

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.

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

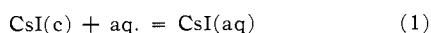
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The "integral heat method" developed in these laboratories has been used to obtain the standard partial molal heat capacities for the key electrolyte cesium iodide in the temperature range 0 to 100° . At 25° a value of -36.6 cal. mole⁻¹ deg.⁻¹ for $\overline{C}_{p_2}^\circ$ 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).

TABLE I
 HEATS OF SOLUTION AND ρ -VALUES FOR CsI

No. of determinations	$m \times 10^3$, moles/kg. of H ₂ O	ΔH_s , cal./mole	$-A_H I^{1/2} \alpha$, cal./mole	ρ , cal./mole	No. of determinations	$m \times 10^3$, moles/kg. of H ₂ O	ΔH_s , cal./mole	$-A_H I^{1/2} \alpha$, cal./mole	ρ , cal./mole
5.00°					55.00°				
1	1.03	8970	-11	8959	5	1.89	6657 ± 18	-30	6627
3	1.90	9034 ± 31 ^a	-14	9020	6	3.75	6688 ± 8	-42	6646
2	3.79	9034 ± 2	-20	9014	7	5.64	6695 ± 11	-50	6645
2	5.69	9022 ± 8	-24	8998	4	7.52	6694 ± 6	-58	6636
2	7.59	9030 ± 1	-27	9003	2	11.27	6695 ± 14	-70	6625
$\Delta H_s^\circ = 9024$					$\Delta H_s^\circ = 6636$				
15.00°					65.00°				
2	1.90	8472 ± 4	-17	8455	3	1.86	6273 ± 37	-33	6240
3	3.79	8444 ± 14	-23	8421	4	3.70	6296 ± 21	-47	6249
3	5.70	8454 ± 12	-28	8426	4	5.57	6219 ± 19	-56	6263
3	7.59	8444 ± 14	-32	8412	4	7.40	6229 ± 7	-64	6265
$\Delta H_s^\circ = 8434$					1	11.11	6337	-79	6258
25.00°					$\Delta H_s^\circ = 6254$				
3	2.38	7939 ± 15	-22	7917	74.95°				
3	4.72	7954 ± 11	-30	7924	2	1.87	5893 ± 38	-38	5855
2	7.14	7950 ± 5	-37	7913	2	3.69	5950 ± 1	-52	5898
1	9.46	7942	-42	7900	2	5.56	5954 ± 11	-64	5890
1	12.50	7943	-47	7896	2	7.38	5974 ± 3	-73	5901
$\Delta H_s^\circ = 7920$					$\Delta H_s^\circ = 5893$				
35.11°					85.01°				
2	1.07	7566 ± 48	-18	7548	3	1.84	5586 ± 12	-42	5544
5	2.30	7512 ± 14	-25	7487	3	3.71	5601 ± 80	-59	5542
4	4.80	7505 ± 7	-35	7470	3	5.53	5620 ± 8	-73	5547
1	7.50	7494	-43	7451	1	7.44	5612	-83	5529
1	8.17	7526	-45	7481	1	11.09	5651	-101	5550
1	9.74	7500	-49	7451	$\Delta H_s^\circ = 5543$				
$\Delta H_s^\circ = 7474$					94.96°				
44.99°					2	1.86	5289 ± 38	-49	5240
4	1.90	7036 ± 27	-26	7018	3	3.73	5273 ± 37	-68	5205
3	3.79	7083 ± 7	-36	7047	3	5.55	5246 ± 99	-83	5163
4	5.69	7080 ± 6	-44	7036	1	11.10	5307	-115	5192
3	7.59	7092 ± 4	-50	7042	$\Delta H_s^\circ = 5198$				
1	11.36	7098	-61	7037	$\Delta H_s^\circ = 5198$				
$\Delta H_s^\circ = 7043$									

^a Standard deviation of individual measurements from the average.

Materials.—Water used in these measurements was prepared by passing distilled water through a pair of acid-base ion-exchange columns to remove trace ionic contaminants.

Cesium iodide samples were prepared by grinding pieces of a spectroscopic grade Harshaw single crystal. The resulting powder was dried at 400° and stored in a desiccator over magnesium perchlorate. Samples of a few hundred milligrams were weighed into thin-walled Pyrex sample bulbs, heated to 400° for 8 hr., cooled in a vacuum desiccator, and sealed under reduced pressure (~0.1 mm.).

Procedure.—Because CsI has an endothermic heat of solution over the entire temperature range under investigation, it was possible to operate the calorimeter under nearly isothermal conditions. The technique used involved the addition of electrical energy at the same time the sample was being dissolved. Particularly at the higher temperatures, the rate of solution was so rapid that it was not possible to completely eliminate temperature fluctuations by this compensation technique. However, by delaying the initiation of the chemical reaction for an appropriate time *after* the start of electrical heating, the small initial "overheating" could be made to balance out the small "overcooling" in the latter part of the run, and the net temperature change was rarely in excess of 1×10^{-4} °. The energy equivalence of this net temperature change could be determined rather accurately by appropriate calibrations of the bridge system.

Experimental Data

Table I summarizes the results of 128 separate heat of solution measurements for cesium iodide. The number of replicate determinations at each concentration, the

heat of solution, the adopted heat of solution at infinite dilution, and parameters used in the extrapolations are indicated at each temperature. Wherever possible, the standard deviations are indicated for each concentration.

Calculations and Thermodynamic Data

An extended form of the Debye-Hückel theory was used to extrapolate the heats of solution to infinite dilution.⁹ Essentially, the heat of dilution of the electrolyte, Φ_L , was taken as

$$\Phi_L = \frac{\nu}{2} A_H |Z_+ Z_-| I^{1/2} \alpha - 2.303 RT^2 \nu_+ \nu_- \left(\frac{dB}{dT} \right) m \quad (4)$$

where

$$\alpha = (1 + I^{1/2})^{-1} - \frac{\sigma(I^{1/2})}{3} \quad (5)$$

The $\sigma(I^{1/2})$ function has been tabulated elsewhere.¹⁰ A_H is the theoretical Debye-Hückel heat slope. The

(9) 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, p. 642.

(10) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958, p. 176.

TABLE II
HEAT CAPACITIES OF AQUEOUS AND CRYSTALLINE
CESIUM IODIDE^a

t_{av} , °C.	ΔC_p°	$\overline{C}_{p_2}^\circ$
10.0	-59.0	-46.6
20.0	-51.4	-39.0
30.0	-44.1	-31.7
40.0	-43.6	-31.2
50.0	-41.1	-28.6
60.0	-40.4	-27.9
70.0	-36.3	-23.8
80.0	-35.2	-22.7
90.0	-33.4	-20.8

^a Units in cal. mole⁻¹ deg.⁻¹.

TABLE III

SMOOTHED VALUES OF THE PARTIAL MOLAL HEAT CAPACITY
FOR AQUEOUS CESIUM IODIDE

t , °C.	$\overline{C}_{p_2}^\circ$, cal. mole ⁻¹ deg. ⁻¹
0	-57 ^a
10	-46.6
20	-39.0
25	-36.6
30	-34.7
40	-31.0
50	-28.3
60	-25.9
70	-23.9
80	-22.6
90	-21.8
100	-21.8 ^a

^a Extrapolated values.

other symbols have their usual meaning.⁹ A function ρ is defined as

$$\rho = \Delta H_s^\circ - \frac{\nu}{2} A_H |Z_+ Z_-| I^{1/2} \alpha =$$

$$\Delta H_s^\circ - 2.303RT^2 \nu_+ \nu_- \left(\frac{dB}{dT} \right) m \quad (6)$$

Consequently, a plot of ρ against m should be linear and extrapolate to ΔH_s° at $m = 0$. Our previous experience with this function has shown this procedure to be satisfactory for 1:1 electrolytes at dilutions below 0.05 m , even up to 100°. The values of $(\nu/2)A_H|Z_+Z_-|I^{1/2}\alpha$ and ρ are given at each temperature and concentration in Table I.

In making the extrapolations in the manner just indicated, it is usually possible to find a range of values for ΔH_s° from these linear extrapolations which fit the experimental data equally well. Consequently, another useful aid in helping reduce the error in ΔH_s° at any temperature is the reasonable requirement that $d\rho/dm$ be a smooth function of temperature. This is a powerful aid in helping fix a unique value of ΔH_s° at a given temperature since in effect it is a cooperative use of the data at neighboring temperatures. The slope that was obtained at 25° for CsI is in excellent agreement with the heat of dilution data for closely similar CsCl pre-

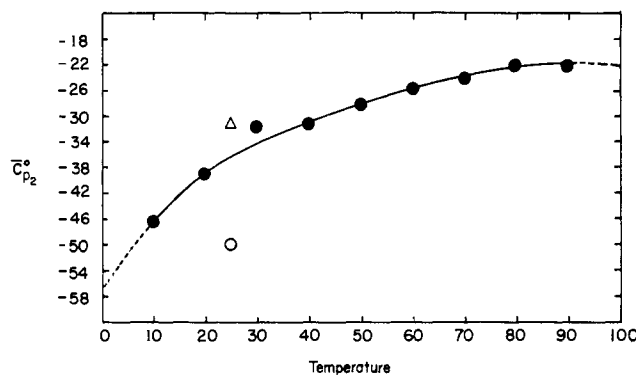


Fig. 1.—Standard partial molal heat capacities for cesium iodide as a function of temperature: ●, from this investigation¹²; and ○,¹³ from previously reported specific heat data.

viously reported by others¹¹; these are the only applicable data available in the literature for comparison.

Table II is a summary of the values of ΔC_p and $\overline{C}_{p_2}^\circ$ calculated from the ΔH_s° entries in Table I and eq. 2 and 3.

The partial molal heat capacities as a function of temperature are given as closed circles in Fig. 1; the smooth curve shown was used to provide the final recommended values tabulated in Table III from 0 to 100°. The only other $\overline{C}_{p_2}^\circ$ data reported in the literature are at 25° and come from interpretation of specific heats of concentrated CsI solutions.^{12,13}

The data obtained from the smooth curve in Fig. 1 and tabulated in Table III are estimated to be accurate to about 0.5 cal. mole⁻¹ deg.⁻¹ between 10 and 90°; the errors in the extrapolated values at 0 and 100° are perhaps two or three times this large. At the present time we can give no completely reasonable explanation for the apparently larger deviation of the value of $\overline{C}_{p_2}^\circ$ at 30° compared to the data at other temperatures. It may be the result of an unfortunate accumulation of errors, or it may signify some real effect due to "structural" changes taking place in the solvent system in this temperature range.

It is interesting to note that CsI is the first electrolyte that we have observed which does not display a maximum in the $\overline{C}_{p_2}^\circ$ temperature curve before 80°; if CsI has such a maximum, it is delayed until nearly 100° or even higher. Calculations from the correspondence principle¹⁴ indicate that it should reach a maximum value of $\overline{C}_{p_2}^\circ$ at 100°. The heat capacities of CsI(aq) are more negative at all temperatures studied than the corresponding values for NaCl(aq). This once again illustrates a point¹⁴ frequently overlooked in various explanations of electrolyte behavior. While the entropies of aqueous ions become more positive with increasing ionic size, the heat capacities have exactly the opposite trend. Yet the effect of ionic charge is exactly the same for both $\overline{C}_{p_2}^\circ$ and \overline{S}_2° (i.e., increasing negative values with increasing charge).

(11) E. Lange and J. Messner, *Z. Elektrochem.*, **33**, 431 (1927).

(12) A. F. Kapustinskii, I. I. Lipilina, and O. Ya. Samoilov, *J. chim. phys.*, **54**, 343 (1957).

(13) M. Eigen and E. Wicke, *Z. Elektrochem.*, **55**, 354 (1951).

(14) C. M. Criss and J. W. Cobble, *J. Am. Chem. Soc.*, **86**, 5385 (1964).