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## PHYSICAL AND INORGANIC CHEMISTRY

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

### The Thermodynamic Properties of High Temperature Aqueous Solutions. II. Standard Partial Molal Heat Capacities of Sodium Perrhenate and Perrhenic Acid from 0 to 100°C<sup>1</sup>

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The integral heat method developed in these laboratories has been used to determine the partial molal heat capacities at infinite dilution of aqueous sodium perrhenate and perrhenic acid from 0 to 100°. Such measurements provide data of interest to high temperature solution chemistry on a representative stable complex ion,  $\text{ReO}_4^-$ , as well as calibrating the differences in behavior between  $\text{Na}^+(\text{aq})$  and  $\text{H}^+(\text{aq})$ . Both  $\text{HReO}_4(\text{aq})$  and  $\text{NaReO}_4(\text{aq})$  have positive values of  $\overline{C}_{p,2}^\circ$  at some of the temperatures studied.

#### Introduction

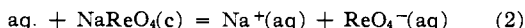
In the first communication of this series,<sup>3</sup> the integral heat method of obtaining accurate values of the partial molal heat capacities of electrolytes at infinite dilution was proposed. This method involved determination of the integral heats of reaction at infinite dilution and at several temperatures of a system which involves the electrolyte in question. Such a procedure results in values of  $\Delta C_p^\circ$  for the reaction from the relation

$$\Delta C_p^\circ = \left( \frac{d\Delta H^\circ}{dT} \right)_p \quad (1a)$$

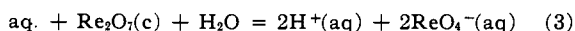
From this value of  $\Delta C_p^\circ$ ,  $\overline{C}_{p,2}^\circ$  for the desired electrolyte can be obtained if the heat capacities for all other species involved in the reaction are known over the temperature range involved. Thus the problem essentially reduces to one of obtaining a series of heats of reaction, extrapolated to infinite dilution, at closely enough spaced temperature intervals so that

$$\frac{\Delta(\Delta H^\circ)}{\Delta t} = \frac{d(\Delta H^\circ)}{dt} \quad (1b)$$

One of the most useful reactions involves the simple heats of solution of a pure substance to give the electrolyte in question. The present research involves determination of the integral heat of solution of sodium perrhenate



and the heat of solution of perrhenic acid anhydride,  $\text{Re}_2\text{O}_7$



as a function of concentration and temperature.<sup>4</sup>

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

(2) From the Ph.D. Thesis of J. C. Ahluwalia, Purdue University, June, 1963.

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

(4) Perrhenic acid is a moderately strong acid at 25°, with a reported  $pK$  of  $-1.25$ .<sup>5</sup> While accurate additional thermochemical data are lacking,

From these data, partial molal heat capacities of  $\text{NaReO}_4(\text{aq})$  and  $\text{HReO}_4(\text{aq})$  from 0 to 100° have been calculated. These heat capacities appear to be the first such extensive data on a complex ion, and also provide data on the relative  $\overline{C}_{p,2}^\circ$  differences between  $\text{Na}^+(\text{aq})$  and  $\text{H}^+(\text{aq})$  as a function of temperature.

#### Experimental

**Apparatus.**—The submarine calorimeter used for the heat measurements has previously been described.<sup>3</sup> However, for the present measurements the sensitivity was increased further by substitution of a Fenwal thermistor (having a negative temperature coefficient of approximately 4% per degree) for the temperature-sensing element. Various thermistors were used which had increasing room temperature resistances (in the 1–10 kilohm range) as the temperature of the calorimeter was increased from 0 to 100°. The bridge itself was constructed from precision helipot and a precision dial-type decade resistor (Dekastat) manufactured by the Electro Scientific Industries. Three legs of the Wheatstone bridge consisted of the thermistor (1–10 kilohms), the Dekastat (12 kilohms) with a series fixed 45-kilohm resistor, and 50-kilohm resistor. The fourth leg was made from the helipot (100 ohms, 10 kilohms) in series. The resistors were arranged so that the thermistor and fixed 50-kilohm resistor were on opposite sides of the bridge. A mercury cell was located between the thermistor–Dekastat junction and its opposite 50-kilohm resistor. An amplifier was fixed at the two remaining junction points. The two ten-turn 100- and 10,000-ohm helipot resistors were used to provide coarse balance for the bridge circuit at each temperature. This procedure essentially provides for approximately equal bridge sensitivity, per ohm, in the fine resistance adjustment (Dekastat) used to balance the bridge before and after a calorimetric run. Such a bridge is particularly useful for high-ohmage thermistors which change resistance rapidly over even limited temperature ranges. The amplifier was a Liston-Becker (Model 14) breaker type which in turn was used to drive a Texas

it can be shown that the  $\Delta S^\circ_{\text{ioniz}}$  will be at least zero or slightly positive at 25°. This is because of the very large entropy of the  $\text{ReO}_4^-(\text{aq})$  ion (48.3). However, the average value of  $\Delta C_p$  of ionization between 25 and 100° will be about  $-40 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$  from the data of Table V, and an estimated heat capacity for undissociated  $\text{HReO}_4$  of 40 units over this temperature range. Consequently perrhenic acid can be expected to be even a stronger acid at higher temperatures, and the measurements of the heats of solution are not complicated either by incomplete dissociation or, in the case of sodium perrhenate, by hydrolysis.

(5) A. F. Clifford, "Inorganic Chemistry of Qualitative Analysis," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1961, p. 445.

TABLE I  
 THE INTEGRAL HEATS OF SOLUTION AND  $\rho$ -VALUES FOR SODIUM PERRHENATE

Number of determinations	$m \times 10^3$ , moles/kg. of $H_2O^a$	$\sqrt{m}$	$\Delta H_s$ , cal./mole	$-AH_1^{1/2}\alpha$ , cal.	$\rho$ , cal./mole	Number of determinations	$m \times 10^3$ , moles/kg. of $H_2O^a$	$\sqrt{m}$	$\Delta H_s$ , cal./mole	$-AH_1^{1/2}\alpha$ , cal.	$\rho$ , cal./mole
1.00°											
2	1.77	0.0421	7927 ± 19 <sup>b</sup>	13	7914 ± 19	1	2.64	0.0514	6703	31	6672
1	3.43	0.0586	7936	18	7918	2	5.42	0.0734	6699 ± 2	42	6657 ± 2
1	4.94	0.0730	7929	21	7908	2	11.55	0.1075	6726 ± 4	60	6666 ± 4
2	6.71	0.0820	7925 ± 25	25	7900 ± 25	1	14.00	0.1183	6731	67	6664
2	10.38	0.1020	7939 ± 9	29	7910 ± 9	$\Delta H_s^\circ = 6663 \pm 5$ cal./mole					
$\Delta H_s^\circ = 7917 \pm 5^\circ$ cal./mole											
4.95°											
2	3.06	0.0553	7728 ± 6	17	7711 ± 6	2	2.48	0.0498	6518 ± 5	34	6484 ± 5
1	5.26	0.0725	7719 ± 9	23	7696	1	4.77	0.0690	6521	44	6477
2	8.28	0.0910	7734 ± 4	28	7706 ± 4	1	5.63	0.0750	6522	51	6482
2	11.84	0.1087	7732 ± 2	33	7701 ± 2	1	8.40	0.0916	6537	61	6476
$\Delta H_s^\circ = 7712 \pm 3$ cal./mole						1	10.28	0.1014	6543	65	6478
$\Delta H_s^\circ = 7712 \pm 3$ cal./mole						2	12.21	0.1105	6545 ± 6	71	6474 ± 6
$\Delta H_s^\circ = 6483 \pm 3$ cal./mole											
15.01°											
2	2.71	0.0567	7332 ± 32	20	7310 ± 32	65.16°					
2	5.89	0.0767	7343 ± 3	28	7315 ± 3	1	2.80	0.0529	6377	41	6336
2	7.66	0.0875	7356 ± 6	32	7324 ± 6	2	5.37	0.0734	6385 ± 7	56	6329 ± 7
2	11.68	0.1081	7349 ± 30	38	7311 ± 30	2	8.80	0.0937	6356 ± 30	70	6334 ± 30
$\Delta H_s^\circ = 7313 \pm 10$ cal./mole						1	12.20	0.1105	6407	82	6325
$\Delta H_s^\circ = 7313 \pm 10$ cal./mole						2	15.70	0.1253	6424 ± 25	92	6332 ± 25
$\Delta H_s^\circ = 6330 \pm 6$ cal./mole											
25.20°											
2	2.74	0.0523	7068	23	7045	75.07°					
2	4.63	0.0680	7073	30	7040	1	4.01	0.0632	6235	55	6183
2	5.51	0.0742	7069 ± 14	32	7037 ± 14	2	5.65	0.0752	6245 ± 20	65	6180 ± 20
2	7.27	0.0852	7088 ± 9	37	7051 ± 9	2	8.4	0.0916	6261 ± 19	79	6182 ± 19
2	8.40	0.0916	7083 ± 20	40	7043 ± 20	2	11.55	0.1075	6271 ± 10	91	6179 ± 10
2	11.96	0.1096	7091 ± 11	45	7046 ± 11	$\Delta H_s^\circ = 6187 \pm 7$ cal./mole					
1	16.16	0.1271	7107	53	7054	84.90°					
1	22.64	0.1504	7092	62	7030	1	2.83	0.0532	6113	53	6050
$\Delta H_s^\circ = 7043 \pm 4$ cal./mole						1	5.40	0.0735	6127	73	6047
$\Delta H_s^\circ = 7043 \pm 4$ cal./mole						3	8.69	0.0932	6129 ± 18	89	6040 ± 18
35.12°											
2	2.46	0.0496	6870 ± 20	25	6845 ± 20	2	12.07	0.1100	6149 ± 13	105	6044 ± 13
1	3.14	0.0560	6859	27	6832	1	15.27	0.1236	6166	119	6045
2	5.40	0.0735	6867 ± 15	36	6831 ± 15	$\Delta H_s^\circ = 6045 \pm 5$ cal./mole					
2	8.43	0.0918	6891 ± 7	46	6843 ± 7	95.03°					
2	11.82	0.1086	6902 ± 14	52	6850 ± 14	2	2.32	0.0482	5928 ± 28	53	5875 ± 28
$\Delta H_s^\circ = 6836 \pm 7$ cal./mole						1	3.66	0.0605	5934	68	5866
$\Delta H_s^\circ = 6836 \pm 7$ cal./mole						1	5.58	0.0747	5927	83	5844
$\Delta H_s^\circ = 6836 \pm 7$ cal./mole						1	8.16	0.0903	5977	100	5877 ± 22
$\Delta H_s^\circ = 6836 \pm 7$ cal./mole						1	12.54	0.1119	5986	121	5865
$\Delta H_s^\circ = 5878 \pm 7$ cal./mole											

<sup>a</sup> In those cases where the concentrations of successive determinations were not exactly reproduced, the concentration listed is the average. <sup>b</sup> Standard deviation of individual measurements from the average. <sup>c</sup> Estimated probable error.

Instrument Co. 0-2.5-mv. recorder. The details of this bridge design and accompanying equipment appear elsewhere,<sup>6</sup> and will be published in a further communication of this series. The sensitivity of the system was such that full scale of the recorder corresponded to about  $10^{-3}^\circ$ . Temperature differences of  $\sim 2 \times 10^{-6}^\circ$  could be detected over the complete temperature range covered.

**Materials.**—Water used in the measurements and in the calorimeter was made by passing distilled water through a pair of acid-base ion-exchange columns to remove all traces of ionic impurities.

Rhenium heptoxide was prepared by subliming the material obtained from the University of Tennessee in a stream of dry oxygen at  $300^\circ$ . The tube containing the purified material was sealed under vacuum and transferred to a small drybox containing either  $P_2O_5$  or magnesium perchlorate, or both. Small sample bulbs which had been stored in the same drybox were weighed, both empty and filled with  $Re_2O_7$ , by placing them in previously dried plastic capped vials. These vials were in turn placed in

glass-stoppered weighing bottles and removed from the drybox through a suitable air-lock arrangement. After weighing, they were transferred back into the drybox and connected to a previously dried stopcock with a short piece of tubing. The sample bulb was then taken out of the drybox, connected to a vacuum pump, and sealed. This procedure was devised so that the  $Re_2O_7$  never came into contact with laboratory air.

Sodium perrhenate was made by neutralizing perrhenic acid with analytical grade sodium hydroxide. Slow evaporation produced crystals which were recrystallized once from hot water. The sodium perrhenate was powdered, dried at  $280^\circ$ , and stored over  $P_2O_5$  in a desiccator. Samples were transferred to a bulb, weighed in air, heated at  $280^\circ$ , and sealed *in vacuo*.

**Procedure.**—The operating procedure has been described previously.<sup>3</sup> One modification was used in the heat of solution measurements of sodium perrhenate. This salt has an endothermic heat of solution and it was convenient to operate the calorimeter under near-isothermal conditions. This was done by electrically heating the calorimeter as the sample of sodium perrhenate was dissolving. Rarely was the chemical heat of reaction

(6) R. E. Mitchell, Ph.D. Thesis, Purdue University, Feb., 1964.

TABLE II  
 THE INTEGRAL HEATS OF SOLUTION OF RHENIUM HEPTOXIDE<sup>a</sup> AND  $\rho$ -VALUES FOR PERRHENIC ACID

Number of determinations	$m \times 10^3$ , moles/kg. of H <sub>2</sub> O <sup>b</sup>	$\sqrt{m}$	0.96°			Number of determinations	$m \times 10^3$ , moles/kg. of H <sub>2</sub> O <sup>b</sup>	$\sqrt{m}$	55.01°		
			$-\Delta H_s$ , cal./mole	$-A_{HI}^{1/2\alpha}$ , cal.	$-\rho$ , cal./mole				$-\Delta H_s$ , cal./mole	$-A_{HI}^{1/2\alpha}$ , cal.	$-\rho$ , cal./mole
1	2.82	0.0531	4812	16	4828	1	2.82	0.0531	6673	36	6709
1	3.50	0.0592	4805	18	4823	1	4.40	0.0663	6668	44	6712
1	7.20	0.0848	4803	24	4827	1	5.90	0.0768	6676	51	6727
1	13.24	0.1149	4793	34	4827	1	6.60	0.0812	6677	54	6731
1	14.20	0.1192	4796	36	4832	1	10.00	0.1000	6682	65	6747
			$\Delta H_s^\circ = -4824 \pm 3^\circ$ cal./mole			2	12.23	0.1100	6678 ± 12	73	6751 ± 12
			4.94°			1	14.90	0.1220	6674	77	6751
1	3.02	0.0550	5045	17	5062	2	17.99	0.1334	6671 ± 5	81	6752 ± 5
1	4.24	0.0651	5042	22	5064	1	19.0	0.1378	6675	88	6763
1	4.78	0.0691	5043	23	5066				$\Delta H_s^\circ = -6707 \pm 4$ cal./mole		
3	8.79	0.0937	5043 ± 7 <sup>d</sup>	29	5072 ± 7				74.87°		
2	11.88	0.1091	5029 ± 2	33	5062 ± 7	1	3.22	0.0567	7235	52	7287
1	16.30	0.1277	5032	40	5072	1	6.06	0.0779	7218	67	7285
			$\Delta H_s^\circ = -5065$ cal./mole			2	8.46	0.0920	7223 ± 2	78	7301 ± 2
			14.94°			2	11.40	0.1008	7234 ± 2	90	7324 ± 2
2	2.18	0.0467	5457 ± 19	19	5476 ± 19	1	13.92	0.1179	7220	100	7320
1	4.20	0.0648	5466	26	5492	1	21.20	0.1456	7206	120	7326
1	6.20	0.0787	5452	30	5482	1	26.36	0.1622	7239	130	7369
1	7.60	0.0872	5451	32	5483				$\Delta H_s^\circ = -7272 \pm 5$ cal./mole		
1	11.32	0.1063	5447	37	5484				85.03°		
1	15.14	0.1230	5441	43	5484	2	3.02	0.0550	7521 ± 3	55	7576 ± 3
1	19.18	0.1386	5464	49	5513	2	5.25	0.0725	7511 ± 2	72	7583 ± 2
			$\Delta H_s^\circ = -5473$ cal./mole			3	7.39	0.0860	7531 ± 12	85	7616 ± 12
			24.96°			1	11.40	0.1068	7530	98	7628
1	4.15	0.0645	5783	29	5812	1	12.20	0.1104	7510	106	7616
2	5.89	0.0764	5781 ± 2	33	5814 ± 2	1	14.71	0.1212	7521	117	7638
1	8.65	0.0930	5787	40	5827				$\Delta H_s^\circ = -7574 \pm 6$ cal./mole		
1	9.52	0.0976	5790	42	5832				95.05°		
2	13.0	0.1140	5784	47	5831 ± 12	1	2.12	0.0460	7878	53	7931
1	17.0	0.1304	5775	57	5832	2	4.28	0.0659	7883	74	7957 ± 2
			$\Delta H_s^\circ = -5807 \pm 5$ cal./mole			2	7.16	0.0846	7882 ± 27	94	7976 ± 27
			45.00°			2	9.62	0.0981	7866 ± 38	108	7974 ± 38
1	2.28	0.0478	6386	30	6416	1	13.20	0.1149	7885	126	8011
2	6.37	0.0798	6382 ± 31	47	6429 ± 31	1	14.04	0.1183	7822	129	7951
3	12.40	0.1113	6389 ± 19	64	6453 ± 19	1	17.76	0.1332	7833	143	7976
1	17.70	0.1330	6376	74	6450				$\Delta H_s^\circ = -7940 \pm 10$ cal./mole		
1	20.54	0.1432	6400	79	6479						
			$\Delta H_s^\circ = -6411 \pm 7$ cal./mole								

<sup>a</sup> For the reaction  $0.5\text{Re}_2\text{O}_7(\text{c}) + 0.5\text{H}_2\text{O} + \text{aq.} = \text{HReO}_4(\text{aq})$ . <sup>b</sup> In those cases where the concentrations of successive determinations were not exactly reproduced, the concentration listed is the average. <sup>c</sup> Estimated probable error. <sup>d</sup> Standard deviation of individual measurements from the average.

exactly compensated for by electrical heating; however, the discrepancy was never large and the heat gain or loss could be accurately determined by rebalancing the bridge. Heat of solution measurements for sodium perrhenate (eq. 2) and rhenium heptoxide (eq. 3) were made from 1 to 95° at eight to ten reasonably spaced intervals.

The only perrhenate for which heat capacity data are available for the solid is potassium perrhenate. Unfortunately, this substance is not very soluble at lower temperatures and therefore not very satisfactory for heat of solution measurements. Further, partial molal heat capacities at elevated temperatures are not available for any other potassium-containing electrolyte, whereas such information is available for sodium ion systems. For these reasons, sodium perrhenate appeared to be a more desirable choice. This necessitated estimating heat capacities for this substance from the chemically and physically similar material  $\text{KReO}_4$ . Separate measurements were made on the heat capacity of solid  $\text{NaReO}_4$  at 25° by using an adiabatic microcalorimeter.

This calorimeter was designed and has been used in measuring heats of solution of small amounts of inaterials,<sup>7</sup> but it was also

satisfactory for heat capacity measurements on small samples of  $\text{NaReO}_4$  to the desired accuracy ( $\pm 5\%$ ). The calorimeter itself was calibrated by measuring the heat capacity of the system containing  $\text{KCl}$  and  $\text{KClO}_4$ . The value obtained for  $\text{NaReO}_4$  at 25° was  $C_{p2}^\circ = 31.95$  cal. mole<sup>-1</sup> deg.<sup>-1</sup>. A similar measurement on  $\text{NaCl}$  at 25° yielded the value 11.59 cal. mole<sup>-1</sup> deg.<sup>-1</sup> compared to the literature<sup>8</sup> value of 11.88 cal. mole<sup>-1</sup> deg.<sup>-1</sup>. At other temperatures, the heat capacity of  $\text{NaReO}_4$  was assumed to maintain the difference of 2.6 cal. mole<sup>-1</sup> deg.<sup>-1</sup> greater than the known heat capacities of  $\text{KReO}_4$ .<sup>9</sup> While the errors so introduced in the evaluation of  $\bar{C}_{p2}^\circ$  for  $\text{NaReO}_4(\text{aq})$  are not believed to be significant compared to the other experimental errors, the heat capacities reported for this electrolyte should nevertheless be considered somewhat tentative.

### Calculations and Results

The results of over 150 integral heats of solution for  $\text{NaReO}_4$  and  $\text{Re}_2\text{O}_7$  are summarized in Tables I and II.

(8) National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1949, p. 450.

(9) J. W. Cobble, G. D. Oliver, and W. T. Smith, Jr., *J. Am. Chem. Soc.*, **75**, 5786 (1953).

(7) G. R. Argue, E. E. Mercer, and J. W. Cobble, *J. Phys. Chem.*, **66**, 2041 (1961).

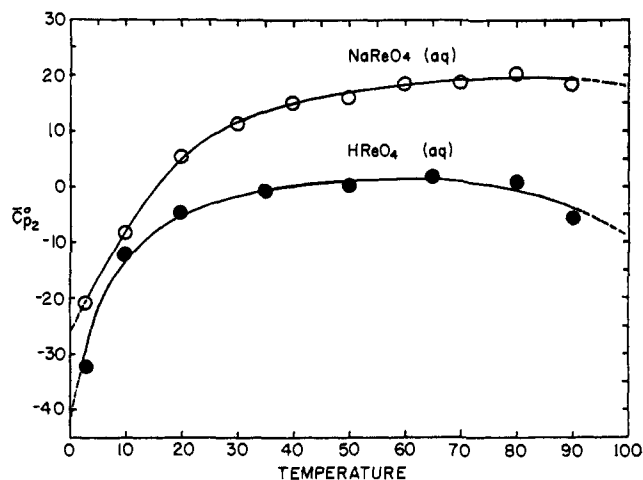


Fig. 1.—Standard partial molal heat capacities of NaReO<sub>4</sub> (upper) and HReO<sub>4</sub> (lower) from 0 to 100°.

The heats of solution, extrapolated to infinite dilution, are listed under each temperature entry. These extrapolated heats were obtained by essentially subtracting the theoretical Debye-Hückel heat of dilution from each heat of solution at a given concentration

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

where  $A_H$  is the limiting Debye-Hückel slope and  $\alpha$  is the function

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

The  $\sigma$ -function has been evaluated elsewhere.<sup>10</sup> Such a procedure takes advantage of the fact that the theoretical two-term Debye-Hückel expression

$$\Phi_L = \frac{\nu}{2} A_H |Z_+ Z_-| I^{1/2} \left[ (1 + I^{1/2})^{-1} - \frac{\sigma(I^{1/2})}{3} \right] - 2.303RT^2 \nu_+ \nu_- \left( \frac{dB}{dT} \right) m \quad (6)$$

leads to a better approximation of the heat of dilution than use of the first term alone. In the present research, a value of  $\rho$  is calculated for each heat of solution measurement and is plotted against  $m$  at each temperature. The advantages of this method<sup>11</sup> have been discussed previously.<sup>3</sup>

The heat data of Tables I and II have been used to calculate  $\Delta C_p^\circ$ , and, from these, the corresponding partial molal heat capacities  $\overline{C}_{p2}^\circ$ , for NaReO<sub>4</sub>(aq) and HReO<sub>4</sub>(aq). These calculations are summarized in Tables III and IV. The relative accuracy of the data can be seen from Fig. 1. Smoothed values of the partial molal heat capacities for the two electrolytes from 0 to 100° are summarized in Table V. The absolute accuracy of the smoothed HReO<sub>4</sub>(aq) data is probably better than  $\pm 0.5$  cal. mole<sup>-1</sup> deg.<sup>-1</sup> except for the 0 and 100° extrapolated values. The accuracy of the Na-

(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.

(11) E. A. Guggenheim and J. E. Prue, *Trans. Faraday Soc.*, **50**, 710 (1954).

TABLE III  
HEAT CAPACITY DATA FOR CRYSTALLINE AND AQUEOUS SODIUM PERRHENATE

$t_{av}$ , °C.	$\Delta C_p^\circ$ , cal. mole <sup>-1</sup> deg. <sup>-1</sup>	$C_{p2}^\circ$ , cal. mole <sup>-1</sup> deg. <sup>-1</sup>	$\overline{C}_{p2}^\circ$ , cal. mole <sup>-1</sup> deg. <sup>-1</sup>
3.0	-51.9	31.0	-20.9
10.0	-39.7	31.3	-8.4
20.1	-26.4	31.7	5.3
30.2	-20.9	32.2	11.3
40.1	-17.5	32.6	15.1
50.3	-17.1	33.0	15.9
60.4	-15.1	33.5	18.4
70.1	-15.4	33.9	18.5
80.1	-14.4	34.5	20.1
90.0	-16.5	34.7	18.2

<sup>a</sup> See text for method of obtaining heat capacities for pure sodium perrhenate.

TABLE IV  
HEAT CAPACITY DATA FOR AQUEOUS PERRHENIC ACID

$t_{av}$ , °C.	$\Delta C_p^\circ$ , cal. mole <sup>-1</sup> deg. <sup>-1</sup>	$0.5C_p$ (Re <sub>2</sub> O <sub>7</sub> ), cal. mole <sup>-1</sup> deg. <sup>-1</sup>	$0.5C_p$ (H <sub>2</sub> O), cal. mole <sup>-1</sup> deg. <sup>-1</sup>	$\overline{C}_{p2}^\circ$ (HReO <sub>4</sub> ), cal. mole <sup>-1</sup> deg. <sup>-1</sup>
3.0	-60.6	19.25	9.0	-32.4
10.0	-40.7	19.4	9.0	-12.3
20.0	-33.4	19.7	9.0	-4.7
35.0	-30.1	20.2	9.0	-0.9
50.0	-29.6	20.6	9.0	0.0
65.0	-28.4	21.1	9.0	1.7
80.0	-29.7	21.5	9.0	0.8
90.0	-36.5	21.7	9.0	-5.8

TABLE V  
SMOOTHED VALUES OF THE STANDARD PARTIAL MOLAL HEAT CAPACITIES OF SODIUM PERRHENATE AND PERRHENIC ACID

$t$ , °C.	NaReO <sub>4</sub> (aq), $\overline{C}_{p2}^\circ$ , cal. mole <sup>-1</sup> deg. <sup>-1</sup>	HReO <sub>4</sub> (aq), $\overline{C}_{p2}^\circ$ , cal. mole <sup>-1</sup> deg. <sup>-1</sup>
0 <sup>a</sup>	-26.3	-42.0
5	-16.7	-23.0
10	-8.1	-13.2
20	5.2	-5.2
25	8.8	-3.2
30	11.3	-1.7
40	14.9	0.2
50	16.8	1.2
60	18.1	1.5
70	19.1	1.0
80	19.5	-0.7
90	19.3	-3.7
100 <sup>a</sup>	18.0	-9.0

<sup>a</sup> Extrapolated values.

ReO<sub>4</sub>(aq) data is more difficult to estimate since detailed information on the heat capacity of pure NaReO<sub>4</sub> is presently not available. However, the estimated accuracy for this electrolyte is probably the same as for HReO<sub>4</sub>(aq).

The positive heat capacity of the NaReO<sub>4</sub>(aq) is undoubtedly due to the more positive contribution of the ReO<sub>4</sub><sup>-</sup> with respect to the less complex halide ions. Part of this positive contribution is due to the internal degrees of freedom of the ReO<sub>4</sub><sup>-</sup>. For example, the known internal heat capacity of OsO<sub>4</sub>(g) is 14.9 cal. mole<sup>-1</sup> deg.<sup>-1</sup> at 25°.<sup>12</sup> The heat capacities of NaCl(aq) and NaReO<sub>4</sub>(aq) at 25° are -18.9 and 8.8 cal. mole<sup>-1</sup> deg.<sup>-1</sup>, respectively. The difference of about 28 cal. mole<sup>-1</sup> deg.<sup>-1</sup> should be reduced by the esti-

(12) K. K. Kelley, Bureau of Mines Bulletin 584, U. S. Government Printing Office, Washington, D. C., 1960, p. 137.

mated 15 cal. mole<sup>-1</sup> deg.<sup>-1</sup> of internal heat capacity in  $\text{ReO}_4^-$  if the solvent interactions between  $\text{Cl}^-(\text{aq})$  and  $\text{ReO}_4^-(\text{aq})$  are to be compared. The remaining net difference of 13 cal. mole<sup>-1</sup> deg.<sup>-1</sup> does not seem so large that it cannot be accounted for reasonably by one

or two water molecules less of primary hydration in  $\text{ReO}_4^-(\text{aq})$  than are present in  $\text{Cl}^-(\text{aq})$ .

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

## The Thermodynamic Properties of High Temperature Aqueous Solutions. III. The Partial Molal Heat Capacities of Hydrochloric Acid from 0 to 100° and the Third-Law Potentials of the Silver-Silver Chloride and Calomel Electrodes from 0 to 100°<sup>1</sup>

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The heat capacities of aqueous hydrochloric acid from 0 to 100° have been calculated from previous data in the literature. These heat capacity data are used in combination with the cell potentials of the silver-silver chloride electrode from 0 to 100° to derive third-law potentials and new thermodynamic functions of the chloride ion. A similar treatment is applied to the less complete data of the calomel electrode system.

### Introduction

In the previous paper of this series,<sup>3</sup> the thermodynamic properties of aqueous sodium perrhenate and perrhenic acid at infinite dilution were determined from 0 to 100° by the integral heat method.<sup>4</sup> In effect, these measurements established the thermodynamic differences between  $\text{H}^+(\text{aq})$  and  $\text{Na}^+(\text{aq})$  over this range of temperature. When combined with previous data on  $\text{NaCl}(\text{aq})$ ,<sup>4</sup> values of  $\overline{C}_{p_1}^\circ$  for the important electrolyte  $\text{HCl}(\text{aq})$  can be derived.

This communication also describes an interesting application of electrolyte heat capacity data to the examination of electrode systems at elevated temperatures. As far as can be determined, this is the first instance where third-law potentials have been derived from cell measurements and heat capacities involving aqueous systems. Such a procedure provides a powerful method of investigating the reliability of chemical cells.

### The Heat Capacity of $\text{HCl}(\text{aq})$

The heat capacity data required to generate values of  $\overline{C}_{p_1}^\circ$  for  $\text{HCl}(\text{aq})$  have been published<sup>3,4</sup>:  $\overline{C}_p^\circ(\text{HCl}) = \overline{C}_p^\circ(\text{HReO}_4) - \overline{C}_p^\circ(\text{NaReO}_4) + \overline{C}_p^\circ(\text{NaCl})$ . Values of the heat capacities of  $\text{HCl}(\text{aq})$  are given in Table I,

TABLE I

#### PARTIAL MOLAL HEAT CAPACITIES FOR HYDROCHLORIC ACID

$t, ^\circ\text{C.}$	$-\overline{C}_{p_1}^\circ,$ cal. mole <sup>-1</sup> deg. <sup>-1</sup>	$t, ^\circ\text{C.}$	$-\overline{C}_{p_1}^\circ,$ cal. mole <sup>-1</sup> deg. <sup>-1</sup>
0 <sup>a</sup>	56.2	50	30.2
5	40.7	60	31.6
10	34.7	70	33.9
20	31.2	80	36.9
25	30.5	90	40.3
30	30.2	100 <sup>a</sup>	45.8
40	30.0		

<sup>a</sup> From extrapolated values.

calculated from smoothed functions for the other three electrolytes involved. The errors in the tabulated

values of  $\overline{C}_{p_1}^\circ$  should be less than 1 cal. mole<sup>-1</sup> deg.<sup>-1</sup> at all temperatures except at 0 and 100°.

Previous values of  $\overline{C}_{p_1}^\circ$  of  $\text{HCl}(\text{aq})$  have been reported.<sup>5-9</sup> The best data at 25° appear to be those of Gucker and Schminke,<sup>5</sup> who report  $\overline{C}_{p_1}^\circ = -29.2$  cal. mole<sup>-1</sup> deg.<sup>-1</sup> at 25°. Three other compilations list  $-29.2$ <sup>10</sup> and  $-30$  cal. mole<sup>-1</sup> deg.<sup>-1</sup>,<sup>8,11</sup> the latter apparently from a revised extrapolation of previous specific heat and other thermodynamic data.

The situation with regard to the present "integral heat" data and previously<sup>9</sup> published  $\overline{C}_{p_1}^\circ$  data on  $\text{HCl}(\text{aq})$  at temperatures other than 25° is illustrated in Fig. 1. The quantitative agreement is not very good. Part of the difference can be attributed to the well-known difficulty in extrapolating specific heat data from higher concentrations. Further, the authors of these data chose the older<sup>6,7</sup> and more negative values of  $\overline{C}_{p_1}^\circ$  at 18 and 25° as a guide in these extrapolations to infinite dilution. In addition, however, it seems apparent that some small but important systematic error has entered into the previous specific heat measurements. A very small error in specific heats leads to much larger errors in  $\phi_{c_p}$  and  $\overline{C}_{p_1}^\circ$ .

It is of interest to note the experimental problem in obtaining partial molal heat capacity data. Specific heat measurements are easier to make in the sense that a larger amount of data can be obtained in a shorter time than required to make the detailed concentration calorimetric study of the heats of solution. However, a precision some ten times greater is required in specific heat measurements, if the dilute ( $\leq 0.1 m$ ) region of electrolyte behavior is to be studied. Unfortunately, extrapolation of  $\phi_{c_p}$  from this region is still largely empirical. The present  $\text{HCl}(\text{aq})$  system leads us to

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