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
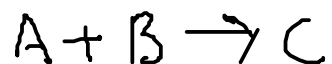
change in time

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:

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

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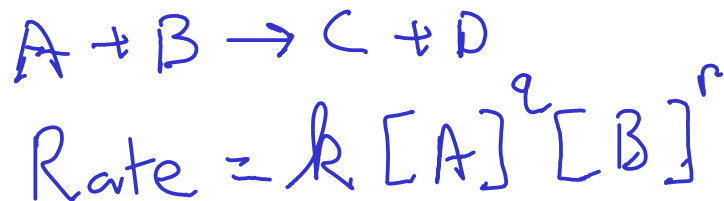
... we want to find the rate constant 'k', and the orders 'q' and 'r'.

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:

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

... 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!

$$(2 * [Add])^q = 2 * Rate \; ; \; q = 1$$

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

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

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

Trial	$[A]$	$[B]$	Rate $\frac{\Delta [A]}{S}$	Calculated 'k'
1	0.156	0.180	0.0016875	0.500
2	0.300	0.156	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
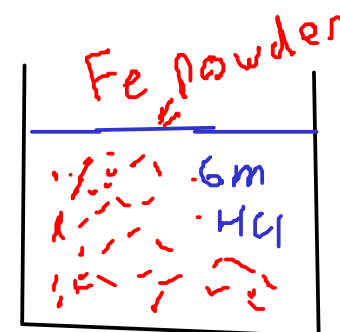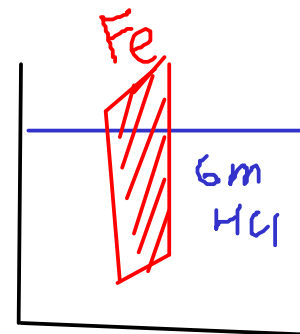
CONCENTRATION OF REACTANTS

- 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!
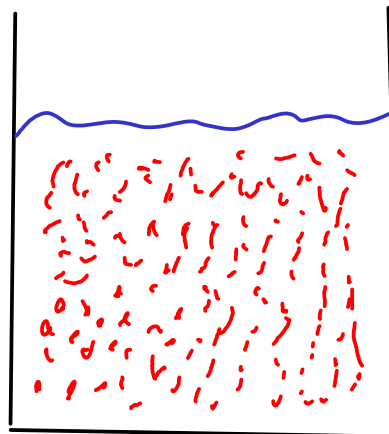
SURFACE AREA OF CONTACT BETWEEN REACTANTS

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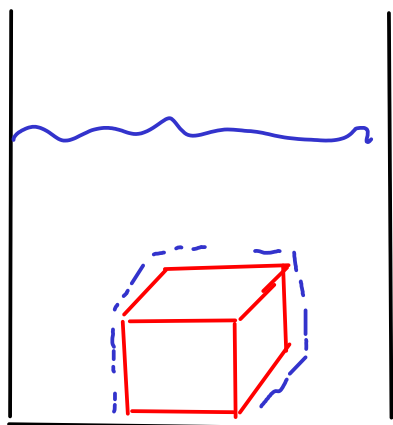
The reaction takes place only on the surface of the cube.

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.

Note: Changing temperature affects the RATE CONSTANT, k !

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.
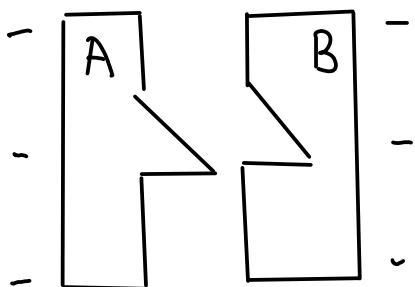
COLLISION THEORY

- 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)
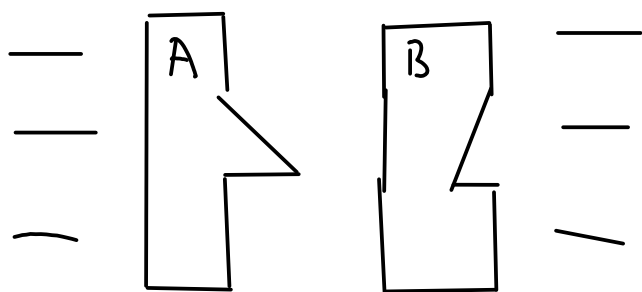
A collision like this - even an energetic one, would lead to NO REACTION, since the molecules are not aligned properly to react. This is particularly important for larger molecules (like biomolecules) where reactive parts of the molecule are small compared to the size of the whole molecule!

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.
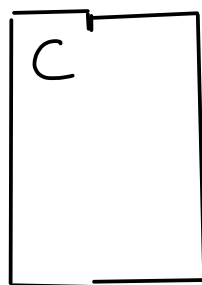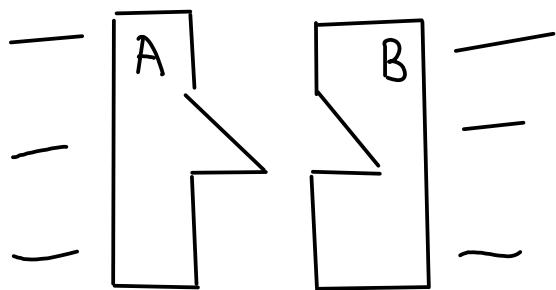
A collision where molecules hit each other with the correct orientation AND enough energy may lead to a reaction!

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:

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

rate
constant

Ea = 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 "Ea". 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

$$A + B \longrightarrow C + D$$

Activation energy

AB^* Transition state

$C + D$

E_A

Products

ΔH_r

Enthalpy of reaction

E
N
E
R
G
Y

$A + B$
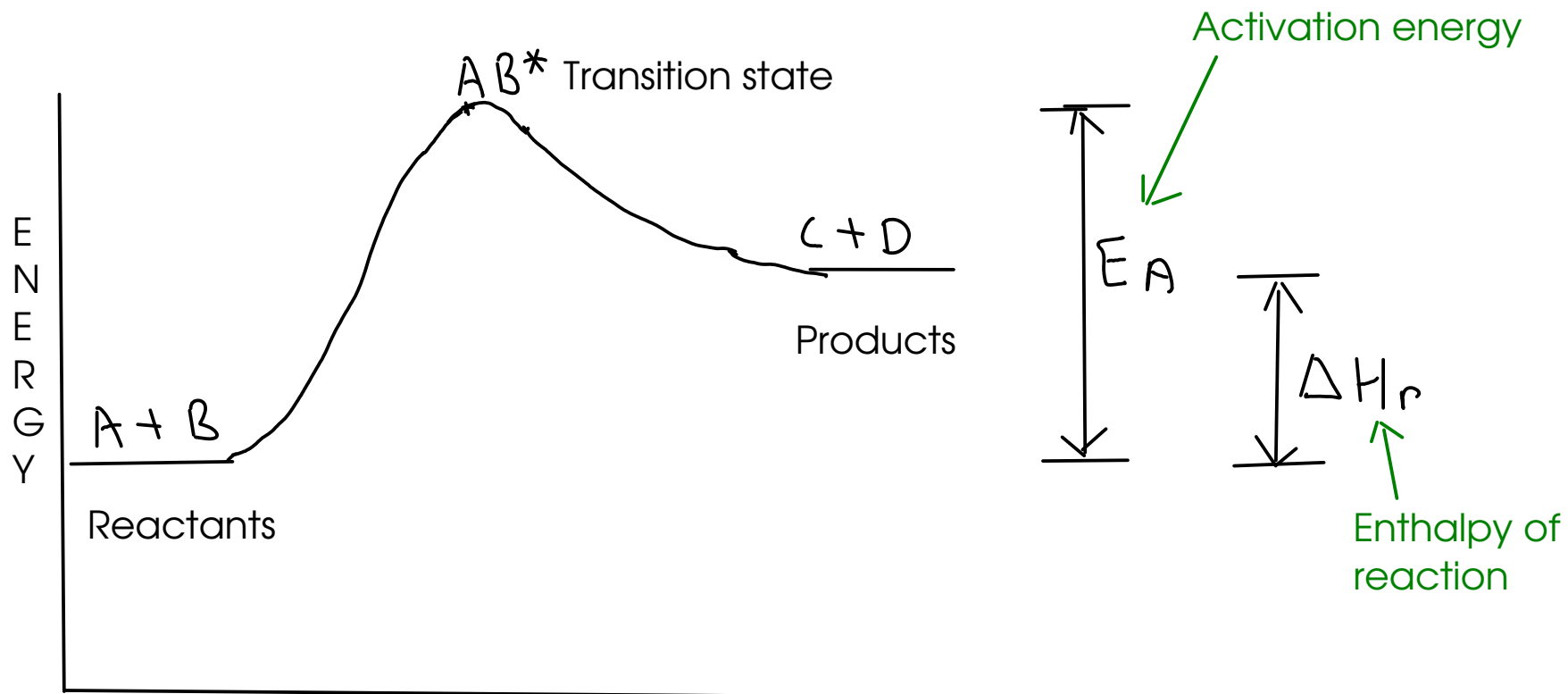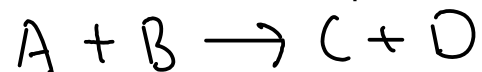
Reactants

REACTION COORDINATE
- a measure of how far the reaction has proceeded

For an EXOTHERMIC REACTION, the products have a lower energy than the reactants

$$A + B \longrightarrow C + D$$

AB* Transition state

E
N
E
R
G
Y

E_A

A + B

Reactants

$-\Delta H_r$

C + D

Products

REACTION COORDINATE
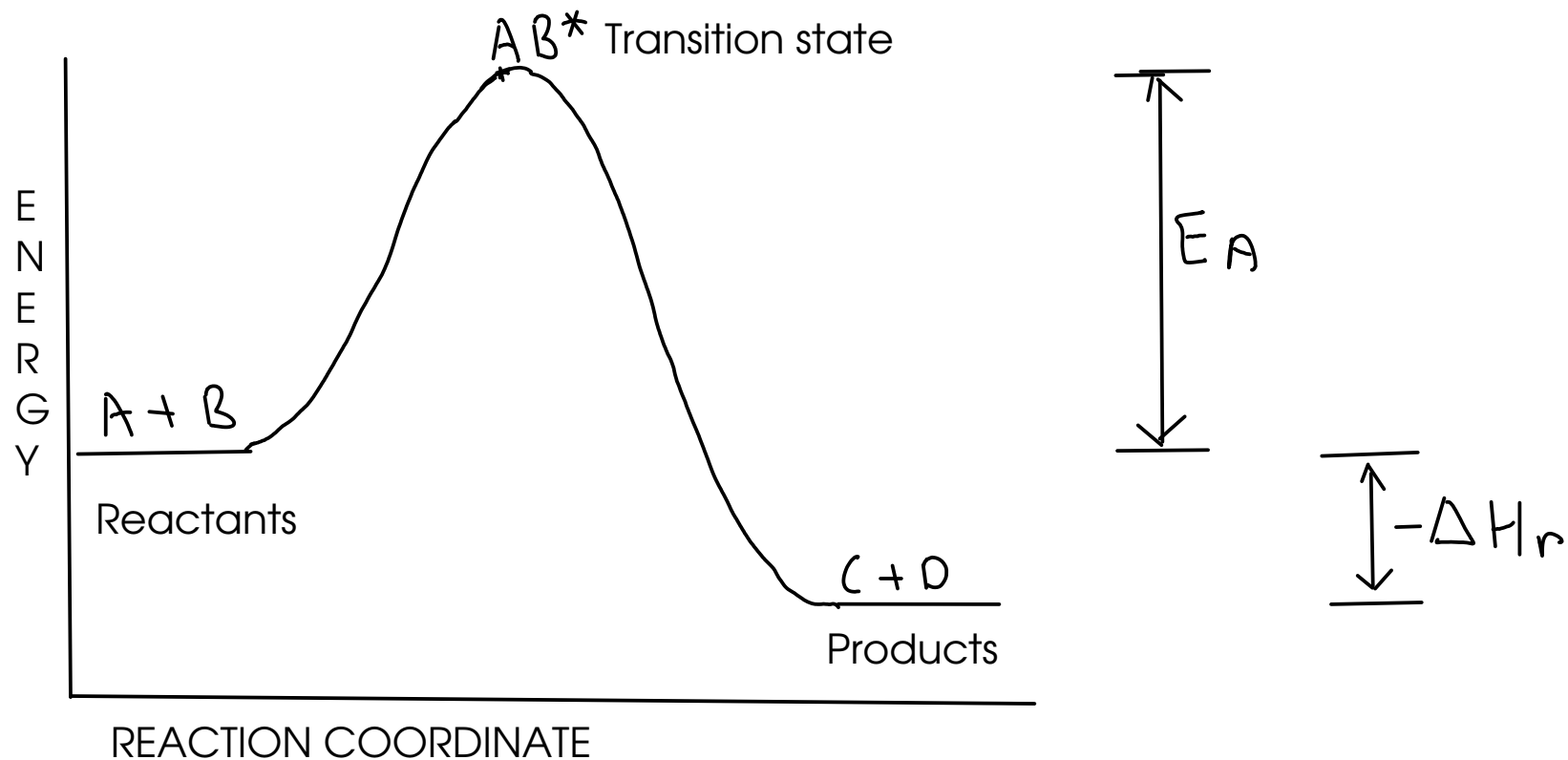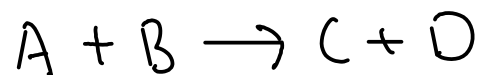
- Whether a reaction is endothermic OR exothermic, there is still an activation energy barrier that must be crossed in order to react.

- This explains why a pile of wood that's exposed to air doesn't just burst into flames. Even though the cdombustion of wood is EXOTHERMIC, there's still an activation energy barrier preventing the reaction from occurring without an initial input of energy - a "spark"!

CATALYSTS?

- So how does a catalyst fit into this picture? A catalyst LOWERS the activation energy for a reaction

catalyst "K"

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

AB^* Transition state

Transition state with catalyst

ABk^*

E N E R G Y

A + B

Reactants

E_A

E_a with catalyst

C + D

Products
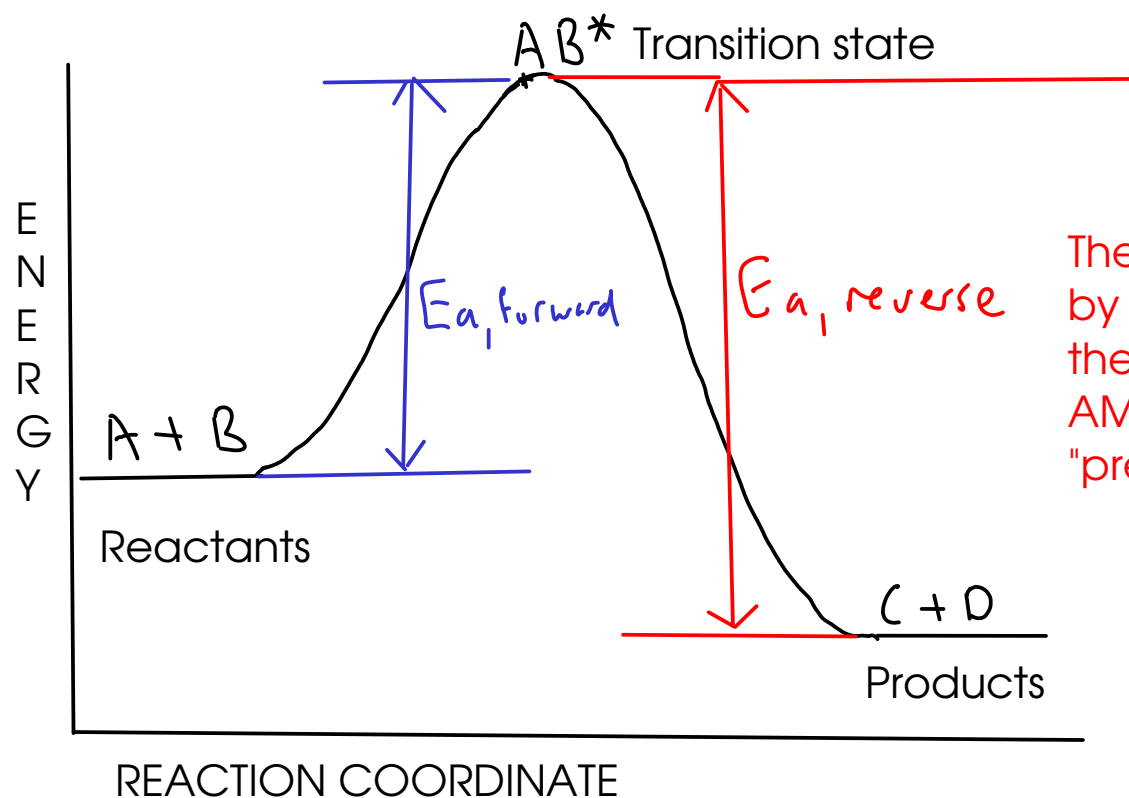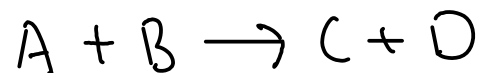
$-\Delta H_r$

REACTION COORDINATE
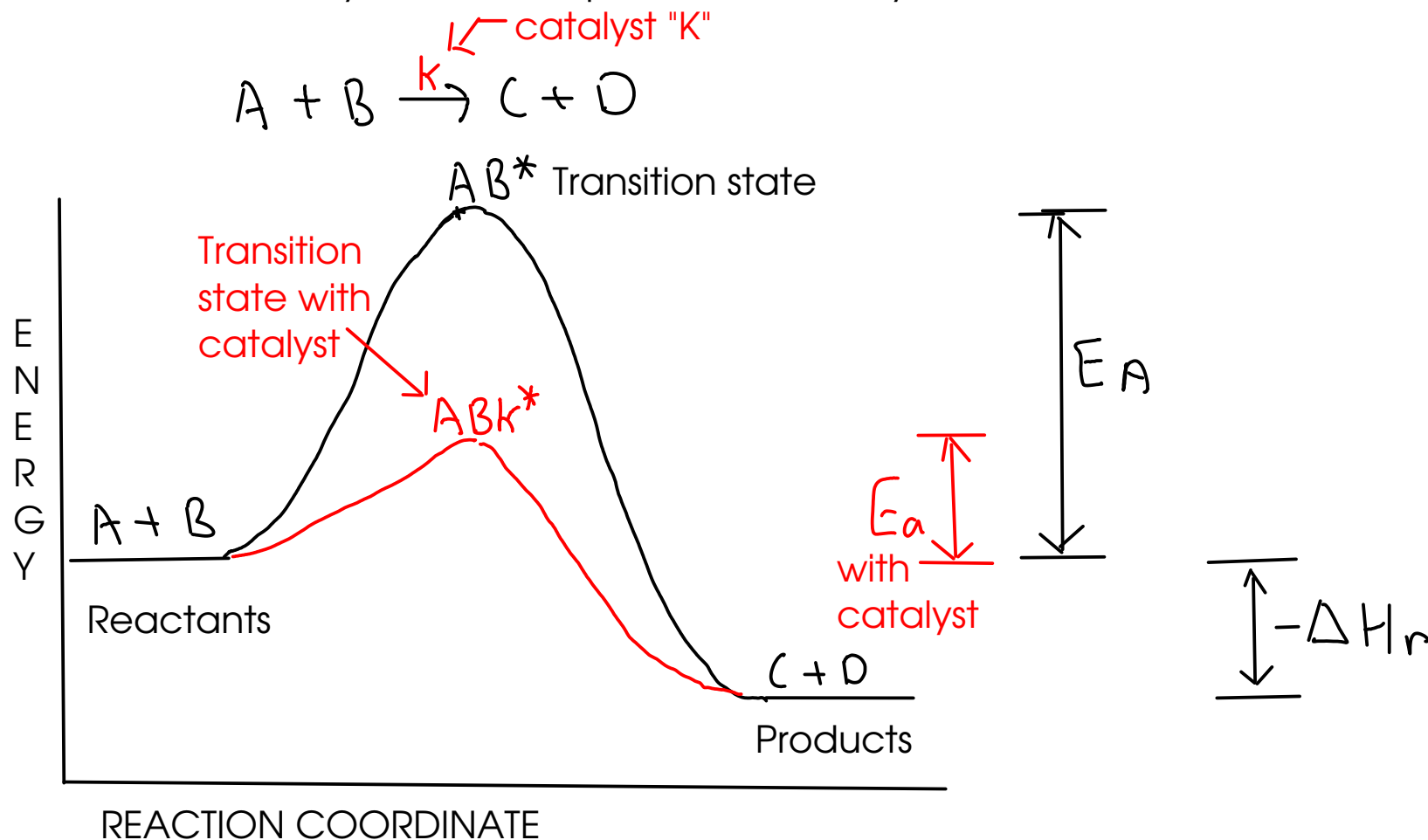
- The exact mechanism by which a catalyst lowers the energy of the transition state may be simple ... or complex. As we mentioned before, some catalysts hold molecules so that it's easier for reactants to come together, some react with reactant molecules to produce an intermediate that reacts more easily with other reactants to make the final product, etc.

WHAT KEEPS A REACTION FROM GOING BACKWARDS?

$A + B \longrightarrow C + D$

reactants   products

$C + D \longrightarrow A + B$

reactants   products

... what keeps the reaction on the right from occurring?

$A + B \longrightarrow C + D$

AB* Transition state

E
N
E
R
G
Y

A + B

Ea, forward

Ea, reverse

Reactants

C + D

Products

REACTION COORDINATE

The reverse reaction is "prevented" by an activation energy barrier - the same thing (if not the same AMOUNT of energy) that "prevents" the forward reaction!

So what really happens during a reaction? Both forward and reverse reactions occur!
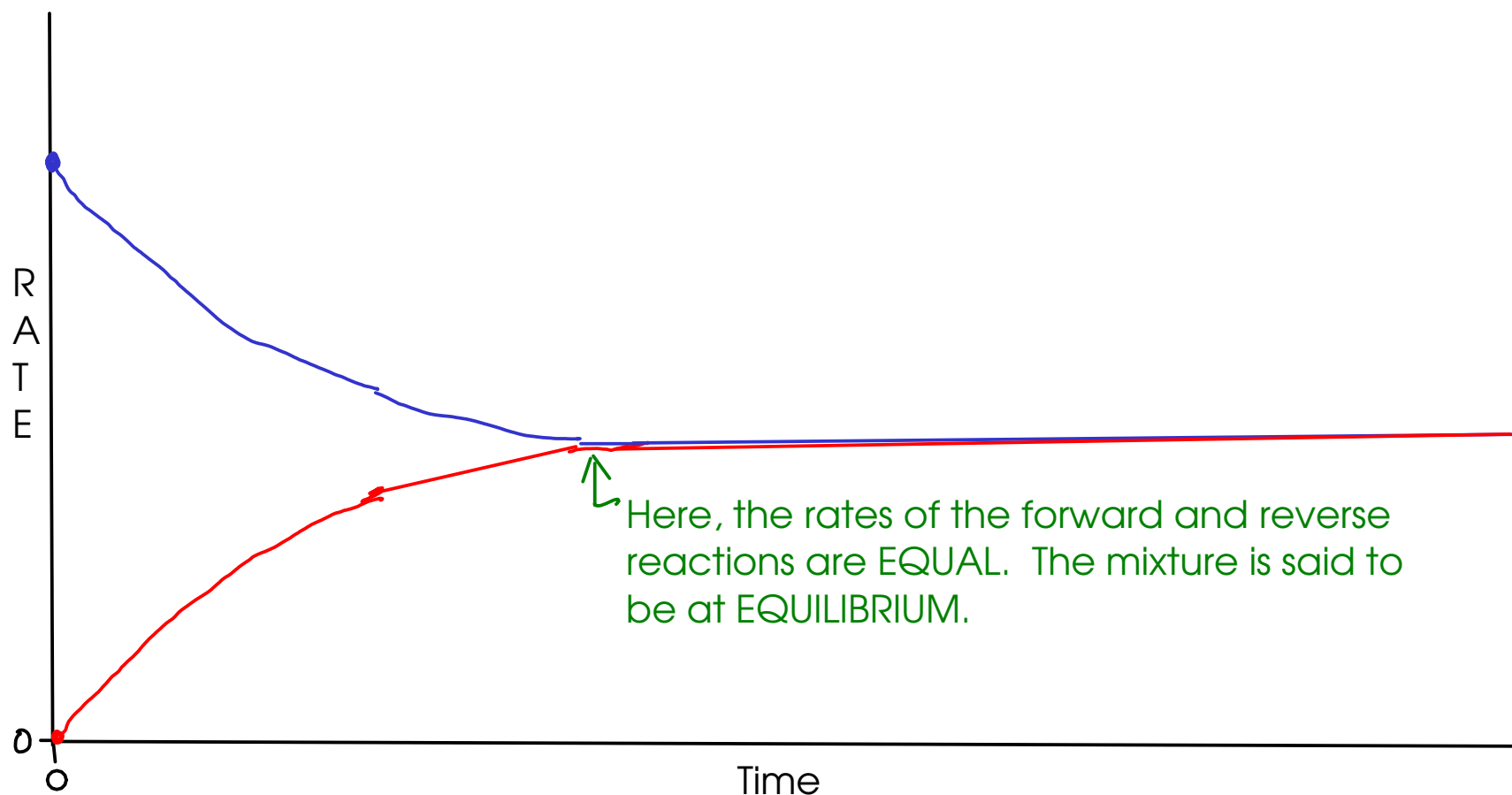
$$A + B \longrightarrow C + D$$
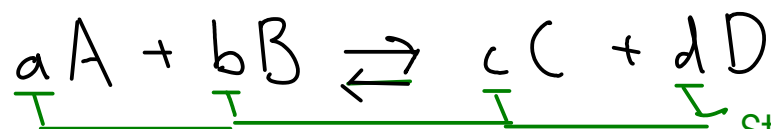
reactants   products

$$Rate = k_F [A][B]$$

$$C + D \longrightarrow A + B$$

reactants   products

$$Rate = k_r [C][D]$$

- Let's look at the RATES of both the forward and reverse reactions over time.

R
A
T
E

0

O   Time

Here, the rates of the forward and reverse reactions are EQUAL. The mixture is said to be at EQUILIBRIUM.

- Initially, the mixture is all A and B. As C and D are formed, the rate of the reverse reaction increases while the rate of the forward reaction decreases. Eventually, these rates become equal.

- At EQUILIBRIUM, the concentrations of A, B, C, and D stop CHANGING. The reaction doesn't stop, but it appears stopped to an outside observer.

$$aA + bB \rightleftarrows cC + dD$$

Stoichiometric coefficients

- Double-headed arrow is often used to show that both the forward and reverse reactions are important.

[ ] : molar concentrations of reactants and products AT EQUILIBRIUM.

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Equilibrium constant (concentration based)

- At equilibrium, the ratio above equals a constant number - the EQUILIBRIUM CONSTANT. The equilibrium constant depends on TEMPERATURE, but not on other factors.

- Not all reactants and products are included in the equilibrium constant expression!

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$
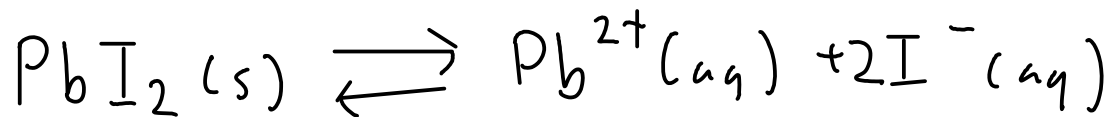
$$K_c = \frac{[Pb^{2+}][I^-]^2}{[PbI_2]}$$

Since the concentration of SOLID lead(II) iodide is fixed by the crystal structure of the solid and does not change over the course of the reaction, we "fold it" into the equilibrium constant.

$$K_c = [Pb^{2+}][I^-]^2 = 6.5 \times 10^{-9}$$

- Species whose CONCENTRATIONS do not change do not appear in the equilibrium constant expression. PURE SOLIDS and PURE LIQUIDS. Also, bulk SOLVENTS (like water when dealing with a reaction that takes place in water).

$$HC_2H_3O_2(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$$

$$K_c = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.7 \times 10^{-5}$$

Since water is the solvent, there's enough of it so that the reaction doesn't really change the concentration of the water itself.
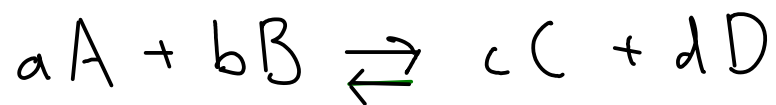
$[H_2O] = ?$ $1 g/mL$, $1 L$ water $= 1000 g \, H_2O$

$1000 g \, H_2O \times \dfrac{mol}{18.02 g} = 55.5 mol \, H_2O/1L = 55.5 \underline{M}$

WHAT DOES AN EQUILIBRIUM CONSTANT TELL US?

(1) - Whether the final reaction mixture consists of mainly products or mainly reactants. In other words, which side of the reaction is "favored".

(2) - Whether a reaction will proceed to the left or to the right when the reaction is not yet at equilibrium.

(3) - With more math, we can actually determine the final composition of an equilibrium mixture from the initial amount of reactant present WITHOUT doing an experiment!

WHICH IS FAVORED? PRODUCT OR REACTANT?

$$aA + bB \rightleftharpoons cC + dD$$

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$HC_2H_3O_2 (aq) + H_2O(l) \rightleftharpoons H_3O^+ (aq) + C_2H_3O_2^- (aq)$$

$$K_c = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.7 \times 10^{-5}$$

To get a small value like this one, the DENOMINATOR of the equilibrium expression must be a lot larger than the NUMERATOR.

Since REACTANTS are the denominator of this fraction, this reaction favors REACTANTS at equilbrium!

- If Kc is small (<<1), then REACTANTS are favored at equilibrium

- If Kc is large (>>1), then PRODUCTS are favored at equilibrium.

HOW TO TELL IF A REACTION IS AT EQUILIBRIUM?

- Use REACTION QUOTIENT (Q)

$$a A + b B \rightleftharpoons c C + d D$$
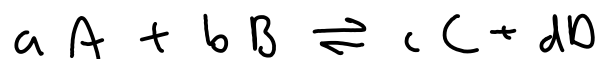
$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Reaction quotient = equilbrium expression using NON-EQUILIBRIUM concentrations.

- If Q = Kc, then reaction is at equiilibrium.

- If Q < Kc, then reaction is NOT at equilibrium and proceeds to the right, forming more products.

- If Q > Kc, then reaction is NOT at equilibrium and proceeds to the left, forming more reactants.

$$2 NOBr(g) \rightleftharpoons 2 NO(g) + Br_2(g) ; \quad K_c = 3.07 \times 10^{-4}$$

$$[NOBr] = 0.0720 \, M, \quad [NO] = 0.0162 \, M, \quad [Br_2] = 0.0123 \, M$$

Is mix at equilibrium? If not, which direction will reaction proceed?

$$K_c = \frac{[NO]^2 [Br_2]}{[NOBr]^2} = 3.07 \times 10^{-4} \quad \bigg| \quad Q = \frac{(0.0162)^2 (0.0123)}{(0.0720)^2} = 6.23 \times 10^{-4}$$

$$6.23 \times 10^{-4} > 3.07 \times 10^{-4}$$

$$Q > K_c ;$$

Since Q > Kc, the reaction is NOT at equilibrium and will proceed to the LEFT, making more NOBr at the expense of the two products (NO and bromine gas).
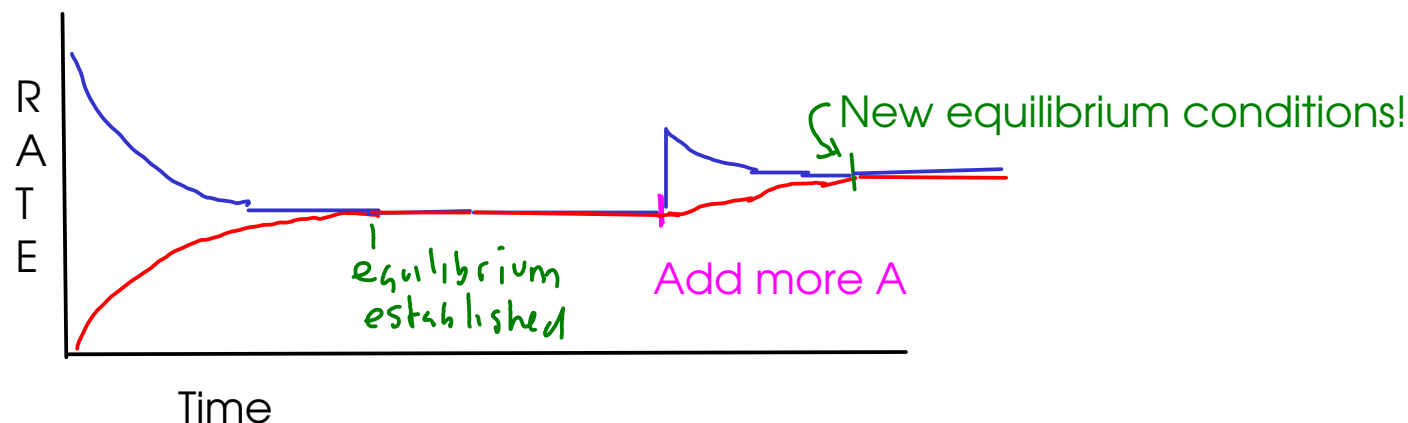
MODIFYING EQUILIBRIUM

- Remember, at equilibrium the reaction has not actually STOPPED. Both forward and reverse processes are still happening - just at the same rate so there's no overall concetration change.

- If you do something to the reaction mixture that changes the rates of the forward or the reverse reaction (or sometimes BOTH), the mixture will no longer be at equilibrium.

Simplest case is to add or remove a substance, changing its concentration.

$$A + B \rightleftharpoons C + D$$
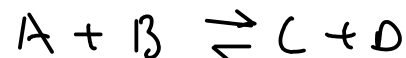
$$Rate_{,fwd} = k_F [A][B]$$

$$Rate_{,rev} = k_r [C][D]$$

R
A
T
E

equilibrium established

Add more A

New equilibrium conditions!

Time

- After adding A, the rate of the forward reaction increased. As more C and D were produced by the (faster) forward reaction, the forward reaction and reverse reaction came back to equilibrium, but at a new set of conditions.

- The addition of A caused our equilibrium to SHIFT towards the RIGHT - consuming some of the extra A to form more products (C and D).

- LE CHATELEIR'S PRINCIPLE states that if an equilbrium is disturbed, it will SHIFT in such a way as to counteract the disturbance and restore equilibrium.

For concentrations:

* Increasing the concentration of a REACTANT will cause the equilibrium to shift to the RIGHT, making more products.

* Decreasing the concentration of a REACTANT will cause the equilibrium to shift to the LEFT, making more reactants.

* Increasing the concentration of a PRODUCT will cause the equilibrium to shift to the LEFT, making more reactants.

* Decreasing the concentration of a PRODUCT will cause the equilibrium to shift to the RIGHT, making more products.

This one can be used to DRIVE a reaction to produce product, even if the Kc value is NOT favorable.

- TEMPERATURE can also cause equilibrium shifts. These temperature-caused shifts can be easily illustrated with Le Chaleleir's principle.

endothermic reaction:

$$A + B + heat \rightleftharpoons C + D$$

- Heat, here, is represented as if it's a reactant!

- If temperature INCREASES, the equilibrium shifts to the RIGHT, making more products.

- If temperature DECREASES, the equilibrium shifts to the LEFT, making more reactants.

exothermic reactions:

$$A + B \rightleftharpoons C + D + heat$$

- In the exothermic case, heat is a product!

- If temperature INCREASES, then the equilibrium shifts to the LEFT, making more reactants.

- If temperature DECREASES, then the equilibrium shifts to the RIGHT, making more products.

- Optimization:
* For ENDOTHERMIC reactions, run as hot as possible. You make MORE products FASTER.
* For EXOTHERMIC reactions, you want to run the reaction cooler (for more products), but not so cool as to make the reaction slow!

EQUILIBRIUM CALCULATIONS

- We're often interested in figuring out what happens at equilibrium BEFORE we do an experiment!

- What's the problem? Initially, we know only ... INITIAL concentrations. Since these are NOT equilibrium concentrations, we cannot simply plug them into an equilbrium expression and solve.

So how do we find out what the concentrations are at equilibrium if we initially know NONE of them?

- To solve an equilibrium problem, write out the equilibrium constant expression. Then, try to RELATE ALL THE EQUILIBRIUM CONCENTRATIONS TO ONE ANOTHER using the chemical equation.

- It helps to assign a variable based on one of the substances in the reaction, then write the concentrations of the other substances based on that variable. How to do this? Take a look at the following examples...

EXAMPLE: Calculate the grams per liter of silver(i) chloride (AgCl) in a solution that is at equilibrium with solid AgCl.

$$AgCl\,(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \; ; \; K_c = 1.8 \times 10^{-10}$$

$$K_c = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$$

Species	[Initial]	Δ	[Equilibrium]
Ag^+	0	$+X$	X
Cl^-	0	$+X$	X

Assign a variable, 'x', to equal the change in concentration of the silver(I) ion...

Each time we make a silver(I) ion, we also make a chloride ion. See the equation ... there's a 1:1 ratio of silver to chloride.

$$[Ag^+][Cl^-] = 1.8 \times 10^{-10}$$

$$(x)(x) = 1.8 \times 10^{-10}$$

Substitiute the variable 'x' into the equilibrium experssion, then solve for 'x'.

$$x^2 = 1.8 \times 10^{-10}$$

$$x = 1.34 \times 10^{-5} \; ; \; [Ag^+] = [Cl^-] = 1.34 \times 10^{-5}\,\underline{m}$$

The concentration of DISSOLVED AgCl also equals 'x' ... since for every dissolved AgCl you have a dissolved Ag.ion:

$$[AgCl]_{dissolved} = 1.34 \times 10^{-5}\frac{mol}{L} \times \frac{143.35\,g\,AgCl}{mol\,AgCl} = \boxed{0.0019\,{}^g/_L}$$

Equivalent to 1.9 ppm (parts per million). ppm is same as mg/L for dilute aqueous solutions