Physical Chemistry Laboratory I
CHEM 445
Experiment 2
Partial Molar Volume
(Revised, 01/13/03)

Volume is, to a good approximation, an additive property. Certainly this approximation is used in preparing solutions whose concentrations are not needed with a high degree of accuracy. However, the standard method of preparing solutions of accurately known concentrations is <u>not</u> the addition of a weighed amount of solid to a known volume of solvent, but the addition of solvent, with mixing, to a weighed amount of solid until the final volume reaches the desired value: 1.000 g{X}/10.00 mL H_2O and 1.000 g{X}/10.00 mL solution are not identical solutions.

If one adds salt to a full glass of water, does the water flow over the rim of the glass? According to Millero [1], it was reported in 1770 that the volume decreases when salts are added to a fixed volume of water. An early theory of electrolyte solutions (which may even be held by people today) is that when salts dissolve in water, they fill the empty space in the liquid. Obviously that theory is not correct. The general reduction in volume on adding a salt to water is attributed to electrostriction, the contraction in volume of the polar solvent around the ions.

If one takes 100.0 g C_2H_5OH (= 126.7 mL at 20.0 °C) and 900.0 g H_2O (= 901.6 mL at 20.0°C) and mixes these liquids, one obtains a solution with a density of 0.9820 g/mL (all density values from CRC Handbook of Chemistry and Physics) and an actual volume of 1018.3 mL, compared with the additive volume of 1028.3 mL. Consequently there is a <u>decrease</u> in volume of ~ 10 mL or ~ 1 % on mixing these two liquids. {See Ref. 2 for experiments showing the decrease in volume on mixing for some aqueous systems.} The fractional decrease in volume is an indication of the differences between intermolecular interactions of the two species.

Partial molar quantities are key elements in the thermodynamics of solutions. The most important of these is the partial molar free energy or chemical potential,

$$\mu_j \equiv \left(\frac{\partial G}{\partial n_j}\right)_{T,P,n\neq j} \tag{1}$$

However, the partial molar volume is the easiest to measure, and perhaps, to understand:

$$\overline{V_j} \equiv \left(\frac{\partial V}{\partial n_j}\right)_{T,P,n\neq j} \tag{2}$$

The standard treatment of partial molar quantities considers the differential change in that property with the addition of more (mol) of material. Hence, for volume, one has the following equation,

$$dV = \overline{V_1}\, dn_1 + \overline{V_2}\, dn_2 \tag{3}$$

The partial molar volume of each component, $\overline{V_j}$, is likely to be a function of concentration, but it does not depend on the total number of moles. Therefore, one can represent the total volume of the solution by the following equation,

$$V = n_1 \overline{V_1} + n_2 \overline{V_2} \tag{4}$$

In the subsequent discussions, the solvent (water, in these experiments) is component 1 and the salt (sample) is component 2. One can determine the volume of solution for a fixed amount of one component, n_l mol of solvent, and variable amounts of sample (in these experiments for 1000.0 g H_2O and molality, m, mol of sample). An aqueous solution of molality, m, contains m moles of salt per 1000 g of water. From the density of this solution, d, in g/mL, one may calculate the volume (in mL) of a solution that contains 1000 g of H_2O (or n_l = 1000/18.015 = 55.508 mol of water) and m (= n_2) mol of salt of molecular weight MW in g/mol:

$$V = \frac{1000 + m*(MW)}{d} \tag{5}$$

The data for volume as a function of molality, V{m}, can be fitted to an equation, generally a power series in m or $m^{1/2}$. The derivative of this function with respect to n_2 (or m mol of sample) is the partial molar volume of the sample as a function of molality, m. Again, m is the number of moles of sample for 1000 g of water.

$$\overline{V_2} = \left(\frac{\partial V}{\partial n_2}\right)_{T,P,n1} = \left(\frac{\partial V}{\partial m}\right)_{T,P} \tag{6}$$

Rearrange Eq. (4) to solve for $\overline{V_1}$, the partial molar volume of the solvent. Then replace $\overline{V_2}$ by its equivalent from Eq. (6). Because we are using the molality of aqueous solutions, n_2 = m and n_l = 1000/18.015 = 55.508 mol of H_2O. One obtains the following equation for the partial molar volume of the solvent, $\overline{V_1}$:

$$\overline{V_1} = \frac{1}{n_1}\left(V - n_2\overline{V_2}\right) = \frac{1}{n_1}\left(V - m\left(\frac{\partial V}{\partial m}\right)\right) \tag{7}$$

Because manipulation of numerical data wasn't always as easy as it is now and because of historical development, the partial molar volume of the sample, $\overline{V_2}$, is also obtained from another quantity, the apparent molar volume of the sample, φ. The apparent molar volume of the sample, φ, is calculated with the assumption that the molar volume of the solvent remains constant (is the same in solution as it is in the pure solvent) and any change in volume is due only to the sample. This assumption is false, but it fits a simplified picture of solvent/sample interactions in which only the sample properties change.

The definition of V remains the same (Equation 4); therefore,

$$V = n_1\overline{V^o{}_1} + m\varphi \tag{8}$$

In this equation n_2 = m, because we are considering m moles of sample in 1000 g of water (n_l = 1000/18.015 = 55.508 mol for all solutions; however, $\varphi \neq \overline{V_2}$, because $\overline{V_1} \neq \overline{V^o{}_1}$. That is, the partial molar volume of the solvent in the solution, $\overline{V_1}$, is not the same as the partial molar volume of the solvent in the pure solvent, $\overline{V_1^\circ}$, which is the volume occupied by one mole of water in pure water. However, Lim(φ{m}) as m → 0 = $\varphi^o = \overline{V^o{}_2}$.

For aqueous solutions at 25.0 °C, $n_1 \overline{V_1^o}$, is the volume of 1000 g of pure water: 1002.96 mL = 1000 g/(0.997044 g/mL). Consequently, φ, in mL, is very easy to calculate.

$$\phi = \frac{V - 1002.96}{m} \tag{9}$$

Because V is generally approximately 1000 mL/mol, the apparent partial molar volume, φ, is determined as a small difference between two large numbers. Consequently, very accurate data for V (and, therefore, of d) are required to obtain precise values for φ.

One can fit the data numerically to obtain φ{m} (that is, φ as a function of m), generally as a power series in m or $m^{½}$. If one differentiates V{m} from Equation (8) with respect to m, one obtains an equation to calculate the partial molar volume of the sample from φ{m},

$$\left(\frac{\partial \mathrm{V}}{\partial \mathrm{m}}\right)_{\mathrm{T,\,P}} = \overline{\mathrm{V}_2} = \varphi + \mathrm{m}\left(\frac{\partial \varphi}{\partial \mathrm{m}}\right)_{\mathrm{T,\,P}} \tag{10}$$

One can calculate $\overline{\mathrm{V}_1}$, the partial molar volume of the solvent, from φ as a function of molality, m, by combining Equations (4), (8), and (10), Remember that n_2 and m are the same, that n_1 = 1000/18.015 = 55.508 mol, and that $\overline{\mathrm{V}_1^\circ}$ = 1002.96/55.508=18.069 mL/mol at 25.0 °C

$$\overline{\mathrm{V}_1} = \overline{\mathrm{V}_1^\circ} - \left(\frac{\mathrm{m}^2}{\mathrm{n}_1}\right)\left(\frac{\partial \varphi}{\partial \mathrm{m}}\right) \tag{11}$$

In the past, calculations with large numbers of decimal places were difficult and it was advantageous to simplify the arithmetic to reduce rounding errors. Now, calculations with a large number of decimal places are easily done with a calculator, a spreadsheet, or another mathematical program. It is easy to carry out the individual steps with more decimal places than are warranted and to round back at the end to the accuracy warranted by the data.

The partial molar volumes of the salts, $\overline{\mathrm{V}_2}$, are functions of concentrations of the solutions. Using Debye-Huckel theory, one may extrapolate these values to infinite dilution, where ionic interactions are no longer observed and the extrapolated values for $\overline{\mathrm{V}^\circ_2}$ are related to properties of the solvated ions and their effects on the structure of water. Unfortunately, extrapolations to infinite dilution require very precise determinations of densities at low concentrations of salts because the densities are not very different from the density of pure water and the uncertainties in the measurements often give significant scatter to the data.

Partial molar volumes can be measured only for salts, not individual ions, but with models, one can assign values to individual ions. One convention to obtain values for individual ions is to assign $\overline{\mathrm{V}^\circ\{\mathrm{H}^+,\mathrm{aq}\}} = 0\ \mathrm{mL/mol}$. The values for ionic sizes are not the same as those obtained from crystalline radii because the ions are solvated in solution. The partial molar volumes at infinite dilution, $\overline{\mathrm{V}^\circ_i}$ for the alkyl ammonium ions, $C_nH_{2n+1}NH_3^+$ increase with increasing chain length and hence ionic size, as one would expect. The partial molar volumes at infinite dilution of the alkali metal ions increase with increasing atomic number as one would expect from trends in the periodic table, but $\overline{V^0\{Li^+\}}$ *and* $\overline{V^o\{Na^+\}}$ are negative! The partial molar volumes at infinite dilution of most multiply charged cations are negative. The partial molar volumes of most anions at infinite dilution are positive. [1]

Experimental Procedure:

Determine the densities of solutions of different concentrations of NaCl. The densities of these salt solutions and V{m}increase monotonically with increasing concentration, m or M. $CuSO_4$ or $CuSO_4.5H_2O$ is a more interesting salt to use because V{m} is not a monotonically increasing function of concentration, but more, and more accurate, data are needed to define the V{m} curve accurately for copper sulfate.

You will measure the densities by two methods. If the experiments are done properly, the densities obtained by the two methods will fit a single curve.

A. **<u>Use a 100 mL Cassia volumetric flask to determine the densities of the solutions</u>**.

This type of volumetric flask has graduations on the neck of the flask at 0.10 mL intervals, like a buret (and costs ~ $90, so be careful!). Consequently, you may read volumes of solutions over a range. The volumetric flask has been calibrated by the manufacturer at 20.0 ^{o}C; however, you should calibrate it at 25.0 ^{o}C. You will determine the volume of the flask from the weight (and, therefore, volume) of distilled water contained. (If you use more than one Cassia flask, keep the stoppers separate. They will not have identical weights.)

1. The flask should have been dried in the oven previous to your use to ensure that there is no liquid inside. To get the weight of the dry flask that is representative of these experiments, wet the outside of the flask with distilled water and then dry the outside of the flask thoroughly and weigh. Weigh the dry flask (with stopper) twice because this is a critical number that is used in all of your calculations, Weight 1. Use the analytical balance for these measurements. There may be differences in the last decimal place (± 0.1 mg or so), but your duplicate weights for the flask should not differ by more than ± 1 mg.

2. Fill the flask to the 100 mL mark (or slightly higher) with distilled water that is at a temperature slightly below 25.0 ^{o}C. Immerse the flask (with stopper) in the bath for ~ 15 minutes. Record the volume after the solution has equilibrated at 25.0 ^{o}C (which must be ≥ 100 mL) to ~ ± 0.02 mL (by interpolation between the 0.10 mL graduation marks as you did when reading burets for titrations in QUANT). Dry the outside of the flask and weigh on the analytical balance, Weight 2. Weigh twice: the two values should agree within a few mg, although perhaps not to ± 1 mg. The difference between Weight 1 and Weight 2 is the weight of water contained by the volumetric flask.

Use the density of water of 0.997044 g/mL at 25.0 ^{o}C to calculate the volume of the flask. This value should be very close to 100.00 mL (or whatever volume you read from the graduations on the neck of the flask), but it is unlikely to be exactly that value. From the weight of the water, ~ 100.xxx ± 0.00y g, the volume of the volumetric flask is known to an accuracy of better than 1/10,000.

3. Fill the volumetric flask to ~ 105 mL, immerse in the 25.0 ^{o}C bath for ~ 15 minutes, dry, and weigh (twice). Read the volume after equilibration to ~ ± 0.02 mL. Calculate the volume from the weight of water and its density as in 2. Make a two-point calibration curve or equation: Volume{calculated from density} vs. Volume{read from flask}.

4. You are to measure the densities of **five** solutions of NaCl of different concentrations from ~ 0.1 M to ~ 3.0 M. The densities of each solution should be reported to an accuracy of ~ 1/10,000, that is 1.00xx g/mL. The molarities of the solutions should be reported to four decimal places (the accuracy of the analytical balance): 1.xxxx mol/kg

Prepare the solutions by adding NaCl to the volumetric flask and weighing (analytical balance, ± 0.1 mg) then adding ~ 100 g H_2O (above the 100 mL mark) and weighing again (analytical balance, ± 0.1 mg). **Because the volumetric flask will be wet inside, you must obtain the weight of the wet flask before adding the salt**. Distilled water is not a contaminant here. Mix well until the salt dissolves and equilibrate at 25.0 ^{o}C for ~ 15 min. Read the volume of solution to ± 0.02 mL and calculate the correct volume from the two-point calibration curve obtained above. You can calculate both the molarity and molality directly from these measurements.

Begin with the most concentrated solution and finish with the least concentrated solution. The volumetric flask must be thoroughly rinsed with distilled water after each solution is prepared and its density measured. The flask cannot be dried on the inside. Distilled water is not a contaminant in preparing these solutions, **but each preceding solution is a contaminant**. Do not rinse with acetone and attempt to dry in the oven.

If you use more than one Cassia volumetric flask, you must calibrate each one. Be careful to remember which flask and which stopper you use for each density determination. The flasks and stoppers are not identical.

When you have completed the experiments, rinse the Cassia volumetric flask(s) **several times with distilled water. That is, fill partially and shake.** Put it (them) into the oven to dry so that they will be clean and dry for use in subsequent labs! Do not rinse with acetone. If you do not rinse the Cassia flasks thoroughly, a deposit of salt will appear on the inside of the flask and greatly annoy those who do the experiment after you.

B. Use a 25 mL pycnometer to measure the densities of solutions.

The pycnometer has a small capillary with a ground glass joint that fits into a small vial. Use a small amount of stopcock grease on the tapered joint of the capillary.

1. Determine the volume of the pycnometer as you determined the volume of the Cassia volumetric flask. Weigh the dry pycnometer and capillary on the analytical balance twice and use the average value. Then weigh (twice) the pycnometer and capillary filled with water

after it has equilibrated in the constant temperature bath for ~ 15 minutes (analytical balance). Calculate the volume of the pycnometer from the weight of water and the known density of water. The volume will be close to, but not exactly, 25.0000 mL. Each pycnometer has a number. Each capillary has a number. If you use two pycnometers, you must calibrate each one. Remember to keep the capillary and vial together. The weights and volumes of the pycnometers are not identical. Report the volume as 25.xxx ± 0.00x mL or 25.xxxx ± 0.000x mL, depending on the precision of your measurements. Use this value in your calculations.

2. Prepare **five** solutions of NaCl in water of concentrations similar to, but not the same as, the solutions in A. Prepare these by weight in a snap top jar using an analytical balance, ~ 60 g of water (to ± 0.1 mg) and an appropriate weight of salt. The molality is determined from the weights of water and salt. This amount of material will give enough solution to rinse the pycnometer and do two determinations of density, if necessary.

Begin with the most concentrated solution and finish with the least concentrated solution. Rinse the pycnometer with small amounts of each new solution. Both the preceding solution and distilled water are contaminants in this experiment. Fill the pycnometer and equilibrate at 25.0 ^{o}C with solutions that are initially at a temperature below 25.0 ^{o}C. Dry the outside of the pycnometer and weigh (analytical balance to ± 0.1 mg). Calculate the density of each solution.

When you have completed the experiment, rinse the pycnometer several times with distilled water to remove any remaining salt solution and place into the oven to dry.

Calculations and Discussion:

Present your primary data for experiments from the **Cassia flask** in a table that contains the weight of salt, the weight of water, the volume of the solution, the molarity, molality (four decimal places), and density for each solution (four decimal places). For the pycnometer experiments, present your primary data in a table as weight of salt, weight of solution, weight of water, volume of pycnometer (to 3 - 4 decimals), molality (four decimals), and density (four decimals).

Plot density vs. molality using a spreadsheet or other data analysis program. For the NaCl/H_2O system the density is a monotonically increasing function of molality, but not a linear function. Both sets of data should fit to a single, smooth curve. If your data do not give a smooth curve, check the calculations**. Make this plot before the second week for this experiment.** If your data are bad or inconsistent, repeat some density measurements.

Present your results in another table that contains molality, m; V = volume of solution containing 1000 g of water from Equation (5); and φ = apparent molar volume of the salt from Equation (9) for each solution. Identify the data from the Cassia flask and from the pycnometer.

Plot V{m} and φ\{m\} vs. m and vs. $m^{1/2}$ and fit the data to a power series in m and in $m^{1/2}$ with a spreadsheet or other program. V{m} and φ\{m\} are monotonically increasing, but not necessarily linear functions of m or $m^{1/2}$. If V{m} is not a monotonically increasing function of m, something is seriously wrong with your experimental data. Irregularities in a plot of ϕ\{m\} vs.

m may occur at the lowest concentrations because very accurate density measurements are needed to give reliable values for ϕ. (See Eq. (9).)

When you fit the data to an equation, check the deviations at each point to see if there is systematic variation that suggests another term in the power series. One uses the minimum number of terms in a power series that will fit the data. The empirical equations should be clearly identified in the text. Give uncertainties in the coefficients when possible.

In another table, present your results for each solution as molality and partial molar volume of salt and of water calculated by the different techniques given above. That is, one may calculate both $\overline{V_1}$ and $\overline{V_2}$, from $V\{m\}$ and from $\varphi\{m\}$. The values for each partial molar volume may be different depending on the method of analyzing the data. Plot $\overline{V_2}$ vs m and $m^{1/2}$ and extrapolate to zero (plot and data analysis) to obtain $\overline{V^o{}_2}$, the partial molar volume of NaCl at infinite dilution.

Compare your results with literature values.

The following data are taken from an old CRC Handbook of Chemistry and Physics for the density of aqueous NaCl solutions as a function of concentration. These densities were obtained at 20.0 ^{o}C and are not identical to your data. Calculate, tabulate, and plot these data: d{m}, V{m}, φ{m}, and $\overline{V_2}$ {m}. There is a relatively simple relation between M and m for any solution. In the following equation, d = density in g/mL (= kg/L) and MW is the molecular weight (relative molar mass) in g/mol:

$$m = \frac{M}{d - \frac{M * MW}{1000}}$$

Density of Aqueous NaCl
20.0 ^{o}C
CRC Handbook of Chemistry and Physics, 47th Ed, 1966-67

Molarity, mol/L	Density, g/mL
0	0.9982
.086	1.0017
.172	1.0053
.346	1.0125
.523	1.0195
.703	1.0267
.885	1.0340
1.069	1.0412
1.445	1.0559
1.734	1.0670
2.229	1.0857
2.637	1.1008
3.056	1.1162

References

1. F. J. Millero, Chem. Rev. 71, 147 (1971)
2. J. Olmsted, III, J. Chem. Ed.