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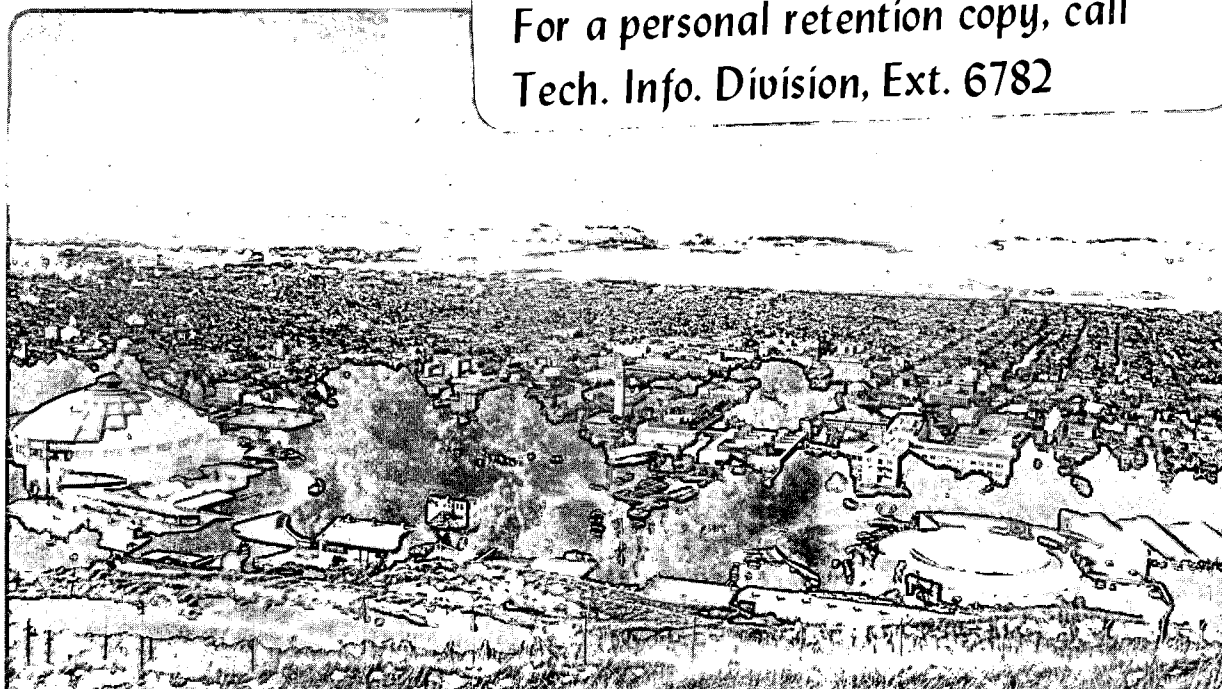
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FROM 75°C TO 200°C AT 20 BAR

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Densities of Aqueous Sodium Chloride Solutions from 75°C to 200°C at 20 bar

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(Abstract)

A high pressure dilatometer has been used to measure the densities of aqueous sodium chloride solutions from .05 to 4.4 molal. The precision of a density determination is $\pm 2 \times 10^{-4}$ g cm^{-3} at 100°C and decreases to $\pm 5 \times 10^{-4}$ g cm^{-3} at 200°C. Within these limits, the density data are in agreement with the low concentration measurements reported by Ellis at the same temperatures and pressure.

Introduction

The thermodynamic properties of aqueous sodium chloride solutions are of interest for research and engineering design in such areas as desalination, geothermal energy development, geothermal brine exploration, and hydrothermal ore deposition. Volumetric properties at high temperatures are of direct significance for their use in determining the pressure dependence of high temperature activity coefficients, enthalpies, and heat capacities. Much of the data on thermal properties are reported at the saturation pressure, so precise volumetric data in this region, as well as at higher pressures, are required for calculations of pressure dependence. In preparation for a program to calculate the pressure dependence of thermal properties, we reviewed the literature data for sodium chloride solutions and found that the density data available at low pressures were inconsistent. The data of Khaibullin and Borisov (1), reported at saturation pressure, are of low precision. They differ by as much as .01 g cm^{-3} from the data of Fabuss, Korosi, and Hug (2).

The more precise data of Ellis (3) are limited to concentrations below one molal. We have used a high pressure dilatometer to measure the densities of sodium chloride solutions to 4.4 molal, at 20.27 bar, from 75°C to 200°C.

Apparatus

The dilatometer is similar to that used by Ellis (3), in which changes in the volume of a solution are measured as a function of temperature. The apparatus is illustrated in Figure 1. A pressure vessel, constructed of corrosion resistant Haynes[R] Alloy No. 625, contains approximately 9 cm^3 of salt solution. The pressure vessel is connected to a mercury reservoir by .062 inch outside diameter, .007 inch inside diameter, stainless steel capillary tubing. The mercury reservoir, which is made of a coil of .125 inch outside diameter stainless steel tubing, is in turn connected to a glass capillary column. The entire system is pressurized with a high pressure nitrogen gas cylinder.

To avoid possible hysteresis in the volume of the sample cell when the system is pressurized and depressurized, a double vessel is used as shown in Figure 2. The sample cell is welded to a thick top cap, so that it is permanently sealed except for the inlet and outlet ports. A thick outer vessel surrounds the sample cell and is sealed using an annealed copper gasket. The inner and outer vessels are connected on the gas side of the apparatus, so that both can be slowly pressurized at the same time. Thus there is never a pressure difference between the inner and outer vessels.

The high pressure glass to metal seals, used to connect the glass capillary to the stainless steel tubing system, are constructed of standard swagelock fittings (1/8 inch tubing to 1/4 inch MNPT) which

have been drilled out to provide a loose fit for the glass tubing. The glass is simply glued into the fittings with epoxy (G. C. Electronics). Precision bore glass tubing, 1.6 mm internal diameter, is carefully annealed before use. The combination of glass tubing and epoxy seal can contain 1 kbar pressure. For safety, the glass tubing is always surrounded by a plexiglass pressure shield.

Temperature control is achieved using two separate systems. The mercury reservoir and most of the capillary connecting tube are thermostated at 30°C with a well stirred water bath and circulation pump. The temperature of the water bath fluctuates by less than .01 K. The sample cell is surrounded by a large aluminum block and is placed in a high temperature fluidized bath. Temperature control of the fluidized bath is good only to a few tenths of a degree, but the aluminum block serves as a heat sink to reduce temperature fluctuations. With the aluminum block, the temperature of the sample cell is stable to +.01 K over a period of 30 minutes.

Experimental Method

The solution density was determined by measuring the change in the volume of the solution as the temperature was raised. To begin a measurement, solution of known molality was prepared with freshly degassed water which had been distilled and passed through a Millipore Q filter system (final resistivity was greater than 18 megaohm). Baker reagent grade NaCl was used without further purification. The salt was dried overnight at 200°C and cooled under vacuum before being weighed.

The procedure used to fill the sample cell without introducing any air bubbles was somewhat complicated. The cell was filled and emptied

by syringe a minimum of five times to eliminate contamination by any old solution still in the cell. As the final slug of solution was placed in the sample cell, a fine needle was used to stir the solution in the inlet hole and dislodge any air bubbles trapped in the narrow opening. A syringe containing 10 ml of the solution was then attached to the inlet fitting, and the solution was forced through the sample cell, the connecting tube, and then out an opening at the mercury/solution interface. A Swagelock cap used to close this opening was tightened while pressure was applied by the syringe. The syringe was removed and the inlet fitting was topped off with a few drops of solution. As the inlet cap was tightened, solution was forced out through the cracks, displacing any remaining air. Finally the apparatus was pressurized. Any air bubbles in the system could be detected immediately by a large displacement in the level of the mercury column.

The sample cell was then placed in the fluidized bath and the solution was allowed to come to equilibrium at room temperature. The pressure of the system and the level of the mercury column were monitored overnight to check for leakage. The temperature of the sample was increased in 25 K increments, and the height of the mercury column was measured to $\pm.01$ mm at each step using a Wilde cathatometer. The temperature of the sample cell was determined to $\pm.005$ K using a 25 Ω, calibrated platinum resistance thermometer and G-2 Mueller bridge. A bourdon tube pressure gauge (Ashcroft Digiguge Model 7781), calibrated with a Ruska Deadweight Tester, was used to determine the pressure of the system to $\pm.1$ bar. The temperature of the water bath and the room temperature were measured with mercury-in-glass thermometers.

Derivation of Equations

The change in the height of the mercury column can be related to the density of the solution as follows. Let T be the experimental temperature, T_R the reference temperature, and T_B the water bath temperature, in degrees Celcius. The density of the solution at the experimental temperature, ρ_T, is equal to the mass of solution in the cell divided by the volume of the cell,

$$\rho_T = \frac{g_T}{V_T} .\tag{1}$$

The mass of solution in the sample cell at temperature T is equal to the mass in the cell at the reference temperature T_R, less the amount that has expanded from the cell. The mass of solution expanded is equal to

$$\Delta h A \rho_{T_B} ,\tag{2}$$

where Δh is the total change in the height of the mercury column between temperatures T_R and T, A is the cross-sectional area of the mercury column, and ρ_{T_B} is the density of the solution at the temperature of the water bath. Thus the density of the solution is given by

$$\rho_T = \frac{1}{V_T} [\rho_{T_R} V_{T_R} - \Delta h A \rho_{T_B}].\tag{3}$$

Assume that the temperature dependence of the volume of the sample cell is

$$V_T = V_0 e^{\alpha T},\tag{4}$$

where V_0 is the volume of the cell at 0°C and α is the unknown expansivity of the cell. Substituting Equation (4) into Equation (3) one

obtains

$$\rho_T = \rho_{T_R} e^{-\alpha(T-T_R)} - \frac{A}{V_0} \Delta h \rho_{T_B} e^{-\alpha T}.$$

Expansion of the exponential yields

$$\rho_T = \rho_{T_R} [1-\alpha(T-T_R)] - \Delta h \frac{A}{V_0} \rho_{T_B} [1-\alpha T] ,$$

or

$$\rho_T = \rho_{T_R} - \frac{A}{V_0} \Delta h \rho_{T_B} + \alpha \rho_{T_R} (T_R-T) + \alpha \frac{A}{V_0} T \Delta h \rho_{T_B} . \tag{5}$$

This is the final equation relating the density of the solution to the observed change in the height of the mercury column.

Small corrections to the observed column height were made to account for variations in water bath temperature, room temperature, hydrostatic head, and system pressure. These corrections are discussed in detail in Reference 4. A correction for the variable mass of solution in the connecting tube was found to be negligible to 200°C.

Calibration

Equation (5) contains two unknowns, the expansivity of the sample cell, α, and the ratio of the cross sectional area of the column to the volume of the cell at $0°C$, A/V_0. Six calibration runs, using pure water in the solution cell, were performed to evaluate these two constants. Observed values of Δh were combined with known densities of water (5) in a nonlinear least squares regression to determine the values $\alpha = (3.81 \pm .04) \times 10^{-5} \ K^{-1}$ and $(A/V_0) = (2.333 \pm .001) \times 10^{-3} \ cm^{-1}$. The value for the expansivity of the sample cell is in good agreement with the expansivity of a similar Hastelloy[R] alloy, $3.6 \times 10^{-5} \ K^{-1}$ (6). The overall standard deviation of fit for all calibration data was $4 \times 10^{-5} \ g \ cm^{-3}$ in the density values for pure water.

Results and Discussion

The results of density measurements for sodium chloride solutions, from .05 to 4.4 molal, are given in Table I. Observed values of Δh were used directly in Equation (5), in combination with the known calibration constants, to obtain densities which were then corrected to rounded temperatures and 20.27 bar. The largest temperature correction was over a 2.5 K interval and introduced a maximum error of $2 \times 10^{-5} \ g \ cm^{-3}$.

Densities of sodium chloride solutions at the reference temperature and at the water bath temperature also are required in Equation (5). These were obtained from an analysis of literature data (4). While the reference temperature varied for each experimental run (generally between $20°C$ and $25°C$), the water bath temperature remained constant at $30°C$. Densities at this temperature also are included in Table I. Complete listings of the raw data for both sodium chloride solutions and calibration runs are included in Reference 4.

The precision of the density data can be estimated by examining the data as a function of molality at constant temperature. The estimated uncertainty increases from $\pm 2 \times 10^{-4}$ g cm^{-3} at 100°C to $\pm 5 \times 10^{-4}$ g cm^{-3} at 200°C. This uncertainty is larger than that quoted by Ellis (3), but it is at least a factor of two smaller than the uncertainty in the best density data (7) available at higher pressures. Within these uncertainty limits, the present measurements are in agreement with the low concentration data of Ellis at the same temperatures and pressure. The data greatly extend the concentration range covered by Ellis, and thus fill an important void in the sodium chloride data base.

A comprehensive equation of state for aqueous sodium chloride has been developed on the basis of these measurements and many literature data extending to 300°C and 1 kbar. This will be published separately, together with a general discussion of the volumetric properties of aqueous sodium chloride.

Acknowledgment

Glossary

A   cross-sectional area of mercury column (cm^2)

T   temperature (°C)

V   volume of sample cell (cm^3)

α   expansivity of sample cell (K^{-1})

ρ   density of solution (g/cm^3)

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Table I. Density of Aqueous NaCl at 20.27 bar

| molality	T = 30°C[a] density (g/cm^3)	T = 75°C density (g/cm^3)	T = 100°C density (g/cm^3)	T = 125°C density (g/cm^3)	T = 150°C density (g/cm^3)	T = 175°C density (g/cm^3)	T = 200°C density (g/cm^3)
.0530	.99867	.97782	.96141	.94216	.92021	.89549	.86767
.2719	1.00743	.98633	.96995	.95085	.92920	.90494	.87774
.5571	1.01854	.99695	.98068	.96184	.94055	.91676	.89024
.9775	1.03444	1.01230	.99615	.97764	.95689	.93388	.90847
1.0360	1.03662	1.01439	.99821	.97970	.95894	.93592	.91042
3.0610	1.10622	1.08202	1.06604	1.04839	1.02912	1.00820	.98556
3.2428	1.11200	1.08764	1.07156	1.05382	1.03446	1.01348	.99081
4.3933	1.14704	1.12190	1.10594	1.08859	1.06986	1.04976	1.02831

[a] Determined from literature data (4).
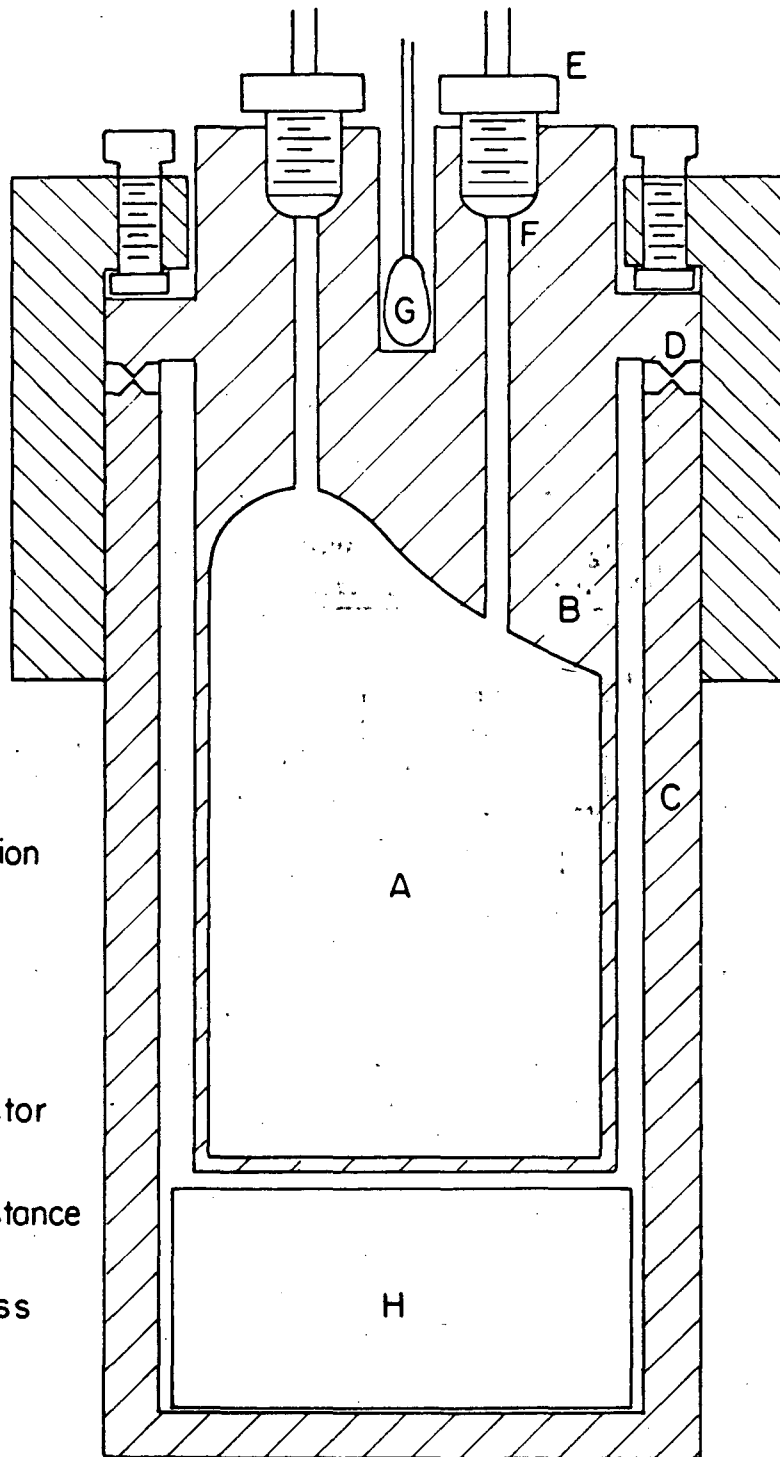
Figure Captions

Figure 1. Schematic diagram of high pressure dilatometer.

Figure 2. Schematic diagram of high pressure solution cell.

High Pressure Dilatometer
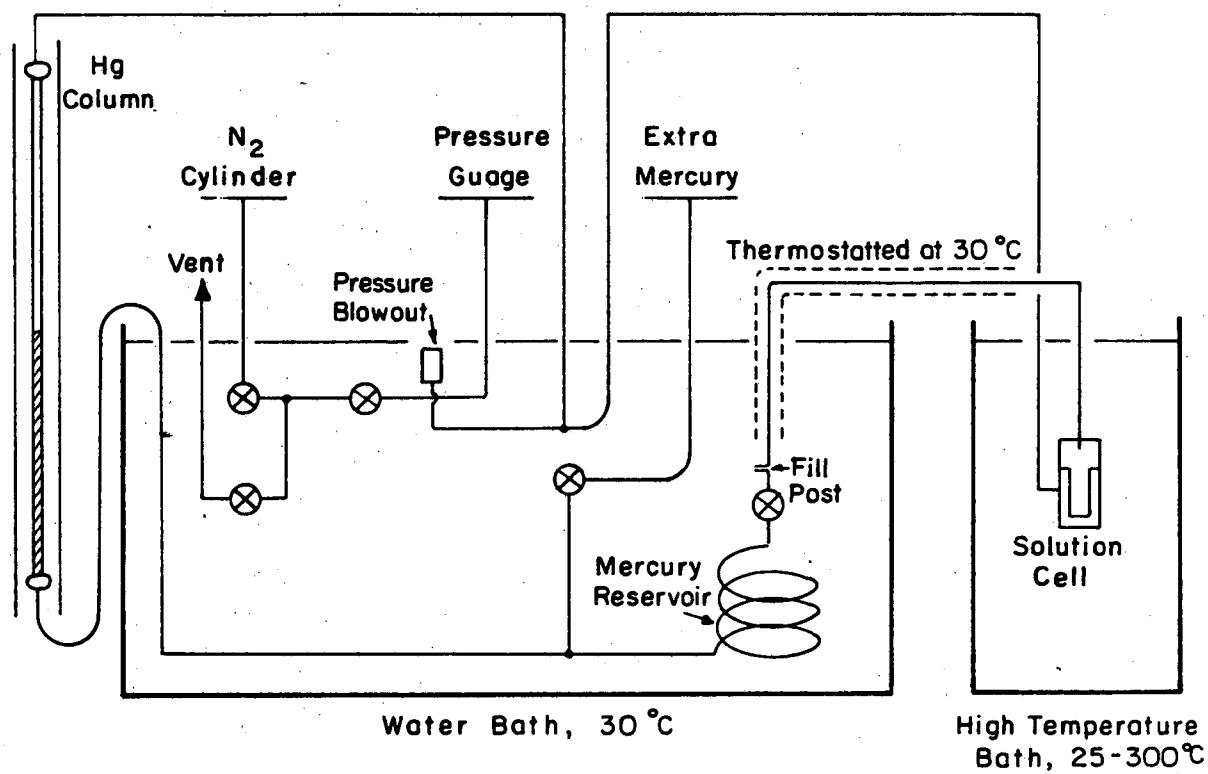
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A Aqueous solution
B Inner vessel
C Outer vessel
D Copper seal
E Swage type
  tubing connector
F Cone
G Platinum resistance
  thermometer
H Thermal mass

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