

## Chapter 14. Solutions

We have been studying primarily pure elements and compounds (Chapters 8 and 9). But substances in nature usually occur as mixtures and properties of mixtures are often very different from the original substances. And so, we will study solutions and their properties.

**Solution:** a homogeneous mixture of pure substances in which no settling occurs. consists of solvent and one or more solutes. The solvent is the medium in which the solutes are dissolved; the amount of solvent is greater than the amount of solute.

Examples:

| Solvent \ Solute | Solid    | Liquid                  | Gas                         |
|------------------|----------|-------------------------|-----------------------------|
|                  | Solid    | Liquid                  | Gas                         |
| Solid            | alloys   | dental fillings         | ?                           |
| Liquid           | seawater | vodka (alcohol + water) | carbonated H <sub>2</sub> O |
| Gas              | ?        | ?                       | air                         |

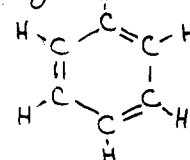
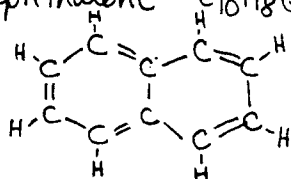
of more interest here  $\Rightarrow$

?: maybe you can think of an example

We are primarily interested in the dissolution of gases, liquids and solids in liquids.

### Dissolution of Solids in Liquids

- (1) "like dissolves like" - 2 substances with similar structure attract each other.  
 polar solvents tend to dissolve polar solutes with similar structures. Eg  
 eg. H<sub>2</sub>O (very polar) dissolves many ionic compounds (ultimate in polarity)  
 nonpolar solvents tend to dissolve nonpolar solutes with similar structure  
 eg. naphthalene C<sub>10</sub>H<sub>8</sub>(s) dissolves in benzene, C<sub>6</sub>H<sub>6</sub>(l)



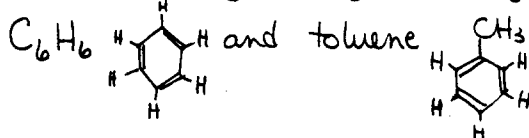
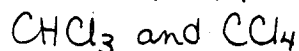
- (2) ionic salts with highly charged ions AlF<sub>3</sub>, MgO, Cr<sub>2</sub>O<sub>3</sub> have very high ion-ion interactions (Coulomb's Law  $F \propto \frac{q_1 q_2}{d^2}$ ) and require much energy to break apart. Hence these salts are not very soluble in water.  
 In general, many solids require heat to dissolve.

## Dissolution of Liquids in Liquids - Miscibility

(1) "like dissolves like" : liquids with similar structures are miscible.

eg liquids exhibiting H-bonding are miscible:  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$

non polar or slightly polar liquids with similar structures are miscible



whereas  $\text{C}_6\text{H}_6$  and  $\text{H}_2\text{O}$  are not miscible.

## Dissolution of Gases in Liquids

(1) "like dissolves like"

(2) the only gases that dissolve appreciably in water (our usual solvent) are

- those capable of H-bonding ( $\text{HF}$ )

- those that ionize ( $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ )

- those that react with water ( $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq})$ )  
very important in seawater.

## Concentration Units of Solutions - A Review PLUS

(1) Percent by mass

$$\% \text{ solute} = \frac{\text{mass of solute}}{\text{mass of SOLUTION}} \times 100$$

(2) Molarity ( $\frac{\text{mol}}{\text{L}}$ )

$$M = \frac{\text{number of moles of solute}}{\text{number of liters of SOLUTION}}$$

(3) Molality ( $\frac{\text{mol}}{\text{kg}}$ )

$$m = \frac{\text{number of moles of solute}}{\text{number of kilograms of SOLVENT}}$$

(4) Mole fraction

$$X_{\text{solute}} = \frac{\text{number of moles of solute}}{\text{no. moles solute} + \text{no. moles solvent}}$$

$$X_{\text{solvent}} = \frac{\text{number of moles of solvent}}{\text{no. moles solute} + \text{no. moles solvent}}$$

by definition  $X_{\text{solute}} + X_{\text{solvent}} = 1$

Example: Calculate % by mass, molarity, molality and mole fraction of benzoic acid in a solution containing 3.45 g of benzoic acid,  $\text{C}_6\text{H}_5\text{COOH}$  (MW = 122 g/mol) in 200 mL of benzene,  $\text{C}_6\text{H}_6$  (MW = 78.1 g/mol). The density of pure benzene is 0.879 g/mL; the density of the solution is 0.890 g/mL.

|                                                                                                                                                                                                                                                                                                                                                                                                    |                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p>(1) % by mass = <math>\frac{\text{g benzoic acid}}{\text{g solution}} \times 100</math></p> <p>= <math>\frac{3.45 \text{ g}}{179 \text{ g}} \times 100</math></p> <p>= 1.93 % benzoic acid</p>                                                                                                                                                                                                  | <p>Extra calculations</p> <p>Recall <math>\text{g solution} = \text{g solute} + \text{g solvent}</math><br/> <math>\text{acid} \quad \text{(benzene)}</math></p> <p>but <math>\text{g solvent} = D_{\text{benzene}} \times \# \text{ mL}</math><br/> <math>\text{(benzene)} = 0.879 \text{ g/mL} \times 200 \text{ mL}</math><br/> <math>= 176 \text{ g}</math></p> <p><math>\therefore \text{g soln} = 3.45 \text{ g} + 176 \text{ g} = 179 \text{ g}</math></p> |
| <p>(2) molarity = <math>\frac{\text{mol benzoic acid}}{\text{L solution}}</math></p> <p>(M)</p> <p>= <math>\frac{0.0283 \text{ mol}}{0.201 \text{ L}}</math></p> <p>= 0.141 M</p>                                                                                                                                                                                                                  | <p>mol benzoic acid = <math>\frac{3.45 \text{ g}}{122 \text{ g/mol}} = 0.0283 \text{ mol}</math></p> <p>mL solution = <math>\frac{\text{g soln}}{D_{\text{soln}}} = \frac{179 \text{ g}}{0.890 \text{ g/mL}}</math><br/> <math>= 201 \text{ mL}</math></p>                                                                                                                                                                                                        |
| <p>(3) molality = <math>\frac{\text{mol benzoic acid}}{\text{kg benzene only}}</math></p> <p>(m)</p> <p>= <math>\frac{0.0283 \text{ mol}}{0.176 \text{ kg}}</math></p> <p>= 0.161 m</p>                                                                                                                                                                                                            | <p>kg benzene found in (1)</p>                                                                                                                                                                                                                                                                                                                                                                                                                                    |
| <p>(4) <math>X_{\text{benzoic acid}} = \frac{\text{mol benzoic acid}}{\text{mol benzoic acid} + \text{mol benzene}}</math></p> <p>= <math>\frac{0.0283 \text{ mol}}{0.0283 \text{ mol} + 2.25 \text{ mol}}</math></p> <p>= 0.0124</p> <p><math>X_{\text{benzene}} = 1 - 0.0124 = 0.9876</math></p> <p>(= <math>\frac{\text{mol benzene}}{\text{mol benzoic acid} + \text{mol benzene}}</math>)</p> | <p>mol benzene = <math>\frac{176 \text{ g}}{78.1 \text{ g/mol}} = 2.25 \text{ mol}</math></p>                                                                                                                                                                                                                                                                                                                                                                     |

But what are molality and mole fraction good for?

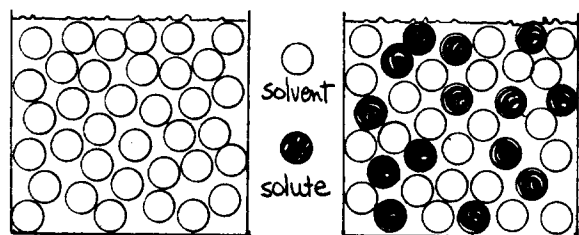
## Colligative Properties

Colligative properties of solutions are physical properties which depend only on the NUMBER of solute particles in solution and NOT the KIND of particle. These particles can be molecules or ions or both!

Colligative properties include : lowering of vapor pressure, which causes  
boiling point elevation  
freezing point depression  
membrane osmotic pressure

## Vapor Pressure Lowering of a Liquid

Vapor pressure of liquids always decrease when NONVOLATILE solutes (molecules or ions) are dissolved in them.



before dissolution

after dissolution

After dissolution, there are fewer solvent molecules at the surface to vaporize  
 $\therefore$  vapor pressure is decreased.

Raoult's Law quantifies the vapor pressure lowering of a solvent due to the presence of a nonvolatile, nonionizing solute :

Raoult's Law: The vapor pressure of a solvent in a solution decreases as the mole fraction of the solvent decreases.

$$P_{\text{solvent}} = X_{\text{solvent}} P^{\circ}_{\text{solvent}}$$

where  $X_{\text{solvent}}$  = mole fraction of solvent

$P^{\circ}_{\text{solvent}}$  = vapor pressure of pure solvent

$P_{\text{solvent}}$  = vapor pressure of solvent in solution

The lowering of vapor pressure is defined as  $\Delta P_{\text{solvent}} = P_{\text{solvent}}^{\circ} - P_{\text{solvent}}$   
 $\therefore$  substituting into this definition the expression for  $P_{\text{solvent}}$  from Raoult's Law

$$\begin{aligned}\Delta P_{\text{solvent}} &= P_{\text{solvent}}^{\circ} - X_{\text{solvent}} P_{\text{solvent}}^{\circ} \\ &= P_{\text{solvent}}^{\circ} (1 - X_{\text{solvent}})\end{aligned}$$

Recall :

$$\begin{aligned}X_{\text{solvent}} + X_{\text{solute}} &= 1 \\ X_{\text{solute}} &= 1 - X_{\text{solvent}}\end{aligned}$$

Then:

$$\Delta P_{\text{solvent}} = X_{\text{solute}} P_{\text{solvent}}^{\circ}$$

Note: Solutions that obey this relationship are called IDEAL solutions.

Example: (Similar to Ch 14 #43, #44)

Calculate the lowering of vapor pressure and the vapor pressure of the solution prepared by dissolving 75.0 g of sucrose  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$  (MW = 342 g/mol) in 300.0 g of  $\text{H}_2\text{O}$  at  $25.0^{\circ}\text{C}$ . The vapor pressure of water at  $25^{\circ}\text{C}$  is 23.76 torr.

equations :

|                            |                                                                            |
|----------------------------|----------------------------------------------------------------------------|
| vapor pressure lowering    | $\Delta P_{\text{solvent}} = X_{\text{solute}} P_{\text{solvent}}^{\circ}$ |
| vapor pressure of solution | $P_{\text{solvent}} = X_{\text{solvent}} P_{\text{solvent}}^{\circ}$       |

Plan\*:

- (1) calculate moles of sucrose and moles of  $\text{H}_2\text{O}$
- (2) calculate  $X_{\text{solvent}}$
- (3) calculate  $P_{\text{solvent}}$ , the vapor pressure of the solution directly
- (4) use  $\Delta P_{\text{solvent}} = P_{\text{solvent}}^{\circ} - P_{\text{solvent}}$  to calculate the vapor pressure lowering.

Note: An alternative method would be to calculate  $\Delta P_{\text{solvent}}$  directly using  $X_{\text{solute}}$ , then find  $P_{\text{solvent}}$  since  $P_{\text{solvent}} = P_{\text{solvent}}^{\circ} - \Delta P_{\text{solvent}}$ .

\* this is only 1 way to do problem. There are many other variations (see Note)

$$(1) \text{ moles H}_2\text{O (solvent)} = \frac{300.0 \text{ g}}{18.0 \text{ g/mol}} = 16.7 \text{ moles}$$

$$\text{moles C}_{12}\text{H}_{22}\text{O}_{11} \text{ (solute)} = \frac{75.0 \text{ g}}{342 \text{ g/mol}} = 0.219 \text{ moles}$$

$$(2) X_{\text{solvent}} = \frac{\text{moles solvent}}{\text{moles solvent} + \text{moles solute}} = \frac{16.7 \text{ mol}}{16.7 \text{ mol} + 0.219} = 0.987$$

$$(3) P_{\text{solvent}} = X_{\text{solvent}} P_{\text{solvent}}^{\circ} = 0.987 \times 23.76 \text{ torr} = \underline{23.45 \text{ torr}}$$

$$(4) \Delta P_{\text{solvent}} = P_{\text{solvent}}^{\circ} - P_{\text{solvent}} = 23.76 \text{ torr} - 23.45 \text{ torr} = \underline{0.31 \text{ torr}}$$

The lowering of the vapor pressure of a solvent by adding a non-volatile solute has two very useful consequences: (Fig 12-15 shown below):

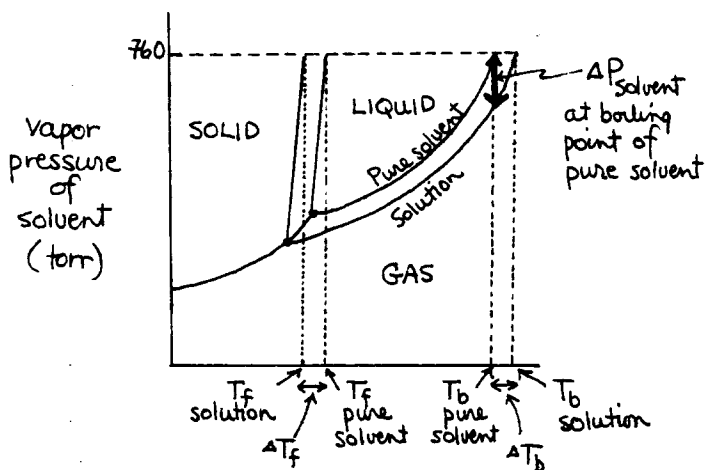


FIGURE 12-15 Because a nonvolatile solute lowers the vapor pressure of a solvent, the boiling point of a solution is higher and the freezing point lower than the corresponding points for the pure solvent. The magnitude of boiling point elevation,  $\Delta T_b$ , is less than the magnitude of freezing point depression,  $\Delta T_f$ .

- (1) the solution has a higher boiling point than the pure solvent
- (2) the solution has a lower freezing/melting point than the pure solvent.

The difference between the boiling points of the pure solvent and the solution ( $\Delta T_b$ ) depends only on the number of particles dissolved in the solution. The particles can be molecules, ions or both.

The same is true for the  $\Delta T_f$ , the difference between the freezing points of the pure solvent and the solution.

For a solution of a nonvolatile compound in a solvent:

|                                                   |
|---------------------------------------------------|
| Boiling point elevation, $\Delta T_b = i K_b m$   |
| Freezing point depression, $\Delta T_f = i K_f m$ |

where  $\Delta T_b = \text{B.P. solution} - \text{B.P. solvent}$

$K_b = \text{molal boiling point elevation constant } (^{\circ}\text{C}/m)$

$\Delta T_f = \text{F.P. (M.P.) pure solvent} - \text{F.P. (M.P.) solution}$

$K_f = \text{molal freezing point depression constant } (^{\circ}\text{C}/m)$

$m = \text{molality}$

$i = \text{van't Hoff factor}$

Notes:  $\Delta T_b$  and  $\Delta T_f$  are always positive numbers

$K_f$  and  $K_b$  are different for different solvents. - found on back of exam envelope

### Van't Hoff Factor, $i$

The van't Hoff factor,  $i$ , is a measure of the number of particles that result from the dissociation of 1 formula unit or molecule of a substance. We will only consider the ideal van't Hoff factor for those substances that dissociate 100% into their ions.

| Compound                                           | Complete dissociation reaction                                     | $i$ , ideal van't Hoff factor |
|----------------------------------------------------|--------------------------------------------------------------------|-------------------------------|
| sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ | -                                                                  | 1                             |
| nonelectrolyte                                     | -                                                                  | 1                             |
| $\text{NaCl (aq)}$                                 | $\text{NaCl(aq)} \rightarrow \text{Na}^+ + \text{Cl}^-$            | 2                             |
| $\text{KOH (aq)}$                                  | $\text{KOH(aq)} \rightarrow \text{K}^+ + \text{OH}^-$              | 2                             |
| $\text{HCl (aq)}$                                  | $\text{HCl(aq)} \rightarrow \text{H}^+ + \text{Cl}^-$              | 2                             |
| $\text{K}_2\text{SO}_4\text{(aq)}$                 | $\text{K}_2\text{SO}_4 \rightarrow 2\text{K}^+ + \text{SO}_4^{2-}$ | 3                             |
| $\text{Ba(OH)}_2\text{(aq)}$                       | $\text{Ba(OH)}_2 \rightarrow \text{Ba}^{2+} + 2\text{OH}^-$        | 3                             |
| $\text{K}_3\text{PO}_4\text{(aq)}$                 | $\text{K}_3\text{PO}_4 \rightarrow 3\text{K}^+ + \text{PO}_4^{3-}$ | 4                             |

Example: Calculate the boiling and freezing point for a solution containing 8.50 g of benzoic acid (MW 122) in 75.0 g benzene (MW 78.1).

For benzene  $K_b: 2.53\text{ }^{\circ}\text{C/m}$  boiling point:  $80.10\text{ }^{\circ}\text{C}$   
 $K_f: 5.12\text{ }^{\circ}\text{C/m}$  freezing point:  $5.48\text{ }^{\circ}\text{C}$

(a) boiling point elevation  $\Delta T_b = i K_b m$  where  $m = \frac{\text{\# moles solute}}{\text{kg solvent}}$   
 $= 1 \times 2.53\text{ }^{\circ}\text{C/m} \times 0.929\text{ m}$   
 $= 2.35\text{ }^{\circ}\text{C}$   
 $= 0.929\text{ m}$

$\therefore$  new boiling point =  $80.10\text{ }^{\circ}\text{C} + 2.35\text{ }^{\circ}\text{C} = 82.45\text{ }^{\circ}\text{C}$

(b) freezing point depression  $\Delta T_f = i K_f m$   
 $= 1 \times 5.12\text{ }^{\circ}\text{C/m} \times 0.929\text{ m}$   
 $= 4.76\text{ }^{\circ}\text{C}$

$\therefore$  new freezing point =  $5.48\text{ }^{\circ}\text{C} - 4.76\text{ }^{\circ}\text{C} = 0.72\text{ }^{\circ}\text{C}$

Example: Calculate the freezing point of a 0.100 m  $\text{K}_2\text{SO}_4$  solution (Assume complete dissociation of the salt)  $K_f$  for  $\text{H}_2\text{O} = 1.86\text{ }^{\circ}\text{C/m}$ .

$\Delta T_f = i K_f m$  since  $\text{K}_2\text{SO}_4 \rightarrow 2\text{K}^+ + \text{SO}_4^{2-}$   
 $= 3 \times 1.86\text{ }^{\circ}\text{C/m} \times 0.100\text{ m}$   
 $= 0.558\text{ }^{\circ}\text{C}$

$\therefore$  freezing point of solution =  $0.000\text{ }^{\circ}\text{C} - 0.558\text{ }^{\circ}\text{C}$   
 $= -0.558\text{ }^{\circ}\text{C}$

# Determination of Molecular Weight by Freezing Point Depression (or Boiling Point Elevation) of a nonvolatile nonelectrolyte:

We know:  $\Delta T_f = i K_f m = K_f m$  since  $i = 1$  for a nonelectrolyte

∴ if we know the freezing point of the solution,  $K_f$ , mass of solute and solvent, we can calculate molecular weight.

$$\Delta T_f = K_f \frac{(\text{g solute} / \text{MW})}{\text{kg solvent}} \quad \text{since } m = \frac{\text{mols solute}}{\text{kg solvent}} = \frac{(\frac{\text{g solute}}{\text{MW}})}{\text{kg solvent}}$$

Example: A 5.12 g sample of a new nonvolatile nonelectrolyte was dissolved in 250 mL benzene to give a solution that boils at  $96.87^\circ\text{C}$ . Calculate the molecular weight. For benzene, Density =  $0.8765 \text{ g/mL}$ ,  $K_b = 2.53^\circ\text{C/m}$ , b.p. =  $80.1^\circ\text{C}$

$$\Delta T_b = K_b m = K_b \frac{(\text{g solute} / \text{MW})}{\text{kg solvent}}$$

$$(96.87^\circ\text{C} - 80.1^\circ\text{C}) = 2.53^\circ\text{C/m} \frac{(5.12 \text{ g} / \text{MW})}{0.219 \text{ kg}}$$

$$\text{since kg benzene} = 250 \text{ mL} \times \frac{0.8765 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.219 \text{ kg}$$

$$\text{Solving, MW} = 35.2 \text{ g/mol}$$

Alternative method: Do problem stepwise:  $\Delta T_b, K_b \xrightarrow{(1)} m \xrightarrow{(2)} \text{moles} \xrightarrow{(3)} \text{MW}$

$$(1) m = \frac{\Delta T_b}{K_b} = \frac{(96.87^\circ\text{C} - 80.1^\circ\text{C})}{2.53^\circ\text{C/m}} = 6.63 \text{ m}$$

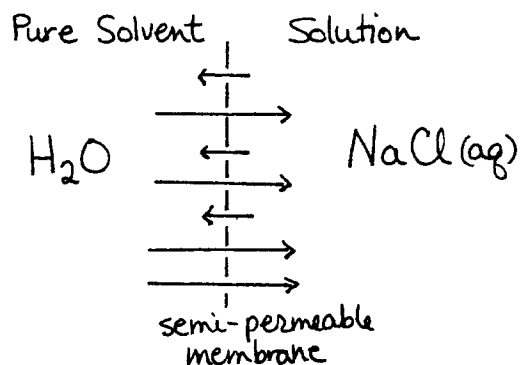
$$(2) \text{ mol unknown} = m \times \text{kg benzene} = 6.63 \text{ m} \times 0.219 \text{ kg} = 1.45 \text{ mol}$$

$$(3) \text{ MW} = \frac{\# \text{g}}{\# \text{mol}} = \frac{5.12 \text{ g}}{1.45 \text{ mol}} = 35.3 \text{ g/mol}$$

The other colligative property we need to discuss is

## Membrane Osmotic Pressure

Osmosis: a spontaneous process by which solvent molecules pass through a semi-permeable membrane from a solution of low concentration of solute to a solution with a high concentration of solute.



the pressure exerted under this condition is called osmotic pressure ( $\pi$ )

These pressures are very powerful.  
1 M nonelectrolyte  $\Rightarrow$   $\sim 22.4$  atm of osmotic pressure in  $\text{H}_2\text{O}$

osmotic pressure (atm)  $\propto M$   
but in dilute aqueous solutions,  $M \cong m$

$$\frac{\text{moles}}{\text{kg solvent (H}_2\text{O)}} \approx \frac{\text{moles}}{\text{L solution (H}_2\text{O)}}$$

$\therefore$  we have:  $\pi = MRT$   
better yet  $\pi = iMRT$

where  $\pi$  osmotic pressure (atm or torr)  
 $M$  molarity ( $\frac{\text{mol}}{\text{L}}$ )  
 $R$   $0.0821 \frac{\text{L atm}}{\text{mol K}}$   
or  $62.4 \frac{\text{L torr}}{\text{mol K}}$

[Note: the similarity to  $P = \frac{nRT}{V}$ , the ideal gas equation]

Osmotic pressure is used routinely to estimate the molecular weights of very large molecules: polymers + biological macromolecules.

Example: A 1.00 g sample of biological material was dissolved in enough water to give 100 mL of solution. The osmotic pressure was 2.80 torr at 25°C. Calculate molarity and approximate molecular weight.

$$\pi = iMRT = MRT \quad \text{for nonelectrolyte}$$

$$(1) \quad \therefore M = \frac{\pi}{RT} = \frac{2.80 \text{ torr}}{62.4 \frac{\text{L} \cdot \text{torr}}{\text{mol} \cdot \text{K}} \times (25^\circ\text{C} + 273^\circ)} \\ = 1.51 \times 10^{-4} \text{ M}$$

$$(2) \quad M = \frac{\# \text{ mol}}{\# \text{ L}} \quad \therefore \# \text{ mol} = M \times \# \text{ L} \\ = 1.51 \times 10^{-4} \text{ M} \times 0.100 \text{ L} \\ = 1.51 \times 10^{-5} \text{ mol}$$

$$\text{MW} = \frac{\# \text{ g}}{\# \text{ mol}} = \frac{1.00 \text{ g}}{1.51 \times 10^{-5} \text{ mol}} = 6.64 \times 10^4 \text{ g/mol}$$

We could solve for the molecular weight directly:

$$\pi = MRT = \left( \frac{\text{mol}}{\text{L}} \right) RT = \left( \frac{\text{g/MW}}{\text{L}} \right) RT$$

$$\text{rearranging, } \text{MW} = \frac{(\# \text{ g}) RT}{\pi (\# \text{ L})} \\ = \frac{1.00 \text{ g} \times 62.4 \text{ L} \cdot \text{torr} / \text{mol} \cdot \text{K} \times (25 + 273) \text{ K}}{2.80 \text{ torr} \times 0.100 \text{ L}} \\ = 6.64 \times 10^4 \text{ g/mol}$$

For interest: read introduction to colloids.