

Partial Molal Volume

Purpose: Determine the partial molal volumes of sodium chloride and water in a series of solutions from 0.3 to 3.0 m.

Reading Assignment: Section 7.1, P. W. Atkins, *Physical Chemistry, 7th Ed.*

Introduction

Partial molal quantities tell us how the properties of solutions change with concentration. We need to know partial molal quantities for all the extensive properties of a solution, including V, G, H, S, and A. For example, the partial molal volume is important in oceanography and aquatic environmental science, which is why we measure the partial molal volume of NaCl solutions in this lab. Another example is that partial molal volume is needed in biochemistry for careful calculations of the molecular weights of proteins and nucleic acids using ultracentrifugation. The partial molal Gibbs Free energy, which is called the chemical potential, is central to the study of solutions.

Take an example of a two-component solution with n_1 moles of component 1 and n_2 moles of component 2. The change in Gibbs Free Energy with concentration at constant temperature and pressure is

$$dG = \left(\frac{\partial G}{\partial n_1}\right)_{n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{n_1} dn_2 \quad 1$$

The partial molal Gibbs Free Energy with respect to changes in the number of moles of component 1 is

$$\left(\frac{\partial G}{\partial n_1}\right)_{n_2} = \mu_1 \quad 2$$

The partial molal Gibbs Free Energy is the Gibbs Free Energy per mole of compound in the solution. The partial molal Gibbs Free Energy with respect to changes in the number of moles of component 2 is

$$\left(\frac{\partial G}{\partial n_2}\right)_{n_1} = \mu_2 \quad 3$$

Substituting these definitions into Equation 1 gives:

$$dG = \mu_1 dn_1 + \mu_2 dn_2 \quad 4$$

which determines the change in Gibbs Free Energy for changes in concentration. The important

point is that the partial molal properties depend on concentration. Hence knowing the concentration dependence is crucial for understanding solutions.

Of all the extensive thermodynamic properties, the volume is the easiest to visualize; this also holds true for the partial molal volumes, which are defined as

$$\left(\frac{\partial V}{\partial n_1}\right)_{n_2} = V_1 \quad \text{and} \quad \left(\frac{\partial V}{\partial n_2}\right)_{n_1} = V_2 \quad 5$$

The partial molal volume of component 1 is the volume per mole of compound 1 in the solution. Similarly, the partial molal volume of component 2 is the volume per mole of compound 2 in the solution. The total change in volume for changes in the concentration of the solution is

$$dV = \left(\frac{\partial V}{\partial n_1}\right)_{n_2} dn_1 + \left(\frac{\partial V}{\partial n_2}\right)_{n_1} dn_2 \quad 6$$

More compactly, using Eqs. 5 we write:

$$dV = V_1 dn_1 + V_2 dn_2 \quad 7$$

To integrate this expression we need to note that V_1 and V_2 depend on concentration, so we must be careful to do the integrals in a way that keeps the concentration of the solution constant. To do this, we simply add the two components together keeping the concentration the same as we add the total number of moles of both components; drop by drop we add 1 to 2 in the proper ratio so that the solution always has the same concentration, Figure 1. The integral is then said to be done at constant composition¹.

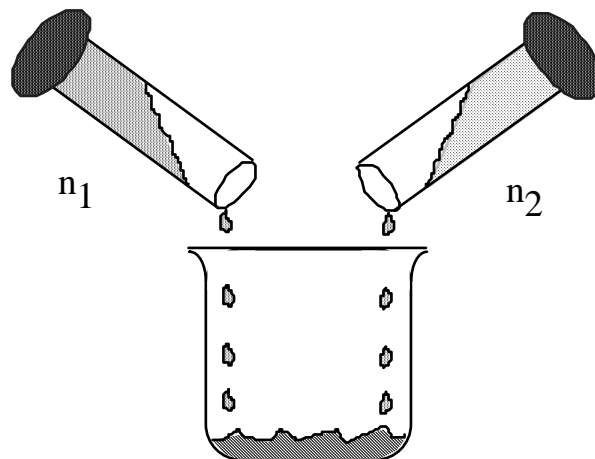


Figure 1. Integration at constant composition can be viewed as adding the components of the solution at the same time, always at the same concentration until n_1 moles of 1 and n_2 moles of 2 have been added to the beaker.

Since V_1 and V_2 are now constants, the integrated form of this equation is

$$V = n_1 V_1 + n_2 V_2 \quad 8$$

This equation is an interesting and surprisingly simple result. Let us see why.

Partial Molal Volume of Some Real Solutions²

If a solution is ideal, then its volume is just the sum of the volumes of the pure solute and pure solvent:

$$V = n_1 V_{m,1}^* + n_2 V_{m,2}^* \quad 9$$

where $V_{m,1}^*$ is the molar volume of pure component 1 and $V_{m,2}^*$ is the molar volume of pure component 2. Benzene and toluene form an ideal solution. The volume of 1 mole pure benzene is 88.9 ml; the volume of 1 mole pure toluene is 106.4 ml. Equation 8 states that 88.9 ml benzene mixed with 106.4 ml toluene results in 88.9 ml + 106.4 ml, or 195.3 ml of solution. Common sense suggests that the volumes add up, since the volumes of substances in solution are extensive properties.

On the other hand, water and ethanol do not form an ideal solution. The volume of 1 mole pure ethanol is 58.0 ml and the volume of 1 mole pure water is 18.0 ml. However, 1 mole water mixed with 1 mole ethanol does not result in 58.0 ml + 18.0 ml, or 76.0 ml, but rather 74.3! According to Equation 7, it is the partial molal volumes that are additive or extensive properties. When the mole fraction is 0.5, the partial molal volume of ethanol is 57.4 ml and the partial molal volume of water is 16.9 ml. With Equation 8, we can now calculate the volume of the solution:

$$1 \text{ mole} \times 57.4 \text{ ml/mol} + 1 \text{ mole} \times 16.9 \text{ ml/mol} = 74.3 \text{ ml} \quad 10$$

which is exactly what is observed. Note that the values just cited for the partial molal volumes of ethanol and water are only for a particular concentration; in this case, the mole fraction equal 0.5 and applies only to the water-ethanol system.

Apparent Molal Volume^{2,3}

The apparent molal volume of the solute, ϕ_V , is closely related to the partial molal volume of the solute. The apparent molal volume is often more useful in conjunction with other experiments than the partial molal volume itself. For example, in pressure perturbation calorimetry and analytical ultracentrifugation the apparent molal or specific volume is used. The apparent molal volume is commonly quoted in the literature and tabulated. The experimental determination of partial molal volumes is, in principle, quite simple and involves the careful measurement of the densities of solutions of known concentrations. The calculations in the past⁴ were simplified by the use of the apparent molal volume. Currently, polynomial curve fitting allows the calculation of the partial molal properties more directly. So we should also determine the apparent molal

volume. Consider the volume of a solution as n_2 moles of a solute are added to a fixed n_1 moles of solvent. The volume of the solution might change as shown in Figure 2. The volume due to the added solute (per mole) is called the apparent molal volume ϕ_V .

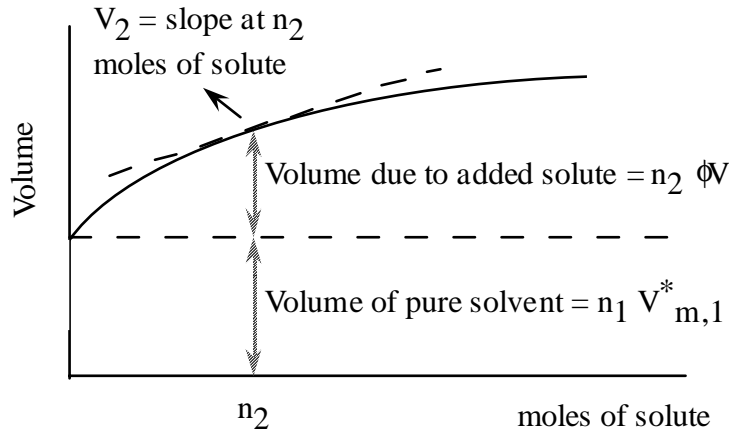


Figure 2. How the total volume of a solution V depends on the volume of the pure solvent and the apparent molal volume of the solute ϕ_V .

Figure 2 shows that

$$\phi_V = \frac{V_{\text{solution}} - V_{\text{solvent}}}{\text{moles of solute}} \quad 11$$

or

$$\phi_V = \frac{V - n_1 V_{m,1}^*}{n_2} \quad 12$$

Thus, in Figure 2, the volume V of the solution at any particular added n_2 moles of solute is given by a rearrangement of Equation 12:

$$V = n_1 V_{m,1}^* + n_2 \phi_V \quad 13$$

The apparent molal volume differs from the partial molal volume in that for the partial molal volume, the volume effects are divided between the solute and the solvent. In other words, the partial molal volume of the solute is the effective volume of the solute and the partial molal volume of the solvent includes the changes in volume of the solvent that are caused by the interaction with the solute. Eq. 13 shows that the apparent molal volume takes a different perspective. The effective volume of the solvent is assumed to remain the pure molar volume, while all of the volume changes in solution are accounted for in the apparent molal volume of the solute. In a sense, partial molal volume is more “democratic” with the volume effects shared between the solvent and solute, while the apparent molal volume ascribes all the volume changes to the solute alone. In application, the choice between partial and apparent molal volume depends on the experimental reference point.

The apparent specific volume, v , is the apparent volume on a per gram basis instead of a per mole basis, $v = \phi_V/M_2$, where M_2 is the molar mass of the solute. The apparent specific volume is

$v = \phi_V/M_2$ or it can also be calculated directly by

$$v = \frac{V - (V d_{\text{soln}} - w)/d_1}{w} \quad 14$$

For organic ionic compounds, such as amino acids, the apparent specific volume is often quite close to 0.7 mL/g.

Partial and Apparent Molal Volumes from Density Measurements

The Solute. We need to relate the partial molal volume to the molality m and the density d of the solution. The volume V of solution can be expressed as

$$V = \frac{\text{Wt. solvent} + \text{Wt. solute}}{d} \quad 15$$

Since density is an intensive quantity we can choose any amount of solution as a starting point. If we choose an amount of solution containing 1kg of solvent then the number of moles of solute in that same solution is $n_2 = m(1\text{kg})$, where m is the molality. Then the volume for the solution containing 1kg of solvent is

$$V^{1\text{kg}} = \frac{n_1 M_1 + n_2 M_2}{d} = \frac{1000 + m(1\text{kg})M_2}{d} \quad 16$$

where M_1 and M_2 are the molar masses of the solvent and solute, respectively. We then fit the volumes to a cubic polynomial in the molality:

$$V^{1\text{kg}} = a m^3 + b m^2 + c m + d \quad 17$$

To calculate the partial molal volume of the solute, we need to take the derivative of Equation 16:

$$V_2 = \left(\frac{\partial V}{\partial n_2}\right)_{n_1} = \left(\frac{\partial V}{\partial m}\right)_{n_1} \left(\frac{\partial m}{\partial n_2}\right)_{n_1} = \left(\frac{\partial V}{\partial m}\right)_{n_1} \frac{1}{\text{kg}} \quad 18$$

because the molality is just the number of moles of 2 in 1kg of solvent.

Then, taking the derivative of Equation 16 gives:

$$V_2 = \left(\frac{\partial V}{\partial n_2}\right)_{n_1} = \left(\frac{\partial V}{\partial m}\right)_{n_1} = 3 a m^2 + 2 b m + c \quad 19$$

To calculate the apparent molal volume, the term $n_1 V_{m,1}^*$ in Equation 12 is just the volume of the pure solvent; when the concentration is expressed in molality, the mass of solvent is 1000 g, so the volume of the solvent is

$$n_1 V_{m,1}^* = 1000/d_1 \quad 20$$

Substitution of $n_1 V_{m,1}^*$ from Equation 19 into Equation 12 gives us our working equation for experimentally measuring ϕ_V , the apparent molal volume, with n_2 equal to $m(1\text{kg})$:

$$\phi_v = \frac{V^{1\text{kg}} - 1000/d_1}{m(1\text{ kg})} \quad 21$$

where d_1 is the density of the pure solvent.

where w is the weight in grams of the solute in volume V of solution, for any volume of solution.

The Solvent. In order to calculate to calculate the partial molal volume of the solvent, we simply use the total volume and the partial molal volume of the solute and Equation 8. For V the volume of the solution containing 1kg of solvent, and $n_2 = m(1\text{kg})$, then Equation 8 becomes:

$$V^{1\text{kg}} = (1000/M_1) V_1 + m(1\text{kg}) V_2 \quad 22$$

Measuring the Density. The density will be measured using a density meter. The meter has a glass U-tube that is filled with the sample. The U-tube is made to vibrate and the vibration frequency is measured. The vibration frequency is a sensitive measure of the density of the solution. The more dense the solution, the smaller the vibration frequency. The meter is computer controlled, and the computer converts the vibration frequency into the measured density using a polynomial calibration equation. Density is a strong function of temperature. The meter also determines the temperature and applies a correction for the density calculation. The meter is calibrated using reagent grade water.

To cause the U-tube to vibrate, a small magnet is glued onto the end of the U-tube. The magnet is placed in a coil that has an oscillating current in it, Figure 3. The frequency of the oscillating current is varied until the natural vibration frequency, that is the resonance frequency, of the U-tube is found. In operation, the density meter is very similar to the speaker on a stereo.

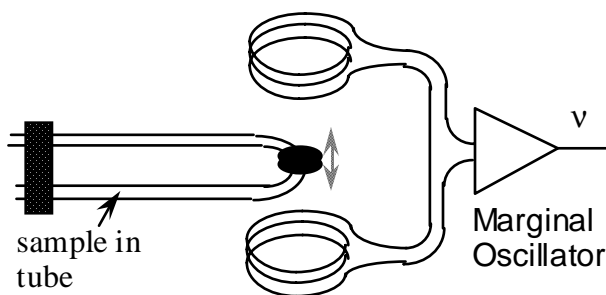


Figure 3. The operation of the density meter.

Experimental

Apparatus

In addition to sodium chloride, the experiment requires a Mettler density meter, five 50-ml stoppered flasks, and a constant temperature bath set to 25.0°C.

Procedure

Prepare about 25 ml of five solutions of sodium chloride in distilled water ranging in molal concentration from about 0.3 to 3.0. Weigh the solute with an analytical balance and solvent with a milligram balance into dry stoppered flasks. You should calibrate the density meter while you are making the solutions, to save time. Degass the sample for about a minute to avoid bubble formation in the density meter. Suspend the flasks in the 25°C bath to reach constant temperature.

The densities of the solutions are measured with a Mettler density meter that has been calibrated by determining the density of water (see tables in the CRC or page 6 of the meter instructions) at the temperature of the measurement using the following instructions. First, rinse the meter with a few portions of reagent grade water using the following steps. Fill the meter by dipping the inlet tube into the liquid and pulling the liquid into the oscillator U-tube using the syringe. Carefully examine the U-tube to ensure that there are no bubbles. Select "DENS" as the measured value by pressing the "MEAS" key and then pressing the Δ or ∇ . Monitor the density reading for 30 sec. If the reading doesn't stabilize there is an air bubble in the measurement U-tube: empty and refill if necessary. Press the "ENTER" and "CALIB" key simultaneously. The "CALIB" symbol will be flashing and "AUTO" is displayed. The automatic calibration is at an end when "MEAS" is again displayed, which can take a minimum of one minute and a maximum of 15 minutes.

Check the calibration by emptying the measuring tube and refilling with reagent grade water. If the difference between the measured and tabulated values is greater than 0.001 g/cm³, check to see that the measuring U-tube is clean and repeat the measurement. If the difference is less than 0.001 g/cm³, repeat the determination two more times and use the average difference between the measured and tabulated values to correct all subsequent readings.

Exercise extreme care in filling, rinsing, cleaning, and handling the meter.

Measure the density of the sodium chloride solutions, taking the same care used in calibrating the meter. Keep the sample flask immersed in the thermostat bath while filling the meter.

Results and Calculations

Equations 16-22 are all based on using the volume of the solution that contains 1 kg of solvent. Use Equation 16 to calculate the volume of each solution for 1000g of solvent. Fit the V using a cubic polynomial in m, Eqn. 17; include pure water in your fit. From the fit coefficients and Equation 18, calculate the partial molal volume of the solute at each molality. Then use Equation 22 to calculate the partial molal volume of the solvent for each solution. With Equation 21 calculate the apparent molal volumes of the solute for each solution^{6,7}. Plot the partial molal volumes versus m. Also, separately, plot the apparent molal volume versus m.

For the error analysis we need to get estimates of the uncertainty in the fit coefficients. Use the Nonlinear Least Squares Curve Fitting- 4 Parameters applet⁵ that calculates the uncertainties in the fit coefficients. Alternatively, you can also use a curve fitting spreadsheet that calculates the uncertainties. The cubest.xls spreadsheet has a link from the lab manual page. Based on the fit coefficient uncertainties, use significant figure rules or propagation of errors to calculate the uncertainty in a typical partial molal volume for one solution for the solute and the solvent.

Report

Tabulate all your information necessary to repeat your calculations. Include all the fit coefficients and their uncertainties. Report the uncertainty in a typical partial molal volume for one solution for the solute and the solvent. What is the predominant error in this experiment? How do your results compare to the literature values⁷? What is the chemical significance of this experiment? Why is this experiment important? Answer the following questions:

1. Is the total volume greater or less than the sum of the volume of the pure components?
2. Are the partial molal volumes of the solute and solvent greater or less than the pure molar volumes?
3. What forces in solution cause the differences that you see in questions 1 and 2? Draw a model of the solution using solute ions as spheres and water molecules as stick structures to aid in your explanation.

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