66 An aqueous solution is 8.50% ammonium chloride by mass. The density of the solution is 1.024 g/mL
Find: molality, mole fraction, molarity.

NH_4Cl : 53.491 g/mol H_2O: 18.016 g/mol

Find molality:

$$\frac{8.50\,g\ NH_4Cl}{100\,g\ \text{solution}} \longrightarrow \frac{\text{mol}\ NH_4Cl}{kg\ H_2O}$$

mass percent   molality

Assuming 100 g solution, find mol ammonium chloride

$$8.50\,g\ NH_4Cl \times \frac{\text{mol}\ NH_4Cl}{53.491\,g\ NH_4Cl} = 0.1589052364\ \text{mol}\ NH_4Cl$$

Find mass water

$$100\,g\ \text{solution} - 8.50\,g\ NH_4Cl = 91.50\,g\ H_2O = 0.09150\ kg\ H_2O$$

So molality is:

$$\frac{0.1589052364\ \text{mol}\ NH_4Cl}{0.09150\ kg\ H_2O} = \boxed{1.74\,m\ NH_4Cl}$$

If we keep our basis of 100 g solution, we've already calculated the moles of ammonium chloride. All we need is moles water - and we already have mass!

Mole fraction:

$$\frac{8.50\,g\ NH_4Cl}{100\,g\ \text{solution}} \longrightarrow \frac{\text{mol}\ NH_4Cl}{\text{mol}\ NH_4Cl + \text{mol}\ H_2O}$$

mass percent   mole fraction

An aqueous solution is 8.50% ammonium chloride by mass. The density of the solution is 1.024 g/mL
Find: molality, mole fraction, molarity.

NH_4Cl : 53.491 g/mol H_2O: 18.016 g/mol

Find moles water

$$91.50\,g\ H_2O \times \frac{mol\ H_2O}{18.016\,g\ H_2O} = 5.078818828\ mol\ H_2O$$

$$X_{NH_4Cl} = \frac{0.1589052364\ mol\ NH_4Cl}{0.1589052364\ mol\ NH_4Cl + 5.078818828\ mol\ H_2O}$$

$$= \boxed{0.0303}$$

(If we wanted Xwater, Xwater=1-Xammonium chloride)

Molarity:

$$\frac{8.50\,g\ NH_4Cl}{100\,g\ solution} \longrightarrow \frac{mol\ NH_4Cl}{L\ solution}$$

mass percent

If we keep our basis of 100g, we already know moles of ammonium chloride. We also know the mass of the solution and can convert that to volume using the density.

$$100\,g\ solution \times \frac{mL}{1.024\,g} = 97.65625\ mL = 0.09765625\ L$$

$$\frac{0.1589052364\ mol\ NH_4Cl}{0.09765625\ L} = \boxed{1.63\ \underline{M}\ NH_4Cl}$$

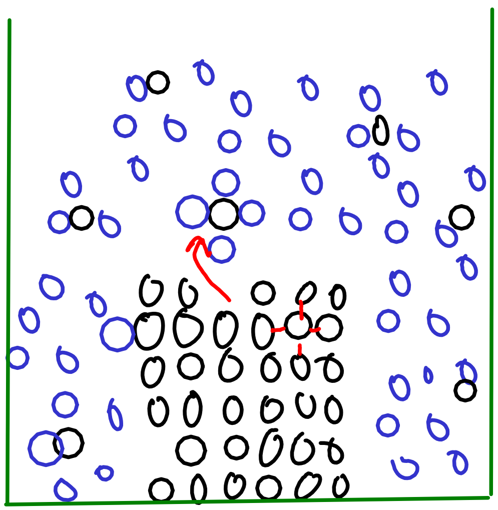
HOW THINGS DISSOLVE

- Let's look at how things dissolve into water, since aqueous solutions are quite common.

sucrose (table sugar)

$$C_{12}H_{22}O_{11}(s) \underset{}{\overset{H_2O}{\rightleftharpoons}} C_{12}H_{22}O_{11}(aq)$$

... what happens?



- Water molecules pull the sugar molecules out of the sugar crystal and into solution.

- Attractions between sugar molecules and water allow this to happen.

- The solubility of the sugar depends on how well water and sugar interact (HYDRATION) versus how well the sugar molecules are held in the crystal (LATTICE ENERGY)

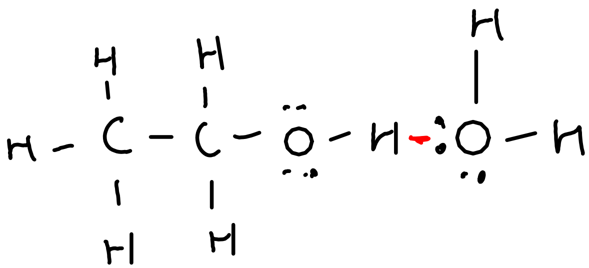
- "like dissolves like": Substances held together by similar (or at least compatible) kinds of attractive forces can dissolve in each other. Substances that are held together by very different kinds of attractive forces will not dissolve in one another!

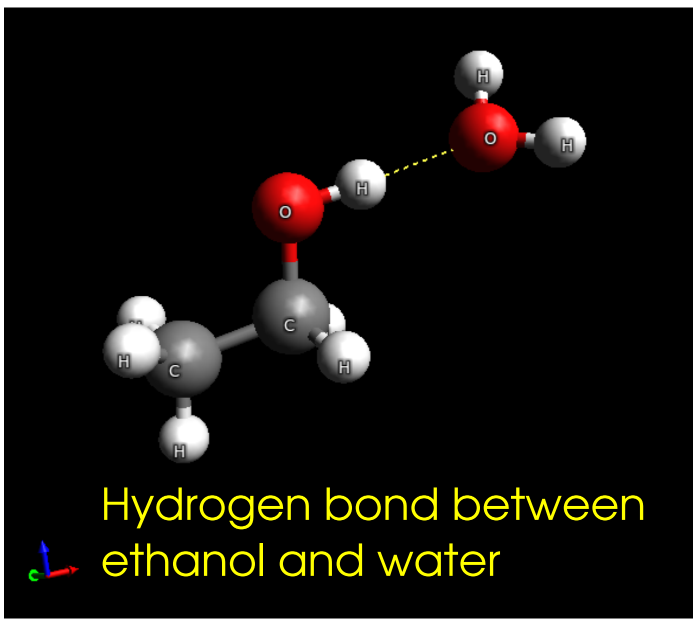
Consider WATER:

HYDROGEN BONDS

↓

Water mixes well with other substances that can hydrogen bond, like ETHANOL!





Hydrogen bond between ethanol and water

POLAR

↓

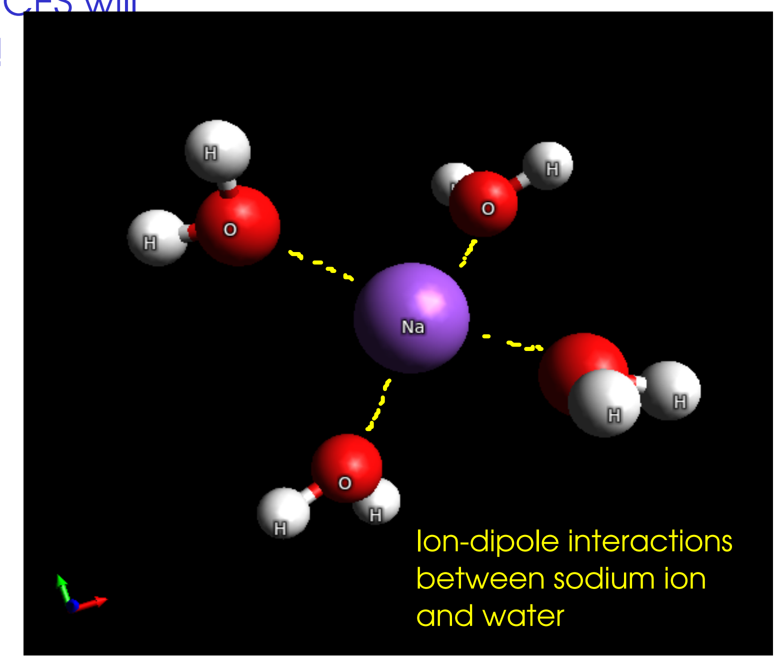
Water can dissolve polar substances!

(SUCROSE is polar!)

↓

Since IONIC BONDS are also interactions between opposite charges (You can think of an ionic bond here as an extreme case of dipole-dipole interaction), many IONIC SUBSTANCES will also dissolve in water!

$Na^+ - Cl^-$



Ion-dipole interactions between sodium ion and water

SMALL (little London force)

↓

large and/or nonpolar solutes do not dissolve well in water!

(example: OILS and WAXES)

MOLECULAR AND IONIC SOLUTIONS

- MOLECULAR solutions:

Contain MOLECULES dissolved in one another.

(1) - Any mixture of GASES

- all gases mix with one another, since gas molecules (effectively) do not interact with one another.

(2) - Liquids

- Liquids dissolve well in one another only if they are held together by similar kinds of forces

(3) - Solids and liquids

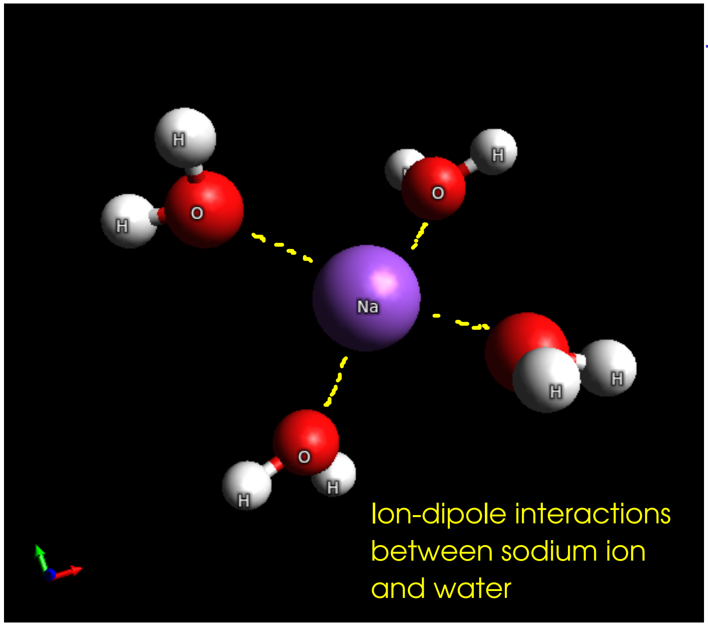
- MOLECULAR SOLIDS will dissolve well in liquids if they are held together by similar forces.

- IONIC SOLIDS will sometimes dissolve in POLAR liquids, but not in nonpolar liquids

- COVALENT NETWORK solids don't generally dissolve well in other substances

IONIC solutions

- form when ions from IONIC SUBSTANCES interact with POLAR solvents - often WATER.



The charged ends of the water molecule HYDRATE the ions.

vs. $Cl^- - Na^+ - Cl^-$

$Na^+ - Cl^- - Na^+$

- The solubility of an ionic compound depends on whether HYDRATION (attraction of water molecules for an ion) is greater than LATTICE ENERGY - the attrraction of ions in a crystal lattice for one another..

- SMALLER IONS are usually easier to enclose in water than larger ones, and ions with larger charges are attracted to water molecules.

- But solubility is also determined by LATTICE ENERGY - which holds the solid ionic compound together. Ions with high charges tend to be strongly attracted to other ions in a crystal, meaning lattice energy is high. Smaller ions also tend to have higher lattice energies. Lattice energy and hydroation are competing trends!

COLLIGATIVE PROPERTIES

- properties unique to solutions.

- depend only on the CONCENTRATION of a solution and not the IDENTITY of the solute**

**ionic solutes: Remember that they dissociate into MULTIPLE IONS!

1. Freezing point depression
   - The freezing temperature of a SOLUTION gets lower as the CONCENTRATION of a solution increases.

2. Vapor pressure lowering
   - The vapor pressure of a solution (pressure of sovent vapor over a liquid surface) goes DOWN as solution concentration goes UP

3. Boiling point elevation
   - The boiling temperature of a solution increases as the concentration of the solution increases.

4. Osmotic pressure
   - The pressure required to PREVENT the process of osmosis

FREEZING POINT DEPRESSION

$$\Delta T_f = K_f \times c_m$$

- c_m — concentration of solute (molality)
- K_f — Freezing point depression constant (for SOLVENT)
- ΔT_f — Freezing point depression: The amount the freezing temperature is LOWERED by the solute.

- Applications: In chemistry, this effect is often used to determine the molecular weight of an unknown molecule.

A solution of 2.500g of unknown dissolved in 100.0 g of benzene has a freezing point of 4.880 C. What is the molecular weight of the unknown?

$K_{f,\text{benzene}} = 5.065\ ^{\circ}C/m$, $T_{f,\text{benzene}} = 5.455^{\circ}C$ (see p500 9th, p509, 10th)

$$\Delta T_f = K_f \times C_m \quad C_m = \frac{\text{mol unknown}}{\text{kg benzene}}$$

ΔT_f: $5.455^{\circ}C - 4.880^{\circ}C = 0.575^{\circ}C$

K_f: $5.065^{\circ}C/m$

To find molecular weight, we need to know the moles of unknown!

Finding Cm will give us the moles of unknown, since we already know the mass of benzene

First, calculate the MOLAL CONCENTRATION based on freezing point depression!

$$0.575^{\circ}C = \left(5.065\ ^{\circ}C/m\right) \times C_m$$

$$C_m = 0.1135241856\ m = 0.1135241856\ \text{mol unknown}/\text{kg benzene}$$

To find moles unknown, multiply the mass of benzene by the molal concentration:

$$0.1000\ \text{kg benzene} \times \frac{0.1135241856\ \text{mol unknown}}{\text{kg benzene}} = 0.01135241856\ \text{mol unknown}$$

MOLECULAR WEIGHT is mass per mole, so:

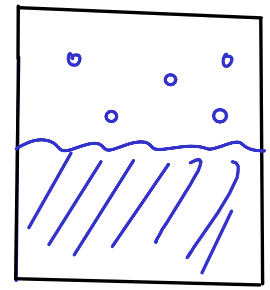
$$MW = \frac{\text{mass unknown}}{\text{mol unknown}} = \frac{2.500\,g}{0.01135241856\ \text{mol unknown}} = \boxed{220.\ g/mol}$$

VAPOR PRESSURE LOWERING

- Described by RAOULT'S LAW

$$P_A = P_A^* \times X_A$$

- X_A: mole fraction of component A
- P_A^*: vapor pressure of pure component A (depends on temperature)
- P_A: partial pressure of component A in a solution



P_A = partial pressure of the VAPOR of solvent molecules.

... but component "A" above is actually the SOLVENT. If we want to describe this as a colligative property, we want to express Raolt's law in terms of the SOLUTE! Assuming a two-component mixture, we get...

$$\Delta P = P_A^* \times X_B$$

- X_B: mole fraction of component B (the SOLUTE in a two-component mixture)
- ΔP: Vapor pressure lowering. This is the DECREASE in the vapor pressure of the solvent due to the presence of solute.

BOILING POINT ELEVATION

- Since the vapor pressure is lowered by the presence of a solute, AND since boiling occurs when the vapor pressure of a liquid equals the external pressure - solutes also cause BOILING POINT ELEVATION.

- The equation for boiling point elevation looks almost exactly like the equation for the freezing point depression, and is used in almost the same way.

$$\Delta T_b = K_b \times c_m$$

c_m: concentration of solute (molality)

K_b: Boiling point elevation constant (for SOLVENT) (p500, 9th; p509, 10th)

ΔT_b: Boiling point elevation: The amount the boiling temperature is RAISED by the solute.

What is the boiling point of a solution that contains 2.817 g of molecular sulfur S_8) dissolved in 100.0 grams of acetic acid?

$T_b = 118.5°C$ $K_b = 3.08°C/m$ (see p500 for data) p509, 10th

$\Delta T_b = K_b \times C_m$ (K_b = 3.08°C/m)

$C_m = \frac{\text{mol } S_8}{\text{kg } HC_2H_3O_2}$ (kg $HC_2H_3O_2$ = 0.1000 kg $HC_2H_3O_2$)

First, find the moles of sulfur. Then fnd Cm and calculate the boiling point elevation.

S_8: 8 × 32.07 = 256.56 g S_8 = mol S_8

$2.817 \text{ g } S_8 \times \frac{\text{mol } S_8}{256.56 \text{ g } S_8} = 0.01097988777 \text{ mol } S_8$

Find Cm:

$C_m = \frac{0.01097988777 \text{ mol } S_8}{0.1000 \text{ kg } HC_2H_3O_2} = 0.1097988775 \text{ } \underline{m} \text{ } S_8$

Finding boiling point ELEVATION:

$\Delta T_b = 3.08 °C/m \times 0.1097988775 \text{ } \underline{m} \text{ } S_8 = 0.3382 °C$

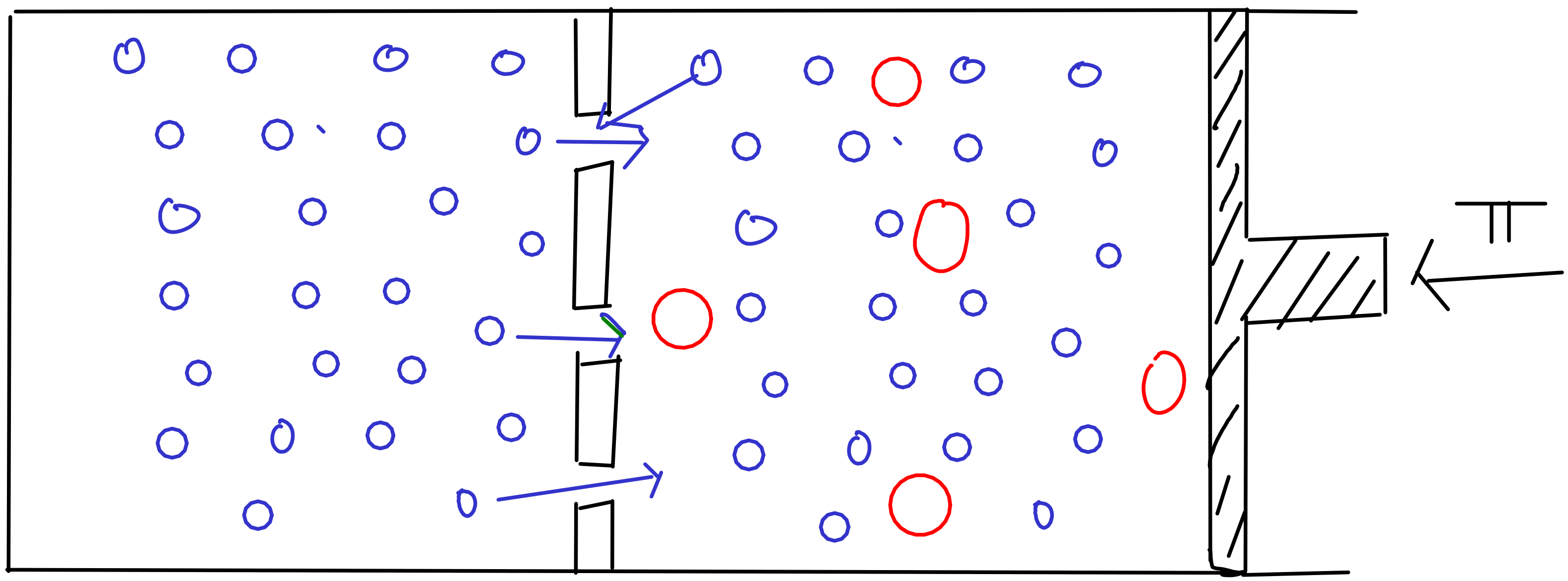
Now, find the boiling point by ADDING the elevation to the original boiling point:

$T_{b,\text{solution}} = 118.5°C + 0.3382°C = \boxed{118.8°C}$

OSMOTIC PRESSURE

permits flow of solvent, but not solute particles

- OSMOSIS: the flow of solvent molecules through a SEMIPERMEABLE membrane to equalize concentration of solute on each side of the membrane.



The rate of solvent migration towards the RIGHT is greater than that towards the LEFT.

If you apply enough pressure to the piston, osmosis will not occur. This pressure is called the OSMOTIC PRESSURE

$$\pi = M \times R \times T$$

- T: temperature
- R: ideal gas constant
- M: molar concentration of solute

IONIC COMPOUNDS and colligative properties

- Ionic compounds DISSOCIATE in water into their component ions. Each ion formed can act as a solute and influence the colligative properties!

$$NaCl(s) \longrightarrow Na^{+}(aq) + Cl^{-}(aq)$$

2 ions!

... so the concentration of IONS here is TWICE the nominal NaCl concentration.

$$CaCl_2(s) \longrightarrow Ca^{2+}(aq) + 2\,Cl^{-}(aq)$$

3 ions!

... so the concentration of IONS here is THREE TIMES the nominal calcium chloride concentration.

- Ions interact with each other in solution, so unless an ionic solution is DILUTE, the effective concentrations of ions in solution will be less than expected. A more advanced theory (Debye-Huckel) covers this, but we'll assume that our solutions are dilute enough so that we can use the concentration of the ions in solution to determine the colligative properties!

If you are at an altitude high enough for the boiling point of water to be 95.00 C, what amount of sodium chloride would you need to add to 1.000 kg of water to raise the boiling point to 100.00 C?

$K_b = 0.512\ ^\circ C/m$ NaCl: 58.443 g/mol

$\Delta T_b = K_b \times C_m$

K_b: 0.512 °C/m

ΔT_b: 100.00°C − 95.00°C = 5.00°C

$C_m = \frac{\text{mol ions}}{\text{kg } H_2O}$ [1.000 kg

Find Cm (molal concentration of IONS)

$5.00^\circ C = 0.512\ ^\circ C/m \times C_m$; $C_m = 9.765625\ m$ ions

Find moles ions

$1.000\text{ kg } H_2O \times 9.765625 \frac{\text{mol ions}}{\text{kg } H_2O} = 9.765625\text{ mol ions}$

$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$; so mol NaCl = 2 mol ions

Find moles NaCl (from the moles of ions), then convert to mass:

$9.765625\text{ mol ions} \times \frac{\text{mol NaCl}}{2\text{ mol ions}} \times \frac{58.443\text{ g NaCl}}{\text{mol NaCl}} = \boxed{285\text{ g NaCl}}$

EXTERNAL FACTORS AFFECTING SOLUBILITY

- There are a few external factors that affect the solubility. (By external, we mean other than the chemical identity of the solute and solvent).

1) TEMPERATURE

-For gases dissolved in liquids, the solubility DECREASES as the temperature INCREASES

- This is why THERMAL POLLUTION is bad! Hot water holds less oxygen than cooler water.

- For solids dissolved in liquids, solubility USUALLY increases with temperature. This is not true for ALL solid/liquid solutions.

2) PRESSURE

- For gases dissolved in liquids, solubility INCREASES when the partial pressure of the solute gas over the solution INCREASES.

- Consider soft drinks. They go flat after opening because the pressure of carbon dioxide over the liquid goes down.

- No significant pressure effects for solid/liquid solutions.