

# Bartender's Conundrum: Partial Molar Volume in Water-Ethanol Mixtures

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**Goal:** Density measurements are presented at two temperatures (22 °C and 40 °C) for mixtures of water and ethanol. The data are analyzed in order to calculate the partial molar volumes of each component and the excess volume.

**Prerequisites:** An introductory knowledge of the thermodynamics of mixtures and using density data to determine the volume of a solution.

**Resources you will need:** This exercise should be carried out within a software environment that is capable of simple data manipulation and graphing.

## Background:

Every bartender knows well that mixing 50 ml of water with 50 ml of ethanol does not give an alcohol drink of 100 ml; the difference is called the excess volume. This excess volume can be expressed in terms of the mole fraction of either ethanol or water, and the magnitude of the excess volume provides a measure of non-ideal mixing of water and ethanol molecules. The existence of the excess volume indicates that molar volumes are non-additive. Instead, thermodynamics dictates that only the partial molar properties are additive.

Partial molar (or molal) quantities relate changes in extensive properties of the solution (such as  $V$ ,  $G$ ,  $H$ ,  $S$ , and  $A$ ) to changes in concentration. Of all the extensive thermodynamic properties, the volume is easiest to visualize.

For a two component system composed of A and B, the partial molar volumes are defined as

$$\bar{V}_A = \left( \frac{\partial V}{\partial n_A} \right)_{n_B} \quad (1)$$

and

$$\bar{V}_B = \left( \frac{\partial V}{\partial n_B} \right)_{n_A} \quad (2)$$

The total differential statement for volume changes in a two component mixture is therefore

$$dV = \bar{V}_A dn_A + \bar{V}_B dn_B \quad (3)$$

Integration of equation (3) gives the Euler relation

$$V = n_A \bar{V}_A + n_B \bar{V}_B \quad (4)$$

indicating that partial molar quantities are indeed additive.

The use of equation (4) requires an accurate knowledge of the partial molar volumes of each component at a given concentration. One of the simplest methods for experimentally determining partial molar volumes involves the careful measurement of solution density at two nearby concentrations. To see how this works,

consider two hypothetical liquid mixtures of A and B: (1) one containing 40% by weight A which has a solution density of 0.8800 g/mL and (2) another containing 50% by weight A which has a solution density of 0.8751 g/mL. Let us further assume that the molar masses of A and B are 35.00 g/mol and 24.00 g/mol, respectively. How do we use this information to determine the partial molar volume of component A?

We first need to think carefully about the meaning of partial molar volume that is implied by equations (1) and (2); the value of the partial derivative can be estimated by calculating how much the volume changes when the moles of only one component is changed by a small amount (holding the moles of the other component constant). Stated symbolically, the partial molar volume of A can be estimated as

$$\bar{V}_A = \left( \frac{\partial V}{\partial n_A} \right)_{n_B} \approx \left( \frac{\Delta V}{\Delta n_A} \right)_{n_B} = \left( \frac{V_2 - V_1}{n_{A,2} - n_{A,1}} \right)_{\text{per 1 mol B}} \quad (5)$$

In equation (5),  $V_2$  and  $V_1$  are the volumes occupied by the two mixtures per 1 mol of component B and  $n_{A,2}$  and  $n_{A,1}$  are the moles of component A per 1 mol of component B; these quantities, in turn, are obtained by dividing the actual volumes and the actual moles of A by the actual moles of B. Using the molar masses and densities from above, we have

#### WORKED EXAMPLE

1) 40% A Solution (assume 100 grams of solution):

$$n_A = 1.143 \text{ mol}, n_B = 2.500 \text{ mol}$$

$$n_{A,1} = n_A/n_B = 0.457$$

$$\text{mass(per 1 mol of B)} = [(0.457 \text{ mol} \times 35.0 \text{ g/mol})/1 \text{ mol}] + [(1.000 \text{ mol} \times 24.0 \text{ g/mol})/1 \text{ mol}] = 39.95 \text{ g/mol}$$

$$V_1 = (\text{mass})/(\text{density}) = (39.95 \text{ g/mol})/(0.8800 \text{ g/mL}) = 45.40 \text{ mL/mol}$$

2) 50% A Solution (assume 100 grams of solution):

$$n_A = 1.429 \text{ mol}, n_B = 2.083 \text{ mol}$$

$$n_{A,2} = n_A/n_B = 0.686$$

$$\text{mass(per 1 mol of B)} = [(0.686 \text{ mol} \times 35.0 \text{ g/mol})/1 \text{ mol}] + [(1.000 \text{ mol} \times 24.0 \text{ g/mol})/1 \text{ mol}] = 48.01 \text{ g/mol}$$

$$V_2 = (\text{mass})/(\text{density}) = (48.01 \text{ g/mol})/(0.8751 \text{ g/mL}) = 54.86 \text{ mL/mol}$$

Plugging into equation (5) yields the partial molar volume of A;

$$\bar{V}_A = \left( \frac{45.40 \text{ mL/mol} - 54.86 \text{ mL/mol}}{0.457 - 0.686} \right) = 41.3 \text{ mL/mol}$$

It is important to realize that this value of partial molar volume of A represents a numerical estimate (valid between the 40 – 50 weight percent A range).

In the exercise below, you will also calculate the excess molar volume,  $V_E$ , which is also related to solution density according to the following equation:

$$V^E = \frac{x_A M_A + x_B M_B}{\rho_L} - x_A V_{m,A} - x_B V_{m,B}$$

(6)

where  $\rho_L$  is the density of the mixture and  $x_A$ ,  $V_{m,A}$ ,  $M_A$ ,  $x_B$ ,  $V_{m,B}$  and  $M_B$  are the mole fraction, molar volume, and molecular weight of pure compounds A and B, respectively.

### Experimental Data:

The density of water-ethanol mixtures were measured by students at the UW-Green Bay campus using a precision density meter (Anton Paar DMA 4500, Ashland, VA). The exact theoretical details about how this instrument works will not be dealt with here. In brief, the instrument has a glass U-tube that is filled with the sample. The U-tube is made to resonate and the resultant vibration frequency is measured. The vibration frequency provides a sensitive measure of the density of the solution (i.e. the denser the solution, the smaller the vibration frequency). The apparatus 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, so the instrument also measures the temperature and applies a correction to the calculated density. The density meter is calibrated using reagent grade water. The temperature of the sample compartment can be varied, so the instrument is capable of measuring densities over a range of temperatures.

The following data was collected for ethanol-water mixtures at 22 °C and 40 °C.

<u>Weight % Ethanol</u>	<u>Density (g/mL) at 22 °C</u>	<u>Density (g/mL) at 40 °C</u>
0	0.99799	0.99220
10	0.98061	0.97060
20	0.96808	0.96130
30	0.95155	0.94160
40	0.93521	0.92070
50	0.91778	0.89863
60	0.89532	0.87070
70	0.86838	0.85213
80	0.84248	0.82622
90	0.81570	0.80074
100	0.78808	0.77240

### Exercise:

1. To calculate the excess volume,  $V_E$ , from equation (6), it is necessary to calculate  $V_{m,A}$  and  $V_{m,B}$ , which represent the molar volumes of water and ethanol, respectively, and  $x_A$  and  $x_B$ , which represent the corresponding mole fractions of water and ethanol. Using information about water and ethanol and the weight percent ethanol information in the table to generate a column of  $x_B$  values.
2. Next, generate  $V_E$  as a function of mole fraction of ethanol ( $x_B$ ) in ethanol-water binary mixtures at both 22°C and 40°C. Comment on the deviation of  $V_E$  from zero at both temperatures. At which temperature is the deviation of  $V_E$  from zero the greatest at each temperature?
3. Making sure that you first completely understand the WORKED EXAMPLE from above, calculate a value for partial molar volume of ethanol at each adjacent set of concentrations at both 22°C and 40°C (you should obtain 10 values for each temperature). Plot the partial molar volume of ethanol as a function of mole fraction

of ethanol at each temperature. Comment on the shapes of the curves.

4. Similarly, calculate values for the partial molar volume of water at each adjacent set of concentrations at each temperature and plot your results as a function of mole fraction of ethanol.

5. Convince yourself of the additivity rule of partial molar quantities implied by equation (4).

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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