Partial Molar Volume

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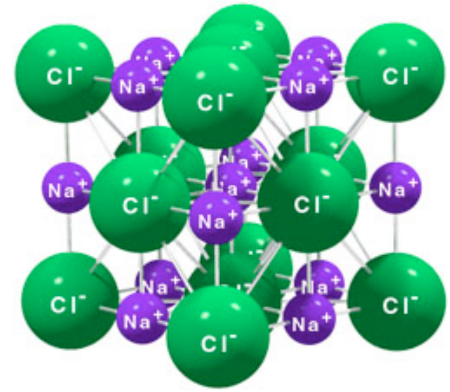
Objectives



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- Use density to calculate the apparent molar volumes of sodium chloride solutions of varying molality (m). The densities will be measured through the use of pycnometers.

- Make a plot of the apparent molar volume as a function of $\sqrt{m}$. Use this graph to determine the partial molar volume of the solute, sodium chloride, at various m.

Theory

- **Partial molar volume** is defined as the change in volume of an infinite amount of solution when one mole of component i is added:

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right) \qquad (1)$$

- The volume of a solution is given by the following equation where n_n is the moles of a component, $\bar{V}_n$ is the partial molar volume of a component, the subscript 1 refers to solvent (in this case water), and the subscript 2 refers to the solute (in this case NaCl):

$$V = n_1\bar{V}_1 + n_2\bar{V}_2 \qquad (2)$$

- The next equation is used to define a non-physical quantity; the **apparent molar volume**. Here $\tilde{V}^0{}_1$ is the molar volume of pure water, **m is the molality of the solution**, and φ is the apparent molar volume:

$$V = n_1\tilde{V}^0{}_1 + n_2\varphi = 55.51\tilde{V}^0{}_1 + m\varphi \qquad (3)$$

- Which is rearranged to give:

$$\varphi = \frac{1}{n_2}\left(V - n_1\tilde{V}^0{}_1\right) = \frac{1}{m}(V - 55.51\tilde{V}^0{}_1) \qquad (4)$$

- When working with molality, assuming solutions contain 1 kg of water allows the number of moles (n) and molality (m) to be interchangeable.

- For this experiment, there is a more convenient way to determine φ. First:

$$V = \frac{(1000+mFW_2)}{d} \qquad (5)$$

- where 1000 is the mass of 1 kg of water in grams, FW_2 is the formula weight of the solute, and d is the density of the solution. Also:

$$n_1\tilde{V}_1^0 = \frac{1000}{d^0} \qquad (6)$$

- where d^0 is the density of pure water. Both equations (5) and (6) have units of mL.
- By substituting equations (5) and (6) into equation (4) we obtain:

$$\varphi = \frac{1}{d}\left(FW_2 - \frac{1000}{m}\frac{d-d_0}{d_0}\right) \qquad (7)$$

- and by rewriting in terms of pycnometer weights:

$$\varphi\left(\boldsymbol{\frac{mL}{mol}}\right) = \frac{1}{d\,\boldsymbol{\frac{g}{cm^3}}}\left(FW_2\,\boldsymbol{\frac{g}{mol}} - \frac{1000\boldsymbol{\frac{g}{Kg}}}{m\boldsymbol{\frac{mol}{Kg}}}\,\frac{W\boldsymbol{g}-W_0\boldsymbol{g}}{W_0\boldsymbol{g}-\langle W_e\rangle\boldsymbol{g}}\right) \ (8)$$

<u>Note:</u> Letters in italics and bold are units!

- $\langle W_e \rangle$: weight of the empty pycnometer
- W_0 : weight of the pycnometer filled with pure solvent
- W : weight of the pycnometer filled with the solution in question.

- By the definition of partial molar volume and equations (2) and (3), we can obtain workable forms of the partial molar volume:

$$\bar{V}_2 = \left(\frac{\partial V}{\partial n_2}\right) = \varphi + n_2\frac{\partial\varphi}{\partial n_2} = \varphi + m\frac{\partial\varphi}{\partial m} \qquad (9)$$

and….

$$\bar{V}_1 = \left(\frac{\partial V}{\partial n_1}\right) = \frac{1}{n_1}\left(n_1\tilde{V}_1^0 - n_2^2\frac{\partial\varphi}{\partial n_2}\right) = \tilde{V}_1^0 - \frac{m^2}{55.51}\frac{\partial\varphi}{\partial m} \qquad (10)$$

- If we plotted φ vs m, we would obtain a curve. We could the find tangents to the curve at our concentrations and determine the slope ($\frac{\partial\varphi}{\partial m}$).
- Luckily for us, it is known that for dilute solutions of electrolytes, molar quantities such as φ vary linearly with $\sqrt{m}$.
- We can rewrite equations (9) and (10) with the following differential (*chain rule*):

$$\frac{\partial\varphi}{\partial m} = \frac{\partial\varphi}{\partial\sqrt{m}}\frac{\partial\sqrt{m}}{\partial m} = \frac{1}{2\sqrt{m}}\frac{\partial\varphi}{\partial\sqrt{m}} \qquad (11)$$

- giving:

$$\bar{V}_2 = \varphi + \frac{m}{2\sqrt{m}}\frac{\partial\varphi}{\partial\sqrt{m}} = \varphi + \frac{\sqrt{m}}{2}\frac{\partial\varphi}{\partial\sqrt{m}} = \overbrace{\varphi^0}^{\text{y-int}} + \frac{3\sqrt{m}}{2}\overbrace{\frac{\partial\varphi}{\partial\sqrt{m}}}^{\text{slope}} \qquad (12)$$

and…

$$\bar{V}_1 = \tilde{V}_1^0 - \frac{m}{55.51}\left(\frac{\sqrt{m}}{2}\overbrace{\frac{\partial\varphi}{\partial\sqrt{m}}}^{\text{slope}}\right) \qquad (13)$$

- where $\varphi^0$is the apparent molar volume extrapolated to $\sqrt{m} = 0$. Now we can work with a linear plot if we know φ and m for each solution.

Procedure

1. Thoroughly clean and dry (Water, Acetone, and compressed air)your pycnometer. Weigh it using the analytical balance. This value is w_e.
2. Fill the pycnometer with distilled water

   and place it in the heat bath for 5 minutes.

   What will happen to the water level in the pycnometer?
3. Record the temperature of the heat bath.

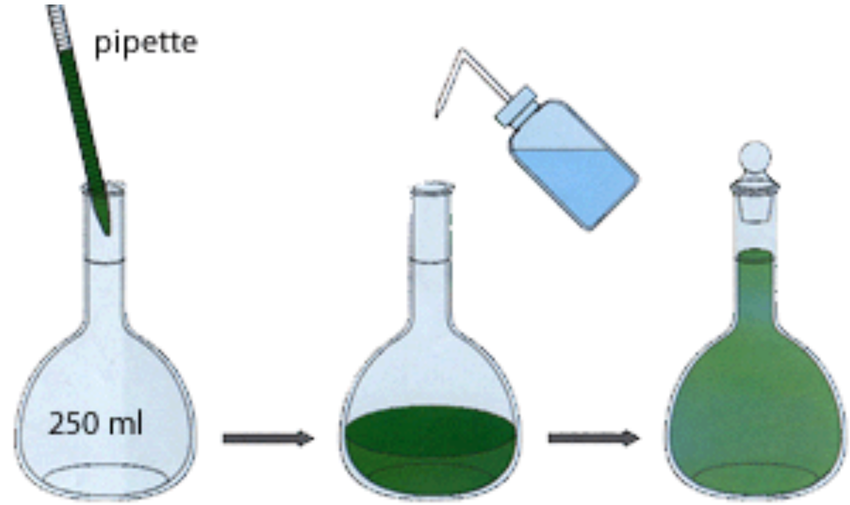
   (must be higher than room temperature)
4. Remove the pycnometer containing DI water, from the heat bath, dry it off, and weigh. This value is w_0.

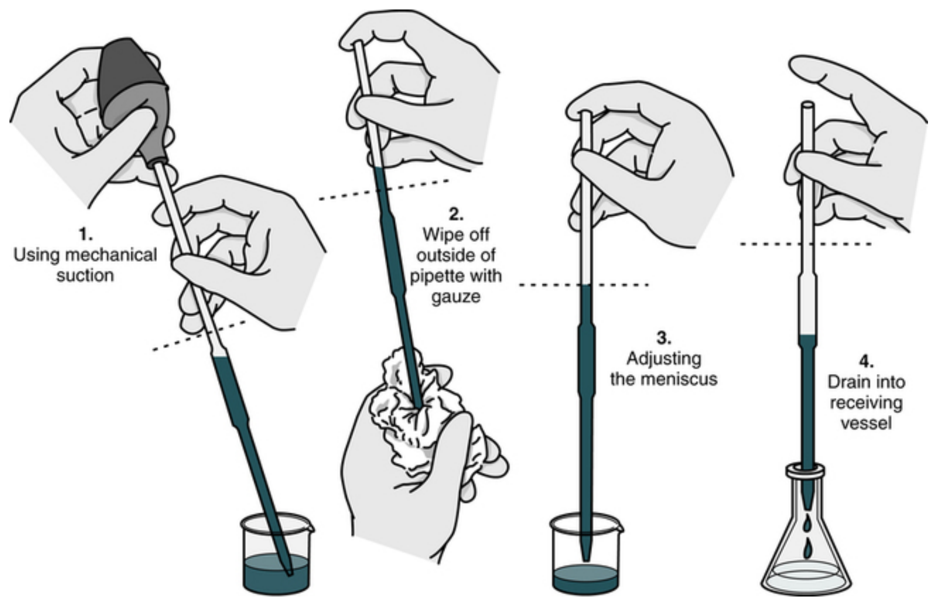
5. Empty the pycnometer and dry it using acetone and the aspirator.

   Hold the pycnometer by the neck with your fingers. Do NOT use your palm to enclose the pycnometer. Why?

6. Weigh the pycnometer again to check if you are getting the same weight as in step one, ± 0.002g (the balance error). This is your 2nd w_e. If your 2nd w_e is outside the balance error, see me immediately.
7. Fill the pycnometer with NaCl solution; place it in heat bath for 5 minutes.
8. Repeat steps 3-6 to get w_s for each solution, and a w_e value after **each solution**. The dilution process is outlined on the next slide.

How to use volumetric flasks and pipettes properly





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Fill a bottle with DI water and leave in the heat bath.

Dilution process:

For dilution #1: Pipette 20 ml of the NaCl stock solution into a 50-ml volumetric flask, add **~10 mL** distilled water and **swirl (don’t invert)**. Fill to ~1cm below the fill line, **swirl again**, and put the flask in the heat bath for 5 min. Fill it to the mark using water from the bottle in the heat bath. Mix well. Repeat with the following volumes of stock solution:

– dilution #2: 25 mL to 50 mL
– dilution #3: 30 mL to 50 mL
– dilution #4: 35 mL to 50 mL
– dilution #5: 40 mL to 50 mL

Why should you use a water bottle that has been in the heat bath to top off your volumetric flask?

Record the Following Data

Solution	Empty weight (Before) W_e	Weight with Solution	Empty weight (After) W_e
DI water (W_o)			
Stock solution (Ws)			
20 ml NaCl (Ws_1)			
25ml NaCl (Ws_2)			
30ml NaCl (Ws_3)			
35ml NaCl (Ws_4)			
40ml NaCl (Ws_5)			

Calculations

1. Determine the volume of each pycnometer using the accurate weight of distilled water and the density. Use the average w_e for this and other calculations (note that each pycnometer will have its own $\langle w_e \rangle$).

$$V_{py} = (w_0 - \langle w_e \rangle)/d_0 \qquad (14)$$

2. Use the volume of the pycnometer to calculate the density of the stock solution and diluted solutions (make sure to use the volume of the pycnometer used for each solution).

$$d = (w_s - \langle w_e \rangle)/V_{py} \qquad (15)$$

3. You will need to graph ϕ vs. $m^{1/2}$ (molality). Please note that a volume/volume dilution cannot be directly applied to calculate molality. For a example, the 2nd dilution m (a 50/50 dilution by volume) is **not** ½ of the stock solution m. Why?

Calculations (cont.)

- Molality is temperature independent (moles & mass are unaffected)
- Molarity is temperature dependent (moles unaffected, but **volume is** affected).
- Dilution calculations are much easier in terms of molarity! Therefore:

a)Use equation **16’** to calculate the stock solution M based on the stock solution m.

b)Use Use $M_iV_i = M_fV_f$ to determine the of M of the each dilution.

c)Then use equation **16** to figure out the m of the each dilution.

d)Use equation **8** to calculate ϕ for each solution.

m stock → M stock → M dilution → m dilution

Equations (For NaCl, MW= 58.45 g/mol)

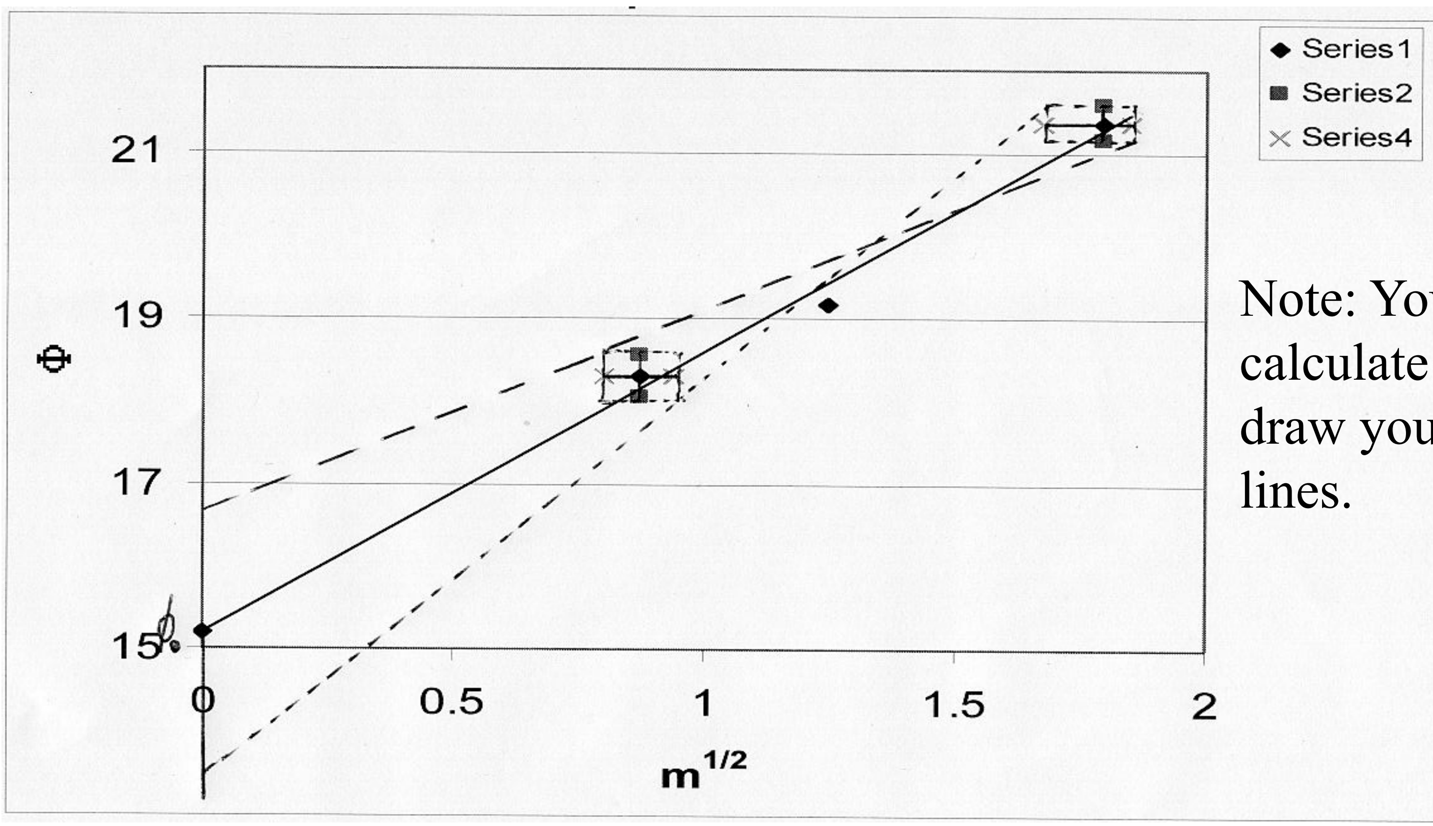
$$\mathrm{m}\left(\frac{mol}{kg}\right)=\frac{1000\ g}{kg}\frac{1}{\left(\frac{\mathrm{d}\ \frac{g}{cm^3}}{\mathrm{M}\ \frac{mol}{L}}\right)\left(\frac{1000\ cm^3}{L}\right)-58.45\ \frac{g}{mol}} \qquad [16]$$

$$\mathrm{M}\left(\frac{mol}{L}\right)=\left(\frac{1000\ cm^3}{L}\right)\left(\frac{\mathrm{d}\ g}{cm^3}\right)\left(\frac{1}{\frac{1000\ \frac{g}{kg}}{\mathrm{m}\ \frac{mol}{kg}}+58.45\ \frac{g}{mol}}\right) \qquad [16']$$

$$\varphi\left(\frac{mL}{mol}\right)=\frac{1}{d\ \frac{g}{cm^3}}\left(FW_2\,\frac{g}{mol}-\frac{1000\frac{g}{Kg}}{m\frac{mol}{Kg}}\,\frac{W\boldsymbol{g}-W_0\boldsymbol{g}}{W_0\boldsymbol{g}-<W_e>\boldsymbol{g}}\right) \qquad (8)$$

Graphical Analysis

- Plot ϕ versus $m^{1/2}$ – (molality, NOT molarity!)



Note: You will need to calculate $\varepsilon(m^{1/2})$ & $\varepsilon(\varphi)$ to draw your error boxes and lines.

Slope = $d(\phi)/d(m^{1/2})$

Y-Intercept = ϕ^0

Calculations (cont.)

- Calculate $\overline{V_1}$ & $\overline{V_2}$ for each solution (stock and all dilutions) using equations 12 & 13.

$$\bar{V}_2 = \varphi^0 + \frac{3\sqrt{m}}{2}\frac{\partial\varphi}{\partial\sqrt{m}} \quad (12)$$

$$\bar{V}_1 = \tilde{V}_1^0 - \frac{m}{55.51}\left(\frac{\sqrt{m}}{2}\frac{\partial\varphi}{\partial\sqrt{m}}\right) \quad (13)$$

Remember:

- Φ^0 is the y-intercept
- $\frac{\partial\varphi}{\partial\sqrt{m}}$ is the slope.
- $\tilde{V}_1^0$ comes from equation 6 where n_1=55.51 mol (***why?***).

Error Analysis

- Calculate the errors in density and molarity for all dilutions.
- Propagate errors to determine errors in ϕ and $m^{1/2}$ for the stock solution and the 1st dilution (20 mL stock → 50 mL).
- Calculate the error in $m^{1/2}$ for all dilutions.
- Plot the error boxes (error of x and y) on your graph to determine errors in the slope and intercept using the "limiting slope/intercept method".
- Determine the error in $\overline{V}_1$ & $\overline{V}_2$ using the error in slope/intercept.
- For this experiment, you **MUST** break the equations into parts and use the "cookie cutter rules." Following directions is very important in a lab environment; this requirement IS part of your grade!

$$\varphi = \frac{1}{d}\left(FW_2 - \frac{1000}{m}\frac{W - W_0}{W_0 - W_e}\right) \qquad (8)$$

Assume the MW of NaCl has no error. Substitute with stand-in variables

Let $a = w - w_0$ and $b = w_0 - \langle w_e \rangle$. This yields:

$\varepsilon(a) = \sqrt{\varepsilon(w)^2 + \varepsilon(w_0)^2}$ and $\varepsilon(b) = \sqrt{\varepsilon(w_0)^2 + \varepsilon(\langle w_e \rangle)^2}$

Also, let $c = \frac{1000a}{mb}$. The error in c is given by:

$$\varepsilon(c) = c\sqrt{\left(\frac{\varepsilon(a)}{a}\right)^2 + \left(\frac{\varepsilon(b)}{b}\right)^2 + \left(\frac{\varepsilon(m)}{m}\right)^2}$$

Let $f = FW_2 - c$

$$\varepsilon(f) = \sqrt{0^2 + \varepsilon(c)^2} = \sqrt{\varepsilon(c)^2} = \varepsilon(c)$$

Combining all the errors together for the total error in ϕ, we get:

$$\varepsilon(\Phi) = \Phi\sqrt{(\varepsilon(f)/f)^2 + (\varepsilon(d)/d)^2}$$

Formulas required for error analysis:*

- $d = \frac{W - W_e}{V_{py}}$ (15)
- $M_1 V_1 = M_2 V_2$
- $V_{py} = \frac{W_0 - \langle W_e \rangle}{d_0}$ (14)
- $\varphi = \frac{1}{d}\left(FW_2 - \frac{1000}{m}\frac{W - W_0}{W_0 - W_e}\right)$ (8)
- $\bar{V}_2 = \varphi^0 + \frac{3\sqrt{m}}{2}\frac{\partial\varphi}{\partial\sqrt{m}}$ (12)
- $\bar{V}_1 = \tilde{V}_1^0 - \frac{m}{55.51}\left(\frac{\sqrt{m}}{2}\frac{\partial\varphi}{\partial\sqrt{m}}\right)$ (13)

*don't forget $m^{1/2}$!

Sources of error (remember to record before leaving lab!):

- Analytical balance: $\varepsilon(\langle w_e \rangle)$, $\varepsilon(w_0)$, $\varepsilon(w_s)$ (use $\pm$0.0005 g)
- Pipette: $\varepsilon(V_{pipette})$ (largest used for each dilution; need for $\varepsilon(M)$)
- Volumetric flask: $\varepsilon(V_{flask})$ (use $\pm$0.05 mL)
- Stock solution molality: $\varepsilon(m_s)$
- Density of pure water: $\varepsilon(d_0) = d_0$(at bath T) – d_0(at bath T+.5°C)

Report

- Title Page: name, partner, title, date performed
- Abstract: Short description of what you did, why you did it, and what your results were (plus error).
- Introduction & theory: Describe the purpose, explain why partial molar volume is important, and define partial and apparent molar volume and explain the relationship between them.
- Signed procedure and signed data
- Calculations: As described earlier
- Error Analysis: As described earlier
- Summary & Discussion: Make a table containing your values for density, molarity, molality, & ϕ, plus errors, and a second table containing your values for $\overline{V}_1$ and $\overline{V}_2$, plus errors. The trend in your values for $\overline{V}_1$ and $\overline{V}_2$ should be very different. <u>Describe</u> each trend and <u>explain</u> whether or not the difference in the trends makes sense. (Not simply a yes or no answer!)

For The Final Write-up…

- **You must bring with you:**
  - Signed data & procedure
  - Calculator (cannot be a phone)
  - Pen, pencil, & eraser

- **You will be provided with:**
  - Lined paper, graph paper, ruler
  - Error Analysis Info: Syllabus, lecture handout, textbook
  - Experimental Info: Syllabus & textbook
  - Copy of this PowerPoint presentation
- **Food and drink are permitted as long as they are not disruptive.**
- **Phones must be turned OFF (vibrate mode is not a substitute).**
- **No electronic devices (e.g. Discman, MP3 player, iPod).**
- **Please do not write on handouts; they will be re-used.**