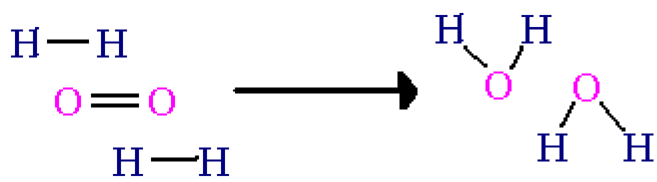
Kinetics and Thermodynamics

Day 17

A Chemical Reaction

•What is happening in a reaction?



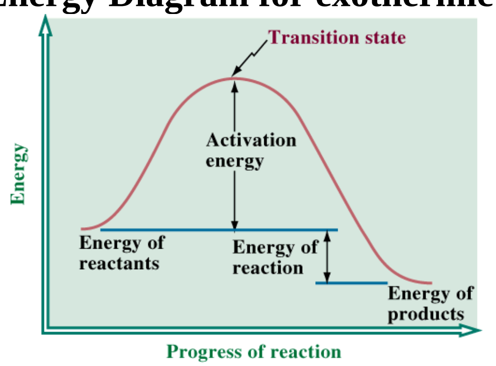
Three things are required for a reaction to occur:

•Molecules must collide.

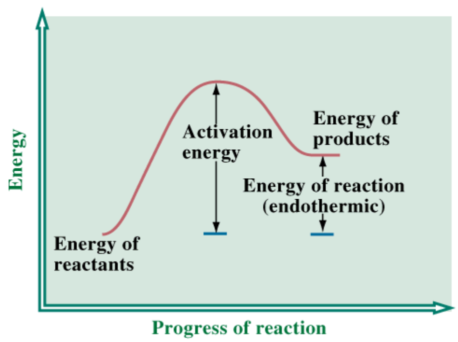
•They must collide with enough energy to break old bonds so new ones can form.

•They must collide in the correct orientation.

Energy Diagram for exothermic reaction



Energy Diagram for endothermic reaction



Kinetics (rate of reaction)

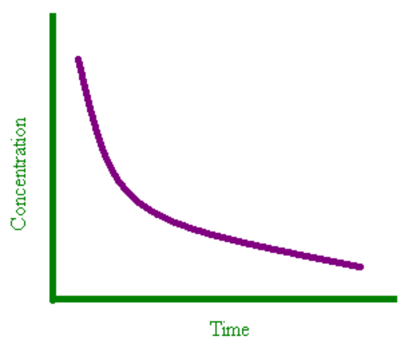
Three ways to increase the rate of a reaction

- ❖ Increase Concentration
  - ➢ Increases number of collisions
- ❖ Increase Temperature
  - ➢ Increases collisions & collisions that have enough energy to break old bonds
- ❖ Use a catalyst.
  - ➢ Lowers energy barrier (Activation energy)

Rate

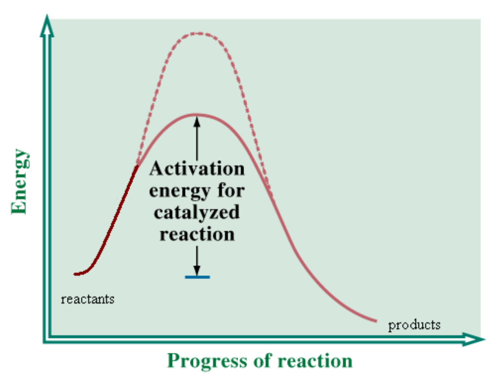
•The rate of a reaction is proportional to concentration.

•As the compounds react, the concentration decreases and the rate slows.



A Catalyst

A compound that increases the rate of a reaction without itself undergoing a permanent change at the end of the process.

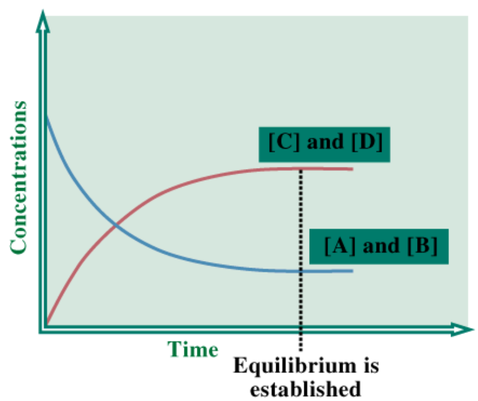


Chemical Equilibrium

•Most reactions are reversible, some are not.
•Reversible reactions are shown with a double arrow.
•An equilibrium condition exists when the rate of the forward reaction equals the rate of the reverse reaction.
•Equilibrium: The exact balancing of two processes that are opposite each other.
•Chemical equilibrium: A dynamic state where the concentrations of all reactants remain constant.

Concentrations as a solution reaches equilibrium

$aA + bB \leftrightarrows cC + dD$



Equilibrium Constant

- For systems at equilibrium, a relationship was discovered by two Norwegian chemists in 1864. (Cata Maxmillian Guldberg and Peter Waage)
- For the reaction $aA + bB \leftrightarrows cC + dD$

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

- [] indicate concentration (typically in molarity)
- Each reaction has its own special K
- Each K is temperature dependent.

K

- For $N_2O_4{}_{(g)} \leftrightarrows 2\ NO_2{}_{(g)}$

$$K = \frac{[NO_2]^2}{[N_2O_4]}$$

Only include aqueous solutions and gases

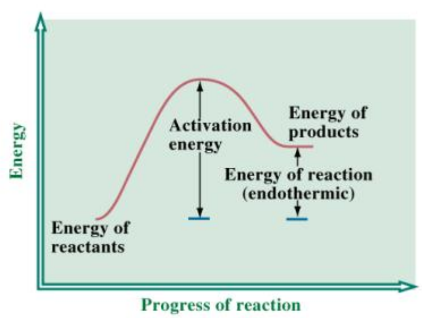
- For $NH_3{}_{(aq)} + H_2O_{(l)} \leftrightarrows NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$

$$K = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Don't show solids or water

K cont.

- When the reaction is exothermic, K is greater than one.
- When the reaction is endothermic, K is less than one.
- Will a catalyst effect equilibrium?



Perturbing a system at equilibrium

- Le Chatelier's principle: When a stress is placed on a system at equilibrium, the equilibrium will shift relieve that stress.
- 4 ways to stress a system

Stress	Shift
Add reactant	right
Add product	left
Remove Reactant	left
Remove Product	right

$A \leftrightarrows B$

- Let's look at a fake equation: The Keq = 1. For this reaction, the concentrations of A & B must be the same at equilibrium.
- Let's assume that there is 1 L of solution and one mole each of A and B. We are at equilibrium.
- Let's perturb the system a couple of different ways

$A \leftrightarrows B$

Add reactant shift right	[A]	[B]	
Initially	1 M	1 M	
Add one mole A	2 M	1 M	Not at equilibrium
Change	-0.5	+0.5	Shift right *(Equation goes to right)*
New equilibrium	1.5 M	1.5 M	Back at equilibrium

By shifting to the right the reaction removes some of the reactant added

Add product shift left	[A]	[B]	
Initially	1 M	1 M	
Add one mole B	1 M	2 M	Not at equilibrium
Change	+0.5	-0.5	Shift left *(Equation goes to left)*
New equilibrium	1.5 M	1.5 M	Back at equilibrium

$A \leftrightarrows B$

Remove product shift right	[A]	[B]	
Initially	1 M	1 M	
Remove one mole B	1 M	0 M	Not at equilibrium
Change	-0.5	+0.5	Shift right *(Equation goes to right)*
New equilibrium	0.5 M	0.5 M	Back at equilibrium

By shifting to the right, the reaction replaces some of the product removed.

$$CH_3COOH_{(aq)} + H_2O_{(l)} \leftrightarrows H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$$

What is K?

- Add CH_3COOH ?
- Add CH_3COO^-?
- Remove H_3O^+ ?
- The reaction is endothermic, What happens when you cool the reaction?
- van't Hoff:
  - Exothermic: heat is a product.
  - Endothermic: heat is a reactant.