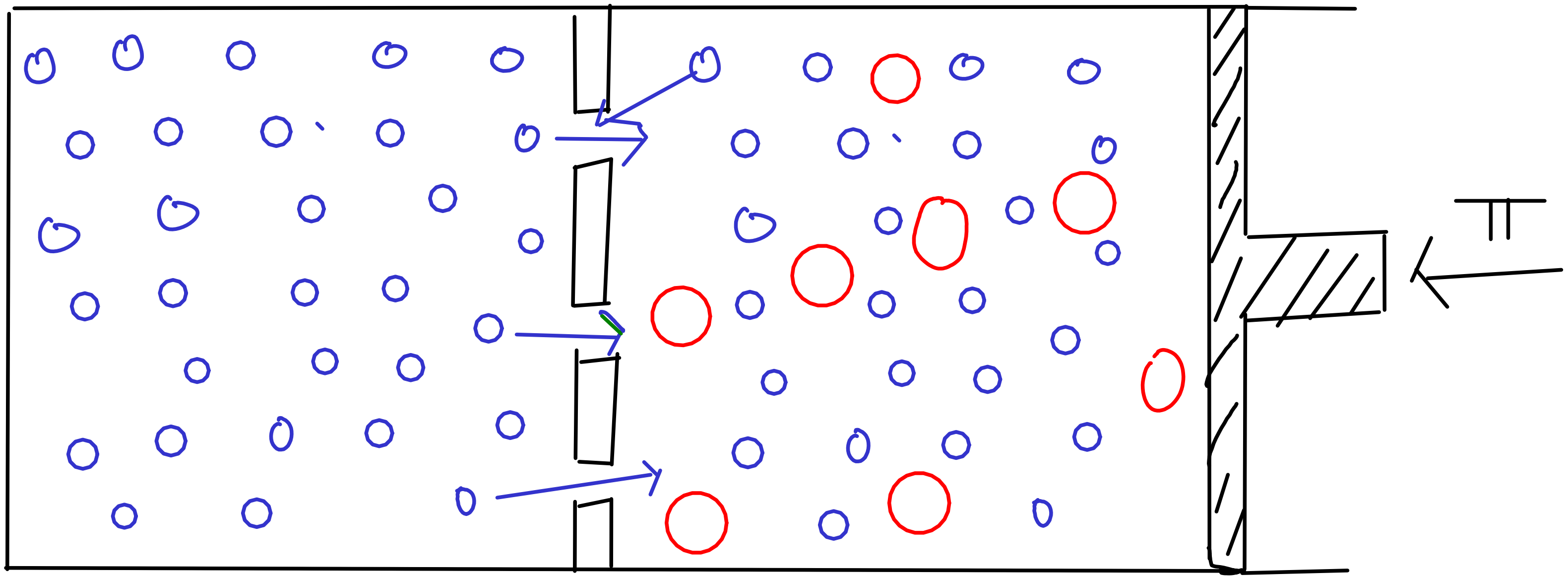
OSMOTIC PRESSURE

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

$$\pi = \underbrace{M}_{\text{molar concentration of solute}} \times \underbrace{R}_{\text{ideal gas constant}} \times \underbrace{T}_{\text{temperature}}$$

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.

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

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?

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

$$\underbrace{\Delta T_b}_{100.00°C - 95.00°C = 5.00°C} = \underbrace{K_b}_{0.512°C/m} \times C_m \qquad C_m = \frac{\text{mol ions}}{\text{kg water}}$$

Find the molal concentration of ions, Cm:

$$5.00°C = (0.512°C/m) \times C_m$$

$$C_m = 9.765625\ m\ \text{ions}$$

Find moles ions:

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

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

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

Now find mass NaCl by using the formula weight ...

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

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

$$A + B \rightarrow C$$

...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.

$$A + B \rightarrow C$$

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

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 $\frac{-\Delta[A]}{s}$	
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

Rate quadruples

The rate law is:

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

... 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!

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

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

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

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

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

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

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

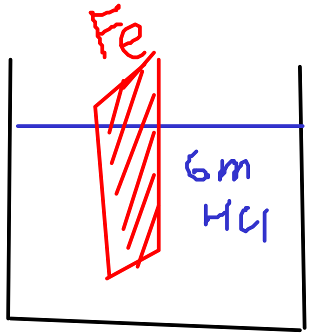
① CONCENTRATION OF REACTANTS

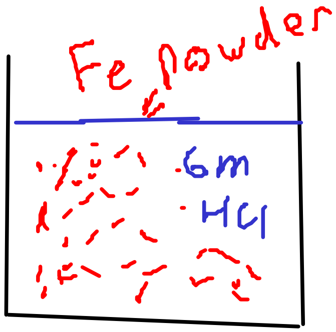
② SURFACE AREA OF CONTACT BETWEEN REACTANTS

③ CONCENTRATION OF / PRESENCE OF A CATALYST

④ TEMPERATURE

$Fe + 2HCl \rightarrow FeCl_2 + H_2$





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!

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

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

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!

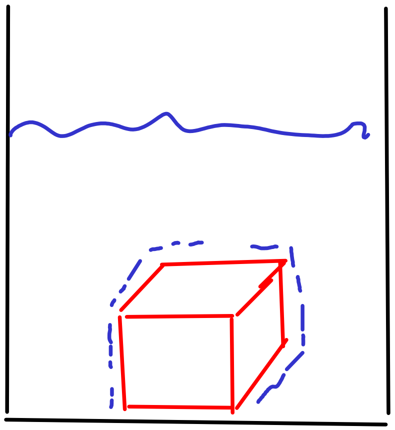
"inhibitor"

- In most cases, reaction orders ARE positive numbers!

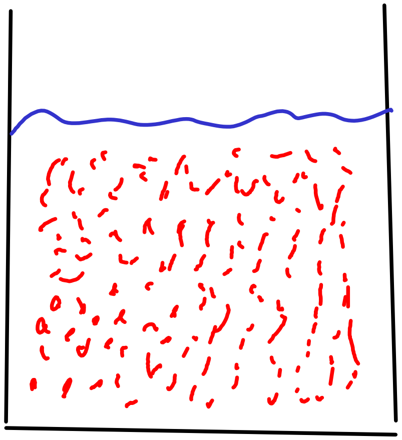
SURFACE AREA OF CONTACT BETWEEN REACTANTS

- 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.

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

$$Rate = k[A]^p[B]^q\underline{[C]^r}$$

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.

Note: Changing temperature affects the RATE CONSTANT, k !