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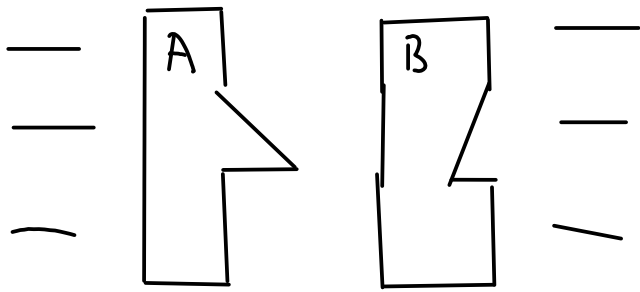
A collision like this - even an energetic one, would lead to NO REACTION, since the molecules are not aligned properly to react. This is particularly important for larger molecules (like biomolecules) where reactive parts of the molecule are small compared to the size of the whole molecule!
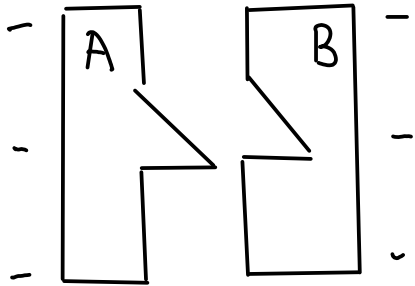
A collision where molecules don't hit each other very hard will not lead to a reaction. There isn't enough ENERGY available for the molecules to react with one another.
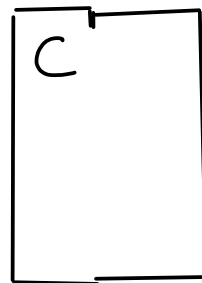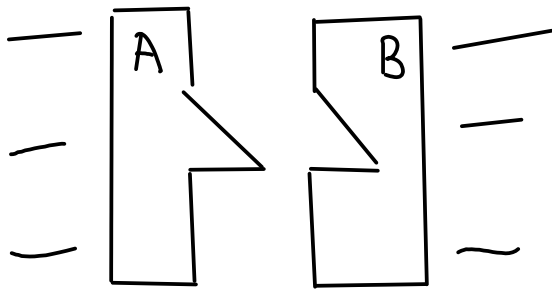
A collision where molecules hit each other with the correct orientation AND enough energy may lead to a reaction!

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

Ea = ACTIVATION ENERGY

R = ideal gas constant
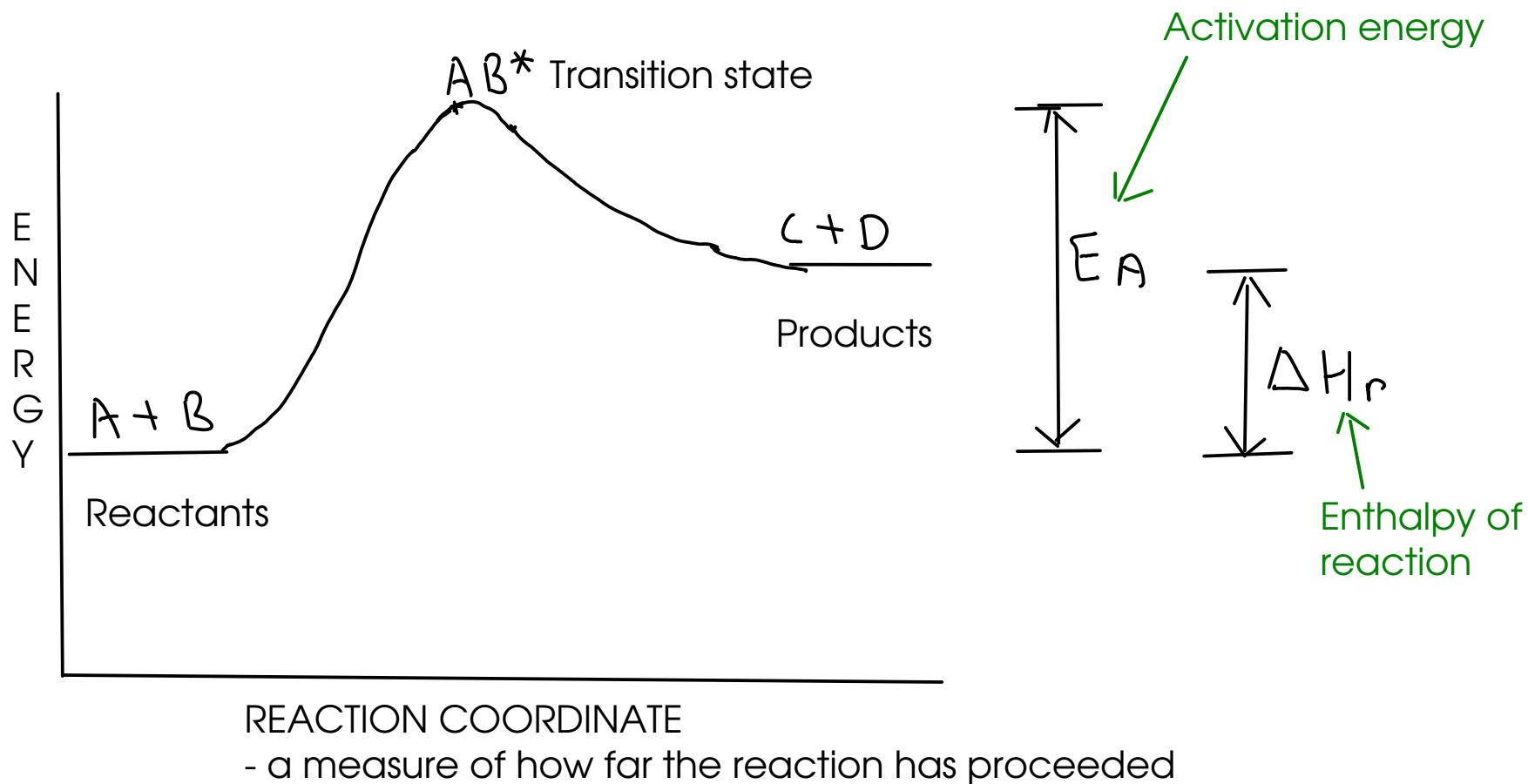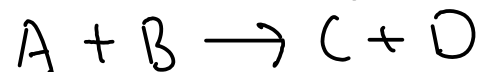
T = absolute temperature

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

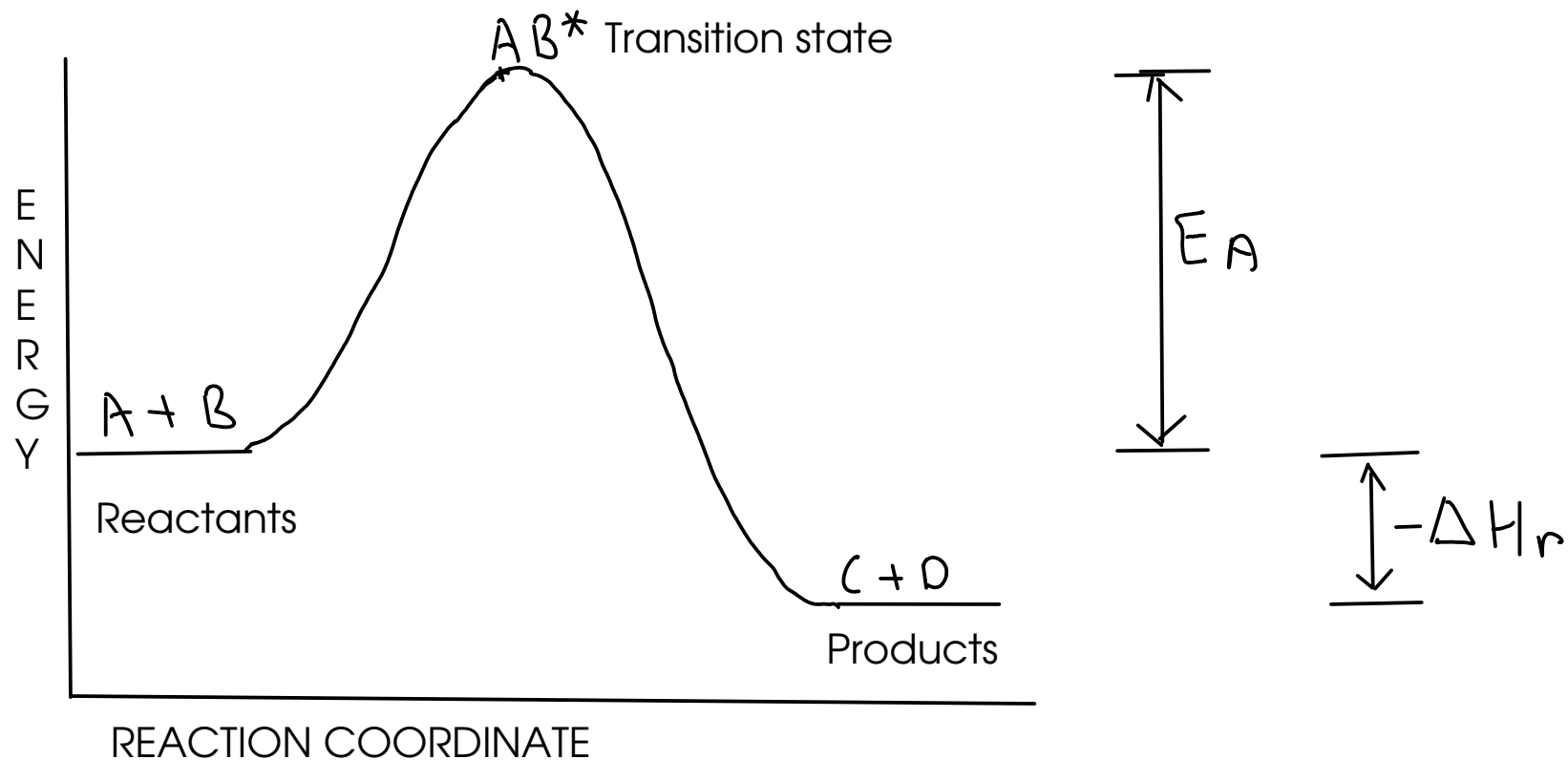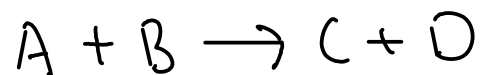- graphically, we can look at transition state theory via an ENERGY DIAGRAM

For an ENDOTHERMIC REACTION, the products have a higher energy than the reactants
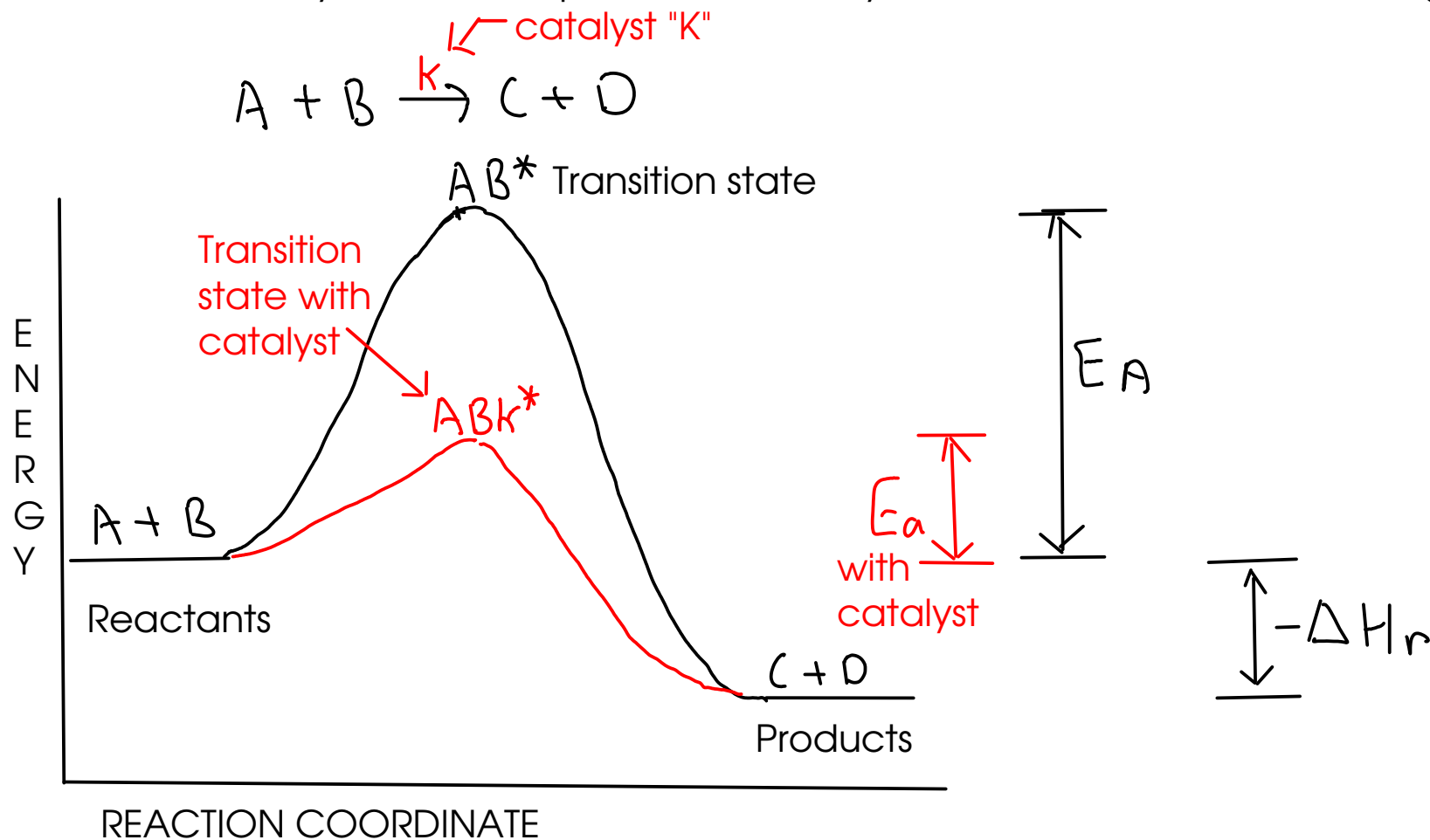
$$A + B \longrightarrow C + D$$

AB^* Transition state

E
N
E
R
G
Y

$A + B$

Reactants

$C + D$

Products

Activation energy

E_A

ΔH_r

Enthalpy of reaction

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

ENERGY (vertical axis label)

A + B

Reactants

C + D

Products

REACTION COORDINATE

E_A

$-\Delta H_r$

- 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^*

ENERGY

A + B

Reactants

E_a with catalyst

E_A

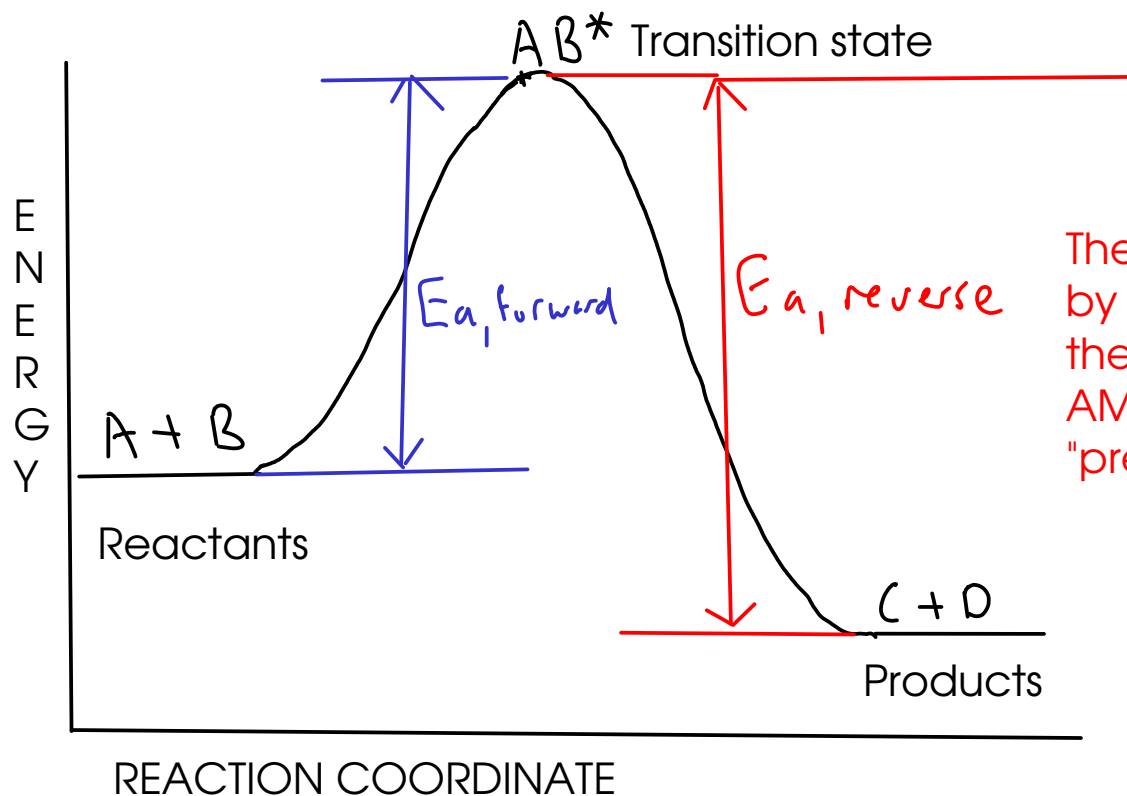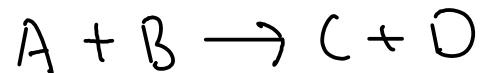$-\Delta H_r$

C + D

Products

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?

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

reactants   products   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

$E_a, \text{forward}$

$E_a, \text{reverse}$

$A + B$

Reactants

$C + D$

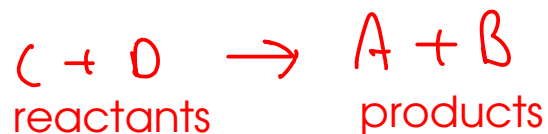Products

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!
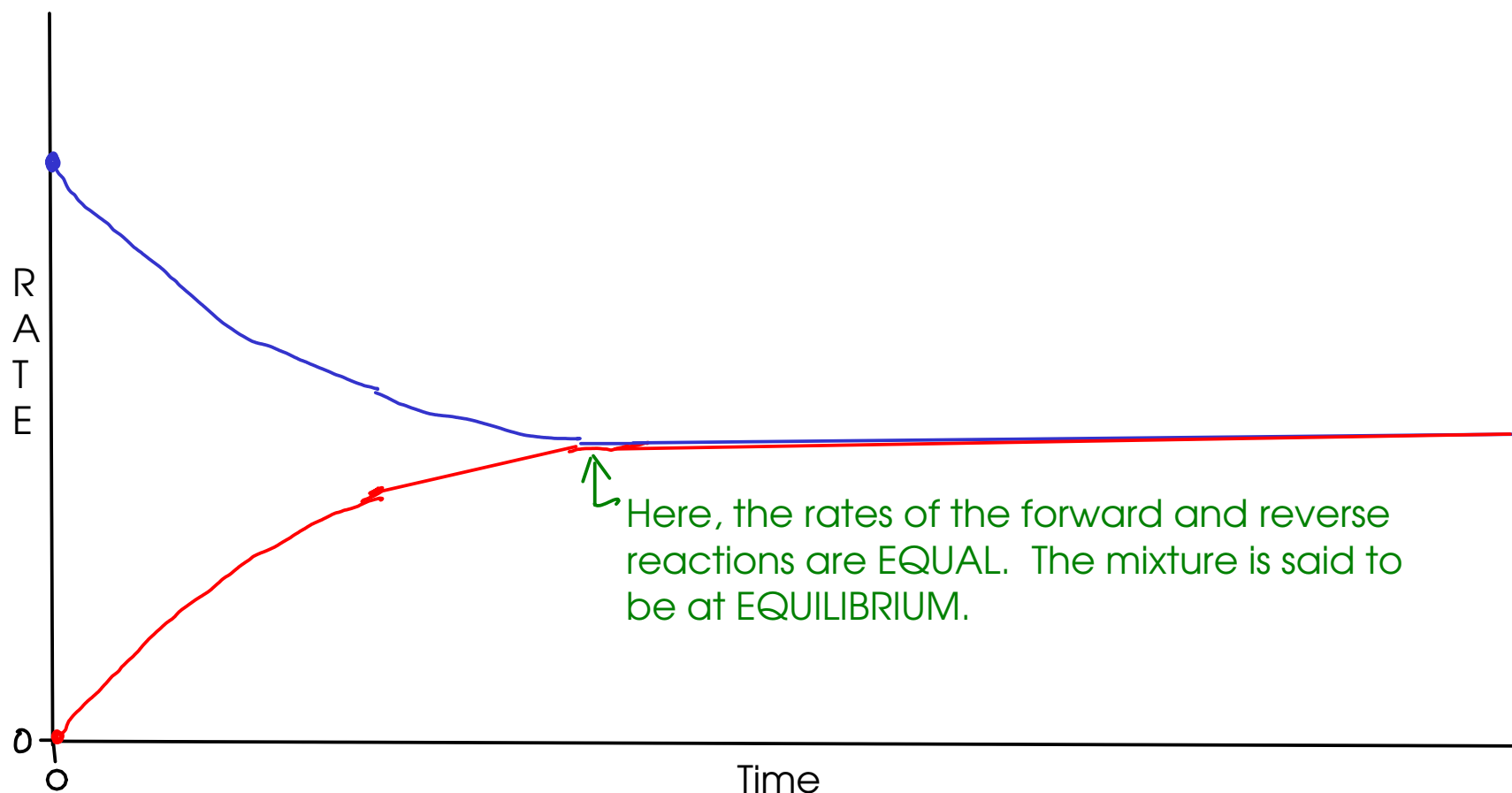
$$A + B \longrightarrow C + D$$
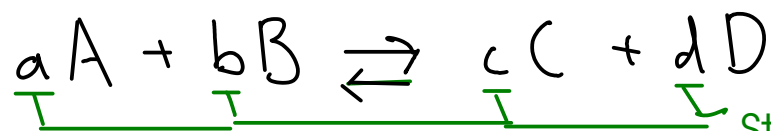reactants   products

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

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

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

0 —

0

Time

- 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.

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

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!

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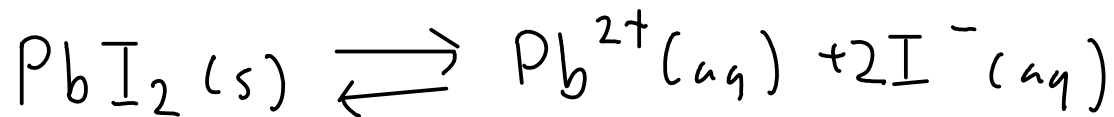
$$K_c = \frac{[Pb^{2+}][I^-]^2}{[PbI_2]}$$

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.
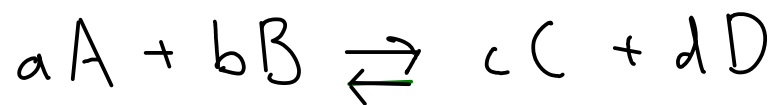
$[H_2O] = ?$

$1 \, g/mL$, $1 \, L$ 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". ("extent" of reaction)

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)

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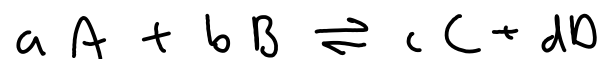
$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

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.

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

$$[NOBr] = 0.0720 \, \underline{M}, \; [NO] = 0.0162 \, \underline{M}, \; [Br_2] = 0.0123 \, \underline{M}$$

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

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

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

... since Q > Kc, the reaction is not at equilibrium and proceeds to the LEFT to make more NOBr ...