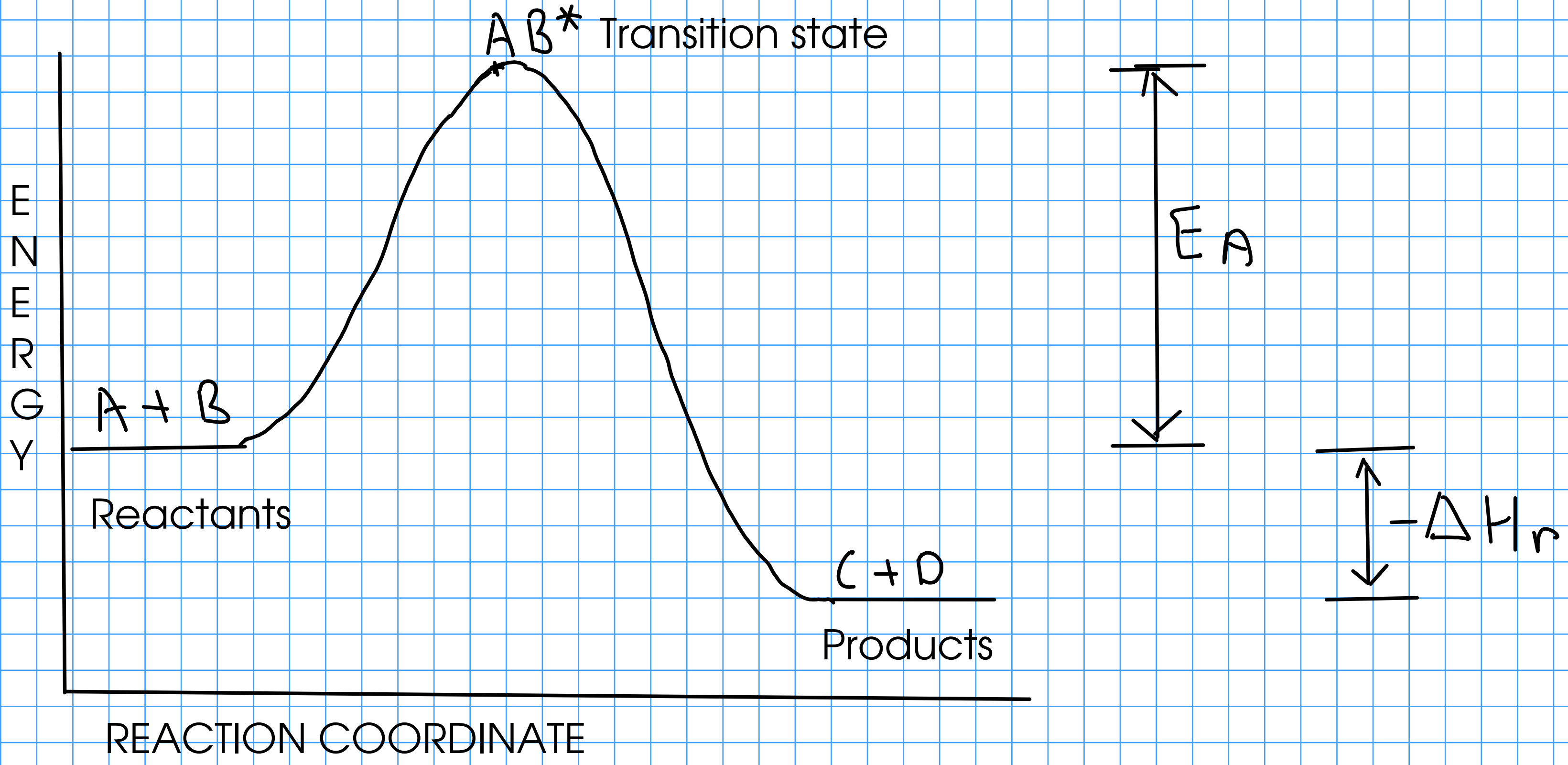
For an EXOTHERMIC REACTION, the products have a lower energy than the reactants

$A + B \rightarrow C + D$



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

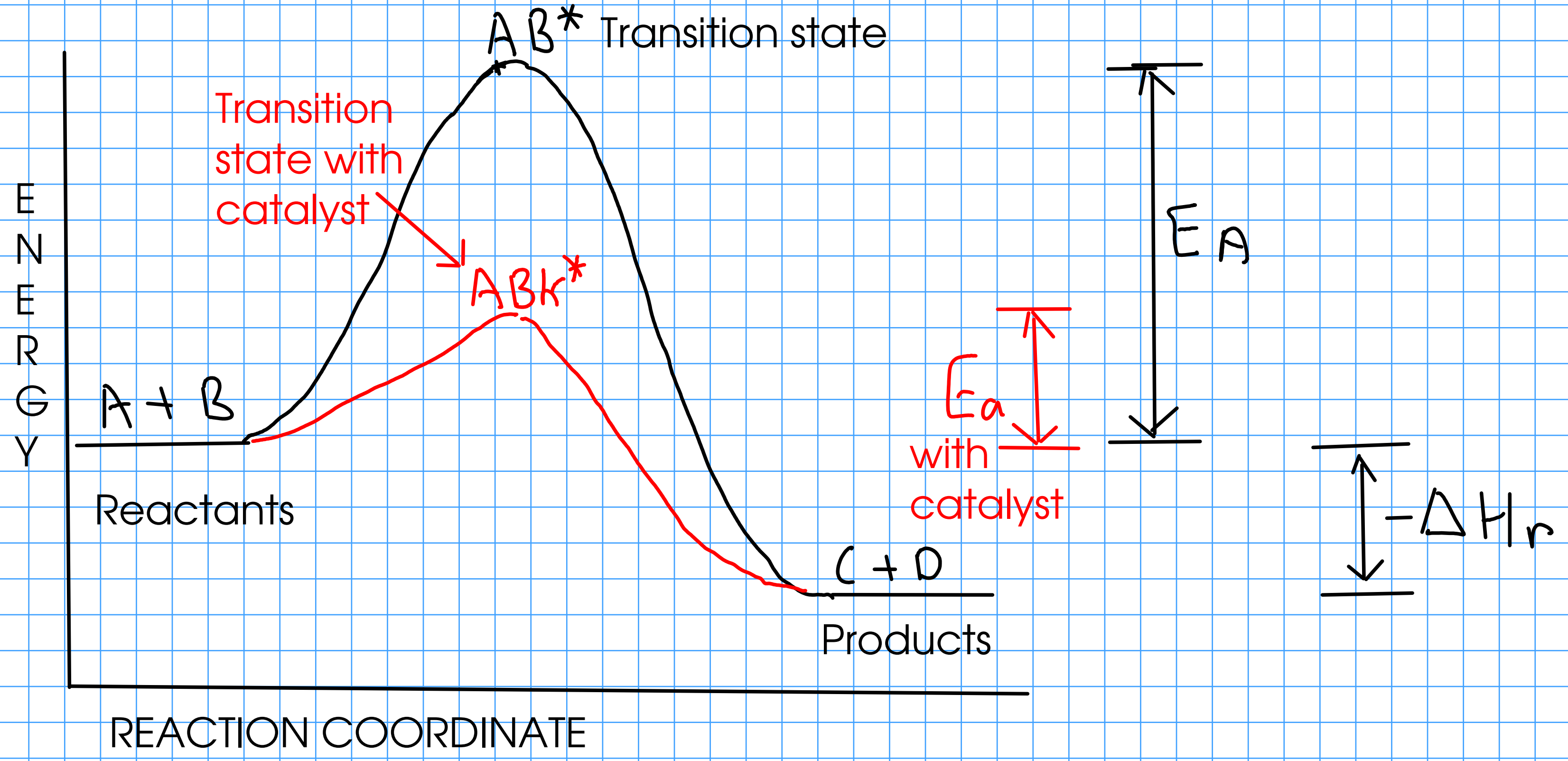
- This explains why a pile of wood that's exposed to air doesn't just burst into flames. Even though the cdombustion of wood is EXOTHERMIC, there's still an activation energy barrier preventing the reaction from occurring without an initial input of energy - a "spark"!

CATALYSTS?

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

catalyst "K"

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



- 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?

$A + B \rightarrow C + D$

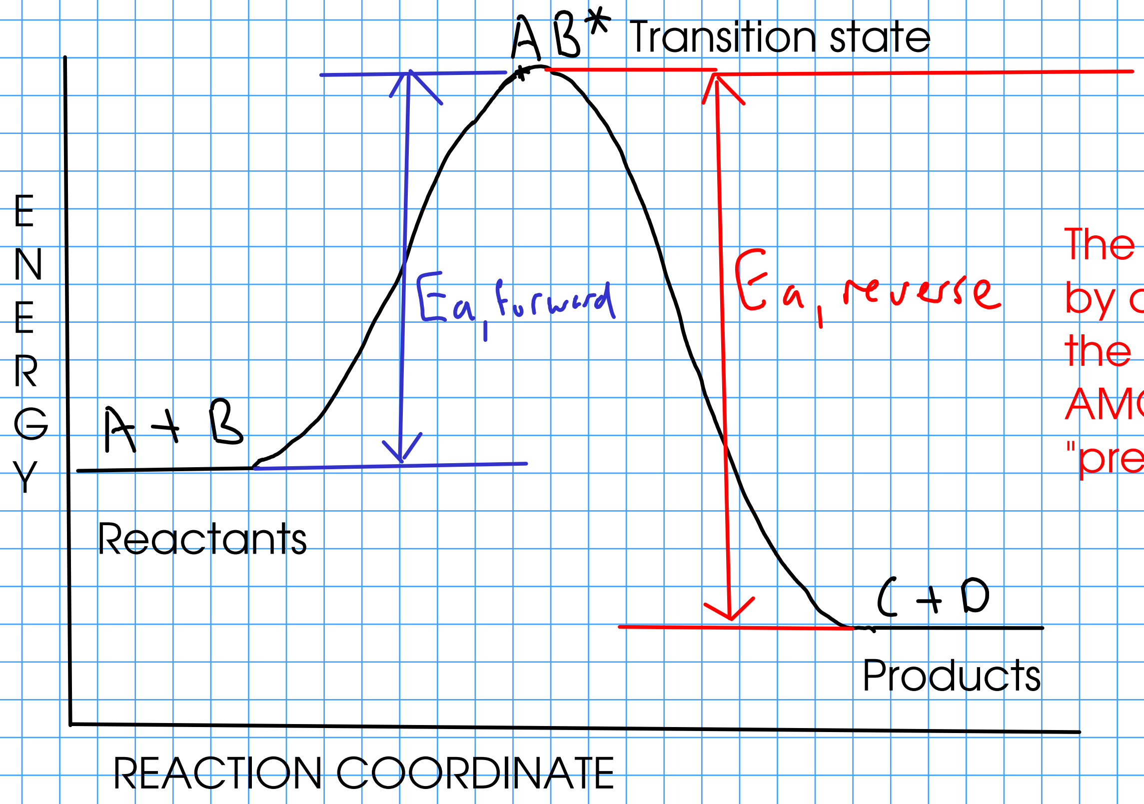
reactants products

$C + D \rightarrow A + B$

reactants products

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

$A + B \rightarrow C + D$



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!

$A + B \rightarrow C + D$

reactants products

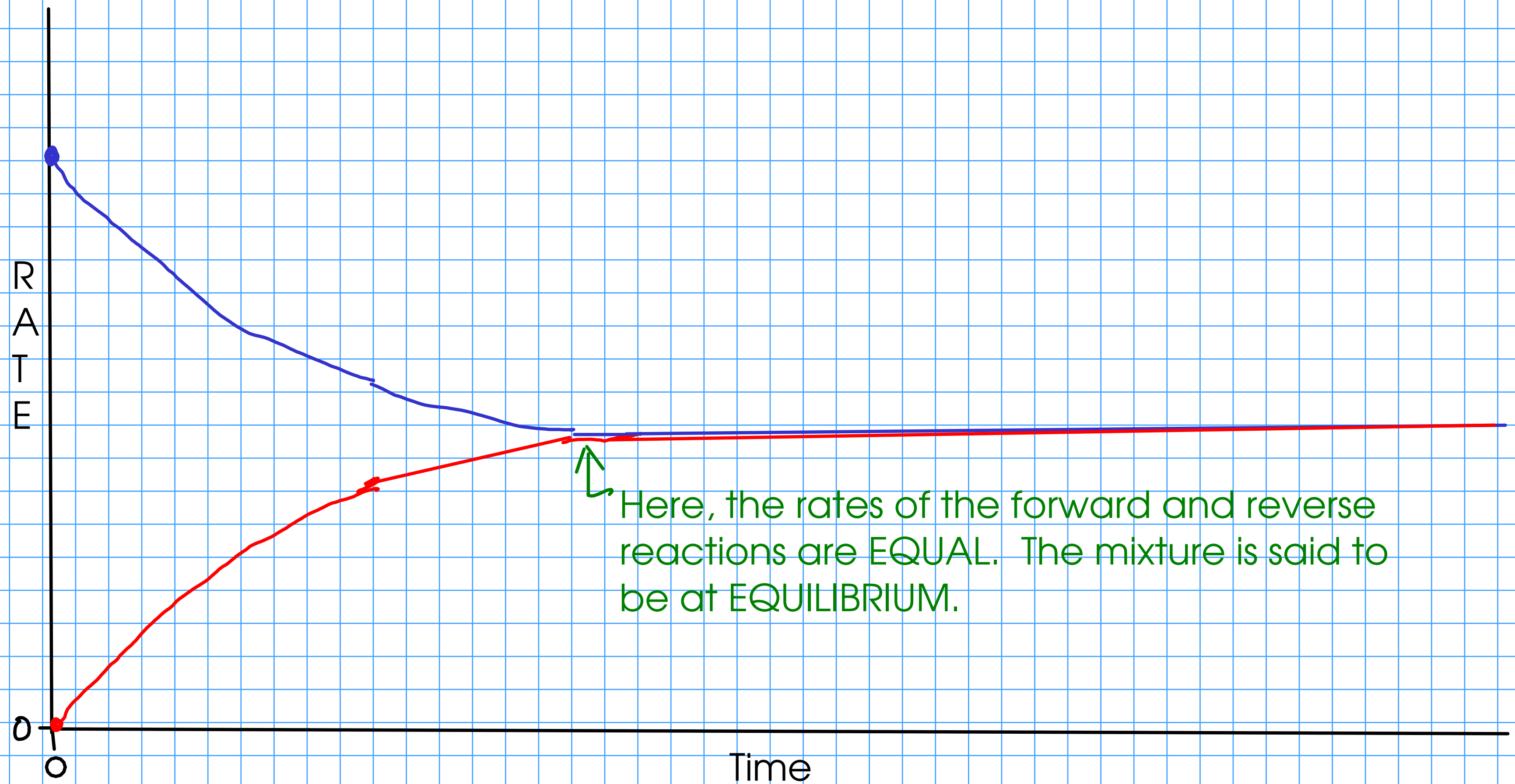
$Rate = k_F[A][B]$

$C + D \rightarrow A + B$

reactants products

$Rate = k_r[C][D]$

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

DESCRIBING EQUILIBRIUM

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

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!

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$

$$K_c = \frac{[Pb^{2+}][I^-]^2}{\boxed{[PbI_2]}}$$

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).

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

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

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

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

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 reacation 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?

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

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

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

$$K_c = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.7\times10^{-5}$$

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 equilibrium!

- 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)

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

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

Reaction quotient = equilbrium expression using NON-EQUILIBRIUM concentrations.

- If Q = Kc, then reaction is at equilibrium.
- 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?

$$K_c = 3{,}07 \times 10^{-4} = \frac{[NO]^2[Br_2]}{[NOBr]^2}$$

$$Q = \frac{(0{,}0162)^2(0{,}0123)}{(0{,}0720)^2} = 6{,}23 \times 10^{-4}$$

$$\underset{Q}{6{,}23 \times 10^{-4}} > \underset{K_c}{3{,}07 \times 10^{-4}}$$

$$Q > K_c$$

Since Q > Kc, this reaction is NOT at equilibrium and will proceed to the LEFT, forming more NOBr.