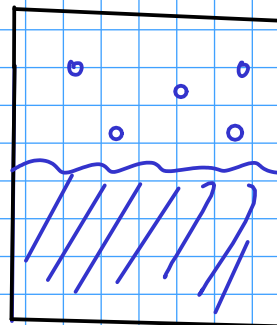


# VAPOR PRESSURE LOWERING

- 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

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... but component "A" above is actually the SOLVENT. If we want to describe this as a colligative property, we want to express Raoult'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.

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

concentration of solute (molality)

Boiling point elevation constant (for SOLVENT)

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?

$$T_b = 118.5^\circ\text{C} \quad K_b = 3.08^\circ\text{C}/m$$

---

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

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

$$C_m = \frac{\text{moles } S_8}{\text{kg } HC_2H_3O_2} \leftarrow 0.1000 \text{ kg}$$

$$2.817 \text{ g } S_8 \times \frac{\text{mol } S_8}{256.56 \text{ g } S_8} = 0.0109799 \text{ mol } S_8$$

$$C_m = \frac{0.0109799 \text{ mol } S_8}{0.1000 \text{ kg } HC_2H_3O_2} = 0.109799 \text{ m}$$

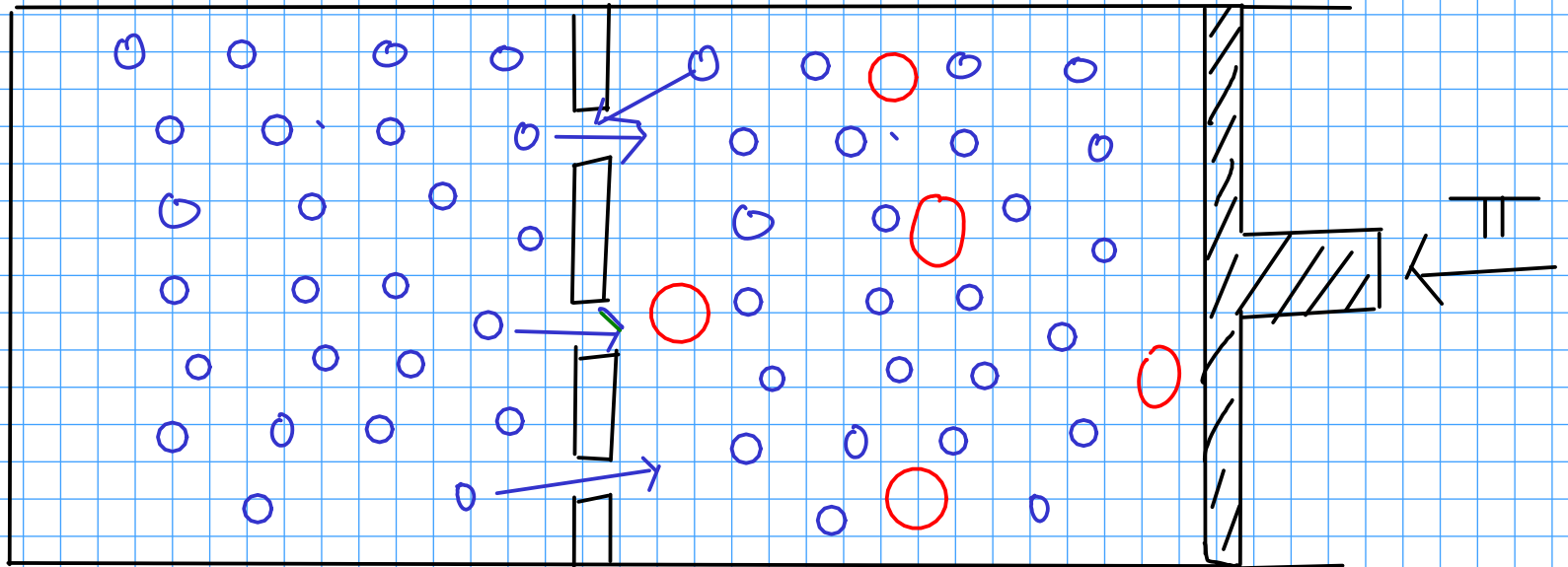
$$\Delta T_b = (3.08^\circ\text{C}/m) \times (0.109799 \text{ m}) = 0.338^\circ\text{C}$$

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

# 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.

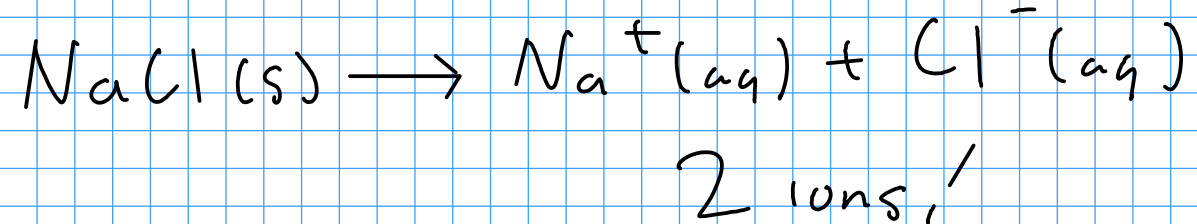
If you apply enough pressure to the piston, osmosis will not occur. This pressure is called the OSMOTIC PRESSURE

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

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!



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

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

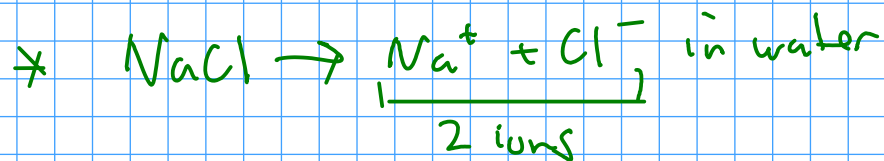
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$$\begin{aligned} \Delta T_b &= K_b \times C_m \\ &= 100^\circ\text{C} - 95^\circ\text{C} \\ &= 5.00^\circ\text{C} \end{aligned}$$

$$C_m = \frac{\text{moles ions}}{\text{kg H}_2\text{O}}$$

$$C_m = \frac{\Delta T_b}{K_b} = \frac{5.00^\circ\text{C}}{0.512^\circ\text{C}/m} = 9.765625 \text{ m ions}$$

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



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

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

## 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

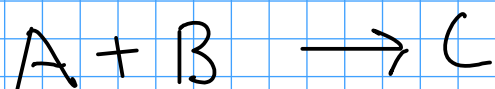
- For gases dissolved in liquids, solubility INCREASES when the partial pressure of the solute gas over the solution INCREASES.
  - Consider soft drinks. They go flat after opening because the pressure of carbon dioxide over the liquid goes down.
- No significant pressure effects for solid/liquid solutions.

# 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

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

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

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.

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

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.

## 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

## 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!

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

$$[A]^0$$

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

$$[A]^1$$

$$[A]^{-1} \quad \frac{1}{[A]}$$

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

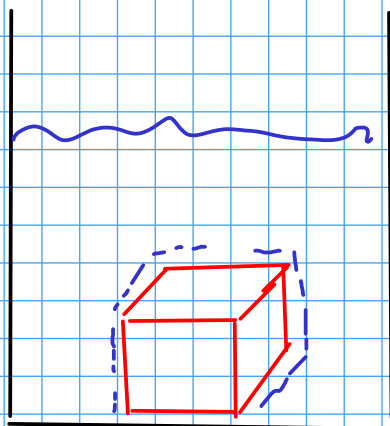
"inhibitor"

- In most cases, reaction orders ARE positive numbers!

## SURFACE AREA OF CONTACT BETWEEN REACTANTS

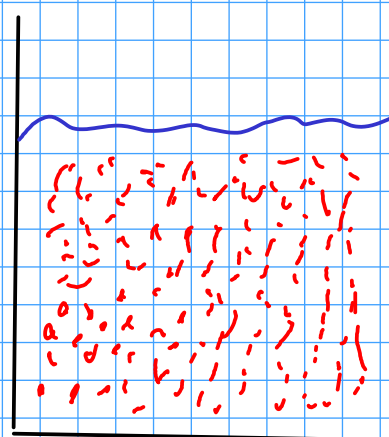
- If a reaction takes place at an INTERFACE, then the reaction rate will depend on the SURFACE AREA of that interface!

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



The reaction takes place only on the surface of the cube.

Next, try the same reaction, but break the cube into small fragments first!



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.

- 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.

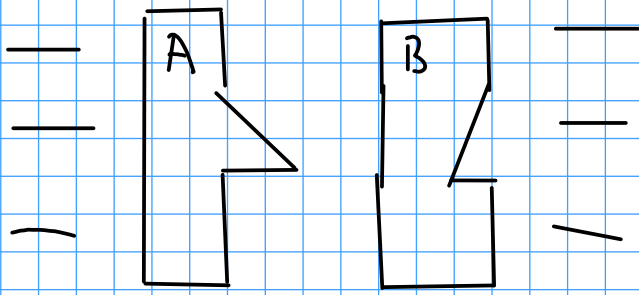
## REACTION RATE THEORY

- 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.

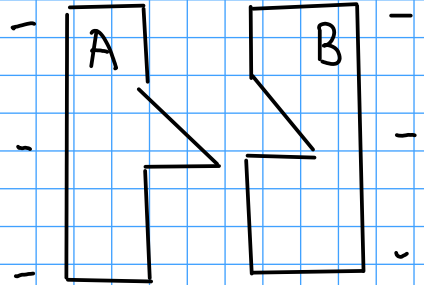
## COLLISION THEORY

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

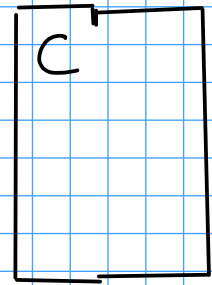
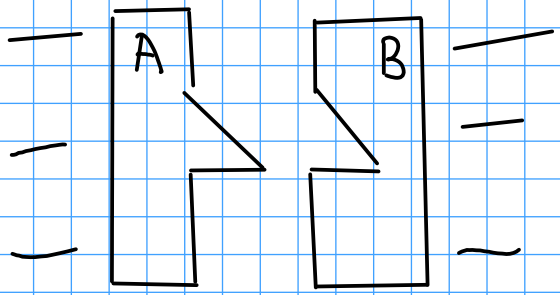
- ① Reactants must COLLIDE with each other.
- ② Colliding reactants must hit each other with the correct ORIENTATION to react.
- ③ Colliding reactants must also hit each other with ENOUGH ENERGY to react (called the ACTIVATION ENERGY)



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!



## EXPLAINING SOME OF THE FACTORS

- Increasing the concentration of reactants increases THE NUMBER OF COLLISIONS that occur in a reaction mixture - increasing rate.
- Increasing SURFACE AREA provides more opportunities for reactant molecules to COLLIDE - increasing rate.
- Increasing temperature INCREASES THE ENERGY (and number) of collisions, since temperature is proportional to the average kinetic energy of molecules. More collisions will have the ACTIVATION ENERGY needed to react, so rate increases.
- Some catalysts work by bending reactant molecules into ORIENTATIONS favorable for reaction - making it easier for large molecules to react with one another.

... but what about this ACTIVATION ENERGY? Let's look at TRANSITION STATE THEORY

## TRANSITION STATE THEORY

- States that when reactant molecules collide, they first form a TRANSITION STATE which then decomposes and/or loses energy to form product molecules.
- A TRANSITION STATE is a high-energy state: It may be an unstable combination of several reactant molecules or an excited (high energy) state of a single product molecule. The transition state breaks down and loses energy to form the products of the reaction.
- The ACTIVATION ENERGY is the energy required to form the transition state, and it acts as a barrier to reaction.
- We model the rate constant "k" using collision and transition state theory with the ARRHENIUS EQUATION:

$$k = A \times e^{\frac{-E_a}{R \times T}}$$

rate  
constant

$E_a$  = ACTIVATION ENERGY

$R$  = ideal gas constant

$T$  = absolute temperature

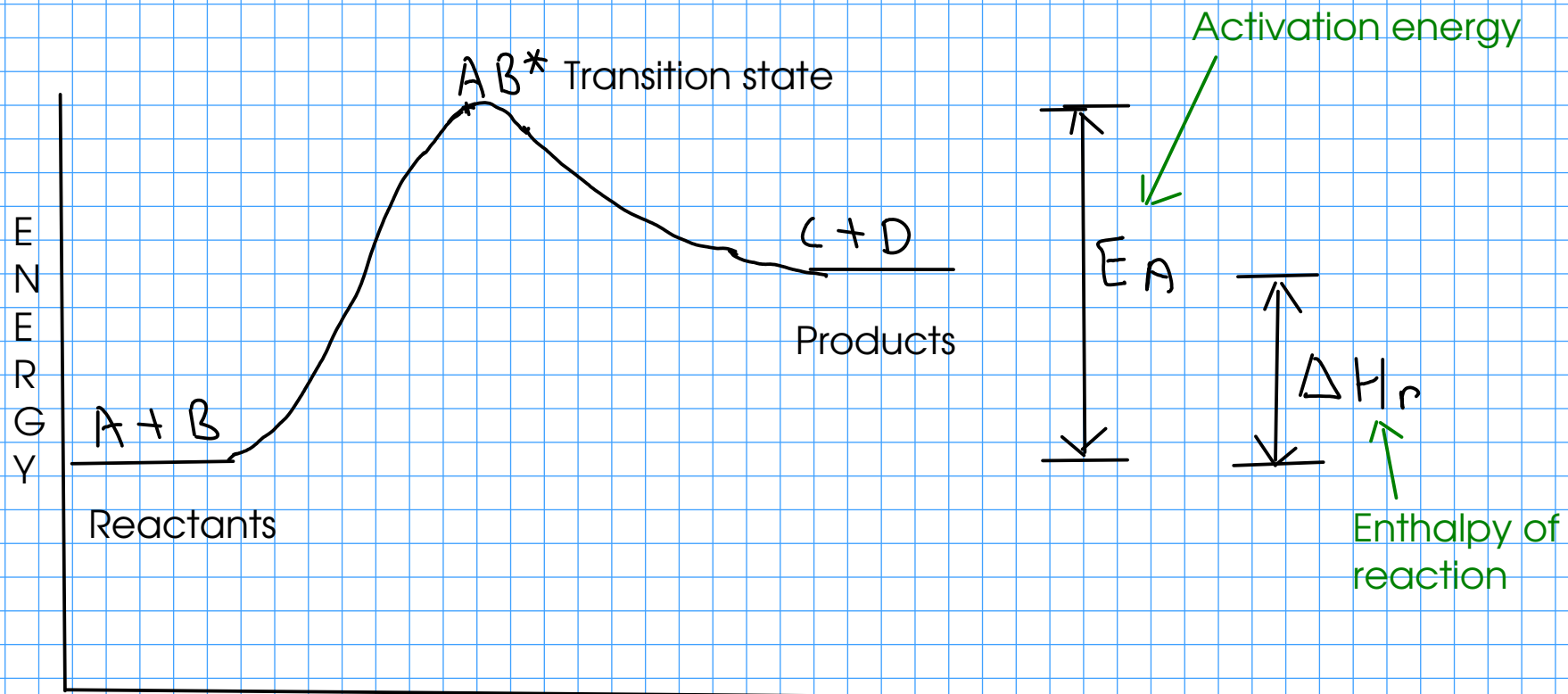
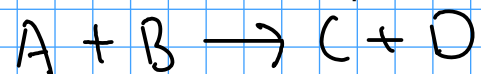
$A$  = frequency factor ... the fraction of collisions with the right orientation to react

... this equation allows us to calculate the rate constant for different temperatures if we have values for "A" and "E<sub>a</sub>". We can get these values by examining a reaction at two (or more) different temperatures.

# ENERGY DIAGRAMS

- graphically, we can look at transition state theory via an ENERGY DIAGRAM

For an ENDOTHERMIC REACTION, the products have a higher energy than the reactants



REACTION COORDINATE

- a measure of how far the reaction has proceeded