Part IV[38] recommends 4.50 for $SO_4^{2-}(aq)$ from a variety of sulfate salts. Since cell A involves an amalgamated lead electrode, the value[39] $\Delta S = 0.93$ cal K^{-1} mol^{-1} must be included for conversion of pure solid lead to lead in mercury. The entropy of H^+ ion is zero by definition. Combination of these values yields the results in the next-to-last column of Table IV. The agreement is very good. But it is equally justifiable to use each set of data to determine a value for the entropy of sulfate ion; the last column gives these values.

Our preferred parameters yield for the heat of dissociation of bisulfate ion $\Delta H_2 = -5.61$ kcal mol^{-1} in excellent agreement with the values −5.2 ± 0.5 and −5.74 ± 0.2 cited above.[25,26] Also one obtains $\Delta S_2° = -27.87$ cal K^{-1} mol^{-1}.

Recently Powell[42] and Cabani and Gianni[43] have discussed the interpretation of data from various sources to yield values of the heat of dissociation of bisulfate ion. These authors showed the sensitivity of these calculations to assumptions about the activity coefficients in the mixed electrolytes involved in these experiments, including those cited[25,26] above. While it should now be possible to remove much of the ambiguity in these assumptions about activity coefficients in mixed electrolytes, it seemed best to base our results on the experiments with pure sulfuric acid solutions.

These data do not have sufficient accuracy over their limited temperature range to yield reliable second temperature derivatives and thereby heat capacities. While three-term expressions were used for the cell potentials, the resulting second derivatives do not yield meaningful ΔC_p values because only two-term expressions were used for K_2 and the other parameters for the aqueous phase. One could introduce independent knowledge of the heat capacity of the solution into the treatment, but the increased complexity did not seem justified.

In view of the interrelationship between parameters it is not useful to set limits of error for most of the individual parameters in Table I. The uncertainties in E_0 values are about 0.3 mV provided the "adopted set" is essentially correct. Alternate E_0 values for $K_2 = 0.0120$ are also given. Even excluding this alternate choice, the value of K_2 is uncertain by a few percent since other parameters can be adjusted to retain the fit at finite concentration.

Table V presents a survey of various properties of aqueous sulfuric acid as calculated from our equations and parameters. For accurate values at other concentrations the equations should be used.

By comparison of our values in Table V at finite concentrations from 1 to 4 M with those of Giauque et al.,[5] one obtains the difference between the properties of sulfuric acid in the solute standard state and those for the pure liquid. Thus for the reaction

$$H_2SO_4(l) = 2H^+(aq) + SO_4^{2-}(aq)$$

we find

$$\Delta G° = -12871 \text{ cal mol}^{-1}$$

$$\Delta H° = -22844 \text{ cal mol}^{-1}$$

$$\Delta S° = -33.45 \text{ cal mol}^{-1} \text{ K}^{-1}$$

If one adds the entropy of pure liquid H_2SO_4, 37.501, to this value for $\Delta S°$, one obtains for the entropy of aqueous SO_4^{2-} the value 4.05 (since the entropy of H^+ is zero by definition). This result agrees reasonably well with those obtained earlier by a different method and we conclude that $S°(SO_4^{2-}) = 4.2 \pm 0.2$ cal mol^{-1} K^{-1}. Combination of this value with $\Delta S_2°$ yields for the entropy of HSO_4^- the value 32.1 ± 0.3 cal K^{-1} mol^{-1}.

The consistency of data in the 1-4 M range is excellent with variations of only a few calories in the $\Delta H°$ and $\Delta G°$ values. However, our absolute knowledge for the dilute range is uncertain to the extent of about 15 cal for $\Delta G°$ and 40 cal for $\Delta H°$ if our adopted parameters are essentially correct. If the

Table V. Properties of H_2SO_4 at 25 °C and at Rounded Molalities

m	$-G^{ex}$	γ	ϕ	a_w	$^{\phi}L$	$-\bar{L}_1$	$\bar{L}_2$
0.0001	58	0.9500	0.981	0.99999	119	0.0002	220
0.0002	87	0.9253	0.971	0.99999	214	0.0006	393
0.0005	150	0.8736	0.949	0.99997	451	0.0032	803
0.001	228	0.8151	0.924	0.99995	757	0.0097	1295
0.002	342	0.7382	0.889	0.99990	1200	0.0265	1936
0.005	568	0.6146	0.833	0.99978	1970	0.083	2891
0.01	802	0.5146	0.787	0.99957	2623	0.171	3571
0.02	1092	0.4190	0.744	0.99920	3261	0.317	4140
0.05	1547	0.3098	0.699	0.99811	3991	0.638	4699
0.1	1934	0.2436	0.676	0.99635	4435	1.034	5008
0.2	2341	0.1918	0.666	0.99283	4793	1.679	5259
0.3	2582	0.1676	0.667	0.98925	4972	2.255	5389
0.5	2880	0.1434	0.678	0.9818	5172	3.318	5540
0.7	3069	0.1311	0.694	0.9741	5292	4.343	5636
1.0	3254	0.1215	0.723	0.9617	5412	6.029	5747
1.5	3436	0.1160	0.778	0.9388	5553	10.23	5932
2.0	3534	0.1171	0.843	0.9129	5677	18.03	6177
2.5	3582	0.1224	0.915	0.8837	5809	31.56	6510
3.0	3598	0.1311	0.992	0.8514	5959	52.12	6924
4.0	3564	0.1563	1.149	0.7801	6318	111.9	7871
5.0	3476	0.1907	1.299	0.7041	6720	184.1	8764
6.0	3357	0.2343	1.437	0.6274	7124	257.1	9503

alternate set were correct these differences become about 50 and 200 cal, respectively.

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Appendix

Values for the Debye-Hückel parameter A_ϕ are well-known;[11,30] the precise values used here were obtained from a careful evaluation of the data on the density and dielectric constant over a very wide temperature range. The resulting equations, valid to 300 °C, are presented elsewhere.[41] A very much simpler equation is adequate for the temperature range 0-55 °C.

$$A_\phi = 0.3770 + 4.684 \times 10^{-4}(T - 273.15) + 3.74 \times 10^{-6}(T - 273.15)^2 \quad \text{(A1)}$$

The value of the parameter for the enthalpy at 25 °C is A_H = 697.5 cal mol^{-1}.

For the mixed electrolyte solutions of cell D, $H_2SO_4(m)$, $HCl(m_3)$, additional terms arise for interactions of Cl^-. Since all of the solutions are very dilute, third virial coefficients may be omitted. Also we neglect terms for interactions of ions of the same sign since these are known[9] to be small for Cl^--SO_4^{2-} and expected to be small also for Cl^--HSO_4^-. One then obtains

$$\tfrac{1}{2}\ln(\gamma_H\gamma_{Cl}) = f^\gamma + (m_3 + m_H)B_{HCl} + m_1B_{H1} + m_2\beta_{H2}^{(0)} + m_Hm_3B_{HCl}' + m_Hm_1B_{H1}' \quad \text{(A2)}$$

$$\ln(\gamma_H\gamma_{SO_4}/\gamma_{HSO_4}) = 4f^\gamma + 2[m_3B_{HCl} + (m_1 - m_H)B_{H1} + (m_H + m_2)\beta_{H2}^{(0)}] + 4m_H[m_3B_{HCl}' + m_1B_{H1}'] \quad \text{(A3)}$$

Other equations continue to apply but m_H and I must include, of course, the contribution m_3 from the HCl. The potential for cell D is then

$$E - E_0 = -(RT/F)[\ln(m_Hm_3) + \ln(\gamma_H\gamma_{Cl})] \quad \text{(A4)}$$

While the parameters for HCl at 25 °C are known,[8] they were reevaluated as a function of temperature by least-squares analysis of the results of Gupta, Hills, and Ives.[40] The results can be expressed as

$$\beta_{HCl}^{(0)} = 0.1754 - 0.0004286(T - 298.15) \quad \text{(A5)}$$

$$\beta_{HCl}^{(1)} = 0.3004 - 0.00406(T - 298.15) + 7.89 \times 10^{-6}(T^2 - 298.15^2) \quad \text{(A6)}$$

These equations (valid 0-50 °C) give slightly different values for the parameters at 25 °C from those given in the earlier treatment[8] which included additional data for HCl; the difference is negligible.

The potential for cell D was calculated with the above parameters for HCl and those of Table I for H_2SO_4. For the set with K_2 = 0.0105 the standard deviation at 25 °C was 0.05 mV while at both 0 and 45 °C the standard deviation was 0.06 mV. In contrast to this excellent agreement, calculations with K_2 = 0.0120 yield systematic disagreement rising from 0.2 to 0.4 mV with increase in concentration.

For the buffer solutions $Na_2SO_4(m_4)$ and $NaHSO_4(m_5)$ in cell B[29] the equations include terms for the interaction of Na^+ with SO_4^{2-}, which are known,[8] and for Na^+ with HSO_4^-, which are not known. For the latter one may take the parameters[8] for $NaClO_4$ as a rough estimate. Now the molality of HSO_4^- is $m_1 = m_5 - m_H$ and for SO_4^{2-} $m_2 = m_4 + m_H$ while for Na^+ $m_{Na} = 2m_4 + m_5$. With very dilute solutions we again omit third virial coefficients and terms for interactions of ions of the same sign and obtain

$$\ln(\gamma_H\gamma_{SO_4}) = 6f^\gamma + 4m_1B_{H1} + 2[m_{Na}B_{Na2} + (m_H + 2m_2)\beta_{H2}^{(0)}] \quad \text{(A7)}$$

$$\ln(\gamma_H\gamma_{SO_4}/\gamma_{HSO_4}) = 4f^\gamma + 2[(m_1 - m_H)B_{H1} + (m_H + m_2)\beta_{H2}^{(0)} + m_{Na}(B_{Na2} - B_{Na1})] \quad \text{(A8)}$$

The calculated cell potentials for the buffer solutions with $NaClO_4$ parameters assumed for $NaHSO_4$ interactions differ by about 1 mV from those observed. This is essentially the same difference as was noted, but not emphasized, in the original paper of Covington, Dobson, and Wynne-Jones.[29] This disagreement is decreased but not removed by the assumption of larger but still reasonable values for $\beta^{(0)}$ and $\beta^{(1)}$ for $NaHSO_4$; it is not appreciably affected by shift to the alternate set of parameters in Table I for H_2SO_4. This discrepancy is small, fortunately, but it is not removed by any plausible change in ionic-interaction parameters provided the consistent E_0 values are used.

References and Notes

(1) S. Shankman and A. R. Gordon, *J. Am. Chem. Soc.*, **61**, 2370 (1939).
(2) R. H. Stokes, *J. Am. Chem. Soc.*, **69**, 1291 (1947); *Trans. Faraday Soc.*, **44**, 295 (1948).
(3) W. H. Beck, K. P. Singh, and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **55**, 331 (1959).
(4) W. H. Beck, J. V. Dobson, and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **56**, 1172 (1960).
(5) W. F. Giauque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, *J. Am. Chem. Soc.*, **82**, 62 (1960).
(6) J. A. Duisman and W. F. Giauque, *J. Phys. Chem.*, **72**, 562 (1968).
(7) K. S. Pitzer, *J. Phys. Chem.*, **77**, 268 (1973).
(8) K. S. Pitzer and G. Mayorga, *J. Phys. Chem.*, **77**, 2300 (1973); **78**, 2698 (1974).
(9) K. S. Pitzer and J. J. Kim, *J. Am. Chem. Soc.*, **96**, 5701 (1974).
(10) W. J. Hamer, "The Structure of Electrolytic Solutions", Wiley, New York, N.Y., 1959, Chapter 15.
(11) K. S. Pitzer and L. Brewer, "Thermodynamics", Revised edition, G. N. Lewis and M. Randall, Ed., McGraw-Hill, New York, N.Y., 1961, pp 587–590.
(12) K. S. Pitzer and L. F. Silvester, *J. Solution Chem.*, **5**, 269 (1976).
(13) T. L. Hill, "Introduction to Statistical Mechanics", Addison-Wesley, Reading, Mass., 1960, Chapter 19.
(14) A. K. Covington, J. V. Dobson, and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **61**, 2050 (1965).
(15) J. Shrawder, Jr., and I. A. Cowperthwaite, *J. Am. Chem. Soc.*, **56**, 2340 (1934).
(16) T. H. Lilley and C. C. Briggs, *Electrochim. Acta*, **20**, 257 (1975).
(17) K. S. Pitzer, *J. Phys. Chem.*, **80**, 2863 (1976).
(18) W. J. Hamer, *J. Am. Chem. Soc.*, **57**, 9 (1935).
(19) H. S. Harned and W. J. Hamer, *J. Am. Chem. Soc.*, **57**, 27 (1935).
(20) S. A. Brown and J. E. Land, *J. Am. Chem. Soc.*, **79**, 3015 (1957).
(21) E. Lange, J. Monheim, and A. L. Robinson, *J. Am. Chem. Soc.*, **55**, 4733 (1933).
(22) J. E. Kunzler and W. F. Giauque, *J. Am. Chem. Soc.*, **74**, 3472 (1952).
(23) W. L. Groenier, Thesis, University of Chicago, 1936.
(24) Y. C. Wu, Thesis, University of Chicago, 1957.
(25) K. S. Pitzer, *J. Am. Chem. Soc.*, **59**, 2365 (1937).
(26) J. M. Austin and A. D. Mair, *J. Phys. Chem.*, **66**, 519 (1962).
(27) V. S. K. Nair and G. H. Nancollas, *J. Chem. Soc.*, 4144 (1958); see also C. W. Davies, H. W. H. Jones, and C. B. Monk, *Trans. Faraday Soc.*, **48**, 921 (1952).
(28) H. S. Dunsmore and G. H. Nancollas, *J. Phys. Chem.*, **68**, 1579 (1964).
(29) A. K. Covington, J. V. Dobson, and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **61**, 2057 (1965).
(30) R. A. Robinson and R. H. Stokes, "Electrolytic Solutions", Butterworths, London, 1959.
(31) J. A. Rard, A. Habenschuss, and F. H. Spedding, *J. Chem. Eng. Data*, **21**, 374 (1976).
(32) K. S. Pitzer, *J. Chem. Soc., Faraday Trans. 2*, **68**, 101 (1972).
(33) T. F. Young, L. F. Maranville, and H. M. Smith, "The Structure of Electrolytic Solutions", W. J. Hamer, Ed., Wiley, New York, N.Y., 1959, Chapter 4.
(34) M. Kerker, *J. Am. Chem. Soc.*, **79**, 3664 (1957).
(35) D. D. Wagman et al., *Natl. Bur. Stand.* (*U.S.*), *Tech. Note*, 270-3 (1968).
(36) K. Gallagher, G. E. Brodale, and T. E. Hopkins, *J. Phys. Chem.*, **64**, 687 (1960).
(37) P. F. Meads, W. R. Forsythe, and W. F. Giauque, *J. Am. Chem. Soc.*, **63**, 1902 (1941).
(38) CODATA, Tentative set of key values for thermodynamics, Part IV (1974).
(39) R. G. Bates, M. Edelstein, and S. F. Acree, *J. Res. Natl. Bur. Stand.*, **36**, 159 (1946).
(40) S. R. Gupta, G. J. Hills, and D. J. G. Ives, *Trans. Faraday Soc.*, **59**, 1874 (1963).
(41) L. F. Silvester and K. S. Pitzer, Lawrence Berkeley Laboratory Report No. 4456 (1976), to be published.
(42) H. K. J. Powell, *J. Chem. Soc., Dalton Trans.*, 1947 (1973).
(43) S. Cabani and P. Gianni, *Anal. Chem.*, **44**, 253 (1972).

Qualitative Potential Energy Surfaces. 5. Sigmatropic Shifts

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Abstract: The LCFC approach is used to generate the manifold of PE surfaces for radical-radical combination reactions and sigmatropic shifts. The effect of polarity on reaction rate and reaction toposelectivity is discussed. It is predicted that (a) within a series of structurally similar compounds, the rate of an *i,j* thermal sigmatropic shift increases as the migration framework and the migration group become a better donor-acceptor pair and (b) a thermal or photochemical sigmatropic shift occurs in the topochemical manner which couples the best donor-acceptor combination of migration framework and migrating group. Experimental data which support the qualitative theory are presented.

In previous papers,[1] we have explored how the linear combination of fragment configurations (LCFC) method can be used to construct qualitative potential energy (PE) surfaces for various classes of chemical reactions. In this paper, we extend our approach to sigmatropic shifts after a background discussion of the LCFC qualitative PE surfaces for radical-radical combination reactions.

(I) Potential Energy Surfaces for Radical–Radical Combination Reactions

We first consider covalent bond formation from a singly occupied X AO and a singly occupied Y AO by reference to the static LCFC diagram shown in Figure 1. The following important trends should be noted: (a) The ground state of the bond has a dominant no bond contribution while the lowest excited state is primarily ionic. (b) The mixing of the no bond and lowest charge transfer configurations, and, hence, X–Y bond strengths, is expected to increase as the ionization potential of one singly occupied AO decreases, the electron affinity of the other singly occupied AO increases, and the corresponding interaction matrix element increases. This situation is illustrated by the greater bond dissociation energy of CH_3-F as compared with that of CH_3-H. However, in situations where an increase of the polarity of the system is counteracted by a "shrinkage" of the AO coefficients of the uniting centers, reduction of the absolute magnitude of the interaction matrix element may dominate the diminution of the energy gap separating the interacting DA and D^+A^- configurations. The smaller C–H bond dissociation energy of $PhCH_2$–H as compared with that of $CH_3CH_2CH_2$–H can be traced to such conflicting trends. The two contrasting cases are illustrated in Figure 2.

The comparison of $CH_3CH_2CH_2$–H and $PhCH_2$–H dissociation energies is instructive and merits attention.

	Donor (D)	Acceptor (A)	$I_D - A_A$, eV	$\langle DA\|\hat{P}\|D^+A^-\rangle$ (in kS units)
CH_3CH_2-CH_2-H	$CH_3CH_2CH_2\cdot$	$H\cdot$	~7.0	~1.00
$PhCH_2$-H	$PhCH_2\cdot$	$H\cdot$	~6.5	0.76

Increased delocalization in D leads to increased polarity cou-