

CHEMISTRY 142 – Example Problems

Solutions and Colligative Properties

To be taken up in class or solutions will be posted

$$N_A = 6.022 \times 10^{23}$$

$K_f(\text{benzene}) = 4.90 \text{ } ^\circ\text{C kg/mol}$	$K_f(\text{ethanol}) = 1.99 \text{ } ^\circ\text{C kg/mol}$
$\text{density of H}_2\text{O} = 1.00 \text{ g/mL}$	$K_f(\text{CCl}_4) = 31.8 \text{ } ^\circ\text{C kg/mol}$
$K_f(\text{H}_2\text{O}) = 1.86 \text{ } ^\circ\text{C kg/mol}$	$K_b(\text{H}_2\text{O}) = 0.51 \text{ } ^\circ\text{C kg/mol}$
$K_b(2\text{-methyl-2-propanol}) = 1.98 \text{ } ^\circ\text{C kg mol}^{-1}$	$P^\circ(\text{H}_2\text{O}) = 23.800 \text{ torr at } 25^\circ\text{C}$
	$K_f(2\text{-methyl-2-propanol}) = 4.68 \text{ } ^\circ\text{C kg mol}^{-1}$

1. Show that for very dilute solutions, molality \cong Molarity.

$$\text{molality} = \frac{n_{\text{solute}}}{\text{mass solvent (kg)}}$$

$$\text{Molarity} = \frac{n_{\text{solute}}}{\text{volume solution (L)}}$$

For dilute aqueous solutions molality \cong Molarity as follows;

$$\text{Since } M = \frac{n_{\text{solute}}}{\text{vol. soln (L)}} \text{ and density soln} = \frac{\text{mass soln}}{\text{vol. soln}}$$

$$\therefore \text{vol. soln} = \frac{\text{mass soln}}{\text{density soln}}$$

Substituting into Molarity expression

$$M = \frac{n_{\text{solute}}}{\left(\frac{\text{mass soln}}{\text{density soln}} \right)} = \frac{n_{\text{solute}}}{\text{mass soln}} \cdot \text{density soln.}$$

and mass soln = mass solvent + mass solute

$$\text{so, } M = \frac{n_{\text{solute}}}{(\text{mass solv.} + \text{mass solute})} \cdot \text{density soln.}$$

For dilute aqueous solns, mass solute $\rightarrow 0$

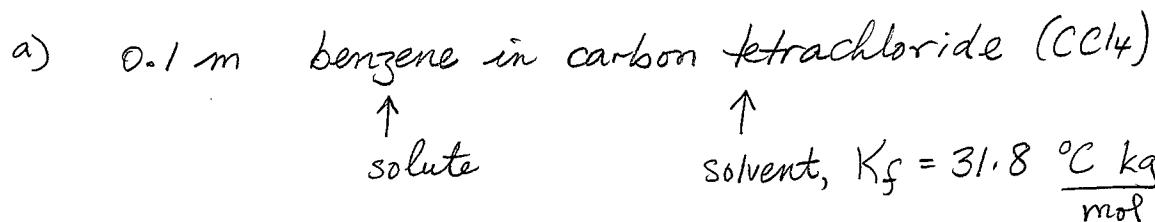
and density soln $\rightarrow 1.0$

$$\text{Therefore } M \cong \frac{n_{\text{solute}}}{\text{mass solvent}} = \text{molality}$$

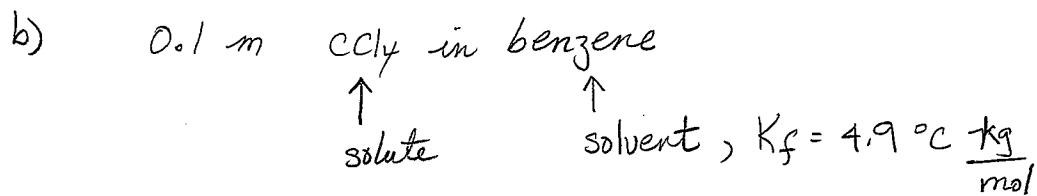
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2. Which will experience a greater freezing point depression, a 0.1 *m* solution of benzene in carbon tetrachloride or a 0.1 *m* solution carbon tetrachloride in benzene? Explain.
 [benzene in CCl_4]

$$\Delta T_f = K_f^{(\text{solvent})} \cdot m$$



$$\therefore \Delta T_f = \left(31.8 \frac{\text{ }^\circ\text{C}}{\text{mol}}\right) \left(0.1 \frac{\text{mol}}{\text{kg}}\right) = 3.18 \text{ }^\circ\text{C}$$



$$\therefore \Delta T_f = \left(4.90 \frac{\text{ }^\circ\text{C}}{\text{mol}}\right) \left(0.1 \frac{\text{mol}}{\text{kg}}\right) = 0.49 \text{ }^\circ\text{C}$$

Therefore, the greater ΔT_f (freezing point depression) occurs for a 0.1 *m* solution of benzene in CCl_4 .

Note: K_f is a property of the solvent and a direct measure of how sensitive a solvent is to a freezing point change per molal unit of solute concentration.

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3. An aqueous sucrose ($C_{12}H_{22}O_{11}$) solution of unknown concentration is found to have a freezing point of -0.912°C . What is the normal boiling point and the partial pressure (in torr) of water at 25°C of this solution. Sucrose is a non-volatile, non-electrolyte.

$[BP = 100.25^{\circ}\text{C}; P_{H_2O} = 23.59 \text{ torr}]$

$$\text{solute} = C_{12}H_{22}O_{11} \quad \text{solvent} = H_2O$$

$$\Delta T_f = 0.912^{\circ}\text{C}$$

$$\Delta T_f = K_f^{(H_2O)} \cdot m$$

$$\therefore \text{Molality} = \frac{\Delta T_f}{K_f^{(H_2O)}} = \frac{0.912^{\circ}\text{C}}{1.86^{\circ}\text{C kg/mol}} = 0.490 \frac{\text{mol}}{\text{kg}}$$

$$\Delta T_b = K_b^{(H_2O)} \cdot m$$

$$= (0.51 \frac{\text{^{\circ}C kg}}{\text{mol}})(0.490 \frac{\text{mol}}{\text{kg}}) = 0.25^{\circ}\text{C}$$

$$\text{so b.p. of soln} = 100.25^{\circ}\text{C}$$

$$P_{\text{soln}} = \chi_{\text{solvent}} \cdot P_{\text{solvent}}^{\circ}$$

\uparrow \uparrow
 $\ddot{\text{?}}$ from molality $23.800 \text{ torr at } 25^{\circ}\text{C}$

$$m = 0.490 \frac{\text{mol}}{\text{kg}} \quad \begin{matrix} \leftarrow \text{sucrose} \\ \leftarrow \text{water} \end{matrix}$$

$$\therefore \chi_{\text{solvent}} = \frac{n_{H_2O}}{n_{H_2O} + n_{\text{sucrose}}} \quad ; \quad n_{H_2O} = \frac{1000.9}{18.02 \text{ g/mol}} = 55.50 \text{ mol}$$

$$= \frac{55.50 \text{ mol}}{(55.50 + 0.490) \text{ mol}} = 0.991$$

$$\begin{aligned} P_{\text{soln}} &= (0.991)(23.800 \text{ torr}) \\ &= 23.59 \text{ torr} \end{aligned}$$

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4. Pure 2-methyl-2-propanol has a freezing point of 25.50 °C, however it absorbs water (as an impurity) on exposure to humid air. If the freezing point of a 100.0 g sample of 2-methyl-2-propanol is 24.59 °C, how many grams of water are present in the sample?

[0.35 g H₂O]

$$f.p. = 25.50 \text{ } ^\circ\text{C} \text{ (pure)}$$

$$f.p. = 24.59 \text{ } ^\circ\text{C} \text{ (impure)}$$

$$\therefore \Delta T_f = 25.50 - 24.59 = 0.91 \text{ } ^\circ\text{C}$$

note: 2-methyl-2-propanol is solvent!
H₂O is solute!

$$\Delta T_f = K_f \cdot m$$

$$\therefore m = \frac{\Delta T_f}{K_f} = \frac{0.91 \text{ } ^\circ\text{C}}{4.68 \frac{\text{ } ^\circ\text{C kg}}{\text{mol}}} = 0.194 \frac{\text{mol}}{\text{kg}}$$

$$\text{Therefore, } \frac{0.194 \text{ mol of solute (H}_2\text{O)}}{\text{kg solvent 2-methyl-2-propanol}}$$

Since mass of solvent is 1000. g,

$$\frac{0.194 \text{ mol H}_2\text{O}}{\text{kg solvent}} \cdot 0.1000 \text{ kg} = 0.0194 \text{ mol H}_2\text{O}$$

$$0.0194 \text{ mol H}_2\text{O} \times 18.02 \frac{\text{g}}{\text{mol}} = 0.350 \text{ g H}_2\text{O}$$

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5. Osmotic pressure is a colligative property that can be used to determine the molar mass of an unknown substance. The osmotic pressure is determined by measuring the height of the column of solution and converting this value to mm of Hg (1 mm Hg = 1 torr, 760 torr = 1 atm). Using, $\Pi V_{\text{solution}} = n_{\text{solute}} R T$ (where Π is the osmotic pressure, R is the universal gas constant and T is the Kelvin temperature), calculate the molar mass of insulin if 20.0 mg is dissolved in 10.0 mL of solution to give a resulting osmotic pressure of 6.48 torr at 25°C. [5740 g/mol]

$$\Pi_{\text{soln}} \cdot V_{\text{soln}} = n_{\text{solute}} RT$$

$$n_{\text{solute}} = \frac{\text{mass solute}}{MM_{\text{solute}}} \leftarrow \begin{matrix} 20.0 \text{ mg} \\ \text{molar mass of solute} \end{matrix}$$

Since Π_{soln} , V_{soln} and T are given;

we can calculate n_{solute} which can
be used in determining MM_{solute} .

$$n_{\text{solute}} = \frac{\Pi V}{R T} = \frac{\left(6.48 \text{ torr} \cdot \frac{1 \text{ atm}}{760 \text{ torr}}\right) \left(10.0 \text{ mL} \cdot \frac{1 \text{ L}}{10^3 \text{ mL}}\right)}{\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) (298 \text{ K})}$$

$$= 3.487 \times 10^{-6} \text{ mol}$$

$$\therefore MM_{\text{solute}} = \frac{\text{mass solute}}{n_{\text{solute}}} = \frac{\left(20.0 \text{ mg} \cdot \frac{1 \text{ g}}{10^3 \text{ mg}}\right)}{3.487 \times 10^{-6} \text{ mol}}$$

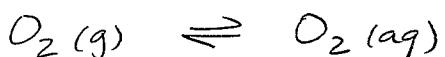
$$= 5736 \text{ g/mol}$$

$$\Rightarrow 5740 \text{ g/mol} \quad (3 \text{ sign. figs.})$$

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6. Henry's Law constant for most gases decreases with increased temperature. Given that K_H for O_2 is $2.20 \times 10^{-3} \text{ M atm}^{-1}$ at 5°C , calculate the percent $\text{O}_2(\text{aq})$ saturation if a lake water sample at 5°C and sea-level is found to contain, 9.20 mg/L of $\text{O}_2(\text{aq})$. (Recall: partial pressure of O_2 at sea-level = 0.2095 atm). [62.3 % sat^d]

For the chemical equilibrium describing the dissolution of a gas;



The equilibrium constant is given by;

$$K_H = \frac{[\text{O}_2(\text{aq})]^{\text{sat}}}{P_{\text{O}_2(\text{g})}}$$

 partial pressure of gas

Henry's Law
constant

$$\text{So, } [\text{O}_2(\text{aq})]^{\text{sat}} = K_H \cdot P_{\text{O}_2}$$

$$\text{and } [\text{O}_2(\text{aq})]^{\text{sat. at } 5^\circ\text{C}} = K_H^{(5^\circ\text{C})} \cdot P_{\text{O}_2}$$

$$= \left(2.2 \times 10^{-3} \frac{\text{M}}{\text{atm}} \right) (0.2095 \text{ atm})$$

$$= 4.61 \times 10^{-4} \text{ M}$$

Converting to $\frac{\text{mg O}_2}{\text{L}}$ yields

$$4.61 \times 10^{-4} \frac{\text{mol O}_2}{\text{L}} \times \frac{32.0 \text{ g}}{\text{mol}} \times \frac{10^3 \text{ mg}}{\text{g}} = 14.7 \frac{\text{mg O}_2}{\text{L}}$$

Therefore % satⁿ = $\frac{9.20}{14.7} \cdot 100\% = 62.3\%$

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7. An Okanagan vintner (that's a winemaker) is waiting for her grapes to freeze in order to make a special batch of holiday ice-wine. Recent analysis has shown that the grapes are currently 28% sugar by mass. Assuming that sugar (formula $C_6H_{12}O_6$) is the only solute present and that water is the solvent, at what temperature will the grapes freeze?

$[-4.0\text{ }^{\circ}\text{C}]$

$$\Delta T_f = K_f \cdot m$$

↑ ↑
 sugar is solute
 H_2O is solvent

$$28\% \text{ mass ratio} = \frac{28\text{ g sugar}}{100.\text{ g soln}}$$

converting to molality yields

$$n_{\text{sugar}} = 28\text{ g} \cdot \frac{1\text{ mol}}{180\text{ g}} = 0.1556\text{ mol}$$

$$\text{mass water} = 100.\text{ g soln} - 28\text{ g sugar} = 78\text{ g } H_2O$$

$$\therefore m = \frac{n_{\text{solute}}}{\text{mass solvent}} = \frac{0.1556\text{ mol}}{0.072\text{ kg}} = 2.16 \frac{\text{mol}}{\text{kg}}$$

$$\text{and } \Delta T_f = (1.86 \frac{{}^{\circ}\text{C kg}}{\text{mol}}) (2.16 \frac{\text{mol}}{\text{kg}})$$

$$= 4.0_2 {}^{\circ}\text{C}$$

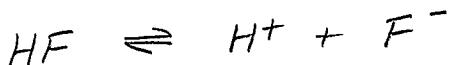
Therefore, grapes freeze at $-4.0\text{ }^{\circ}\text{C}$

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8. Calculate the van't Hoff factor (i) for HF if the freezing point of a 0.50 m aqueous solution has a freezing point of -1.00°C . What percentage of the HF is dissociated at this concentration.

$$[i=1.075; \frac{7.6}{33.8}\% \text{ diss}]$$

Because HF is a weak acid, it will dissociate partially into H^+ and F^- ions:



$$\text{we can define \% dissociation} = \frac{\text{N}_{\text{HF dissociated}}}{\text{N}_{\text{HF initial}}} \cdot 100\%$$

Since all colligative properties depend only on the number of solute particles, the extent of dissociation will affect the magnitude of the freezing point depression.

$$i = \frac{\Delta T_{\text{obs}}}{\Delta T_{\text{calc}}} \leftarrow \begin{array}{l} \text{experimentally observed} \\ \text{based on no dissociation} \\ \text{into ions} \end{array}$$

Note: in this case i will range from $1 \rightarrow 2$ depending on extent of dissociation

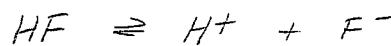
$$\Delta T_{\text{calc}} = K_f^{(\text{H}_2\text{O})} \cdot m = \left(1.86 \frac{\text{ }^\circ\text{C kg}}{\text{mol}}\right) \left(0.50 \frac{\text{mol}}{\text{kg}}\right) = 0.93 \text{ }^\circ\text{C}$$

$$\Delta T_{\text{obs}} = 1.00 \text{ }^\circ\text{C}$$

$$\therefore i = \frac{1.00}{0.93} = 1.075$$

To calculate % HF dissociation at this conc.,
use observed ΔT_f to calculate 'effective' $M_{\text{solute particles}}$
i.e.

$$M_{\text{particles}} = \frac{\Delta T_{\text{obs}}}{K_f} = \frac{1.00 \text{ } ^\circ\text{C}}{1.86 \frac{\text{ } ^\circ\text{C kg}}{\text{mol}}} = 0.538 \frac{\text{mol}}{\text{kg}}$$



I	0.50 m	0	0
C	-x	+x	+x
E	(0.50-x)	x	x

Since the total number particles (HF, H⁺ & F⁻)
is equal to 0.538 $\frac{\text{mol}}{\text{kg}}$ (as determined by ΔT_{obs})

$$(0.50-x) + x + x = 0.538$$

$$\therefore x = 0.038$$

$$n_{\text{HF dissociated}} = 0.038$$

$$n_{\text{HF initial}} = 0.50$$

$$\therefore \% \text{ dissociation} = \frac{0.038}{0.50} \times 100\% = 7.6\%$$