VII

Solutions

EXPERIMENT 9
Partial Molar Volume

In this experiment the partial molar volumes of sodium chloride solutions will be calculated as a function of concentration from densities measured with a pycnometer.

THEORY

Most thermodynamic variables fall into two types. Those representing *extensive* properties of a phase are proportional to the amount of the phase under consideration; they are exemplified by the thermodynamic functions V, E, H, S, A, G. Those representing *intensive* properties are independent of the amount of the phase; they include p and T. Variables of both types may be regarded as examples of homogeneous functions of degree l: that is, functions having the property

$$f(kn_1, \ldots, kn_i, \ldots) = k^l f(n_1, \ldots, n_i, \ldots) \tag{1}$$

where n_i represents for our purposes the number of moles of component i in a phase. Extensive variables are functions of degree 1 and intensive variables are functions of degree 0.

Among intensive variables important in thermodynamics are *partial molar quantities,* defined by the equation

$$\bar{Q}_i = \left(\frac{\partial Q}{\partial n_i}\right)_{p,T,n_{j \neq i}} \tag{2}$$

where Q may be any of the extensive quantities already mentioned. For a phase of one component, partial molar quantities are identical with so-called molar quantities, $\tilde{Q} = Q/n$. For an ideal gaseous or liquid solution, certain partial molar quantities ($\bar{V}_i, \bar{E}_i, \bar{H}_i$) are equal to the respective molar quantities for the pure components while others ($\bar{S}_i, \bar{A}_i, \bar{G}_i$) are not. For nonideal solutions all partial molar quantities differ in general from the corresponding molar quantities, and the differences are frequently of interest.

A property of great usefulness possessed by partial molar quantities derives from Euler's theorem for homogeneous functions, which states that, for a homogeneous function $f(n_1, \ldots, n_i, \ldots)$ of degree l,

$$n_1 \frac{\partial f}{\partial n_1} + n_2 \frac{\partial f}{\partial n_2} + \cdots + n_i \frac{\partial f}{\partial n_i} + \cdots = lf \tag{3}$$

Applied to an extensive thermodynamic variable Q, for which $l = 1$, we see that

$$n_1 \bar{Q}_1 + n_2 \bar{Q}_2 + \cdots + n_i \bar{Q}_i + \cdots = Q \tag{4}$$

Equation (4) leads to an important result. If we form the differential of Q in the usual way,

$$dQ = \frac{\partial Q}{\partial n_1} dn_1 + \cdots + \frac{\partial Q}{\partial n_i} dn_i + \cdots + \frac{\partial Q}{\partial p} dp + \frac{\partial Q}{\partial T} dT$$

and compare it with the differential derived from Eq. (4),

$$dQ = \bar{Q}_1 \, dn_1 + \cdots + \bar{Q}_i \, dn_i + \cdots + n_1 \, d\bar{Q}_1 + \cdots + n_i \, d\bar{Q}_i + \cdots$$

we obtain

$$n_1 \, d\bar{Q}_1 + \cdots + n_i \, d\bar{Q}_i + \cdots - \left(\frac{\partial Q}{\partial p}\right)_{n_i,T} dp - \left(\frac{\partial Q}{\partial T}\right)_{n_i,p} dT = 0 \tag{5}$$

For the important special case of constant pressure and temperature,

$$n_1 \, d\bar{Q}_1 + \cdots + n_i \, d\bar{Q}_i + \cdots = 0 \qquad (\text{const } p \text{ and } T) \tag{6}$$

This equation tells us that changes in partial molar quantities (resulting of necessity from changes in the n_i) are not all independent. For a binary solution we can write

$$\frac{d\bar{Q}_2}{d\bar{Q}_1} = -\frac{X_1}{X_2} \tag{7}$$

where the X_i are *mole fractions,* $X_i = n_i/\Sigma \, n_i$. In application to free energy, this equation is commonly known as the Gibbs–Duhem equation.

We are concerned in this experiment with the partial molar volume $\bar{V}_i$, which may be thought of as the increase in the volume of an infinite amount of solution (or an amount so large that insignificant concentration change will result) when 1 mole of component i is added. This is by no means necessarily equal to the volume of 1 mol of pure i.

Partial molar volumes are of interest in part through their thermodynamic connection with other partial molar quantities such as partial molar Gibbs free energy, known also as *chemical potential.* An important property of chemical potential is that for any given component it is equal for all phases that are in equilibrium with each other. Consider a system

containing a pure solid substance (e.g., NaCl) in equilibrium with the saturated aqueous solution. The chemical potential of the solute is the same in the two phases. Imagine now that the pressure is changed isothermally. Will the solute tend to go from one phase to the other, reflecting a change in solubility? For an equilibrium change at constant temperature involving only expansion work, the change in the Gibbs free energy G is given by

$$dG = V \, dp \tag{8}$$

Differentiating with respect to n_2, the number of moles of solute, we obtain

$$d\bar{G}_2 = \bar{V}_2 \, dp \tag{9}$$

where the partial molar free energy (chemical potential) and partial molar volume appear. For the change in state

$$NaCl(s) = NaCl(aq)$$

we can write

$$d(\Delta\bar{G}_2) = \Delta\bar{V}_2 \, dp$$

or

$$\left[\frac{\partial(\Delta\bar{G}_2)}{\partial p}\right]_T = \Delta\bar{V}_2 \tag{10}$$

Thus, if the partial molar volume of solute in aqueous solution is greater than the molar volume of solid solute, an increase in pressure will increase the chemical potential of solute in solution relative to that in the solid phase; solute will then leave the solution phase until a lower, equilibrium solubility is attained. Conversely, if the partial molar volume in the solution is less than that in the solid, the solubility will increase with pressure.

Partial molar volumes, and in particular their deviations from the values expected for ideal solutions, are of considerable interest in connection with the theory of solutions, especially as applied to binary mixtures of liquid components, where they are related to heats of mixing and deviations from Raoult's law.

METHOD[1]

We see from Eq. (4) that the total volume V of an amount of solution containing 1 kg (55.51 mol) of water and m mol of solute is given by

$$V = n_1\bar{V}_1 + n_2\bar{V}_2 = 55.51\bar{V}_1 + m\bar{V}_2 \tag{11}$$

where the subscripts 1 and 2 refer to solvent and solute, respectively. Let $\tilde{V}_1^0$ be the molar volume of pure water ($= 18.016$ g mol^{-1}/0.997044 g cm$^{-3} = 18.069$ cm^3 mol^{-1} at 25.00°C). Then we define the *apparent molar volume* ϕ of the solute by the equation

$$V = n_1\tilde{V}_1^0 + n_2\phi = 55.51\tilde{V}_1^0 + m\phi \tag{12}$$

which can be rearranged to give

$$\phi = \frac{1}{n_2}(V - n_1\tilde{V}_1^0) = \frac{1}{m}(V - 55.51\tilde{V}_1^0) \tag{13}$$

Now

$$V = \frac{1000 + mM_2}{d} \text{ cm}^3 \tag{14}$$

and

$$n_1 \tilde{V}_1^0 = \frac{1000}{d_0} \text{ cm}^3 \tag{15}$$

where d is the density of the solution and d_0 is the density of pure solvent, both in units of g cm^{-3}, M_2 is the solute molar mass in grams, and 1000 g is the mass of water containing m mol of solute. Substituting Eqs. (14) and (15) into Eq. (13), we obtain

$$\phi = \frac{1}{d}\left(M_2 - \frac{1000}{m} \frac{d - d_0}{d_0} \right) \tag{16}$$

$$= \frac{1}{d}\left(M_2 - \frac{1000}{m} \frac{W - W_0}{W_0 - W_e} \right) \tag{17}$$

In Eq. (17), the directly measured weights of the pycnometer—W_e when empty, W_0 when filled to the mark with pure water, and W when filled to the mark with solution—are used. This equation is preferable to Eq. (16) for calculation of ϕ, as it avoids the necessity of computing the densities to the high precision that would otherwise be necessary in obtaining the small difference $d - d_0$.

Now, by the definition of partial molar volumes and by use of Eqs. (11) and (12),

$$\bar{V}_2 = \left(\frac{\partial V}{\partial n_2} \right)_{n_1, T, p} = \phi + n_2 \frac{\partial \phi}{\partial n_2} = \phi + m \frac{d\phi}{dm} \tag{18}$$

Also

$$\bar{V}_1 = \frac{1}{n_1}\left(n_1 \tilde{V}_1^0 - n_2^2 \frac{\partial \phi}{\partial n_2} \right) = \tilde{V}_1^0 - \frac{m^2}{55.51} \frac{d\phi}{dm} \tag{19}$$

We might proceed by plotting ϕ versus m, drawing a smooth curve through the points, and constructing tangents to the curve at the desired concentrations in order to measure the slopes. However, for solutions of simple electrolytes, it has been found that many apparent molar quantities such as ϕ vary linearly with $\sqrt{m}$, even up to moderate concentrations.[2] This behavior is in agreement with the prediction of the Debye–Hückel theory for dilute solutions.[3] Since

$$\frac{d\phi}{dm} = \frac{d\phi}{d\sqrt{m}} \frac{d\sqrt{m}}{dm} = \frac{1}{2\sqrt{m}} \frac{d\phi}{d\sqrt{m}} \tag{20}$$

we obtain from Eqs. (18) and (19),

$$\bar{V}_2 = \phi + \frac{m}{2\sqrt{m}} \frac{d\phi}{d\sqrt{m}} = \phi + \frac{\sqrt{m}}{2} \frac{d\phi}{d\sqrt{m}} = \phi^0 + \frac{3\sqrt{m}}{2} \frac{d\phi}{d\sqrt{m}} \tag{21}$$

$$\bar{V}_1 = \tilde{V}_1^0 - \frac{m}{55.51}\left(\frac{\sqrt{m}}{2} \frac{d\phi}{d\sqrt{m}} \right) \tag{22}$$

where ϕ^0 is the apparent molar volume extrapolated to zero concentration. Now one can plot ϕ versus $\sqrt{m}$ and determine the best straight line through the points. From the slope $d\phi/d\sqrt{m}$ and the value of ϕ^0, both $\bar{V}_1$ and $\bar{V}_2$ can be obtained.

EXPERIMENTAL

Make up 200 mL of approximately 3.2 m (3.0 M) NaCl in water. Weigh the salt accurately and use a volumetric flask; then pour the solution into a dry flask. If possible, prepare this solution in advance (since the salt dissolves slowly). Solutions of $\frac{1}{2}, \frac{1}{4}, \frac{1}{8}$, and $\frac{1}{16}$ of the initial molarity are to be prepared by successive volumetric dilutions; for each dilution pipette 100 mL of solution into a 200-mL volumetric flask and make up to the mark with distilled water.

Rinse the pycnometer with distilled water and dry it thoroughly before each use. Use an aspirator, and rinse and dry by suction; use a few rinses of acetone to expedite drying. The procedure given here is for the Ostwald–Sprengel type of pycnometer; the less accurate but more convenient stopper type can be used with a few obvious changes in procedure.† To fill, dip one arm of the pycnometer into the vessel containing the solution (preferably at a temperature *below* 25°C) and apply suction by mouth with a piece of rubber tubing attached to the other arm. Hang the pycnometer in the thermostat bath (25.0°C) with the main body below the surface but with the arms emerging well above. Allow at least 15 min for equilibration. While the pycnometer is still in the bath, adjust menisci to fiducial marks with the aid of a piece of filter paper. Remove the pycnometer from the bath and quickly but thoroughly dry the outside surface with a towel and filter paper. Weigh the pycnometer.

The pycnometer should be weighed empty and dry (W_e), and also with distilled water in it (W_0), as well as with each of the solutions in it (W). It is advisable to redetermine W_e and W_0 as a check, inasmuch as the results of all runs depend on them. All weighings are to be done on an analytical balance to the highest possible precision.

As an alternative and very convenient procedure, one can use a Cassia volumetric flask instead of a pycnometer. Although the precision of density measurements made with this flask is not as good as that obtainable with the Ostwald–Sprengel pycnometer, it is adequate for the present purposes. The Cassia flask, shown in Fig. 1c, is a special glass-stoppered volumetric flask with 0.1-mL graduations between 100 mL and 110 mL, calibrated to contain the indicated volume to within ±0.08 mL. Since this flask is 26 cm high and will weigh over 120 g when full, it must be weighed on a top-loading balance. A high-quality balance of this type, capable of weighing to within ±0.01 g, is required.

The Cassia flask should be weighed empty and dry (W_e) and twice with distilled water in it, once with the level near 100 mL (W_0) and once with the level near 105 mL (W_0'). It should then be weighed with each of the solutions in it (W) to a level just above 100 mL. In every case, record the liquid-volume reading to within ±0.05 mL (V_0, V_0', V for each solution). As with the pycnometers, the Cassia flask must be rinsed well and dried prior to each filling. The filled flask is then thermally equilibrated in a constant-temperature bath (25°C) for at least 15 min. On removing the flask from the bath, dry the outside thoroughly before weighing. Since more solution is required to fill a Cassia flask than a pycnometer, you will need *at least* 225 mL of the 3 M stock solution. Using two 200-mL volumetric

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†The filling of a Weld-type pycnometer must be carried out with great care. The temperature of the laboratory must be below the temperature at which the determination is to be made. Fill the pycnometer body with the liquid, and seat the capillary stopper firmly. Wipe off excess liquid around the tapered joint, cap the pycnometer, and immerse it in the thermostat bath to a level just below the cap. When temperature equilibrium has been reached, remove the cap, wipe off the excess liquid from the capillary tip, being careful not to draw liquid out of the capillary, and remove the pycnometer from the bath. As the pycnometer cools to room temperature, the liquid column in the capillary will descend; be careful not to heat the pycnometer with your hands, since this will force liquid out of the capillary. Carefully clean and wipe off the whole pycnometer, including the cap but not including the tip of the stopper. Cap the pycnometer, place it in the balance, and allow it to stand about 10 min before weighing.
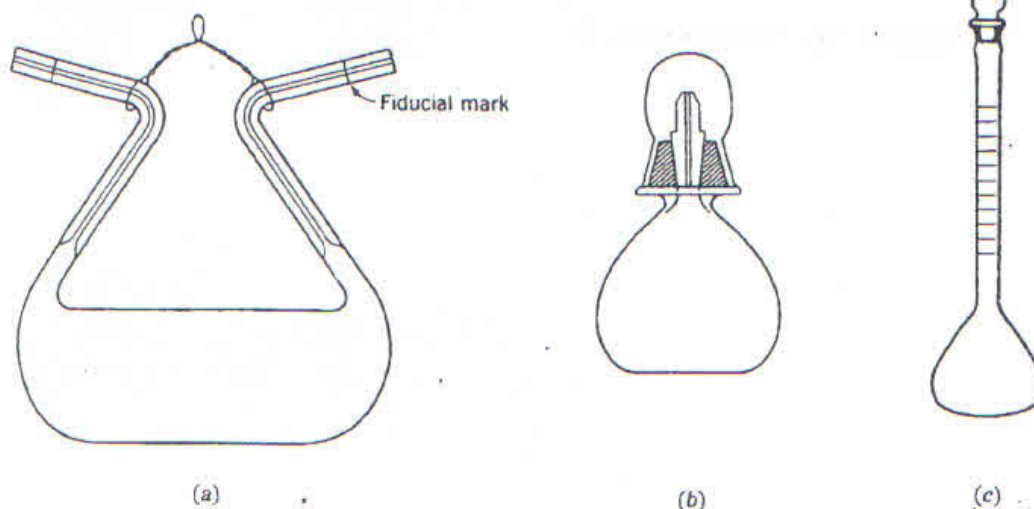
FIGURE 1
Pycnometers:
(*a*) Ostwald–Sprengel type;
(*b*) Weld (stopper) type;
(*c*) Cassia volumetric flask
(not drawn to scale).

flasks and two pipettes (one 50-mL and one 100-mL), you can prepare all the dilutions required.

CALCULATIONS

The success of this experiment depends greatly on the care with which the computations are carried out. For this reason, use of a spreadsheet program for analyzing the data is strongly recommended. If the work is done by two or more students, the partners are encouraged to work together, performing the same calculations independently and checking results after each step.

Calculate the density d of every solution to within an accuracy of at least one part per thousand:

$$d = \frac{W_{\text{soln}}}{V} = \frac{W - W_e}{V} \tag{23}$$

If a pycnometer was used, determine its volume from $W_0 - W_e$ and the density d_0 of pure water at 25°C (0.997044 g cm^{-3}). If a Cassia flask was used, carry out this volume calculation for both fillings with water and compare your results with the direct volume readings V_0 and V_0'. If necessary devise a calibration procedure that can be applied to correct the Cassia volume readings obtained on the solutions.

The molalities m (concentration in moles per kilogram of solvent) that are needed for the calculations can be obtained from the molarities M (concentration in moles per liter of solution) obtained from the volumetric procedures by using the equation

$$m = \frac{1}{1 - (M/d)(M_2/1000)} \cdot \frac{M}{d} = \frac{1}{(d/M) - (M_2/1000)} \tag{24}$$

where M_2 is the solute molar mass (58.45 g mol^{-1}) and d is the experimental density in g cm^{-3} units.

Calculate ϕ for each solution using Eq. (17) for pycnometer data or Eq. (16) for Cassia flask data. Plot ϕ versus $\sqrt{m}$. Determine the slope $d\phi/d\sqrt{m}$ and the intercept ϕ^0 at $m = 0$ from the best straight line through these data points. This should be done with a linear least-squares fitting procedure.

Calculate $\bar{V}_2$ and $\bar{V}_1$ for $m = 0, 0.5, 1.0, 1.5, 2.0$, and 2.5. Plot them against m and draw a smooth curve for each of the two quantities.

In your report, present the curves (ϕ versus $\sqrt{m}$, $\bar{V}_2$ and $\bar{V}_1$ versus m) mentioned above. Present also in tabular form the quantities $d, M, m, (1000/m)(W - W_0)/(W_0 - W_e)$, and ϕ for each solution studied. Give the values obtained for the pycnometer volume V_p and ϕ^0 and $d\phi/d\sqrt{m}$.
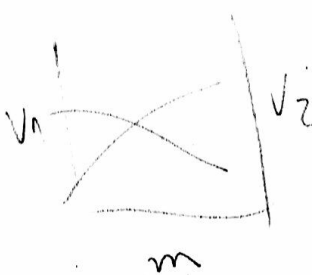
DISCUSSION

The density of NaCl(s) is 2.165 g cm^{-3} at 25°C. How will the solubility of NaCl in water be affected by an increase in pressure?

Discuss qualitatively whether the curves of $\bar{V}_1$ and $\bar{V}_2$ versus m behave in accord with Eq. (7).

SAFETY ISSUES

None.

APPARATUS

Pycnometer (approximately 70 mL) with wire loop for hanging in bath or Cassia flask; one or two 200-mL volumetric flasks; 100-mL pipette, and 50-mL pipette if a Cassia flask is used; pipetting bulb; 250-mL Erlenmeyer flask; one 250- and one 100-mL beaker; large weighing bottle; short-stem funnel; spatula; filter paper and gum-rubber tube (1 to 2 ft long) if an Ostwald–Sprengel pycnometer is used.

Constant-temperature bath set at 25°C; bath hardware for holding flasks and pycnometer; reagent-grade sodium chloride (35 g of solid or 200 mL of solution of an accurately known concentration, 50 g or 285 mL if a Cassia flask is used); acetone to be used for rinsing; cleaning solution.

REFERENCES

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GENERAL READING

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