Introduction to Kinetics

Gathered and edited by Schweitzer 02/10/04

Rate = Δ Stuff/ Δ time

- A reaction can be measured by the appearance or disappearance of a given species with in a reaction.
- Stuff: (Need some way to measure change)
 pH (acids/bases)
 - Color (colorimeter)
 - Pressure (gases)
 - Mass (gain or loss of over all mass)

Rate and Equilibrium

- Rate and equilibrium are NOT related.
- Equilibrium is a ratio of products verses reactants.
- Kinetics is the rate at which a reaction achieves equilibrium.

Collision Theory

- Two or more particles need to collide physically in order for a reaction to take place.
 - Force Particles need a minimum amount of force between particles to trigger a reaction.
 - Geometry- Particles need to collide in a specific fashion or direction in order to have a legitimate chance for a reaction.

Temperature

- Defined strictly as the measure of the movement of particles
- Defined as average kinetic energy. Since not all particles are traveling same speed. (Average temperature)
- Increased temperature = increase Collisions = increased reactions

- Concentration:
 - Increased concentration means increased number of collisions = increased rate
 - This goes for gases as well as solutions.

Surface Area

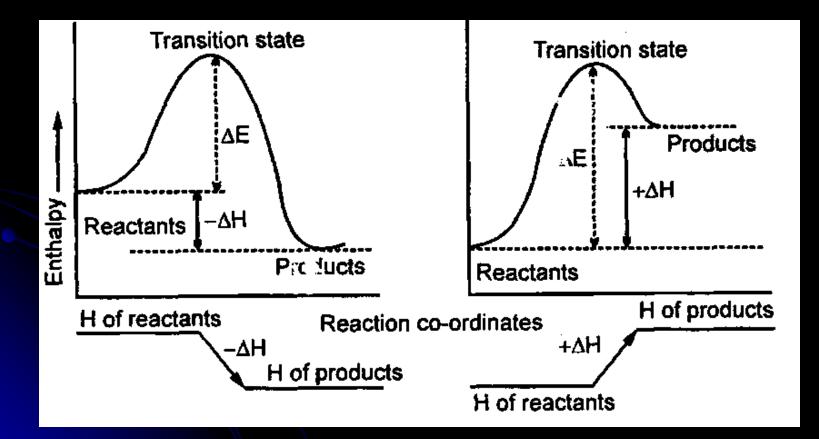
 Increased surface area increases the opportunities for collisions = increased rate

• Ex: If you were to take a two glasses of water. Set one glass on the counter to evaporate and the other is dumped out on the floor. The water on the floor has lots more surface area which allows for a greater rate of evaporation.

- Catalyst
 - A Catalyst Lowers the activation energy of a reaction.
 - This minimizes the amount of energy needed for a reaction to take part in a reaction. Therefore a larger percentage of a given number of particles will have the needed energy to take part.
 - Actually changes the reaction pathway!!!!

Activation Energy

Energy Needed to start a reaction.



- Q: Which accounts for the increase in the rate of reaction when a catalyst is added to a reaction system?
- a. Decrease in ΔH
- b. Increase in ΔS
- c. Increase in potential energy of the reactants
- d. Increase in potential energy of products
- e. Decrease in potential energy of the activated complex.

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Rate with in a Reaction

Stoichiometric ratio

• Ties entire reaction together.

- $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O_2$
- In this case relative to the rate of production of CO₂
- H₂O produced 2 times as fast
- O₂ consumed 2 times as fast
- CH₄ is consumed as the same rate

Example

 $CH_4 + 2O_2 \implies CO_2 + 2H_2O$ If oxygen is being consumed at a rate of 2.5 moles per second. What is the rate of production of the Carbon dioxide?

Relative rates Answer

 $CH_4 + 2O_2 \implies CO_2 + 2H_2O_2$ If oxygen is being consumed at a rate of 2.5 moles per second. What is the rate of production of the Carbon dioxide? **Use stoich ratio** Answer: $2.5 O_2 * (1 CO_2 / 2O_2) =$ 1.25 CO₂ moles/sec

Orders of Reactions

• Zero order

- Concentration of species does not affect rate
- $[2x]^0 = 1$ (no change)
- 1st order
 - Rate increases proportionally with the in the concentration
 - $[2x]^1 = 2 \dots [3x]^1 = 3$

2nd order

- Rate quadruples if concentration doubles
- $[2x]^2 = 4 \dots [3x]^2 = 9$

Rate Equation

- $2H_2 + O_2 \rightarrow 2H_2O$
 - Rate = $k[H_2]^x[O_2]^y$
 - Looks very similar to equilibrium but exponents MUST be determined by experiment NOT by coefficients

Why do we want the rate equation?
Allows us to determine rates at different concentrations.

Determination of exponents (Order)

Experiment--[NO]M--[CI]M ----INITIAL RATE M/s 1 0.0125 0.255 2.27E-5 2 0.0125 0.510 4.45 E-5

- 3 0.0250 0.255 9.08 E-5
- What is the rate equation?
- Rate = k[NO]^x[CI]^y
- X and Y represent the order.
- We need to figure out x, y, and k.

Determination of Exponents (order)

- Experiment--[NO]M--[CI]M ----INITIAL RATE M/s
- 1 0.0125 0.255 2.27E-5
 2 0.0125 0.510 4.45 E-5
- 3 0.025 0.255 9.08 E-5

Isolate a change between trials.

Example between trial 1 and trial 2.

Determination of Exponents (order)

Experiment--[NO]M--[CI]M ----INITIAL RATE M/s

• Isolate a change between trials.

- Example between trial 1 and trial 2.
- Since NO didn't Change and the CI doubled then we can say that all the change in rate was due to the CI.
- Concentration doubled... rate doubled1st order

Determine the order of NO

- Experiment--[NO]M--[CI]M ----INITIAL RATE M/s
- 1 0.0125 0.255 2.27E-5
- 2 0.0125 0.510 4.45 E-5

3 0.025 0.255 9.08 E-5
Determine the order of NO on your own.

Determine the order of NO

Experiment--[NO]M--[CI]M ----INITIAL RATE M/s

• 1	0.0125	0.255	2.27E-5
• 2	² 0.0125	⁰ 0.510	⁴ 4.45 E-5
• 3	0.0250	[↓] 0.255	[↓] 9.08 E-5

More then likely we will want to compare trials 1 and 3. the CI stays the same while the NO doubles. However the rate increases by 4

Concentration doubles rate quadruples...2nd order

Update the Rate equation

- Rate = $k[NO]^2[CI]$
- Lastly We must determine K

How do you determine k and its units!!!

- Pick any one of the Trials.
- Substitute values of concentrations and the rate into rate equation. Solve for K.
- I Chose trial 1.
- Rate = $k[NO]^2[CI]$
- 2.27E-5M/s = k[.0125]²[.225]
- $K = .645L^2/mol^2s$

Where did the units come from??

- Rate = $k[NO]^2[CI]$
- Rate/[NO]²[Cl] = k
- $(Mol/Ls) = k (mol^2/L^{2*} mol/L)$
- L²/ mol²s= k

Question

 a) What would be the initial rate in experiment 4, which has [NO] = M and [CI] = M

Rate = .645 [0.0500]²[0.0255]¹
Rate = 4.11E-5 M/s