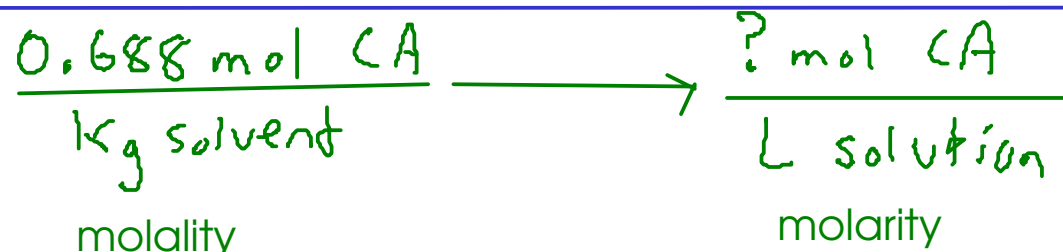
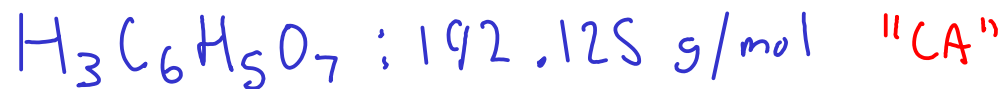


Example: If a solution is 0.688 m citric acid, what is the molar concentration (M) of the solution?  
 The density of the solution is 1.049 g/mL



To solve the problem, we will ASSUME A BASIS of 1 kg of solvent. With a basis of 1 kg solvent, we know that we have 0.688 moles of CA. So to finish solving the problem, we just need to find out the VOLUME of the SOLUTION. To do that, calculate the mass of the solution and then use density to find volume.

$$192.125 \text{ g CA} = \text{mol CA}$$

$$0.688 \text{ mol CA} \times \frac{192.125 \text{ g CA}}{\text{mol CA}} = 132.182 \text{ g CA}$$

So the mass of the solution is ...

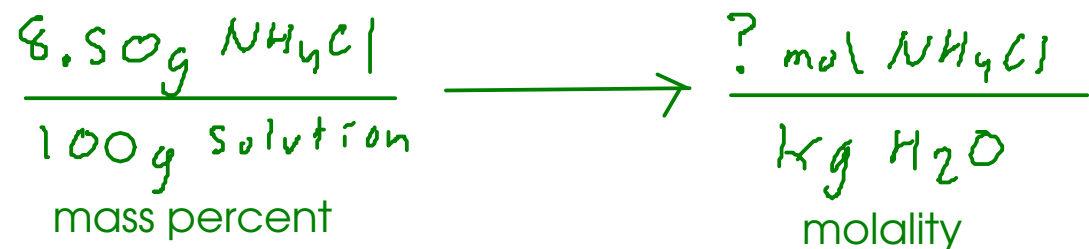
$$1000 \text{ g solvent} + 132.182 \text{ g CA} = 1132.182 \text{ g solution}$$

And the volume is ...

$$1132.182 \text{ g} \times \frac{\text{mL}}{1.049 \text{ g}} = 1079.296473 \text{ mL} = 1.079296473 \text{ L}$$

$$M = \frac{0.688 \text{ mol CA}}{1.079296473 \text{ L}} = \boxed{0.637 \text{ M CA}}$$

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



Assume a basis of 100 g solution. This means we have 8.50 grams ammonium chloride. Find moles ammonium chloride.

$$8.50 \text{ g NH}_4\text{Cl} \times \frac{\text{mol NH}_4\text{Cl}}{53.491 \text{ g NH}_4\text{Cl}} = 0.1589052364 \text{ mol NH}_4\text{Cl}$$

Find mass water.

$$100 \text{ g solution} - 8.50 \text{ g NH}_4\text{Cl} = 91.50 \text{ g H}_2\text{O} = 0.09150 \text{ kg H}_2\text{O}$$

So the molality is ...

$$m = \frac{0.1589052364 \text{ mol NH}_4\text{Cl}}{0.09150 \text{ kg H}_2\text{O}} = \boxed{1.74 \text{ m NH}_4\text{Cl}}$$

An aqueous solution is 8.50% ammonium chloride by mass. The density of the solution is 1.024 g/mL

Find: molality and molarity.



We can use the same basis that we used for finding molality (100 g solution). If we do that, we already know moles. So all we need to do is find out volume...



Find volume of solution...

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

So the molarity is ...

$$M = \frac{0.1589052364 \text{ mol NH}_4\text{Cl}}{0.09765625 \text{ L}} = \boxed{1.63 \text{ M NH}_4\text{Cl}}$$

## 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 solvent 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

$$\Delta T_f = K_f \times C_m$$

— concentration of solute (molality)

— Freezing point depression constant (for SOLVENT)

— 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?

$$K_{f, \text{benzene}} = 5.065 \text{ } ^\circ\text{C}/m, \quad T_{f, \text{benzene}} = 5.455 \text{ } ^\circ\text{C} \quad \left( \begin{array}{l} \text{see} \\ \text{p500 9th} \\ \text{p509, 10th} \end{array} \right)$$

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

$\underbrace{\quad}_{= 5.065 \text{ } ^\circ\text{C}/m}$   
 $\underbrace{\quad}_{5.455 \text{ } ^\circ\text{C} - 4.880 \text{ } ^\circ\text{C} = 0.575 \text{ } ^\circ\text{C}}$

To find molecular weight, we need to know the moles unknown. Then we just divide ...  
2.500g / ?? mol unknown

First, calculate the MOLAL concentration, cm

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

$$C_m = 0.1135241856 \text{ m}$$

To find moles unknown we need to multiply the molal concentration by the mass of benzene.

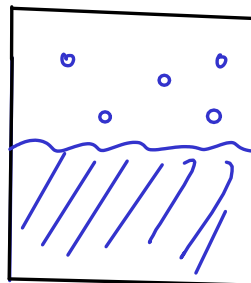
$$0.1000 \text{ kg benzene} \times \frac{0.1135241856 \text{ mol unkr}}{\text{kg benzene}} = 0.0113524186 \text{ mol unkr}$$

And the MOLECULAR WEIGHT is ...

$$MW = \frac{\text{mass unkr}}{\text{mol unkr}} = \frac{2.500 \text{ g}}{0.0113524186 \text{ mol unkr}} = \boxed{220. \text{ g/mol}}$$

## VAPOR PRESSURE LOWERING

- Described by RAOULT'S LAW



$P_A$  = partial pressure of the VAPOR of solvent molecules.

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

mole fraction of component A

vapor pressure of pure component A (depends on temperature)

partial pressure of component A in a solution

... 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...

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

mole fraction of component B (the SOLUTE in a two-component mixture)

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.

$$\Delta T_b = K_b \times C_m$$

$\Delta T_b$  — Boiling point elevation: The amount the boiling temperature is RAISED by the solute.

$K_b$  — Boiling point elevation constant (for SOLVENT)

$C_m$  — concentration of solute (molality)

(pS0C, 9th  
pS09, 10th)



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?

$$T_b = 118.5^\circ\text{C}$$

$$K_b = 3.08^\circ\text{C}/m$$

(see p500 for data)  
p509, 10th

$$\Delta T_b = \frac{K_b \times m}{3.08^\circ\text{C}/m}$$

$$m = \frac{\text{mol } S_8}{\text{kg a.a.}}$$

$$S_8: \frac{8 \times 32.07}{256.56 \text{ g } S_8 = \text{mol } S_8}$$

Find  $m$  using the information given about the solution.

$$2.817 \text{ g } S_8 \times \frac{\text{mol } S_8}{256.56 \text{ g } S_8} = 0.0109798877 \text{ mol } S_8$$

$$\frac{0.0109798877 \text{ mol } S_8}{0.1000 \text{ kg a.a.}} = 0.1097988775 \text{ m}$$

$$\uparrow$$

(100.0 g)

Find  $\Delta T_b$  ...

$$\Delta T_b = (3.08^\circ\text{C}/m) \times (0.1097988775 \text{ m}) = 0.338^\circ\text{C}$$

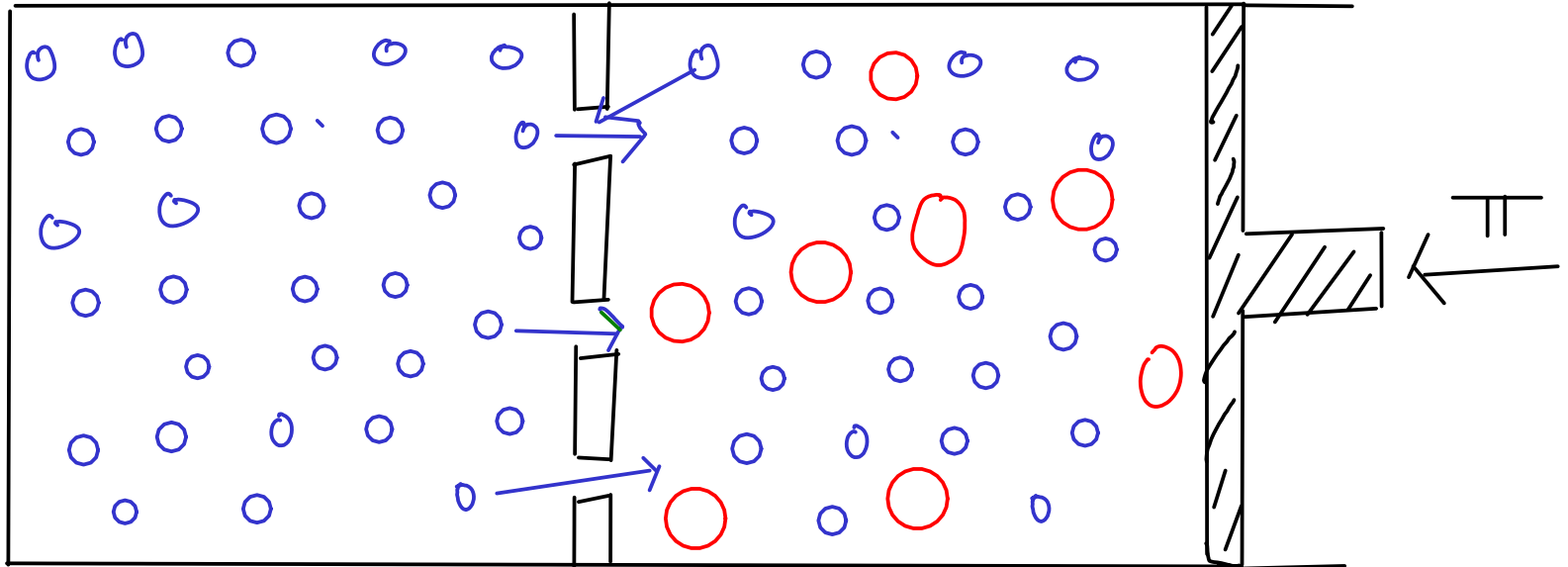
The new boiling point is ...

$$118.5^\circ\text{C} + 0.338^\circ\text{C} = \boxed{118.8^\circ\text{C}}$$

## 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

$$\Pi = M \times R \times T$$

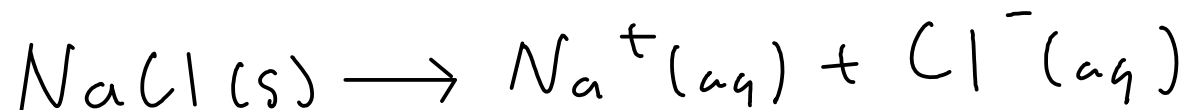
temperature

ideal gas constant

molar concentration of solute

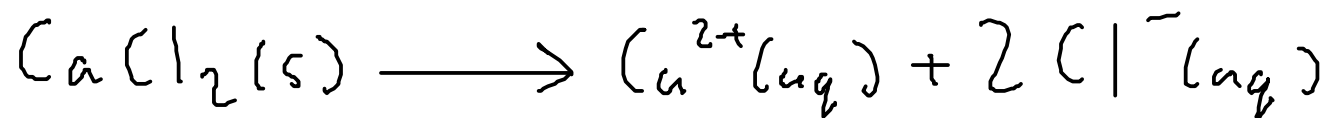
## IONIC COMPOUNDS and colligative properties

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



2 ions!

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



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?

$$K_b = 0.512 \text{ } ^\circ\text{C}/m \quad \text{NaCl: } 58.443 \text{ g/mol}$$

$$\frac{\Delta T_b}{K_b} = \frac{m \text{ ions}}{\text{kg H}_2\text{O}} \quad \left| \quad C_m = \frac{m \text{ ions}}{\text{kg H}_2\text{O}} \right.$$

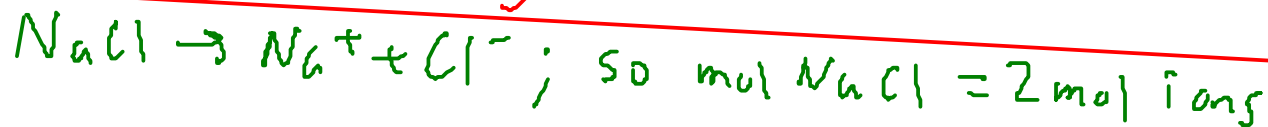
$$\frac{100.00^\circ\text{C} - 95.00^\circ\text{C} = 5.00^\circ\text{C}}{0.512^\circ\text{C}/m} \quad \left| \quad \begin{array}{l} \text{kg H}_2\text{O} \\ \uparrow 1.000 \text{ kg H}_2\text{O} \end{array} \right.$$

Find  $C_m$  (molal concentration of ions):

$$5.00^\circ\text{C} = (0.512^\circ\text{C}/m) \times C_m ; C_m = 9.765625 m \text{ ions}$$

Find moles ions

$$1.000 \text{ kg H}_2\text{O} \times \frac{9.765625 m \text{ ions}}{\text{kg H}_2\text{O}} = 9.765625 m \text{ ions}$$



$$9.765625 m \text{ ions} \times \frac{1 \text{ mol NaCl}}{2 m \text{ ions}} = 4.8828125 m \text{ NaCl}$$

Now find grams ...

$$4.8828125 m \text{ NaCl} \times \frac{58.443 \text{ g NaCl}}{m \text{ NaCl}} = \boxed{285 \text{ g NaCl}}$$

## KINETICS

- the study of the RATE of chemical reactions. Or, the study of the factors affecting how fast chemical reactions proceed.

### DEFINING RATE

- RATE is defined as the change in the molar (M) concentration of a reactant or product over time. Usually, rate is defined in terms of one of the REACTANTS



...Let's look at a simple combination

$$\text{Rate} = \frac{-\Delta[A]}{\Delta t}$$

$[A]$  = "molar concentration of substance "A".

Square brackets ( ) are used to denote MOLAR concentration

change in time

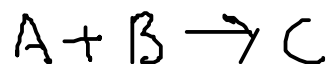
$$\text{Rate} = \frac{\Delta[C]}{\Delta t}$$

You could ALSO define the rate in terms of the disappearance of B or the appearance of C over time! Our choice of A was arbitrary,

Negative sign because we define the rate as a POSITIVE number, and (A) will decrease over time!

## THE RATE LAW

- We express the rate of reaction using an equation called the RATE LAW.



$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k \times [A]^p \times [B]^q$$

This is the RATE CONSTANT. It depends on TEMPERATURE, but does not depend on the CONCENTRATION of any reactant or product.

"p" and "q" are called REACTION ORDERS. They indicate the effect a particular reactant or catalyst has on the rate of a reaction. Reaction orders may be positive, zero (in which case the substance has NO effect on rate) and negative (in which case the substance actually slows the reaction down).

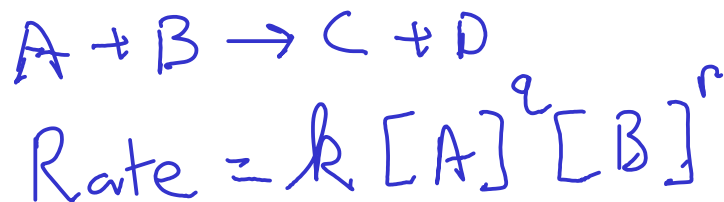
- Rate laws depend on CONCENTRATION of reactants. Since the concentrations of reactants CHANGE throughout the course of the reaction, so does the rate!
- RATE CONSTANTS and REACTION ORDERS are determined experimentally. If you do experiment 13 (the iodine clock reaction), you will see how this can be done in the lab via the INITIAL RATES METHOD.

Initial rates method:

- To determine the rate constant and reaction orders in a reaction, it's possible to monitor the rate of a reaction starting from time zero to a short time later where the concentrations of the reactants haven't changed much. In other words, we look at the INITIAL RATE.

- To determine the rate constant and orders, we need to perform several experiments - one for each order to determine and one baseline experiment to determine the rate constant.

Example:



... we want to find the rate constant 'k', and the orders 'q' and 'r'.

Trial	[A]	[B]	Rate $-\frac{\Delta [A]}{s}$
1	0.150	0.150	Baseline experiment
2	0.300	0.150	Double (A) to find 'q'
3	0.150	0.300	Double (B) to find 'r'

Trial	[A]	[B]	Rate $-\frac{\Delta[A]}{s}$
1	0.150	0.150	0.0016875
2	0.300	0.150	0.0033750
3	0.150	0.300	0.0067500

Rate doubles (green arrow from trial 1 to 2)  
Rate quadruples (orange arrow from trial 1 to 3)

The rate law is:

$$\text{Rate} = k [A]^q [B]^r$$

... so how do we use the data above to find out the values of 'k', 'q', and 'r'?

We observe that in the second trial ((A) doubled), the rate has doubled!

$$(2 \times [A])^q = 2 \times \text{Rate} ; q = 1$$

We observe that in the third trial ((B) doubled), the rate has quadrupled.

$$(2 \times [B])^r = 4 \times \text{Rate} ; r = 2$$

$$\text{Rate} = k [A] [B]^2$$



Trial	[A]	[B]	Rate $\frac{\Delta [A]}{s}$	Calculated 'k'
1	0.150	0.150	0.0016875	0.500
2	0.300	0.150	0.0033750	0.500
3	0.150	0.300	0.0067500	0.500

$$\text{Rate} = k [A][B]^2$$

Now, we'd like to know the value of 'k'. Solve rate law for 'k'.

$$k = \frac{\text{Rate}}{[A][B]^2}$$

Plug in each set of data to this equation and calculate 'k'!

The average of these calculated 'k' values equals the rate constant.  
(For real data, expect some experimental error in these numbers!)

$$\text{Rate} = 0.500 [A][B]^2$$

## FACTORS THAT AFFECT REACTION RATE

- ① CONCENTRATION OF REACTANTS
- ② SURFACE AREA OF CONTACT BETWEEN REACTANTS
- ③ CONCENTRATION OF / PRESENCE OF A CATALYST
- ④ TEMPERATURE

