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Pressure-Volume-Temperature-Concentration Relation of Aqueous NaCl Solutions

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The derivatives $\left(\frac{\partial v}{\partial P}\right)_{T,x}$ of NaCl solutions have been experimentally determined in the temperature range 0° to 175° C. for NaCl concentrations of 0 to 25 grams per 100 grams of solution and pressures up to 350 kg. per sq. cm. An interpolation formula which describes the pressure-volume-temperature-concentration (*P-v-T-x*) relation has been developed to fit these experimental results and the density data from the literature.

BECAUSE of the importance of converting salt water to potable water, there is considerable interest in the thermodynamic properties of aqueous NaCl solutions. The petroleum industry is also interested in these properties for predicting steam drive and aquifer performance. Pressure, specific volume, temperature, and concentration data are the basic data required for calculating thermodynamic properties of solutions. Although no equation can be found to represent the relations among the properties in an absolutely correct manner without understanding the fundamental nature of the substances and their interactions, an empirical equation which adequately represents the property relations can be used to interpolate the experimental data, facilitate calculations involving integration and differentiation, and provide a concise representation of a large mass of data. An efficient evaluation of the properties is nearly impossible without interpolation formulas.

A survey of literature indicated the lack of experimental data on compressibility for NaCl solutions at temperatures above 40° C.; measurements were therefore made to determine the values of the derivative $\left(\frac{\partial v}{\partial P}\right)_{T,x}$ for 0, 5, 10, 15, 20, and 25% of NaCl in solutions at 21.7°, 50.9°, 81.0°, 119.4°, 146.9°, and 174.4° C., up to pressures of 350 kg. per sq. cm. By using test results and low-pressure density data from the literature, a formula was then improvised to describe the *P-v-T-x* relations. The estimated maximum deviation of the observations from this formula was less than 1.5 p.p.t. over the entire region investigated.

EXPERIMENTAL

The compressibilities of a liquid are often experimentally determined by measuring the total change in specific volume caused by the change in pressure from 1 to *P* atm. However, this experiment was designed to obtain the differential change in specific volume associated with a small pressure change at pressure *P*, at the fixed temperature, by using a calibrated positive displacement pump. The apparatus used is shown in Figure 1. The vessel used for testing the solutions was made of stainless steel, surrounded by three electrical heating coils of 650 watts each, and insulated by a 1.5-inch layer of mineral wool. The electric current through the coil was controlled by a variable resistor that maintained the desired temperature of the solution in the vessel. To minimize temperature variation of the solution, 415 feet of 0.01-inch o.d. nickel-chromium wire was placed inside the vessel to distribute the heat uniformly through the solution. The pump piston, which was calibrated to 0.01 cc. of piston displacement, could be advanced or retreated at uniform speed of 0 to 100 cc. of

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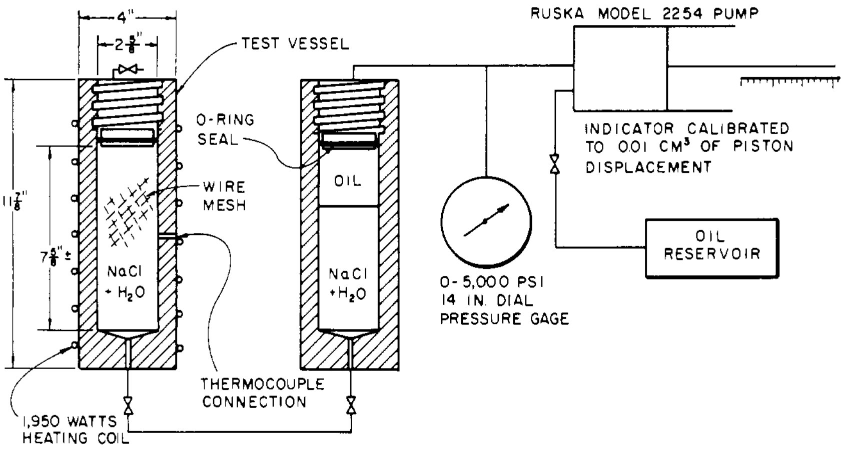

Figure 1. Arrangement of apparatus for determining derivative $\left(\frac{\partial v}{\partial P}\right)_{T,x}$

displacement per minute by a motor and gear box. Soltrol 160, a light oil, was used to separate the solution in the second vessel from the pump and pressure gage. The valve on top of the test vessel was normally closed except when used to bleed the solution to the atmosphere.

The 14-inch Bourdon tube Heiss pressure gage was calibrated with a deadweight tester to establish the pressure scale. The pressure readings were accurate within ±3 p.s.i. The temperature of the solution was measured by a Conax 20-gage iron-constantan thermocouple, which was placed in the middle of the vessel, and a Leeds & Northrup Model 8686 millivolt potentiometer. The precision of temperature readings from potentiometer was within ±0.02° C. Later the thermocouple was calibrated with a platinum resistance thermometer, which had been calibrated by the National Bureau of Standards. The accuracy of temperature readings from the potentiometer is ascertained to be within ±0.1° C.

The solutions were prepared from distilled water and NaCl with a purity of 99.7%. To avoid possible contamination, the interior surface of the vessel was cleaned with a dilute acid solution and thoroughly rinsed with distilled water. After the vessel was filled with solution, any entrained air was carefully driven out through the top of the vessel by boiling and stirring the solution.

Experimental Procedure. The apparatus was assembled, and the pressure of the system was raised to 5000 p.s.i.g. The system was kept at this pressure for at least 30 minutes to ensure no leakage through the joints. The electrical resistor was adjusted, and when thermal equilibrium was established, the pressure of the system was gradually lowered by reversing the motion of the piston at a very slow speed. The piston displacements were recorded at intervals of 250-p.s.i. pressure. During this operation, the temperature of the solution dropped slightly. It was therefore necessary to raise the current through the heating coils in order to maintain a constant temperature. The pressure was lowered to 185 p.s.i.g., and the valve under the test vessel was closed to isolate the solution in this vessel from the system. The pressure was again raised to 5000 p.s.i.g. and then lowered. Piston displacement readings were repeated at intervals of 250 p.s.i. Two sets of data, one taken with the valve open and one with the valve closed, were needed to determine the volume changes of the test vessel and its contents. An average of 6 hours was required to complete each test.

The results of a typical test, taken at 174.4° C. and 25% NaCl, are shown in Figure 2. ΔV is the difference between the two piston displacements taken at each 250-p.s.i. pressure change with the valve under the test vessel open and closed. Data were taken by Chou (*1*) at 21.7°, 50.9°, 81.0°, 119.4°, 146.9°, and 174.4° C. for NaCl concentrations of 0, 5, 10, 15, 20, and 25%. Trial tests were made to determine the degree of consistency of the data; variations of the mean value of ΔV were within 0.5%.

ΔV can be interpreted as the sum of the volume change of the solution in the test vessel and the dilation of this test vessel due to internal pressure. The dilation of the test vessel was determined experimentally by weighing the overflow of distilled water from the top of the test vessel in the following manner. The valve under the vessel was closed at a desired pressure, and the valve on the top was then opened to release the overflow due to the pressure drop. The water temperatures were measured before and after the expansion of water. From the *P-v-T* relation of pure water, the volume changes of the vessel due to pressure drop were determined.

The total volume of the test vessel at room temperature was measured by drying the interior surface and measuring the amount of water required to fill the vessel. The volume change of the vessel due to thermal expansion of metal was determined by recording the piston displacements of different temperatures while the vessel contained distilled water at a fixed pressure.

EVALUATION OF $\left(\frac{\partial v}{\partial P}\right)_{T,x}$

Since the derivative $\left(\frac{\partial v}{\partial P}\right)_{T,x}$ does not vary rapidly with a change in pressure, the mean value of the derivative over a small pressure change can be approximated by the equation

$$-\left(\frac{\partial v}{\partial P}\right)_{T,x} = \frac{\Delta V - \Delta V_e}{M\Delta P} \tag{1}$$

where ΔV represents the volume change of the solution and the dilation of the test vessel (as discussed previously), ΔP is the correspondent change of pressure, ΔV_e is the dilation of the vessel, and M is the mass of solu-

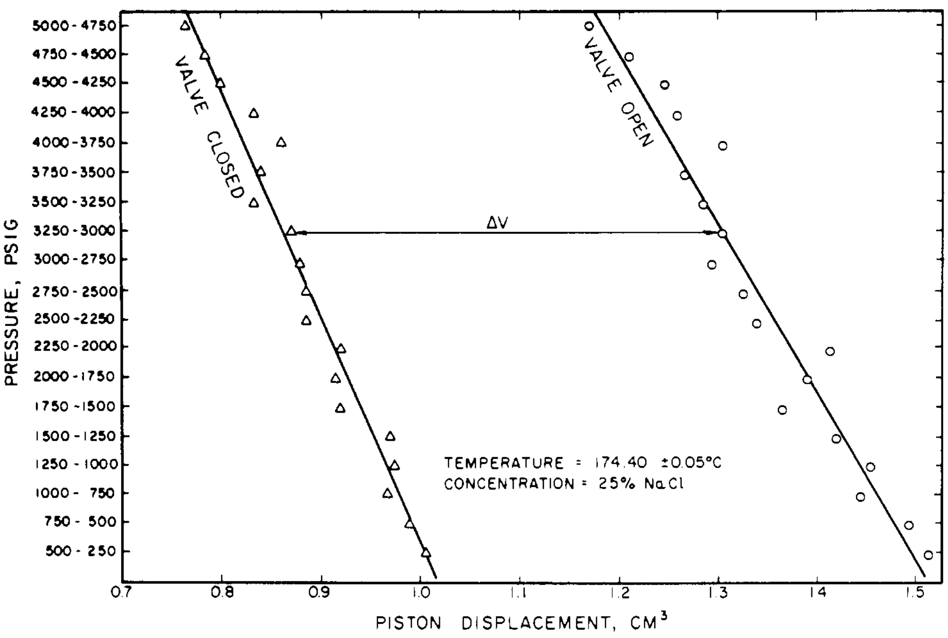

Figure 2. Typical measurements of piston displacement for compression test

tion isolated from the system after closing of the valve under the test vessel. Let v_i be the specific volume of solution at the condition when the valve closes, V_o the volume of the test vessel at room temperature, and ΔV_t the increase of thermal expansion of metal at the testing temperature. Then Equation 1 becomes

$$-\left(\frac{\partial v}{\partial P}\right)_{T,x} = \frac{v_i\,(\Delta V - \Delta V_e)}{(V_o + \Delta V_t)\,\Delta P} \tag{2}$$

The values of ΔV, ΔV_e, V_o, ΔV_t, and ΔP were obtained from Chou's experiment (*1*), and v_i at 185 p.s.i.g. was determined in the following manner. The data on densities of the solutions in the region 0° to 100° C. and 1 to 26 grams of NaCl per 100 grams of solution at 1 atm. are given in the International Critical Tables (*8*). From these data and the data obtained by Fabuss (*2*) at 100°, 125°, 150°, and 175° C., and 0.1, 2.0, and 2.5 moles of NaCl per 1000 grams of water at pressures near the vapor pressures, an interpolation formula was established to represent the specific volume of the solution at low pressures with temperature and concentration as the only independent variables. Since the values of the derivative $\left(\frac{\partial P}{\partial v}\right)_{T,x}$ lie between 0.00008 and 0.00002 cc./g./atm., the change of v_i due to 185 p.s.i. of pressure change is 0.00101 to 0.00025 cc. per gram. The error caused by using the interpolation formula for the specific volume at low pressure to represent v_i at 185 p.s.i.g. —i.e., the pressure of solution when the valve under the test vessel was closed—was not felt to be excessive in comparison to other experimental uncertainties. By substituting the values of ΔV, ΔV_e, V_o, ΔV_t, ΔP, and v_i into Equation 2, the values of the derivative $\left(\frac{\partial v}{\partial P}\right)_{T,x}$ at 0, 5, 10, 15, 20, and 25 grams of NaCl per 100 grams of NaCl per 100 grams of solution were obtained (Table I).

The values of the derivative for pure water obtained from this experiment, those calculated from Smith and Keyes' formula (*5*), and those derived from Equation 3 are compared in Figure 3. Chou (*1*) fitted the data established by the Third International Conference on Steam Tables (*7*) within the internationally acceptable tolerances by using the equation:

$$v = A(T) - P \cdot B(T) - P^2 \cdot C(T) \tag{3}$$

where v is the specific volume in cubic centimeters per gram, P is the absolute pressure in kilograms per square centimeter, and T is the temperature in ° K. The three functions of temperature for specific volumes in the region 0° to 180°C. and up to 400 kg. per sq. cm. were determined as follows:

$$A(T) = 5.916365 - 0.01035794T + 0.9270048 \times 10^{-5}T^2 - 1127.522/T + 100674.1/T^2$$

$$B(T) = 0.5204914 \times 10^{-2} - 0.10482101 \times 10^{-4}T + 0.8328532 \times 10^{-8}T^2 - 1.1702939/T + 102.2783/T^2$$

$$C(T) = 0.118547 \times 10^{-7} - 0.6599143 \times 10^{-10}T$$

The values derived from Smith and Keyes' formulation, although in agreement with others, appear too low at temperatures below 30° C. compared with the values of compressibilities from Kell and Whalley's (*4*) recent investigation at 1 atm.

Freyer (*3*) measured the velocity of sound through aqueous NaCl solutions at atmospheric pressure. The values of the derivative $\left(\frac{\partial v}{\partial P}\right)_{T,x}$ at 20° C. and 1 atm. were calculated according to his measurements, and the results are listed below:

x	0.01	0.06	0.10
u	1497.0	1554.5	1600.6
$-\left(\frac{\partial v}{\partial P}\right)_{T,x} \times 10^6$	45.24	39.41	35.38
x	0.16	0.20	0.24
u	16730.0	1722.5	1771.5
$-\left(\frac{\partial v}{\partial P}\right)_{T,x} \times 10^6$	30.00	26.83	23.97

Table I. Values of $\left(\frac{\partial v}{\partial P}\right)_{T,x}$ in Cubic Centimeters per Gram per Atmosphere, Multiplied by -10^4

Salt, %	t, ° C.	Pressure, Atm. 10	100	200	300
0	21.7	0.466	0.451	0.435	0.419
	50.9	0.463	0.447	0.430	0.412
	81.0	0.489	0.470	0.450	0.429
0	119.4	0.568	0.542	0.513	0.485
	146.9	0.667	0.635	0.600	0.566
	174.4	0.807	0.763	0.715	0.666
5	21.7	0.410	0.398	0.384	0.371
	50.9	0.412	0.399	0.385	0.370
	81.0	0.432	0.418	0.401	0.385
5	119.4	0.494	0.476	0.455	0.435
	146.9	0.570	0.547	0.521	0.495
	174.4	0.666	0.636	0.602	0.568
10	21.7	0.363	0.350	0.336	0.321
	50.9	0.366	0.353	0.339	0.324
	81.0	0.386	0.372	0.356	0.340
10	119.4	0.436	0.419	0.400	0.381
	146.9	0.492	0.472	0.450	0.428
	174.4	0.565	0.542	0.515	0.489
15	21.7	0.323	0.311	0.296	0.282
	50.9	0.330	0.317	0.302	0.287
	81.0	0.348	0.334	0.319	0.303
15	119.4	0.388	0.373	0.356	0.339
	146.9	0.432	0.415	0.397	0.378
	174.4	0.489	0.470	0.449	0.428
20	21.7	0.290	0.277	0.262	0.248
	50.9	0.299	0.286	0.272	0.258
	81.0	0.315	0.302	0.288	0.274
20	119.4	0.347	0.333	0.319	0.304
	146.9	0.382	0.368	0.352	0.336
	174.4	0.425	0.410	0.393	0.376
25	21.7	0.262	0.250	0.235	0.221
	50.9	0.273	0.260	0.247	0.233
	81.0	0.285	0.273	0.259	0.246
25	119.4	0.312	0.299	0.286	0.273
	146.9	0.341	0.328	0.314	0.300
	174.4	0.375	0.361	0.346	0.331

x denotes the weight fraction of NaCl in the solution, u represents the sound velocity in meters per second, and the derivative unit is cubic centimeters per gram atmosphere. These values are plotted on Figure 4 and compared with the values obtained at 21.7° C. in this study. The difference between the two sets of data increases as the NaCl concentration increases. A careful review of the testing procedures gave no reasonable explanation for such large discrepancies. Since the calculation of $\left(\frac{\partial v}{\partial P}\right)_{T,x}$ from sound velocity was based on the assumption that the velocity of wave transmission is dependent solely upon two physical properties of the medium, elasticity and density, a speculative opinion is that the electrostatic pressure due to the electric field around the ions may also have some effect on the velocity of sound through an electrolytic solution.

Another comparison made with isothermal compressibilities is also available. In the literature, data are often reported in terms of mean isothermal compressibility, k_m, defined as

$$k_m = \frac{(v_1 - v_p)}{v_1 (P - 1)} \tag{4}$$

where v_1 and v_p are the specific volumes in cubic centimeters per gram at the same temperature but under pressures of 1 and P atm., respectively. Tait (*6*) has found that his experimental data at 0°C., for pressures up to 450 atm. and NaCl concentrations of 3.88 to 17.63

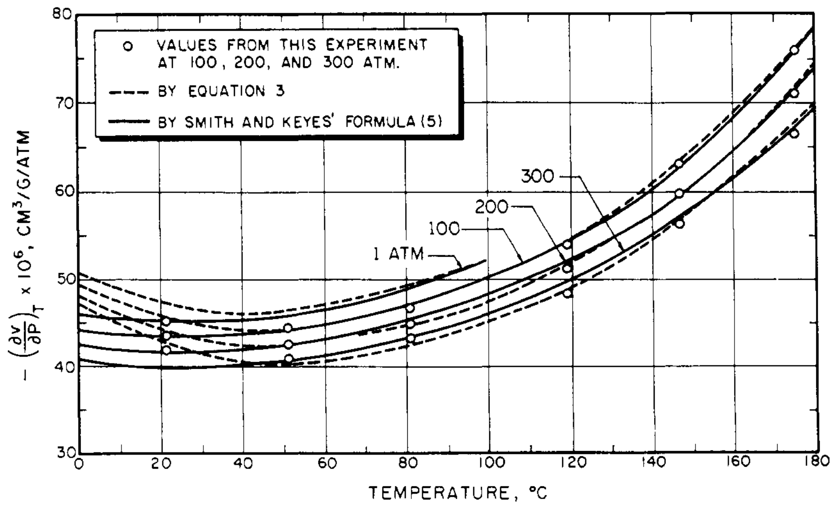

Figure 3. Comparison of $\left(\frac{\partial v}{\partial P}\right)_T$ of water

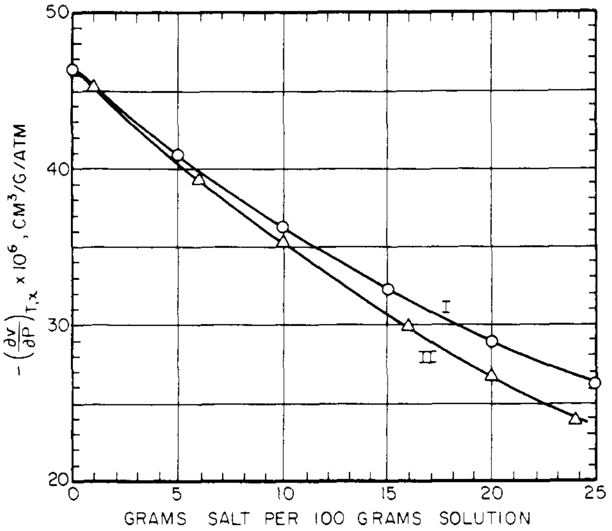

Figure 4. Comparison of $\left(\frac{\partial v}{\partial P}\right)_{T,x}$ of solution

I. Values from this experiment at 21.7° C. and 10 atm.
II. Values at 20° C. and 1 atm., computed from sound velocity by Freyer (*3*)

grams per 100 grams of solution, can be represented by his empirical equation

$$k_m = \frac{0.00186}{(36 + P + w)} \tag{5}$$

where K_m is the mean compressibility in atm.$^{-1}$, P is the pressure in long tons per square inch, and w is the NaCl concentration in grams per 100 grams of solution. The results of this experiment were compared with Tait's results, and the mean compressibilities were computed from values of specific volumes given by Equation 6 which fits the experimental results of this study. The disagreement between the values from Tait's formula and from Equations 4 and 6 is less than 2%, as shown in Table II.

In the design of the experiment, it was intended to check the accuracy by remeasuring pure water in the same equipment used for the solutions. Thus, the absolute precision of measurement would not be so critical. Repeated tests were made, and the deviation in results was less than 1% of the mean value of the derivative $\left(\frac{\partial v}{\partial P}\right)_{T,x}$. Based on the comparison with pure water, the maximum probable errors of the derivatives obtained from this experiment are within 3.0% of the true values.

P-v-T-x RELATION

To fit the experimental data, the following mathematical expression was arbitrarily chosen:

$$v = A(T) - P\cdot B(T) - P^2\cdot C(T) + x\cdot D(T) + x^2\cdot E(T) - xP\cdot F(T) - x^2P\cdot G(T) - \frac{1}{2}xP^2\cdot H(T) \tag{6}$$

where v is the specific volume in cubic centimeters per gram, T is the temperature in ° K., P is the absolute pressure in kilograms per square centimeter, and x is the weight fraction of NaCl in solution. The temperature functions were determined in the following manner. When $x = 0$, Equation 6 reduces to Equation 3, which is for liquid water; functions $A(T)$, $B(T)$, and $C(T)$ have been listed previously.

Table II. Mean Compressibility in Atm.$^{-1}$ at 0° C., Multiplied by 10,000

	Salt Weight, G./100 G. Solution					
	5		10		15	
P, Atm.	[a]	[b]	[a]	[b]	[a]	[b]
10	45.7	45.3	41.0	40.4	37.0	36.4
100	45.2	44.7	40.5	39.9	36.7	36.0
150	44.9	44.3	40.2	39.6	36.4	35.8
200	44.5	44.0	39.9	39.3	36.1	35.6
250	44.2	43.6	39.6	39.0	35.8	35.3
300	43.9	43.3	39.3	38.8	35.5	35.1

[a] By Equations 4 and 6.
[b] By Tait's formula.

In the hypothetical states of zero pressure,

$$v = A(T) + x\cdot D(T) + x^2\cdot E(T) \tag{7}$$

The density data of solutions at 1 atm. or near the vapor pressures are given in the International Critical Tables (*8*) and by Fabuss (*2*). The agreement of data from these two sources is better than 0.5 p.p.t. With the information on compressibilities from the experiment, these data were adjusted to zero pressure for evaluation of the coefficients of the functions $D(T)$ and $E(T)$, listed below:

$$D(T) = -2.5166 + 0.0111766T - 0.170552 \times 10^{-4}T^2$$

$$E(T) = 2.84851 - 0.0154305T + 0.223982 \times 10^{-4}T^2$$

Equation 7 fits the data accurately to three decimal places.

Differentiation of Equation 6 leads to

$$\left(\frac{\partial v}{\partial P}\right)_{T,x=0} - \left(\frac{\partial v}{\partial P}\right)_{T,x} = x\cdot F(T) + x^2\cdot G(T) + xP\cdot H(T) \tag{8}$$

The best coefficients for functions $F(T)$, $G(T)$, and $H(T)$ were determined by fitting the experimental values of the derivatives:

$$F(T) = -0.0014814 + 0.82969 \times 10^{-5}T - 0.12469 \times 10^{-7}T^2$$

$$G(T) = 0.0027141 - 0.15391 \times 10^{-4}T + 0.22655 \times 10^{-7}T^2$$

$$H(T) = 0.62158 \times 10^{-6} - 0.40075 \times 10^{-8}T + 0.65972 \times 10^{-11}T^2$$

The maximum difference between the data and values estimated from Equation 8 is 2.7% of the value of $\left(\frac{\partial v}{\partial P}\right)_{T,x=0}$. Since the magnitude of the derivative is in the order of 10^{-5}, 5% of relative error on the estimated value of the derivative would induce an error of approximately 0.0004 to 0.0006 cc. per gram in the specific volume at 300 atm. Equation 6 may accurately represent the specific volume of the solution to 1.5 p.p.t. for the region 0° to 150° C., 0 to 25% of NaCl weight in solution, and 1 to 350 kg. per sq. cm.

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Heat of Solution of Liquid Bromine in 2*M* NaOH at 27° C.

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The heat of solution of liquid Br_2 in excess 2.0*M* NaOH has been measured in a diphenyl ether, change-of-phase calorimeter at 27° C. and found to be 10.3 ± 0.2 kcal. per mole of Br_2.

THE TWO RECENT DETERMINATIONS of the heat of solution of liquid Br_2 in aqueous NaOH at 25° C. differ by about 5%. Although this difference does not significantly affect values for the thermochemical functions of the hypohalites it is interesting that in one research, done at relatively high NaOH concentrations (0.25 to 1.3*M*) (*4*), no dependence of heat of solution on NaOH concentration was noted, while in the other work (*3*), the heat of solution was observed to increase with increasing NaOH concentration in the range 0.025 to 0.1*M*.

We have used the reaction between liquid Br_2 and excess 2.0*M* NaOH to evaluate the performance of a Bunsen or change-of-phase calorimeter when the reactants are mixed by the up-and-down motion of a hand-operated Teflon disk affixed to a glass breaker. The results are reproducible to within the limits of precision indicated by the calibration constant and agree with the extrapolated value at infinite NaOH dilution obtained by McDonald and Cobble (*3*), 10.35 ± 0.20 kcal. per mole at 25° C.

EXPERIMENTAL AND DISCUSSION

The construction and calibration of the diphenyl ether calorimeter have been described (*1*). The present instrument was calibrated both by electrical heating and by using the standard reaction between 2-amino-2-(hydroxymethyl)-1,3-propanediol (Tris or Tham) and 0.1*N* HCl, for which enthalpies have been measured (*2*). The result of four electrical calibrations was 0.348 ± 0.01 cal. per cm. and for eight Tham calibrations was 0.337 ± 0.01 cal. per cm. These results agree within the limits of their precision. However, since the rate of heat evolution during Tham calibrations was similar to the rate of heat evolution during hydrolysis experiments, the Tham calibration factor was used in calculating heats from the mercury thread extension in the dilatometer tube of the calorimeter.

Table I. Heat of Solution of Liquid Bromine in 2.0*M* NaOH at 27° C.

Br_2, Mmoles	OBr^-, Mmoles	Measured Exothermic Heat, Cal.	Kcal./Mole Br_2
1.008	1.00	10.4	10.3
2.884	. . .	29.0	10.1
1.678	1.69	18.3	10.9
5.320	5.22	53.9	10.1
3.390	3.39	35.7	10.5
2.859	2.80	28.6	9.99
3.702	. . .	38.2	10.3
2.620	2.62	27.8	10.6
3.316	3.30	34.1	10.3
			Av. 10.3 ± 0.2

Analar analytical grade bromine was weighed and sealed into thin-walled glass bulbs which were broken and stirred into 25.0 ml. of 2.0*M* NaOH in a reaction tube placed in the calorimeter. A heat of breaking and stirring was determined in blank experiments (0.56 ± 0.18 cal., exothermic) and subtracted from all heat of solution experiments.

Following the heat determination, if any unreacted Br_2 could be seen in the reaction mixture the experimental result was discarded. In almost all experiments the reaction mixture was analyzed iodometrically for hypobromite ion. The results are given in Table I.

The yield of hypobromite is variable and on the average about 0.7% below that demanded by the stoichiometry:

$$Br_2(liq) + 2NaOH(aq) = NaBr(aq) + NaOBr(aq) + H_2O$$

A similar result was found by McDonald and Cobble