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?

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

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

$$0.512\ ^\circ C/m$$

$$100.00\ ^\circ C - 95.00\ ^\circ C = 5.00\ ^\circ C$$

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

Find Cm (molal concentration of IONS):

$$5.00\ ^\circ C = 0.512\ ^\circ C/m \times C_m, \qquad C_m = 9.765625\ \underline{m}\ ions$$

Find moles ions:

$$1.000\ kg\ H_2O \times \frac{9.765625\ mol\ ions}{kg\ H_2O} = 9.765625\ mol\ ions$$
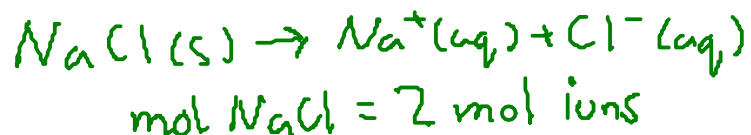
$$NaCl\,(s) \rightarrow Na^+(aq) + Cl^-(aq)$$ Each mole of NaCl dissociates into TWO moles of
$$mol\ NaCl = 2\ mol\ ions$$ ions! (One mole sodium ion, one mole chloride ion)

Find mol NaCl, then convert to mass:

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

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.
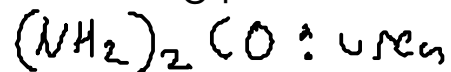
- No significant pressure effects for solid/liquid solutions.

Some sample colligative propoerties problems from the book...

12.97

p 521

What is the freezing point of a 41% solution of urea in water?

$$(NH_2)_2 CO : urea$$

$$\Delta T_F = K_F \times C_m$$

p500, $K_{F, H_2O} = 1.858 \,°C/m$

$T_{F, H_2O} = 0.000 \,°C$

$$C_m = \frac{mol \; urea}{kg \; water}$$

We need to find mol urea and kg water. We know mass percentage, so we'll have to start there.

41% urea : $\dfrac{41 g \; urea}{100 g \; solution}$;

We need mass WATER to find molality!

mass water $= 100g - 41g = 59g$

Find moles urea using formula weight and mass.

$$41g \; urea \times \frac{mol \; urea}{60.062 g \; urea} = 0.682627951 \; mol \; urea$$

$(NH_2)_2 CO :$
N: 2×14.01
H: 4×1.008
C: 1×12.01
O: 1×16.00
$\overline{60.062 \, g) \, mol}$

So, Cm is:

$$C_m = \frac{mol \; urea}{kg \; water} = \frac{0.682627951 \; mol \; urea}{0.059 \; kg \; water} = 11.56996527 \; \underline{m} \; urea$$

$$C_m = \frac{mol\ urea}{kg\ water} = \frac{0.682627951\ mol\ urea}{0.059\ kg\ water} = 11.56996527\ \underline{m}\ urea$$

Now we can find delta Tf:

$$\Delta T_F = \underline{K_F} \times C_m$$

$$p500,\ K_{F,H_2O} = 1.858\ ^oC/m$$

$$\Delta T_F = \left(1.858\ ^oC/m\right) \times \left(11.56996527\ \underline{m}\ urea\right) = 21.49699548\ ^oC$$

$$So,\ T_F = 0.000\ ^oC - 21.49699548\ ^oC = \boxed{-21\ ^oC}$$

12. 105, p 521

A compound (containing Mn, C, O) is 28.17% Mn, 30.80% C. A solution of the compound containing 0.125 g in 5.38 g cyclohexane freezes at 5.28 C. What is the molecular formula?

$$\Delta T_F = K_F \times C_m$$

$$T_{F, cyc} = 6.55°C \ , \ K_{F, cyc} = 20.0°C/m$$

$$C_m = \frac{mol \ unknown}{Kg \ cyc}$$

$$5.38g = 0.00538 \ kg$$

First, find Cm, then find mol unknown.

$$(6.55°C - 5.28°C) = (20.0°C) \times C_m$$

$$C_m = 0.0635 \ m$$

Now find moles unknown

$$0.0635 \ m = \frac{mol \ unknown}{0.00538 \ kg} \ , \ mol \ unknown = 3.4163 \times 10^{-4} \ mol$$

Molecular weight:

$$\frac{mass \ unknown}{mol \ unknown} = \frac{0.125g}{3.4163 \times 10^{-4} mol} = 366 \ g/mol$$

Molecular weight of unknown.

Find empirical formula from the mass data given

28.17 % mn

100% − 28.17% − 30.80% = 41.03 % O

30.80 % C

Convert this mass data to a MOLAR ratio:

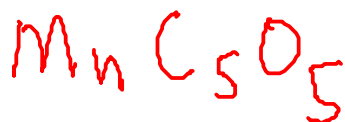to reduce to whole numbers, divide each term by the smallest (in this case, 0.512...)

Assume 100 g

$28.17 \text{ g Mn} \times \dfrac{\text{mol Mn}}{54.94 \text{ g Mn}} = 0.5127911722 \text{ mol Mn}$ 1 mol Mn

$30.80 \text{ g C} \times \dfrac{\text{mol C}}{12.01 \text{ g C}} = 2.564529559 \text{ mol C}$ 5.001 mol C

$41.03 \text{ g O} \times \dfrac{\text{mol O}}{16.00 \text{ g O}} = 2.564375 \text{ mol O}$ 5.001 mol O

So the EMPIRICAL formula is:

$Mn C_5 O_5$

1 Mn : 5 C : 5 O

Mn : 1 × 54.94
C : 5 × 12.01
O : 5 × 16.00
_____
194.99 g/mol ; compare to MW = 366 g/mol

194.99 times 2 is 390, closest to 366. So molecular formula is empirical times 2

$Mn_2 C_{10} O_{10}$

12.91, p 520

56 grams of a sample contain 0.51 mole fraction propane and the remainder butane. What are the masses of propane and butane in the sample?

Know! $X_{C_3H_8} = 0.51$

$X_{C_4H_{10}} = 1 - 0.51 = 0.49$

Want: mass C_3H_8

mass C_4H_{10}

How do we get from mole fraction to the masses in the sample?

$X_{C_3H_8} = 0.51 = \dfrac{moles\ C_3H_8}{total\ moles}$ let's assume ... FOR NOW ... that we have a mole of solution!

mol $C_3H_8 = 0.51 \times 1 = 0.51$ mol C_3H_8 Now, let's convert these to masses!
We need formula weights.

mol $C_4H_{10} = 0.49 \times 1 = 0.49$ mol C_4H_{10}

$C_3H_8 : 44.094\ g/mol$ | $C_4H_{10} : 58.12\ g/mol$

g $C_3H_8 : 0.51$ mol $C_3H_8 \times \dfrac{44.094\ g}{mol} = 22.48794\ g\ C_3H_8$

g $C_4H_{10} : 0.49$ mol $C_4H_{10} \times \dfrac{58.12\ g}{mol} = 28.4788\ g\ C_4H_{10}$

$\overline{\qquad\qquad\qquad}$
50.96674 g total

Use the ratio of mass butane/total mass and mass propane/total mass to find the actual butane and propane content of the sample!

$$g\ C_3H_8 : 0.51\ mol\ C_3H_6 \times \frac{44.094\ g}{mol} = 22.48794g\ C_3H_8$$

$$g\ C_4H_{10} : 0.49\ mol\ C_3H_8 \times \frac{58.12\ g}{mol} \doteq 28.4788g\ C_4H_{10}$$

$$\overline{\qquad\qquad\qquad}$$
$$50.96674g\ total$$

56 g of sample, so ...

$$56g \times \frac{22.48794g\ C_3H_8}{50.96674g\ total} = 24.7\ g\ C_3H_8$$

$$56g \times \frac{28.4788g\ C_4H_{10}}{50.96674g\ total} = 31.2g\ C_4H_{10}$$

So the composition of the sample is 25 g propane, 31 g butane.

12.103, p 521

Commercial sulfuric acid (98% by mass) is 18 M. What is the density of the solution, and what is the molality?

Want: $density = \dfrac{mass\ solution}{volume\ solution}$

know: $18\ M = \dfrac{mol\ H_2SO_4}{L\ solution}$

$98\% = \dfrac{g\ H_2SO_4}{100g\ solution}$

Let's assume we have 1 L of solution.

$\dfrac{18\ mol\ H_2SO_4}{L} \times 1L = 18\ mol\ H_2SO_4$

We need to find mass solution. To do that, we'll first calculate the mass of sulfuric acid.

$H_2SO_4: 98.086\ g/mol$

$18\ mol\ H_2SO_4 \times \dfrac{98.086g}{mol} = 1765.548\ g\ H_2SO_4$

Find mass solution

$1765.548g = 0.98 \times mass\ solution$ 98% of the solution is sulfuric acid!

$1801.5796g = mass\ solution$

Find density

$density = \dfrac{mass\ solution}{volume\ solution} = \dfrac{1801.5796g}{1000mL} = \boxed{1.8\ g/mL}$

$$\text{molality} = \frac{\text{mol } H_2SO_4}{kg \ H_2O}$$

If we keep our assumption of 1L of solution, we know the moles sulfuric acid is 18 mol. We also know the mass of sulfuric acid AND the total mass of the solution!

Find mass water by subtraction:

$1801.5796g \ \text{solution} - 1765.548 \ g \ H_2SO_4 = 36.0315g \ H_2O$

or, $0.0360315 \ kg \ H_2O$

$$\text{molality} = \frac{\text{mol } H_2SO_4}{kg \ H_2O} = \frac{18 \ \text{mol } H_2SO_4}{0.0360315 \ kg \ H_2O} = \boxed{500 \ m \ H_2SO_4}$$

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

$$A + B \longrightarrow C$$

...Let's look at a simple combination

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

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

Square brackets ( ) are used to denote MOLAR concentration
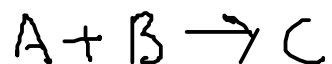
change in time

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

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

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,

THE RATE LAW

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

$$A + B \rightarrow C$$

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

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:

$$A + B \rightarrow C + D$$

$$Rate = k[A]^q[B]^r$$
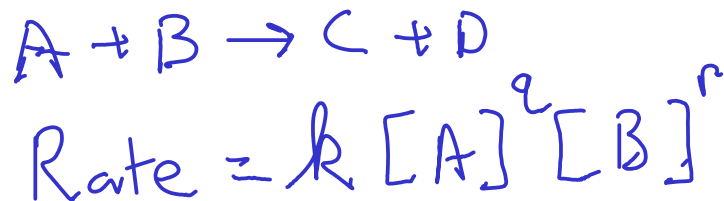
... we want to find the rate constant 'k', and the orders 'q' and 'r'.

Trial	$[A]$	$[B]$	Rate $\dfrac{-\Delta[A]}{s}$	
1	0.156	0.180		Baseline experiment
2	0.300	0.156		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

Rate quadruples

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!

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

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

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

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

Trial	[A]·	[B]	Rate $\frac{\Delta [A]}{s}$	Calculated 'k'
1	0.156	0.150	0.0016875	0.500
2	0.300	0.150	0.0033750	0.500
3	0.150	0.300	0.0067500	0.500

$$Rate = k[A][B]^2$$

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

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

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!)

$$Rate = 0.500[A][B]^2$$

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

$$Fe + 2HCl \rightarrow FeCl_2 + H_2$$

Fe

6m
HCl

Fe powder

6m
HCl
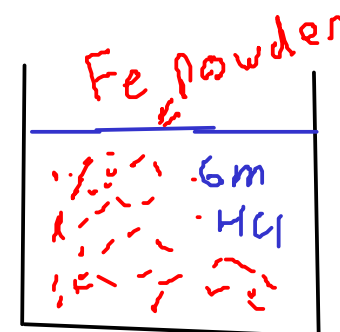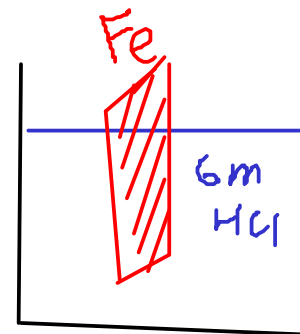
CONCENTRATION OF REACTANTS

- Usually, the reaction rate increases as you increase the concentration of a reactant. This is true if the order for that reactant is greater than zero!

$$Rate = k[A]^q$$

$$[A]^0 \qquad [A]^1 \qquad [A]^{-1} \qquad \frac{1}{[A]}$$

If the order is 0 the value of this term will be 1 no matter what (A) is!

If the order is -1, this term will get SMALLER (reducing rate) as (A) gets larger!

"inhibitor"

- In most cases, reaction orders ARE positive numbers!

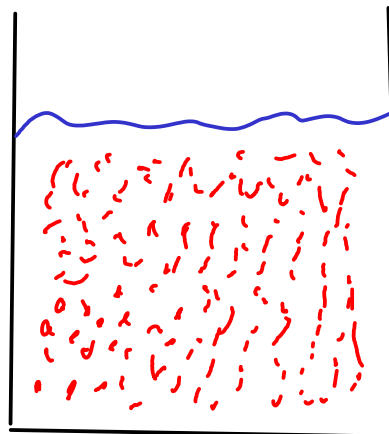# SURFACE AREA OF CONTACT BETWEEN REACTANTS

- If a reaction takes place at an INTERFACE, then the reaction rate will depend on the SURFACE AREA of that interface!

Consider a reaction between a liquid and a solid. The reaction can only take place where the liquid and the solid TOUCH each other,

Next, try the same reaction, but break the cube into small fragments first!
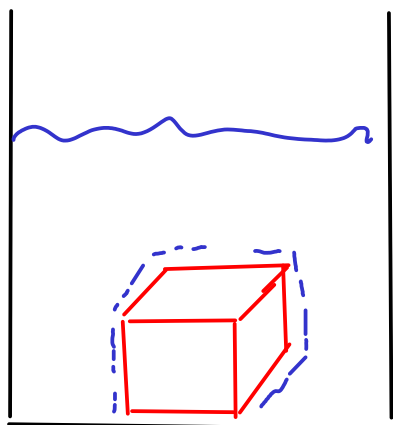
The reaction takes place only on the surface of the cube.

Here, the reaction takes place on the surface area of each fragment. In total, this is a much LARGER surface than the cube.

- The larger the SURFACE AREA of the INTERFACE between the reactants, the faster the reaction will occur!

- This is not an important factor for reactions that take place IN SOLUTION, since there is no interface.

CONCENTRATION OF / PRESENCE OF A CATALYST

-a CATALYST is a substance that INCREASES the rate of a reaction without being consumed in the reaction.

- Appear in the rate law equation, but are written as "reaction conditions" in traditional chemical equations. Typically, the higher the concentration of catalyst, the faster the reaction.

$$A + B \xrightarrow{c} D$$

$$Rate = k[A]^p [B]^q [C]^r$$

The catalyst shows up in the rate law like the reactants!

- Work via many different mechanisms. Some provide surfaces for reactants to bind to and react. Some react with reactant molecules to leave them in a state more suitable for the main reaction (and are then regenerated during the main reaction). Some catalysts bind to and bend reactants into favorable orientations for reactions, etc.

- Biological catalysts are usually called ENZYMES.

TEMPERATURE

- We observe that chemical reactions proceed FASTER at HIGHER temperatures.

... but sometimes reactions are run at low temperatures for other reasons - like safety, decomposition of desired products at high temperatures, formation of competing undesirable products at high temperatures, etc.

REACTION RATE THEORY

- We'd like to have an explanation for how the four factors we discussed affect the reaction rate!

- COLLISION THEORY and TRANSITION STATE THEORY attempt to explain reaction rate.

COLLISION THEORY

- states that for a reaction to occur between atoms or molecules, three things must occur:

① Reactants must COLLIDE with each other.

② Colliding reactants must hit each other with the correct ORIENTATION to react.

③ Colliding reactants must also hit each other with ENOUGH ENERGY to react (called the ACTIVATION ENERGY)
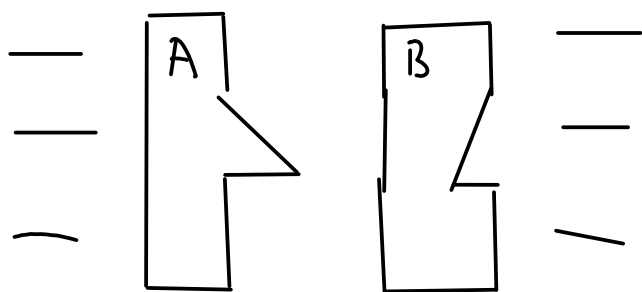
A collision like this - even an energetic one, would lead to NO REACTION, since the molecules are not aligned properly to react. This is particularly important for larger molecules (like biomolecules) where reactive parts of the molecule are small compared to the size of the whole molecule!
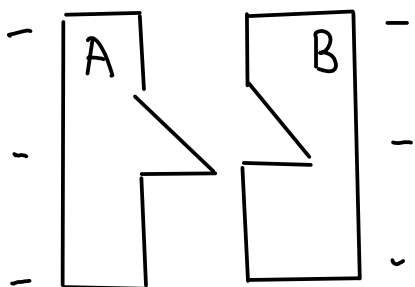
A collision where molecules don't hit each other very hard will not lead to a reaction. There isn't enough ENERGY available for the molecules to react with one another.
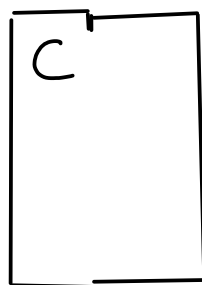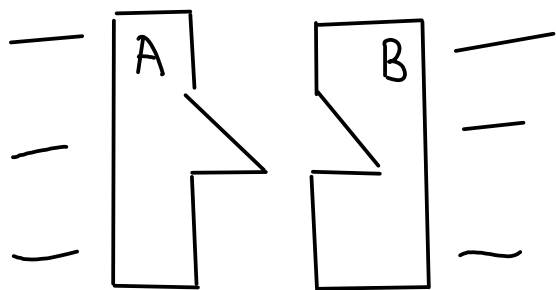
A collision where molecules hit each other with the correct orientation AND enough energy may lead to a reaction!