

Determination of Partial Molar Volumes in Aqueous Solutions of Ionic Compounds

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Goal: Density data are presented for aqueous solutions of three ionic compounds. From this data graphs of the volumes of the solutions containing a fixed amount of solvent vs. moles of solute are constructed, and from these graphs the partial molar volumes with respect to the solutes are determined.

Prerequisites: An introductory knowledge of the thermodynamics of mixtures; a knowledge of the relationships among percent by mass, mass of solution, and mass of solute; and the ability to calculate volumes of solutions from their masses and densities.

Resources you will need: This exercise should be carried out within a software environment that is capable of data manipulation, that can graph an x-y data set and provides a choice of fitting functions, and that can display the equation for the fitting function.

Background:

The dependence of the extensive properties of a system (V , E , H , S , G , etc.) on its composition is given by what are called partial molar quantities. For a general extensive property F the partial molar value with respect to component i is given by

$$\bar{F}_i = \left(\frac{\partial F}{\partial n_i} \right)_{T, P, n_{j \neq i}} \quad (1)$$

In other words, \bar{F}_i equals the partial derivative of F with respect to the number of moles of i with temperature, pressure, and the number of moles of all other components held constant. If temperature and pressure are held constant, then

$$dF = \sum_i \bar{F}_i dn_i \quad (2)$$

In this exercise we will be looking at the volume of a two-component system consisting of water (w) and an ionic solute (s). In this case Equation 2 becomes

$$dV = \bar{V}_s dn_s + \bar{V}_w dn_w, \quad (3)$$

where

$$\bar{V}_s = \left(\frac{\partial V}{\partial n_s} \right)_{T, P, n_{\dots}} \quad (4)$$

and

$$\bar{V}_w = \left(\frac{\partial V}{\partial n_w} \right)_{T, P, n_s} \quad (5)$$

The integration of Equation 3 at constant temperature and pressure from n_s and n_w equal to zero to some final values of n_s and n_w , gives

$$V = \bar{V}_s n_s + \bar{V}_w n_w \quad (6)$$

Equation 6 gives the impression that \bar{V}_s and \bar{V}_w are the volumes of one mole of the solute and water respectively; however Equations 4 and 5 show that this is not true. These equations show that \bar{V}_s and \bar{V}_w are the *rates* at which the volume of the *whole solution changes* as the moles of solute or of water are changed while temperature, pressure, and the moles of the other are held constant. Evidence that \bar{V}_s and \bar{V}_w are not volumes will appear as you do the exercise.

Experimental Data:

Below are tables of densities and percent by mass of solute for aqueous solutions of three compounds: sodium chloride, sodium phosphate, and zinc sulfate. These data are taken from the CRC Handbook of Chemistry and Physics 66th edition (1985-1986) and are used with permission. The data all apply to solutions at 20°C and 1 atm of pressure.

NaCl		Na ₃ PO ₄		ZnSO ₄	
% NaCl	Density of Solution (g/mL)	% Na ₃ PO ₄ by Mass	Density of Solution (g/mL)	% ZnSO ₄ by Mass	Density of Solution (g/mL)
0.0	0.9982	0.0	0.9982	0.0	0.9982
0.4	1.0011	0.5	1.0042	0.5	1.0034
0.8	1.0039	1.0	1.0100	1.0	1.0085
1.2	1.0068	1.5	1.0158	1.5	1.0137
1.6	1.0096	2.0	1.0216	2.0	1.0190
2.0	1.0125	2.5	1.0275	2.5	1.0243
2.4	1.0153	3.0	1.0335	3.0	1.0296
2.8	1.0182	3.5	1.0395	3.5	1.0349
3.2	1.0211	4.0	1.0456	4.0	1.0403
3.6	1.0239	4.5	1.0517	4.5	1.0457
4.0	1.0268	5.0	1.0579	5.0	1.0511
4.4	1.0297	5.5	1.0642	5.5	1.0565
4.8	1.0326	6.0	1.0705	6.0	1.0620
5.2	1.0355	6.5	1.0768	6.5	1.0675
5.6	1.0384	7.0	1.0832	7.0	1.0730
6.0	1.0413	7.5	1.0896	7.5	1.0786
6.4	1.0442	8.0	1.0961	8.0	1.0842
6.8	1.0471			8.5	1.0899
7.2	1.0500			9.0	1.0956
7.6	1.0530			9.5	1.1013
8.0	1.0559			10.0	1.1071

8.4	1.0588				
8.8	1.0618				
9.2	1.0647				
9.6	1.0677				
10.0	1.0707				

Exercise:

Carry out the following steps for each of the three solutions (NOTE: sample calculations are given at the end of this exercise for the 0.4% NaCl solution):

1. Choose an amount of water (it doesn't matter how much as long as it is kept constant for all of the calculations on any given solution). 1000 grams is a value often used.
2. For each concentration of solute
 - a. Use the percent by mass to calculate the mass of solution containing your chosen mass of water.
 - b. Use your chosen mass of water and the mass of solution containing your chosen mass of water calculated in Step a to calculate the mass of solute in that mass of solution.
 - c. Convert the mass of solute calculated in Step b to moles.
 - d. Combine the density value for the given concentration and the mass of solution calculated in Step a to calculate the volume of solution that contains your chosen mass of water.
3. Plot a graph of the volume of solution (Step d) vs. moles of solute (Step c). This will be a graph of volume vs. moles of solute at constant temperature (20°C), pressure (1 atm), and moles of water (because the mass of water is constant throughout the calculations).
4. Experiment with fitting curves to your graph using different functional forms (polynomials of various orders, exponential, etc.) and see which gives the best fit to your data. When you have decided on the best fit, be sure to activate the option that displays the equation for that best fit on the graph.
5. Using the fitted equation for your graph and the definition from Equation 4, determine an equation for \bar{V}_s as a function of the number of moles of solute. Use that equation to evaluate \bar{V}_s for the number of moles of solute corresponding to concentrations of 1.0% and 6.0% solute by mass.

Questions:

1. Do the graphs of volume of solution vs. moles of solute have the same shape for all three solutions?
2. Is there anything unexpected in the way the volume changes as solute is added to any of the solutions? How might you account for any unexpected behavior that you observe?
3. Are the values of \bar{V}_s that you calculated in Step 5 all positive? If any of the values of are negative, what does that say about the validity of thinking of \bar{V}_s as a volume? Can volumes be negative?

Sample Calculations:

Below are the calculations relating to the 0.4% sodium chloride solution. The chosen mass of water is 1000 g.

Step a:

Mass of solution containing 1000 g water

$$= 1000\text{ g} \times \left(\frac{1}{1 - 0.004} \right) = 1004.016\text{ g}$$

Step b:

Mass of solute in the mass of solution calculated in step a

$$= 1004.016\text{ g} - 1000\text{ g} = 4.016\text{ g}$$

Step c:

Moles of solute corresponding to the mass calculated in step b

$$= \left(\frac{4.016\text{ g}}{58.44\text{ g/mol}} \right) = 0.06872\text{ mol}$$

Step d:

Volume of solution containing 1000 g water

$$= \left(\frac{1004.016\text{ g}}{1.0011\text{ g/mL}} \right) = 1002.9\text{ mL}$$

Suggestions for improving this web site are welcome. You are also encouraged to submit your own data-driven exercise to this web archive. All inquiries should be directed to the curator: Tandy Grubbs, Department of Chemistry, Unit 8271, Stetson University, DeLand, FL 32720.

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