

AP Chemistry – Kinetics

Kinetics – the study of how fast reactions occur (from here forward we will call it the “rate of reaction” or just rate)

Factors that affect rate

1. Nature of reactants

- Physical state – solid/liquid/gas/aqueous, has to do with reactants ability to mix
- Chemical identity – ions/# of bonds to be broken/bond energies

2. Concentration of reactants

- Higher conc. means more molecules present, more collisions and faster rate

3. Temperature

- Heat'em up, speed'em up.... Higher temps, more molecules moving faster (Boltzmann), more collisions = faster rate

4. Surface area

- More exposed surface = more collisions

5. Catalysis

- Lowers activation energy (less energy needed which means more molecules can have effective collisions)
- Careful... catalysis will not change equilibrium b/c it lowers E_a of both forward AND reverse rxn (changes rate of both equally). You should be able to draw energy diagram for this!
- In rxn mechanism consumed in early step then produced

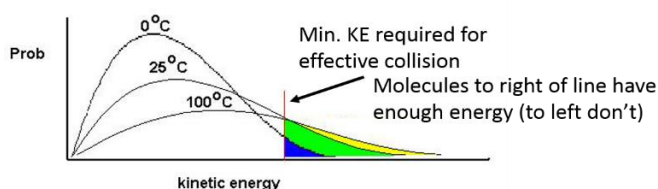
Trick alert: adding INERT gases has no effect on rates!

Collision Model Theory

- Based on KMT and accounts for Temperature and Concentration effects on reaction rates
 - Molecules must collide to react
 - Must collide with sufficient Energy (E_a)
 - Must collide with proper orientation
- If properly oriented and high enough energy will have effective collision that will produce activated complex (also called a transition state)

more collisions and/or higher energies = FASTER RATES

Boltzmann Distribution



Curves flatten out as Temp increases = more molecules have E_a

Relative Rates (reactants are negative rates, products are positive rates)

Individual rates are stoichiometrically equivalent and comparable to each other and overall rate (based on coefficients)



- Rate for A will be same as overall rate (1:1 ratio)
- Rate for B will be twice as fast as A
- Rate for C will be 4x's as fast as A and 2x's as fast as B

Rate Law

Rate – versus – Concentration

$$\text{Rate} = k[A]^X[B]^Y$$

Orders are determined by looking at how a change in concentration effects the rate (Table logic)

k = rate constant

X = order with respect to A

Y = order with respect to B

Trick alert: be able to solve for units of k

1st order
Changes are proportional

Double Conc. = double rate
1.5x Conc. = 1.5x rate
4x Conc. = 4x rate

Zero Order
NO change

Changing Conc. Has
NO EFFECT on rate

2nd order
Changes are exponential

Double conc. = rate x 2²
Triple conc. = rate x 3²
(find the pattern!)

Table Logic to Determine Orders – Rate Law

- You will always be comparing two different trials
 - Hold one concentration constant
 - Determine change in [] of other (multiplier) and the effect on rate (multiplier)
 - Your only choices are 1st, 2nd, or zero order...

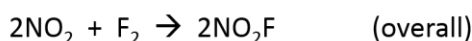
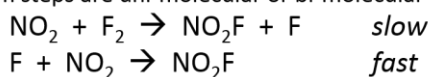
KNOW the effects on rate to the left for each order!!!!!!!!!!

Experiment Number	Initial Rate ($\Delta M/\text{sec}$)	Initial Concentration [A] ₀	Initial Concentration [B] ₀
1	.5	.50	.20
2	.5	.75	.20
3	.5	1.00	.20
4	1	.50	.40
5	1.5	.50	.60

[B] is doubled, Rate is doubled (change is proportional) so B is 1st order
To get order for A, do the same thing but hold [B] constant and change [A]

Reaction Mechanisms – Part 1

- Reactions sometimes occur in steps to get to the final product (reaction mechanism) (steps should add to overall reaction!)
- Most mechanism steps are uni-molecular or bi-molecular



Trick alert: F is a reaction intermediate b/c it is produced in early step then consumed

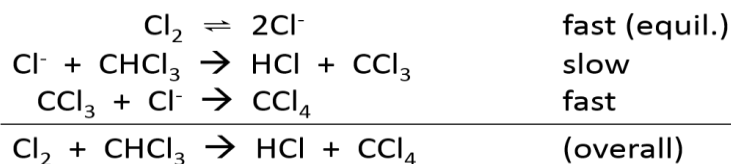
Arrhenius Equation Simplified

$$k \approx e^{\frac{-E_a}{RT}}$$

A bigger ($-E_a$) will make rate constant smaller
---so we expect rxn to go SLOWER

A larger (T) will make the rate constant larger
---so we expect rxn to go FASTER

Reaction Mechanisms – Part 2 (Fast 1st step in Mechanism)



Trick alerts: Can you spot all the reaction intermediates?
When there is a slow second step the steps before it will reach equilibrium
At Equilibrium remember --- Rate Forward Rxn = Rate Reverse Rxn

Rate Law:

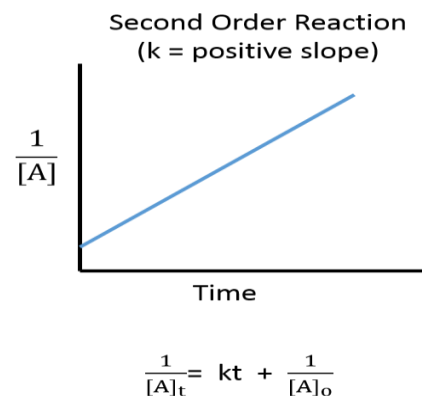
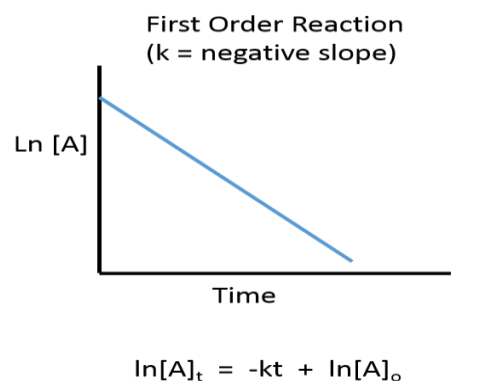
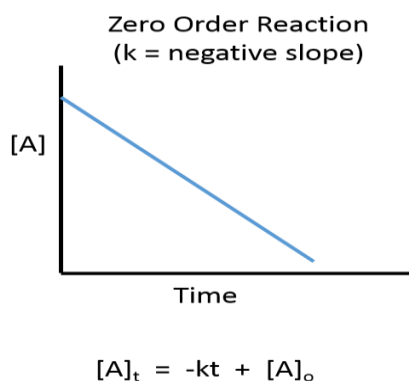
$$\text{Rate} = k[\text{Cl}^-][\text{CHCl}_3]$$

Use slow step, coefficients become orders
NO reaction intermediates can be in rate law!

- To remove intermediate set rates of 1st rxn equal to each other $[\text{Cl}_2] = [\text{Cl}^-]^2$ (For. = Rev.)
- Then solve for the reactant that appears in overall rxn $[\text{Cl}_2]^{1/2} = [\text{Cl}^-]$ (solved for Cl_2)
- Then substitute:
New Rate Law: $\text{Rate} = k[\text{Cl}_2]^{1/2} [\text{CHCl}_3]$

Integrated Rate Law

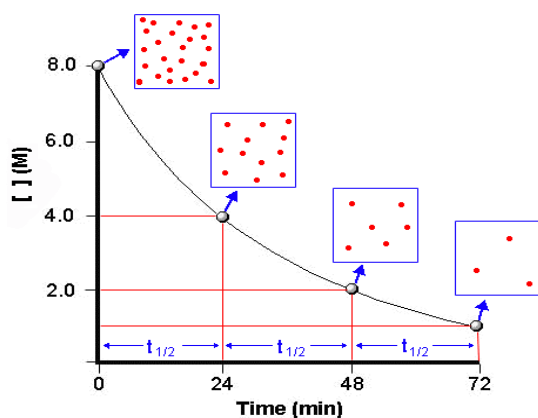
Time – versus – Concentration



Trick alert: WATCH THE AXIS LABELS!

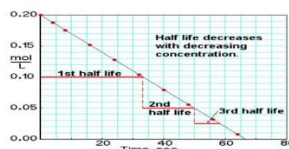
Half-Life

Amount of time it takes for half of a reactant to disappear-- notice it is Concentration versus time!

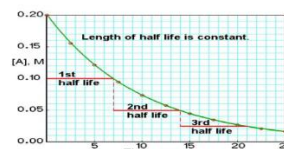


Each half-life cuts original reactant percentage in half (100% → 50% → 25% → 12.5% → etc...)

Zero Order Reaction $\text{A} \rightarrow \text{products}$ & $\text{rate} = k$

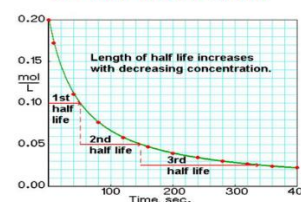


First Order Reaction $\text{A} \rightarrow \text{products}$ & $\text{rate} = k[\text{A}]$



Second Order Reaction

$2\text{A} \rightarrow \text{products}$ or $\text{A} + \text{B} \rightarrow \text{products}$
 $\text{rate} = k[\text{A}]^2$ or $\text{Rate} = k[\text{A}][\text{B}]$



Things to notice about half-life for each order reaction:

Zero order – half life DECREASES

First order – Half-life is CONSTANT (means it is Conc. Independent)

Second order – Half-life INCREASES

Calculating Half-Life – Method 1

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

Relates half-life ($t_{1/2}$) to rate constant (k)

Calculating Half-Life – Method 2

$$\ln \frac{[\text{A}]_t}{[\text{A}]_o} = -kt$$

Use to figure out how long it will take for % of reactant to disappear