

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, INDIANA]

The Thermodynamic Properties of High Temperature Aqueous Solutions. VI. Applications of Entropy Correspondence to Thermodynamics and Kinetics¹

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In previous papers from this laboratory,² the general nature of the principle of entropy correspondence has been demonstrated. This, in turn, has led to reliable predictions of the partial molal heat capacities of ionic species over wide temperature ranges. The present work extends the usefulness of the correspondence principle by illustrating its application in a wide variety of situations of interest to the chemical sciences. In part II, selected high temperature solubilities, dissociation constants, and cell potential data are predicted or evaluated on a more sound thermodynamic basis. In part III, the kinetic consequences of entropy correspondence are examined; this has resulted in the prediction of a class of reactions which will follow "retrograde kinetics."

Part I

In some of the calculations to be given, various thermochemical parameters will be used and are defined as follows. The activity coefficient of an ion will be represented by the equation

$$\log \gamma = -A_\gamma |Z_+ Z_-| \frac{I^{1/2}}{1 + I^{1/2}} + \frac{2\nu_+ \nu_-}{\nu} B_{(m)} m \quad (1)$$

where A_γ is given by³

$$A_\gamma = \left(\frac{2\pi N d_0}{2.303} \right)^{1/2} \left(\frac{e^2}{DkT} \right)^{1/2} \quad (2)$$

D is the dielectric constant, d_0 is the density of the pure solvent, and I is the ionic strength, $0.5 \sum M_i Z_i^2$. A solute is made up of ν_+ cations and ν_- ions ($\nu \equiv \nu_+ + \nu_-$) and $B_{(m)}$ is a concentration-dependent parameter which

TABLE I
THERMOCHEMICAL PARAMETERS

t , °C.	$2.303RT$	$-a_{(t)}^a$	A_γ^b
25	1364	0	0.511
60	1524	1.98	0.545
100	1707	8.73	0.595
150	1936	23.16	0.689
200	2165	43.5	0.809
250	2394	69.2	0.983

^a As defined by eq. 4. ^b As defined by eq. 2; values of A_γ were taken from the compilation of ref. 4, p. 640, at 25, 60, and 100°. Above 100°, values were calculated from eq. 2 using data on D from G. C. Åkerlöf and H. I. Oshry, *J. Am. Chem. Soc.*, **72**, 2844 (1950); the density of pure water above 100° is from the compilation of W. E. Forsythe, "Smithsonian Physical Tables," 9th Ed., Smithsonian Institute, Washington, D. C., 1954, p. 298.

varies from solute to solute. Tabulated values of $B_{(m)}$ for many salts as a function of molality at 25° have been given elsewhere.⁴ The change in the free energy of a reaction between t_2 and 25° is given by

$$\Delta F^\circ_{(t_2)} - \Delta F^\circ_{(25)} = \Delta(\Delta F) = \overline{\Delta C_p}^\circ \Delta T - \Delta S^\circ_{(25)} \Delta T - T_2 \overline{\Delta C_p}^\circ \ln \frac{T_2}{T_1} \quad (3)$$

or

$$\Delta(\Delta F) = \overline{\Delta C_p}^\circ \left[\Delta T - T_2 \ln \frac{T_2}{298.15} \right] - \Delta S^\circ_{(25)} \Delta T = a_{(t)} \overline{\Delta C_p}^\circ - \Delta S^\circ_{(25)} \Delta T \quad (4)$$

(1) Supported by a grant from the National Science Foundation.

(2) C. M. Criss and J. W. Cobble, *J. Am. Chem. Soc.*, **86**, 5385, 5390 (1964); papers IV and V of this sequence.

(3) E. A. Guggenheim, *Phil. Mag.*, **19**, 588 (1935).

(4) G. N. Lewis and M. Randall, "Thermodynamics," 2nd Ed., revised by K. S. Pitzer and L. Brewer, McGraw-Hill Book Co., New York, N. Y., 1961, pp. 643-658.

where $\Delta T = t_2 - 25^\circ$. Table I contains tabulated values of $a_{(t)}$, A_γ , and $2.303RT$ at intermediate temperatures between 25 and 250°.

Part II

A. Cell Potentials.—One of the most precise free energy measurements that can be made is the potential of a reversible electrochemical cell. Precisions of the order of ± 0.1 mv. are not uncommon in such measurements, and in recent years data have been obtained above the older 0-60° temperature range.⁵⁻⁷ In such studies, it is not uncommon to report the resultant E° values as a power series function of the temperature. By such means it is possible to reproduce the experimental data to an *average* error which corresponds to the average experimental error.

Such a procedure is poor in a number of ways. First of all, it tends to smooth out any nonrandom trends in the data, particularly above 60°, where the heat capacities for electrolytes frequently demonstrate maxima. Secondly, it is impossible by such a procedure to determine whether the cell gives thermodynamically meaningful results over all of the temperature range studied since the only proof of such behavior depends upon a *previous* knowledge of the heat capacities involved. However, the most serious defect lies in the fact that a power series expansion of the potential will not usually approximate the true behavior of ΔC_p . Forcing the data into such a form not only gives misleading information on ΔC_p , but does not enable one to use the full accuracy of the free energy data even in obtaining ΔH° and ΔS° .

The most accurate method which can be used to treat cell data over an extended temperature range is one which uses known or estimated heat capacities. As an example, consider the cell potential data reported for the Ag-AgCl electrode between 25 and 275°. The authors of these data have expressed the potential in the form of power series expansion

$$E^\circ = 0.23755 - 5.3783(10^{-4}t) - 2.3728(10^{-6}t^2) \quad (5)$$

which has a "standard error of fit of the data from 25 to 200°... (of)... 0.19 mv." From the previous papers of this series the heat capacity of HCl(aq) can now be estimated² over the temperature range involved. Equa-

(5) R. G. Bates and V. E. Bower, *J. Res. Natl. Bur. Std.*, **53**, 283 (1954).

(6) R. S. Greeley, W. T. Smith, Jr., R. W. Stoughton, and M. H. Lietzke, *J. Phys. Chem.*, **64**, 652 (1960).

(7) M. B. Towns, R. S. Greeley, and M. H. Lietzke, *ibid.*, **64**, 1861 (1960).

tion 4 is conveniently rewritten as

$$E^\circ_{(t)} + \frac{a\Delta C_p}{nF} \Big]_{25}^t = E^\circ_{25} + \frac{\Delta S^\circ_{25}}{nF}(t - 25) \quad (6)$$

where the constant a is the temperature factor as defined previously (eq. 4), and $\Delta C_p \Big]_{25}^t$ is the average value of the heat capacity between t and 25° . If the observed E° values at each temperature are added to the heat capacity term, then a plot of the left side of eq. 6 against t must be linear within the accuracy of the values of ΔC_p and will have a slope equal to ΔS°_{25} . If such a plot is not linear, the cell is not thermodynamically meaningful over part (or all) of the temperature range studied.

A further advantage of this method is also obvious. The intercept of the plot of eq. 6 at 25° is equal to E°_{25} . This value of E°_{25} is then based upon *all* of the e.m.f.-temperature data, and not just on potentials at adjacent temperatures, a restriction which the power series method imposes.

Much better values for E°_{25} , ΔS°_{25} , and ΔH°_{25} result by this "third-law" method of treating the free energy data.

The Ag-AgCl cell data from 25 to 275° ⁶ were analyzed by this method.^{8,9} The plot of $E^\circ_{(t)} - a\Delta C_p/nF \Big]_{25}^t$ against t was linear up to approximately 125° , but then began to show curvature at higher temperatures. The slope of the initial linear portion of the curve gave $\Delta S^\circ_{25} = -14.8 \pm 0.1$ cal. mole⁻¹ deg.⁻¹ compared to the best previously available value of -14.86 cal. mole⁻¹ deg.⁻¹¹⁰; E°_{25} was evaluated at 0.2225 ± 0.0001 v. compared to the best available value of 0.222384 v.¹⁰ The situation above 125° can best be illustrated by using eq. 6 and the experimentally determined value of $\Delta S^\circ_{25} = -14.8$ cal. mole⁻¹ deg.⁻¹ to calculate a value of E°_{25} from each of the $E^\circ_{(t)}$ values (Fig. 1). Such a procedure clearly indicates that some other effect is setting in above 125° which either makes the cell non-reversible or introduces some additional chemical factor. In the present case, it appears that lack of information on the state of Ag^+ from the dissolved AgCl in the HCl solutions involved may have caused increasingly serious errors in the evaluation of $E^\circ_{(t)}$ as the temperatures were elevated.

It may be noted that the power series equation (5) gives $E^\circ_{25} = 0.2224$ v. and $\Delta S^\circ_{25} = 15.1$ cal. mole⁻¹ deg.⁻¹. While the previously reported value of E°_{25} is in good agreement with the new treatment, the value of ΔS°_{25} was not as accurately fixed as is now possible. A more serious criticism can be made of the second temperature differential of eq. 5 which indicates an incorrect trend of ΔC_p with temperature.

A second example can be found in the various electrochemical cells involving $\text{H}_2\text{SO}_4(\text{aq})$.¹¹ Application

(8) Heat capacity data for $\text{HCl}(\text{aq})$ are from ref. 2; corresponding data for Ag, AgCl, and H_2 are from ref. 9.

(9) K. K. Kelley, Bureau of Mines Bulletin 584, U. S. Government Printing Office, Washington, D. C., 1960.

(10) J. C. Ahluwalia and J. W. Cobble, *J. Am. Chem. Soc.*, **86**, 5381 (1964), paper III of this sequence.

(11) R. E. Mitchell, E. C. Jekel, and J. W. Cobble, Abstracts of Papers, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 19, 1964, abstract 17D; to be published.

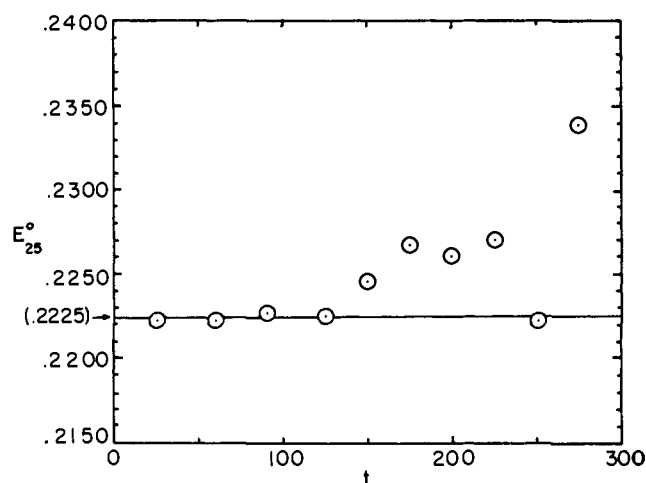
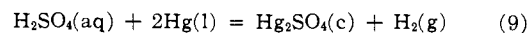
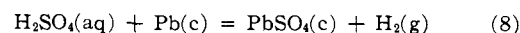
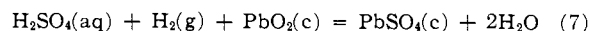


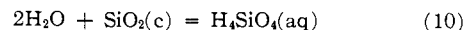
Fig. 1.—Third-law analysis (eq. 6) of the high temperature Ag-AgCl electrode; $\Delta S^\circ_{25} = -14.8$ (cell data are from ref. 6; heat capacity data are from ref. 2 and 9).

of eq. 6 to three different sets of cell reactions indicated only one (eq. 7) sulfate ion electrode appears to be thermodynamically meaningful over even limited temperature ranges. The cell reactions involved are

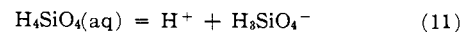


The present type of analysis indicated that the thermodynamic functions for cell reaction 7 should be changed to $E^\circ_{25} = 1.6874$ v. and $\Delta S^\circ_{25} = 18.5$ cal. mole⁻¹ deg.⁻¹ from the quoted range of values of 1.6871 to 1.6848 v. and the presently accepted value¹² of $\Delta S^\circ_{25} = 15.0$ cal. mole⁻¹ deg.⁻¹. Further, none of the data appears to be compatible with the criteria of eq. 6 above 40° for *any* sulfate ion electrode published to date.

B. Dissociation of Weak Acids.—The *a priori* prediction of ionic heat capacities is useful in attempting to use and extend the dissociation constants of weak electrolytes, particularly where these are difficult to obtain experimentally. One such case is the silica-water-silicic acid system up to the critical point. The solubility data of quartz in high temperature solutions have recently again been determined¹³ and the previous data discussed¹⁴ rather extensively. Apparently the concentration of monomeric silicic acid can be determined, and the data are consistent with the reaction



The long times required for equilibria, particularly at lower temperatures, prevent fixing accurate values of $\Delta C_p^\circ_{10}$ and ΔS°_{10} , but these apparently are small if not zero for eq. 10 near room temperature. The structural evidence¹⁵ favors the $\text{H}_2\text{SiO}_4^{-2}$ ion as the predominant species in basic solutions, and we shall write as the dissociation equilibria



(12) Auxiliary thermodynamic data are from W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, New York, N. Y., 1952.

(13) C. W. Morey, R. O. Fournier, and J. J. Roane, *Geochim. Cosmochim. Acta*, **26**, 1029 (1962).

(14) J. A. van Lier, P. L. de Bruyn, and J. Th. G. Overbeek, *J. Phys. Chem.*, **64**, 1675 (1960).

(15) J. E. Earley, D. Fortnum, A. Wojcicki, and J. O. Edwards, *J. Am. Chem. Soc.*, **81**, 1295 (1959).

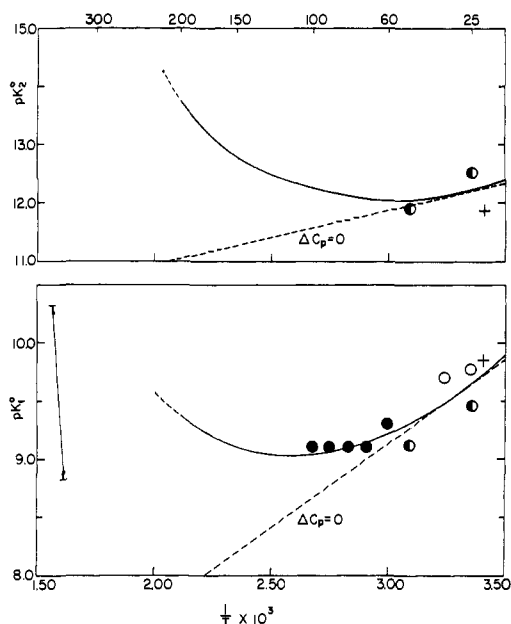
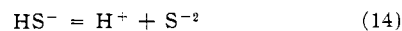
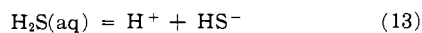


Fig. 2.—Predicted and observed first (lower) and second (upper) dissociation constants for $\text{H}_4\text{SiO}_4(\text{aq})$. The dotted lines represent the thermodynamically improbable cases of $\Delta C_p = 0$. The arrows in the lower section represent the range of values reported near the critical region by J. Vilim, *Collection Czech. Chem. Commun.*, **26**, 1268 (1961); *Chem. Abstr.*, **55**, 16,104a (1961). Other symbols: \circ S. A. Greenberg and E. W. Price, *J. Phys. Chem.*, **61**, 1539 (1957); \bullet G. Lagerström, *Acta Chem. Scand.*, **13**, 722 (1959); \bullet J. A. van Lier, P. L. De Bruyn, and J. Th. G. Overbeek, *J. Phys. Chem.*, **64**, 1675 (1960); $+$ S. A. Greenberg, *J. Am. Chem. Soc.*, **80**, 6508 (1958).

The situation is summarized in Fig. 2. The data for K_{11}° are best fit with a value for $\Delta S_{11}^\circ = -22$ cal. mole $^{-1}$ deg. $^{-1}$ at 25° . The entropies of H_3SiO_4^- and $\text{H}_2\text{SiO}_4^{-2}$ are estimated¹⁶ to be 13 and -32 cal. mole $^{-1}$ deg. $^{-1}$, respectively, and ionic heat capacities calculated as previously discussed.² The heat capacity of $\text{H}_4\text{SiO}_4(\text{aq})$ was fixed as 35, 36, 36, and 37 cal. mole $^{-1}$ deg. $^{-1}$ at 60, 100, 150, and 200° , respectively, from the quartz solubility data. Figure 2 illustrates that extensions of thermodynamic data to higher temperatures can be inaccurate if they are based on the assumption that ΔC_p is zero over even limited temperature ranges. In this respect it should be pointed out that the available data on the second dissociation constant of H_4SiO_4 are so sparse as to make the predicted values of K_{12}° subject to large errors.

A second case of an important and quite unusual weak acid dissociation is hydrogen sulfide



A number of investigators have reported values for the first and second dissociation constants, K_{13}° and K_{14}° from 0 to 60° . ΔS_{13}° has the value of 15.9 cal. mole $^{-1}$ deg. $^{-1}$ at 25° as determined by thermal and free energy measurements.^{12,17} The thermodynamic analysis, using estimated heat capacities as before,² is summarized in Fig. 3. The two lower solid lines are both based on estimated values of $\Delta C_{p,13}^\circ$; solid line 3 assumes that

(16) J. W. Cobble, *J. Chem. Phys.*, **21**, 1443 (1953).

(17) J. W. Kury, A. J. Zielen, and W. M. Latimer, *J. Electrochem. Soc.*, **100**, 468 (1953); the entropy of $\text{H}_2\text{S}(\text{aq})$ has been taken as 30.9 cal. mole $^{-1}$ deg. $^{-1}$ as calculated from data summarized by H. A. Pohl, *J. Chem. Eng. Data*, **6**, 515 (1961). The heat capacity of $\text{H}_2\text{S}(\text{aq})$ can be calculated from this same source.

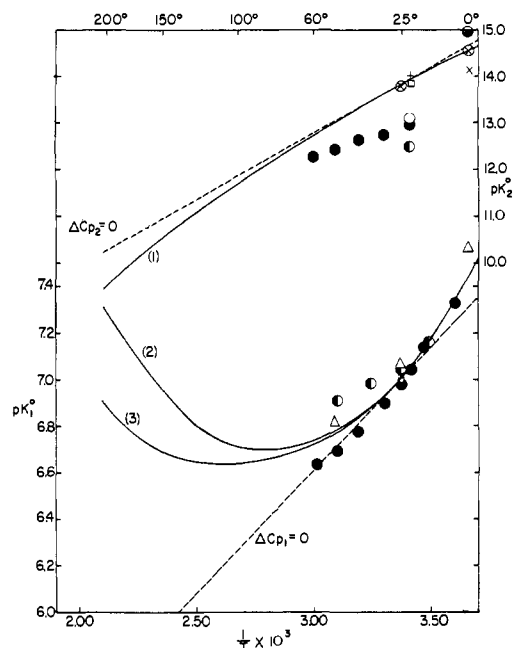


Fig. 3.—Predicted and observed dissociation constants for $\text{H}_2\text{S}(\text{aq})$. Solid lines 1 and 2 are from predicted heat capacities as a function of temperature. Solid line 3 is predicted from the heat capacities at 25° and assuming (erroneously) that ΔC_p is constant. The dotted lines indicate the even more improbable cases of $\Delta C_p = 0$. Upper symbols: \otimes G. Maronny, *Electrochim. Acta*, **1**, 58 (1959); \bullet S. S. Zavodnov and P. A. Kryuhov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1704 (1960); $+$ A. J. Ellis and R. M. Golding, *J. Chem. Soc.*, 127 (1959); \times K. Jellinek and J. Czerwinski, *Z. physik. Chem.*, **102**, 438 (1922); \circ N. Konopik and O. Leberl, *Monatsh. Chem.*, **80**, 781, 788 (1949); \bullet H. Kubli, *Helv. Chem. Acta*, **29**, 1962 (1946); \bullet "International Critical Tables," Vol. 7, McGraw-Hill Book Co., New York, N. Y., 1930, p. 237; \square S. S. Muhammad and E. V. Sundaram, *J. Sci. Ind. Res. (India)*, **20B**, 16 (1961). Lower symbols: $+$ A. J. Ellis and R. M. Golding, *J. Chem. Soc.*, 127 (1959); \bullet R. H. Wright and O. Maass, *Can. J. Res.*, **6**, 588 (1932); \bullet T. A. Tremanova and K. P. Mishenko, *Zh. Neorgan. Khim.*, **2**, 1990 (1957); \triangle H. L. Loy and D. M. Himmelbau, *J. Phys. Chem.*, **65**, 264 (1961); \square same as upper symbol.

$\Delta C_{p,13}^\circ$ has a constant value equal to that at 25° over the entire temperature range indicated. This calculation was made to illustrate that such an assumption may lead to errors in predicting temperature behavior, although not as large as those obtained by assuming $\Delta C_p = 0$.

Because of the predicted "saturation effect" for the heat capacity of the monatomic sulfide ion, the surprising result is obtained that $\Delta C_{p,14}^\circ$ is positive over the temperature range under consideration. This means that there will be no minima in the value of K_{14}° as the temperature is varied, but rather that HS^- will become an increasingly strong acid as the temperature increases. Indeed, if the present analysis is correct, HS^- will become a stronger acid than H_2S at very high temperature ranges, and HS^- will then cease to be an important species in H_2S solutions. In this analysis of the second dissociation constant, the determinations of K_{14}° by Maronny¹⁸ at 0 and 25° were used, and the heat capacity data below 25° are from a recent study¹⁹ at 0° . Maronny's estimate of $\Delta S_{14}^\circ = -21$ cal. mole $^{-1}$ deg. $^{-1}$ at 25° will not be as accurate as the one used in the pres-

(18) G. Maronny, *Electrochim. Acta*, **1**, 58 (1959).

(19) R. E. Mitchell and J. W. Cobble, to be published. See Ph.D. Thesis of R. E. Mitchell, Purdue University, 1964.

ent analysis of $\Delta S^\circ_{14} = -19.0$ cal. mole⁻¹ deg.⁻¹ at 25° because this author assumed $\Delta C_p^\circ_{14}$ to be zero.

C. Solubility of Ca(OH)₂. Activity Coefficients at High Temperatures.—The standard state which has been used up to now has referred to the ions at infinite dilution, the hypothetically ideal 1 *m* solution. In many cases, it is the free energy, equilibrium constant, or concentration at a finite ionic strength which is desired. At lower temperatures, sufficient activity coefficient data are available or can be estimated to treat solutions of finite concentration, but above 100° very few values of γ_{\pm} are known.

One possible solution to the problem would be to assume $\Delta \bar{C}_p$ is not a sensitive function of the concentration. Again, detailed data are lacking for very many systems, but what data do exist indicate that this is not a very satisfactory assumption, particularly for reactions involving both ions and neutral solutes. One can, of course, assume that γ_{\pm} is not a very sensitive function of the temperature. While this is not a particularly bad assumption for 1:1 electrolytes up to 100°, it is not valid at higher temperatures. For example, in 0.1 *m* HCl, γ_{\pm} is 0.796 and 0.58 at 25 and 250°,^{6,7} respectively.

Lietzke and Stoughton,²⁰ in an extensive series of studies on the solubility of silver sulfate in various electrolyte solutions, have shown rather conclusively that activity coefficients can be as easily correlated by various Debye-Hückel expressions up to 250° as they are at room temperature. Further, from a series of studies on the silver-silver halide electrodes,^{6,7} the activity coefficients of HCl and HBr were also interpretable in terms of simple theory. These authors favored use of a variable *A* parameter in the denominator of the simple Debye-Hückel expression: $\log \gamma = -A_{\gamma} |Z_1 Z_2| \mu^{1/2} / (1 + A_{\gamma} \mu^{1/2})$. However, the expression used in the present paper will be that given by the two-parameter eq. 1, where *A* = 1.000. As a first approximation it will be assumed that *B*_(*m*) is independent of the temperature.²¹ From this it follows that

$$(\log \gamma_{\pm}^{\text{ts}})_m = (\log \gamma_{\pm}^{25})_m - \frac{\sqrt{I}}{1 + \sqrt{I}} [A_{\gamma}^{\text{ts}} - A_{\gamma}^{25}] \quad (15)$$

The limiting law coefficients *A*_γ have been tabulated in Table I. In the example referred to above, γ_{\pm}^{250} is calculated to be 0.62 from γ_{\pm}^{25} of 0.796 in 0.1 *m* HCl. The observed value at 250° is 0.58 ± 0.02 ,^{6,7} which is probably satisfactory agreement under these conditions. Tabulated values of the activity coefficients of many electrolytes in terms of *B* in eq. 1 are given by Pitzer and Brewer,⁴ and an equally useful expression in terms of the *B* coefficients in these tables is

$$(\log \gamma_{\pm}^{\text{ts}})_m = -\frac{A_{\gamma}^{\text{ts}} \sqrt{I}}{1 + \sqrt{I}} + B_{(m)}^{25} m \quad (16)$$

In many cases, the activity coefficients of the salt are

(20) M. H. Lietzke and R. W. Stoughton, *J. Phys. Chem.*, **63**, 1183, 1186, 1188, 1190, 1984 (1959).

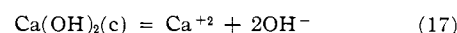
(21) Values of dB/dt and d^2B/dt^2 are available for some electrolytes near room temperature (ref. 4, p. 397). However, over the large temperature intervals being discussed, values of d^2B/dt^2 are simultaneously required; unfortunately the detailed behavior of *B*_(*m*) as a function of temperature above 100° is not known but for a few electrolytes. It is known experimentally that dB/dt and d^2B/dt^2 for NaCl and BaCl₂ are both zero and change sign near 50°. At 100° these values are changing rapidly, but nothing is known of d^2B/dt^2 or d^4B/dt^4 above 100°. In any event, the combination of all of the temperature coefficients may largely cancel at higher temperatures.

not known even at 25°. In such a case, the activity coefficient must be estimated from a chemically similar substitute whose γ_{\pm} values are known.

The validity of these procedures will be illustrated in a comparison of the predicted and observed solubilities of Ca(OH)₂. The data on this salt were not extensive enough at higher temperatures to use in the original entropy calculations.²

The activity coefficients of Ca(OH)₂(aq) at 25° are not known, but can be fixed sufficiently well for the present purposes from data in the literature. The most careful measurements on the solubility of Ca(OH)₂ in the presence of added electrolytes appear to be those of Johnston and Grove on large crystals²² at 25°. The *K*_{sp}° of Ca(OH)₂ is defined as $4\pi i^3$, and the *K*_{sp}° as $4m^3\gamma_{\pm}^3$, where *m* is the molality and γ_{\pm} the mean molal activity coefficient. The expression $\log K_{sp} - 6A_{\gamma} I^{1/2} / (1 + I^{1/2})$ was plotted against the ionic strength; the intercept at *I* = 0 defines $\log K_{sp}^\circ$ as -5.000 ,²³ which corresponds to a *K*_{sp}° of 1.00×10^{-5} , or a solubility of 0.0207 *m* ($\gamma_{\pm} = 0.656$) at 25°. This value of *K*_{sp}° now allows the calculation of γ_{\pm} for Ca(OH)₂ at 25° as a function of the ionic strength in various electrolytes. When these activity coefficients were calculated, they were observed to be almost identical with those of CaCl₂ up to ~1 *m*; consequently the conveniently recorded⁴ values of γ_{\pm}^{25} for CaCl₂ were used in all further calculations on Ca(OH)₂.

The procedure which was adopted was as follows. Theoretical values of pK°_{17} were predicted at higher temperatures for the reaction



using $\Delta F^\circ_{25} = 6820$ cal. and $\Delta S^\circ_{25} = -36.4$ cal. mole⁻¹ deg.⁻¹. The heat capacity of Ca(OH)₂(c) as a function of temperature was interpolated from the measured specific heats,²⁴ and the heat capacities of Ca⁺² and OH⁻ were estimated from the correspondence principle.² The theoretical values of *K*₁₇° are summarized in Table II. In order to directly compare to the solubility

TABLE II
PREDICTED VALUES OF THE SOLUBILITY CONSTANT (*K*₁₇°)
FOR Ca(OH)₂

<i>t</i> , °C.	<i>K</i> ₁₇ °	<i>t</i> , °C.	<i>K</i> ₁₇ °
25	1.00×10^{-5}	150	1.26×10^{-7}
60	3.96×10^{-6}	200	1.58×10^{-8}
100	9.78×10^{-7}	250	1.74×10^{-9}

data, the value of the activity derived from the predicted *K*_{sp}° values ($a_{\text{Ca(OH)}_2} = \sqrt[3]{K_{sp}^\circ}/4$) was used to estimate a γ_{\pm} at that temperature. A preliminary value

(22) J. Johnston and C. Grove, *J. Am. Chem. Soc.*, **53**, 3976 (1931).

(23) It is of interest to compare this value for Ca(OH)₂ with that calculated in another independent manner. The heat of formation of Ca(OH)₂ can be fixed¹² from the calorimetric determination of the reaction with acid at 20° [T. Thorvaldson and W. G. Brown, *J. Am. Chem. Soc.*, **52**, 80 (1930)] as $-235,609$ cal. mole⁻¹ at 25°. This value is superior to that previously accepted¹² since better estimates can now be made of the heat capacity corrections from 20 to 25° and the heats of dilution of HCl and CaCl₂ to infinite dilution. The entropy of formation of Ca(OH)₂ of -72.0 cal. mole⁻¹ deg.⁻¹ is accepted from the literature,¹² and the resulting free energy of formation at 25° becomes $\Delta F^\circ = -214,139$ cal. mole⁻¹. The free energies of Ca⁺²(aq) and OH⁻(aq) also come from independent sources¹² not related to Ca(OH)₂, from which ΔF°_{25} of solution of Ca(OH)₂ is calculated to be 6769 cal. mole⁻¹. This corresponds to a $\log K_{sp}^\circ$ of -4.97 or a *K*_{sp}° of 1.07×10^{-5} at 25°, which is only 7% different from the value adopted above. The difference amounts to only 51 cal., well within the experimental error of the heat of formation of Ca(OH)₂(c).

(24) "International Critical Tables," Vol. 5, McGraw-Hill Book Co., New York, N. Y., 1933, p. 99.

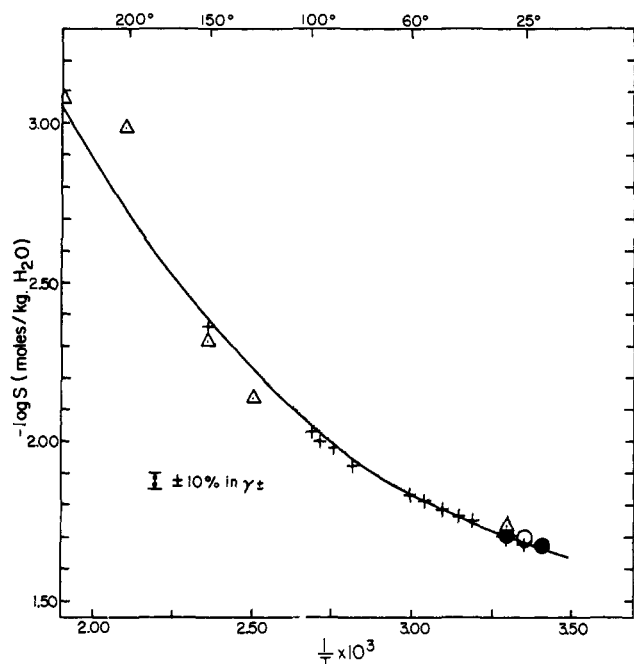


Fig. 4.—Predicted (solid curve) and observed solubilities for $\text{Ca}(\text{OH})_2$ as a function of temperature. Symbols: \circ J. Johnston and C. Grove, *J. Am. Chem. Soc.*, **53**, 3976 (1931); $+$ H. Bassett, *J. Chem. Soc.*, 1270 (1934); \bullet R. G. Bates, V. E. Bower, and E. R. Smith, *J. Res. Natl. Bur. Std.*, **56**, 305 (1956); \triangle R. B. Pepler and L. S. Wells, *ibid.*, **52**, 75 (1954).

of the solubility was then calculated ($m = a/\gamma_{\pm}$) and a new activity coefficient estimated at that concentration. This procedure was repeated until successive determinations of the solubility did not change significantly. The log of the predicted solubilities are plotted against $1/T$ and compared to the observed data in Fig. 4. Considering that there appears to be some question on the effect of particle size on the solubility,²⁵ and that none of the activity coefficients were actually known except at 25°, the agreement is surprisingly good. With the exception of a few points, the difference between the predicted and observed solubility is not larger than $\pm 10\%$.²⁶

Unfortunately, little new can be said regarding the effect of the complexing of Ca^{+2} by OH^- to form the species $\text{Ca}(\text{OH})^+$ at 25°. Previously reported data^{25,27} on this reaction at lower temperatures suggest that the $\text{Ca}(\text{OH})^+$ ion is real ($K_d^{25} \sim 0.06$) although there is no clear-cut determination on the value of the dissociation constant. Bates, *et al.*,²⁷ have questioned whether such a species is even a useful concept in $\text{Ca}(\text{OH})_2$ solutions. At lower temperatures, the present analysis allows one to account for any hydrolysis effects through the activity coefficient of $\text{Ca}(\text{OH})_2$. Since these, in turn, are based upon $\text{CaCl}_2(\text{aq})$, then association effects of Ca^{+2} and OH^- appear to be roughly comparable to similar effects between Ca^{+2} and Cl^- .

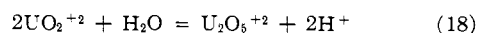
(25) R. G. Bates, *J. Res. Natl. Bur. Std.*, **56**, 305 (1956).

(26) Our analysis appears to be only slightly different from that previously reported [S. A. Greenberg and L. E. Copeland, *J. Phys. Chem.*, **64**, 1057 (1960)]. These authors did not have heat capacity data available and put most of the emphasis on the lower temperature data. The activity coefficients used in the present calculations are also only slightly different. However, the analysis of Greenberg and Copeland gives incorrect values for the $\overline{C}_{p2}^{\circ}$ of Ca^{+2} and OH^- at lower temperatures, and a value for the entropy of Ca^{+2} at 100° which is 9 cal. mole⁻¹ deg.⁻¹ greater than that calculated from the known heat capacity of Ca^{+2} as a function of temperature.²

(27) R. P. Bell and J. H. B. George, *Trans. Faraday Soc.*, **49**, 619 (1953); R. G. Bates, V. E. Bower, R. G. Canham, and J. E. Prue, *ibid.*, **55**, 2062 (1959).

At higher temperatures, the situation is somewhat different. If one uses the low temperature data on the change of the apparent dissociation constant with temperature to derive an "absolute" entropy for $\text{Ca}(\text{OH})^+$, about -4 cal. mole⁻¹ deg.⁻¹ (or alternatively, estimates on entropy by other means), then the dissociation constant of $\text{Ca}(\text{OH})^+$ becomes very small indeed at 200° ($\sim 6 \times 10^{-4}$) and only 10% of the calcium is present as Ca^{+2} in a saturated solution of $\text{Ca}(\text{OH})_2$ ²⁸ at this temperature. The net predicted effect would be to increase the solubility enormously over that observed, assuming that reasonable estimates of the γ_{\pm} for $\text{Ca}(\text{OH})^+$ can be made. Although the calculation is somewhat sensitive to the entropy chosen for $\text{Ca}(\text{OH})^+$ at room temperature, the present analysis apparently does not support extensive complex ion formation in these solutions, at least at higher temperatures.

D. Hydrolysis of Inorganic Ions.—Very little is known regarding the hydrolysis reactions of inorganic ions at higher temperatures. Many of the older data²⁹ on the temperature coefficients of simple cations have been obtained before it was recognized that dimerization and polymerization had to be considered. One example has been studied rather extensively, the hydrolysis of the uranyl ion. Consider one of the possible reactions



The hydrolysis constant, K_{18}° , has been determined for this reaction up to 250°. ^{30,31} Table III gives a com-

TABLE III
THE HIGH TEMPERATURE HYDROLYSIS OF THE URANYL ION^a
 $2\text{UO}_2^{+2} + \text{H}_2\text{O} = \text{U}_2\text{O}_6^{+2} + 2\text{H}^+$

$t, ^{\circ}\text{C}:$	$\Delta S^{\circ}, \text{cal. mole}^{-1} \text{deg.}^{-1}$ (exptl.)	$\Delta S^{\circ}, \text{cal. mole}^{-1} \text{deg.}^{-1}$ (predicted)
20	7.0	7.0 ^b
60	5.2	4.4
100	3.2	2.3
150	0.6	0.5
200	-1.9	-2.3
250	-4.5	-5.5

^a Entropy values were calculated from K_h data given in ref. 30. ^b The experimental value of ΔS at 25° was used to define the entropy of $\text{U}_2\text{O}_6^{+2}$ at this temperature.

parison of the experimental entropies with those calculated from the correspondence relations² using the constants for simple ions. In this comparison, entropies were adjusted to agree at 25°, since there is no independent value for the entropy of $\text{U}_2\text{O}_6^{+2}$. The absolute entropy of UO_2^{+2} was taken as -30 cal. mole⁻¹ deg.⁻¹.³² The excellent agreement lends additional support to both the experimental results and the assumptions made above regarding the heat capacities of cationic hydrolysis species. This is a particularly

(28) Even less if there is any appreciable amount of $\text{Ca}(\text{OH})_2^{\circ}(\text{aq})$ formed.

(29) As summarized by J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants," Part II, "Inorganic Ligands," The Chemical Society, London, 1958.

(30) M. H. Lietzke and R. W. Stoughton, to be published.

(31) C. F. Baes, Jr., and N. J. Meyer, *Inorg. Chem.*, **1**, 780 (1962), have also studied the hydrolysis of UO_2^{+2} more completely but at only two temperatures, 25 and 94°, and give their results for nitrate solutions of $\mu = 0.5$. Estimating $\Delta C_p = -23$ for reaction 18, $\Delta S_{25} (I = 0.5)$ can be calculated from these authors' data as 9.2 cal. mole⁻¹ deg.⁻¹. The agreement is as good as can be expected with that predicted (Table III) considering the high ionic strength.

(32) M. H. Rand and O. Kubaschewski, "The Thermochemical Properties of Uranium Compounds," Oliver and Boyd Ltd., London, 1963, p. 12.

sensitive test since the temperature coefficients are being compared.

E. Thermodynamic Functions above 200°. The Dissociation Constant of Water up to 350°.—A number of authors have discussed the dissociation constants of water as a function of temperature, and various attempts have been made to calculate thermochemical functions for H^+ and OH^- at higher temperatures³³ from the data. However, the heat capacities calculated from such equilibrium constants do not agree with the direct experimental values of $\overline{C}_{p_2}^\circ$ for H^+ and OH^- determined calorimetrically³⁴ from $NaCl(aq)$, $NaOH(aq)$, and $HCl(aq)$ up to 100°. The situation is illustrated in Fig. 5, which summarizes the experimental data on K_w° . The solid curve is predicted from the correspondence principle at higher temperatures² and is, therefore, in agreement with the low temperature heat capacity data. In these calculations, ΔS_{25}° was assumed to be $-19.3 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$, which is based upon $pK_w^\circ = 13.997$ and a ΔH_{25}° of ionization equal to $13,336 \text{ cal. mole}^{-1}$.³⁵ This value for the entropy of ionization is slightly larger than that presently accepted.¹² It is believed that the predicted values (solid curve) represent at the present time somewhat better values for K_w° of water up to 350° than those obtained by extrapolation of equilibrium constants below 100°. The predicted K_w° values are summarized in Table IV.

TABLE IV
THE IONIZATION CONSTANT OF WATER AT
HIGHER TEMPERATURES^a

$t, ^\circ C.$	pK_w°	$t, ^\circ C.$	pK_w°
25	13.997	200	11.30
60	13.05	250	11.18
100	12.21	300	11.19
150	11.65	350	11.33

^a See section F, however, for a discussion concerning possible effects of the solvent pressure upon K_w° .

F. The Effects of Solvent Pressure.—As the temperatures of aqueous solutions approach the critical region, the effect of a rapidly increasing solvent fugacity on the thermodynamic properties of a system must be considered. A pressure effect can influence a chemical equilibria in at least three separate ways. First, the activity of water itself will change, introducing an additional free energy term of the type

$$\Delta F_{19} = \int_1^p V dp \quad (19)$$

if water is involved in the chemical equilibria. Next, there will be a free energy change due to changes in the partial molal volumes of the substances involved in the reaction

$$\Delta F_{20} = \int_1^p \Delta \overline{V} dp \quad (20)$$

Finally, in solutions of finite concentrations, there will be an effect on the activity coefficients of dissolved species

$$\left(\frac{\partial \ln \gamma}{\partial P} \right) = \frac{\overline{V}_i - \overline{V}_i^\circ}{2RT} \quad (21)$$

(33) See H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958, pp. 643-649, for a summary; also J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants," Part II, The Chemical Society, London, 1958, p. 1.

(34) Th. Ackermann, *Z. Elektrochem.*, **62**, 411 (1958).

(35) C. E. Vanderzee and J. A. Swanson, *J. Phys. Chem.*, **67**, 2608 (1963).

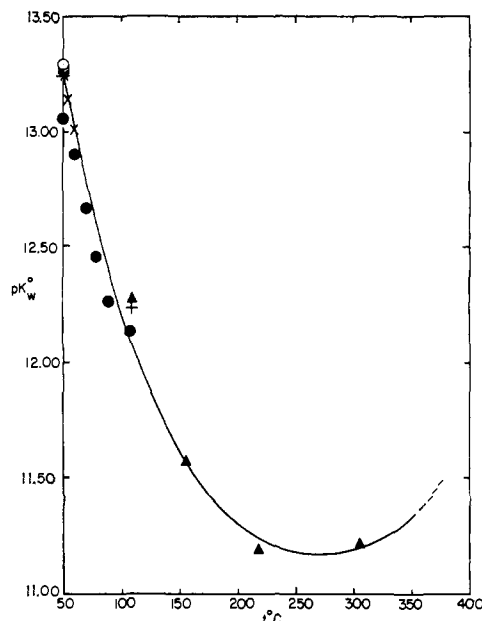


Fig. 5.—The high temperature dissociation of water. The solid curve was predicted; experimental data are as follows: + A. Heydweiller, *Ann. Physik*, **28**, 503 (1909); \circ H. Lunden, *J. chim. phys.*, **5**, 574 (1907); \bullet R. Lorenz and A. Bohi, *Z. physik. Chem.*, **66**, 733 (1909); \blacktriangle A. A. Noyes, Y. Kato, and R. B. Sosnan, *J. Am. Chem. Soc.*, **32**, 159 (1910); \square A. Olander, *Z. physik. Chem.*, **144**, 49 (1929); \times H. S. Harned and W. J. Hamer, *J. Am. Chem. Soc.*, **55**, 2194, 4496 (1933). Values of pK_w° derived from heat capacity measurements on H^+ and OH^- up to 130° by Th. Ackermann [*Z. Elektrochem.*, **62**, 411 (1958)], are not included since these heat capacities contributed to the data which were used in deriving the constants in the correspondence principle relations.

where \overline{V}_i is the partial molal volume of some component at a given concentration. In all of these relations, the pressures involved are those of the solvent at a given temperature.

In general, the first type of correction, ΔF_{19} , can be ignored at modest temperatures. Any reasonable volume estimates at 300° (assuming $\overline{V} - \overline{V}^\circ$ is approximately the same at 300 as at 25°) indicates that the effect on γ will also be less than 1%.

The greatest errors could conceivably come from the second consideration, a change in $\Delta \overline{V}^\circ$ for the reaction at higher temperatures. While it is true, in general, that many substances show increasing values of \overline{V}_2° between 25 and 60°,^{36,37} what little data are available indicate the partial molal volumes then become more negative with increasing temperature.³⁷⁻³⁹ For example, \overline{V}° for $KCl(aq)$ is 26.8 and 24.8 cc. mole⁻¹ at 25 and 100°, respectively, while the similar values for $LiCl(aq)$ are 17.9 and 14.2 cc. mole⁻¹. $HCl(aq)$ behaves similarly, dropping from 18.1 to 14.5 cc. mole⁻¹ between 25 and 100°. If one examines the partial molal volumes of electrolytes⁴⁰ some correlation exists between \overline{V}_2° and S_2° at 25°. Partial molal volumes decrease with increasing charge, as does the entropy, and increase with size, also similar to the entropy.

A plot of the molal volumes of KCl , $LiCl$, and HCl against the corresponding entropies at 25 and 100°

(36) H. S. Harned and B. B. Owen, ref. 33, p. 649.

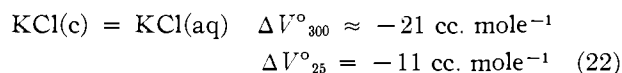
(37) K. Fajans and O. Johnson, *J. Am. Chem. Soc.*, **64**, 668 (1942).

(38) G. C. Akerlof and J. Teare, *ibid.*, **60**, 1226 (1938).

(39) G. P. Baxter and C. C. Wallace, *ibid.*, **38**, 70 (1916).

(40) Recent compilations: L. G. Hepler, *J. Phys. Chem.*, **61**, 1426 (1957); and A. M. Couture and K. J. Laidler, *Can. J. Chem.*, **34**, 1209 (1956).

can be extrapolated to higher temperatures (and pressures) where the entropies are now known.² \bar{V}_2° for KCl at 200° (18 atm.) is estimated to be 25 cc. mole⁻¹ and about 15 cc. mole⁻¹ at 300° (85 atm.). Consequently, in the case of the solubility equilibrium of the



solid the estimated error in the free energy at 300° from eq. 20 would only be a few calories.

For electrolytes of much higher charge types, it is not inconceivable that the effects could run a hundred times this much, since the molal volumes are larger at 25°, and their rate of change with temperature may reasonably be expected to be larger. Errors of a few hundred calories could be introduced at 300° by ignoring ΔV effects. In these cases, a reasonable approximation can be made that the average change in $\Delta \bar{V}^\circ$, for a reaction between 25 and 300° might be about 50% different (the sign depending upon which side ions are involved) per mole of solute than the value at 25°.

If the heat capacities are determined experimentally under the ambient pressure of water at higher temperatures, then the need for any correction on $\Delta F_{(i)}^\circ$ will largely disappear. In this case it may be preferable to experimentally determine C_v rather than C_p .

At much higher temperatures (and pressures), there are no data to guide any possible estimates. At very high solvent pressures, the partial molal volumes will again eventually have to reverse their trend and will probably take on more positive values approaching those of the crystalline salt,^{41,42} and ΔV for ionic reactions could be expected to be very small. Consequently the behavior of the ionic partial molal volumes near the critical region must be rather complicated.

Part III

A. Possible Kinetic Consequences of Correspondence Theory.—It is of interest to question whether the entropy correspondence relationships can be applied to chemical kinetics in the estimating of heat capacities for ionic activated complexes. In general these species will differ from ordinary ions in their geometries, and possibly by the failure of the hydration spheres to properly orient around the newly formed species before their passage over the potential barrier. However, Powell has already demonstrated⁴³ that the entropies of complex ionic activated complexes can be estimated reasonably well by the same methods used for ordinary stable complex ions. This is probably due to the fact that most of the entropy change involved in the association of ions is due to electrical Born effects.

It follows that ionic heat capacities may also be reasonably approximated by the heat capacities of similar stable species. The present analysis, based upon this assumption, would indicate that very large values can be expected for some heat capacities of activation. The very fact that large ΔS^* values have been observed for many such reactions in the past should have been reason enough to suspect that similarly large ΔC_p^* effects should exist. The effects of charge, size, and dielectric constant affect both the ionic entropy and heat capacity, and large and negative values of $\bar{C}_{p_2}^\circ$

(41) L. H. Adams, *J. Am. Chem. Soc.*, **53**, 3769 (1931); **54**, 2229 (1932).

(42) L. H. Adams and R. E. Gibson, *ibid.*, **54**, 4520 (1932).

(43) R. E. Powell, *J. Phys. Chem.*, **58**, 528 (1954).

for ionic solutes are not uncommon.⁴⁴ Further, a number of investigations have actually determined large values of ΔC_p^* for reactions involving polar or charge-separated activated complexes.⁴⁵⁻⁴⁷

It is beyond the scope of this discussion to compile kinetic systems where enough entropy of activation data are known to calculate ΔC_p^* from the correspondence equations.² However, such calculations indicate⁴⁸ that it is not uncommon to find systems for which ΔC_p^* is predicted to run from +100 to -70 units.

B. Treatment of Kinetic Data by Estimating ΔC_p^* .—In the usual statistical thermodynamic treatment of reaction rates for bimolecular reactions, the specific rate constant for the rate-determining step is approximated by

$$k^\circ \cong \left(\frac{kT}{h} \right) e^{-\Delta H^*/RT} e^{+\Delta S^*/R} \quad (23)$$

where (kT/h) has a value of 6×10^{12} sec.⁻¹ at 25°. Most of the present values for ΔS^* solution reactions result from such an analysis of kinetic data over limited temperature ranges. If the functions ΔH^* and ΔS^* have any thermodynamic significance at all, then they must be temperature dependent. Equation 23 can be expanded, using ordinary thermodynamic methods, to give eq. 24 which predicts the extended temperature behavior of the rate constant

$$\ln \frac{k_2^\circ}{k_1^\circ} = \ln \frac{T_2}{T_1} - \frac{\Delta H_1^*}{R} \times \\ \left(\frac{1}{T_2} - \frac{1}{T_1} \right) - \frac{\Delta C_p^*}{R} \int_1^2 \left(\frac{\Delta T}{T_2} - \ln \frac{T_2}{T_1} \right) \quad (24)$$

The value ΔH_1^* will differ significantly from the average value $\bar{\Delta H}^*$ given in eq. 23, if $\Delta C_p^* \int_1^2$ is significant between the temperatures T_1 and T_2 . Previous authors have almost uniformly assumed that the product $(\Delta C_p^* \int_1^2 / R) [(\Delta T/T_2) - \ln (T_2/T_1)]$ is small enough to be ignored. The values now indicate that this may not be a valid assumption, particularly for reactions having modest ΔH^* values. Further, the observation that a plot of $\log k^\circ/T$ vs. $1/T$ appears to be linear over a limited temperature range is not a sufficient criterion for assuming that the ΔC_p^* term is negligible. This method is perhaps the poorest one available for attempting to obtain information on ΔC_p^* , even though slight changes in the slope of such a plot can cause substantial errors in ΔH^* . A far better procedure is to estimate values of ΔC_p^* by the method previously outlined, and to use a rearranged form of eq. 24

$$\ln k_2^\circ - \ln \frac{T_2}{T_1} + \frac{\Delta C_p^*}{R} \int_1^2 \times \\ \left(\frac{\Delta T}{T_2} - \ln \frac{T_2}{T_1} \right) = \ln k_1^\circ - \frac{\Delta H_1^*}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (25)$$

(44) K. S. Pitzer and L. Brewer, ref. 4, p. 400.

(45) B. R. W. Penson, L. Pearson, and F. J. W. Roughton, *Trans. Faraday Soc.*, **52**, 1512 (1956).

(46) E. Appelman, M. Anbar, and H. Taube, *J. Phys. Chem.*, **63**, 126 (1959).

(47) R. E. Robertson, R. L. Heppollette, and J. M. W. Scott, *Can. J. Chem.*, **37**, 803 (1959).

(48) J. W. Cobble, Proceedings of the VIII International Conference on Coordination Chemistry, Vienna, 1954, p. 439.

A plot of the left-hand side of eq. 25 against $1/T$ will give much more accurate values of ΔH_1^* (or ΔH_2^* at any temperature) than will assuming the ΔC_p^* term to be zero.

C. Retrograde Kinetics.—Kinetic reactions can reasonably be divided into two classes: those having positive values of ΔC_p^* , with the others having negative values at 25° (or any other convenient reference temperature). The latter class are particularly interesting. At a temperature such that

$$-\Delta H_1^* = \Delta C_p^* \int_1^2 (t_2 - t_1) \quad (26)$$

ΔH_2^* becomes zero. For temperatures above this inversion point, ΔH_2^* will become negative, and the rate-determining step will proceed more *slowly* as the tem-

perature is increased further. This *retrograde* temperature region depends upon a very literal interpretation of the statistical thermodynamic rate equation (23). Whether the conditions and assumptions involved in the derivation of eq. 23 can accommodate negative activation energies is a mute question. However, there are a number of reactions where this interesting point can be tested between 25 and 100° , particularly for those having already small activation energies at room temperature. (Unless ΔS^* is also rather negative, some reactions will proceed too rapidly to measure over the whole temperature range of interest.) It is perhaps reasonable to inquire whether examples of kinetic systems having negative activation energies at room temperature (for the rate-determining step) have been mistakenly interpreted as being due to some more complex reason than is actually required.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, INDIANA]

The Thermodynamic Properties of High Temperature Aqueous Solutions. VII. The Standard Partial Molal Heat Capacities of Cesium Iodide from 0 to 100°C ¹

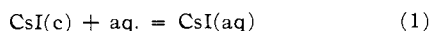
BY R. E. MITCHELL^{2,3} AND J. W. COBBLE

RECEIVED MAY 15, 1964

The "integral heat method" developed in these laboratories has been used to obtain the standard partial molal heat capacities for the key electrolyte cesium iodide in the temperature range 0 to 100° . At 25° a value of -36.6 cal. mole⁻¹ deg.⁻¹ for $\overline{C}_{p_2}^\circ$ was obtained. The heat capacities for this electrolyte show unusual behavior in that no maximum in $\overline{C}_{p_2}^\circ$ was observed over this temperature range. If such a maximum does exist, it is at 100° or higher temperatures.

Introduction

The "integral heat method" of determining partial molal heat capacities at infinite dilution has been described in previous communications from this laboratory.^{4,5} This method has been used to determine values of $\overline{C}_{p_2}^\circ$ for NaCl, BaCl₂, NaReO₄, HReO₄, and HCl from 0- 100° with an average accuracy of better than 0.5 cal. mole⁻¹ deg.⁻¹. Further, the measurements upon which the evaluation of $\overline{C}_{p_2}^\circ$ depends involve concentration ranges of 0.001-0.01 *m*, where methods for extrapolation of heats of solution are reliable. In the present research, the integral heats of solution of pure cesium iodide were determined as a function of concentration at 10° intervals from 5 to 95° .



$\Delta \overline{C}_p^\circ$ for the reaction was computed as

$$\Delta \overline{C}_p^\circ = \frac{\Delta H_s^\circ(t_2) - \Delta H_s^\circ(t_1)}{t_2 - t_1} \quad (2)$$

where $\Delta H_s^\circ(t)$ refers to the heat of solution at infinite dilution at a temperature *t*. $\overline{C}_{p_2}^\circ$ then becomes

$$\overline{C}_{p_2}^\circ = \Delta C_p^\circ + C_{p_2}^\circ \quad (3)$$

The heat capacities of CsI(c), $C_{p_2}^\circ$, over this temperature range have not been experimentally determined, but can

be fixed accurately enough for the present purposes from experimental heat capacity data on other cesium salts and related materials.⁶

Experimental

Apparatus.—A submarine-type heat of solution calorimeter (CS-1) which has been previously described⁴ was used for measurements between 5 and 55° . The sensitivity was increased by replacing the platinum resistance thermometer with a thermistor as the temperature-sensing element.⁵ An improved calorimeter (designated as laboratory calorimeter CS-2) became available during the course of these measurements,⁷ and the data obtained at 55° up to 95° were from this new device. The details of this calorimeter and the associated bridge are described in another communication in this series.⁷

Electrical calibrations of the calorimetric systems were made by using a commercially available Sargent Model IV coulometer as the constant-current source. An electronic timer⁸ accurate to ± 0.01 sec. was used to measure the heating time; this timer was in turn powered by a 60,000-c.p.s. tuning-fork frequency standard accurate to $\pm 0.005\%$. The energy measurements were believed to be accurate to better than 0.1% even for moderately short heating times (~ 10 sec.).

Power inputs were determined in the usual manner by measuring the voltages across the heater at an appropriate point along the heater leads⁷ using a Leeds and Northrup Type K-3 potentiometer with a volt box. Current measurements in the heating circuit were made using an N.B.S. calibrated 10-ohm standard resistor. Corrections for the various lead resistances were applied where necessary.

(6) K. K. Kelly, U. S. Bureau of Mines Bulletin 584, U. S. Government Printing Office, Washington, D. C., 1960.

(7) E. C. Jekel, C. M. Criss, and J. W. Cobble, *J. Am. Chem. Soc.*, **86**, 5404 (1964); see also E. C. Jekel, Ph.D. Thesis, Purdue University, 1964.

(8) This timer was designed and built in our laboratories by R. M. Hayes and is described by J. E. McDonald, Ph.D. Thesis, Purdue University 1961.

(1) Supported in part by a grant from the National Science Foundation.

(2) Ethyl Corporation Fellow, 1961-1962.

(3) From the Ph.D. Thesis of R. E. Mitchell, Purdue University, Jan., 1964.

(4) C. M. Criss and J. W. Cobble, *J. Am. Chem. Soc.*, **83**, 3223 (1961).

(5) J. C. Ahluwalia and J. W. Cobble, *ibid.*, **86**, 5377 (1964).