

Chem 1412  
General Chemistry II  
**Studying Chemical Reactions  
and  
Specialty Topics in Chemistry**

# General Chemistry

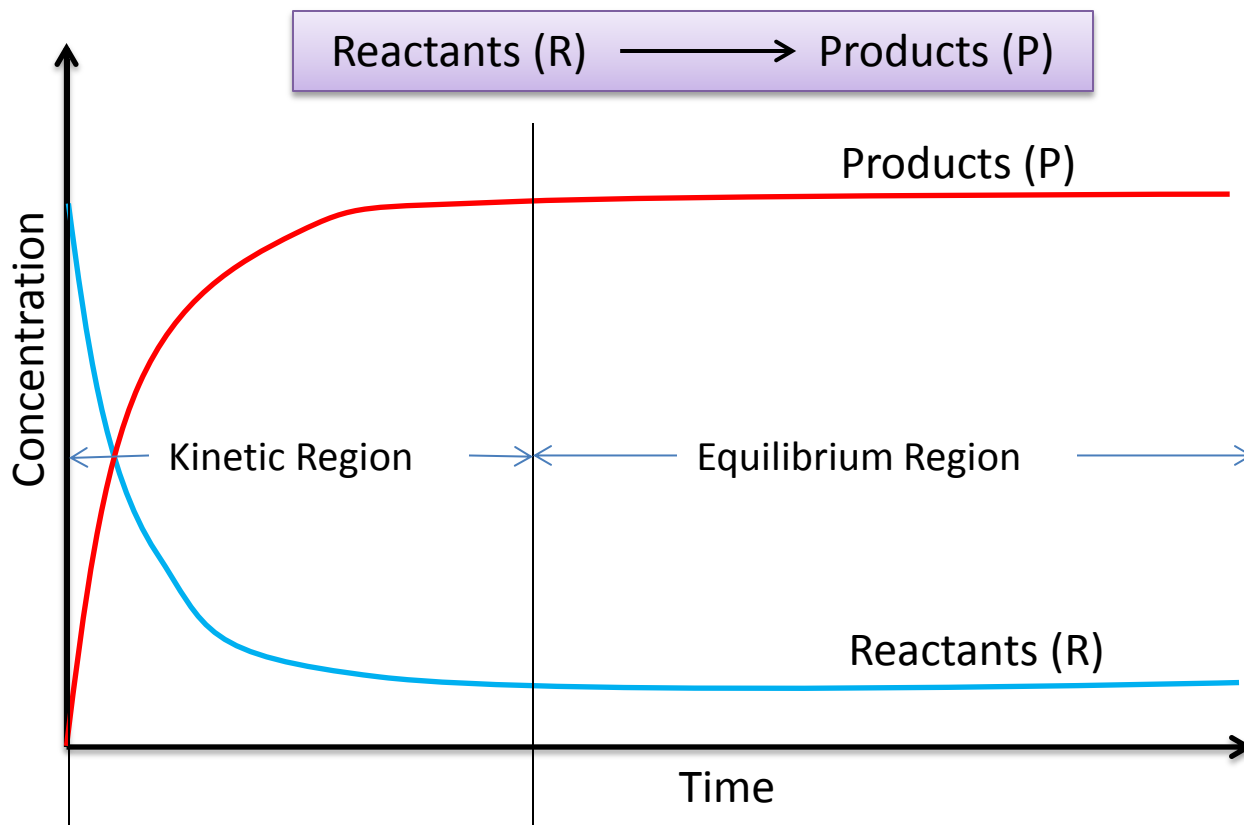
## A Survey Course in Chemical Technology

- **General Chemistry I:** Basic concepts in chemistry based upon Dalton's Atomic Theory.
  - **Organization of Study of Chemistry:** ( $p^+$ ,  $n^0$ ,  $e^-$ ) >> Atoms & Elements >> Molecules & Compounds >> Chem Equations & Reactions >> States of Matter >> Solutions
- **General Chemistry II:** Study of Chemical Reactions and Specialty Topics in Chemistry
  - **Study of Rxns:** Kinetics >> Equilibrium >> Acid/Base Equilibrium >> Solubility Product Equilibrium >> Thermodynamics
  - **Specialty Topics:** Electrochemistry > Nuclear Chemistry > Families of Elements > Organic Chemistry > Polymer Chemistry > Biochemistry > Analytical Chemistry > Medicinal Chemistry > Formulation Chemistry...

# Topics for Study of Chemical Reactions

- Chemical Kinetics – The Study of Rates of Reaction
- Chemical Equilibrium – The Study of Extent of Reaction
- Chemical Thermodynamics – The Study of Reaction Feasibility

# Relationship between Kinetics, Equilibrium and Thermodynamics



# Factors Affecting Reaction Rates

Concentration Effects

Surface Area Effects

Nature of Reacting Substances

Temperature Effects

Catalytic Effects

C.A.N.T.C.

# Factors Affecting Reaction Rates

## 11.4 Factors that affect Reaction Rate



<http://www.youtube.com/watch?v=S1sWvCOTUI8>

# Measuring Rates of Reaction

For any reaction producing products:

$$\text{Rate of Reaction} = \frac{\Delta \text{Rate Factors}}{\Delta \text{Time}} = \frac{\Delta \text{Concentration}}{\Delta \text{Time}}$$

- The central issue in measuring rates of reaction is finding methods of measuring rate factors.
- This could include:
  - Analytical Wet Method Titrations
  - pH Analysis
  - Electrical Conductivity Measurement
  - Infrared Spectroscopy
  - UV/Vis Spectrophotometry
  - Gas Volume Analysis

# Units of Reaction Rates

$$\text{Rate of Reaction} = \frac{\Delta \text{Concentration}}{\Delta \text{Time}}$$

Concentration = moles / liter = Molar

Time = seconds (s)

$$\text{Rate of Reaction Units} = \frac{\text{moles/liter}}{\text{seconds}} = \frac{\text{moles}}{\text{liter-sec}} = \text{moles} \cdot \text{L}^{-1} \text{ s}^{-1}$$

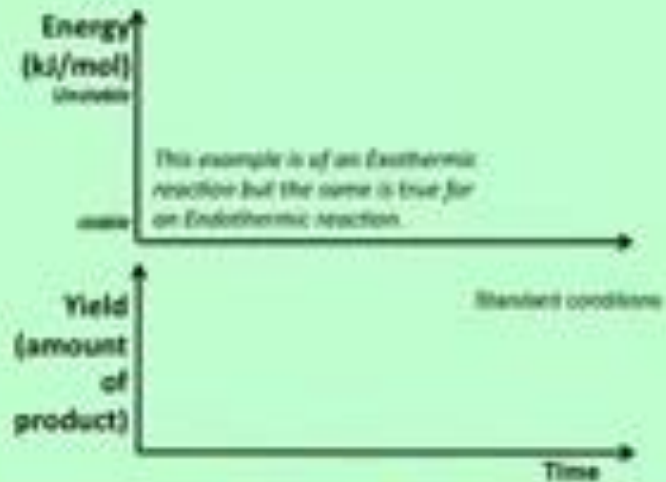


# Rate Laws

- Rate Laws are mathematical relationships that define changes in rate as a function of a rate factor.
- Rate  $\propto$  f(concentration)
- Rate  $\propto$  f(surface area)
- Rate  $\propto$  f(nature)  $\propto$  f(chemical structure)
- Rate  $\propto$  f(temperature)
- Rate  $\propto$  f(catalytic process)

# Rate Laws

## REACTION RATES



Effect of Heat

Effect of Concentration

Effect of Surface Area

Effect of volume

Effect of catalyst

Effect of Heat

End Show

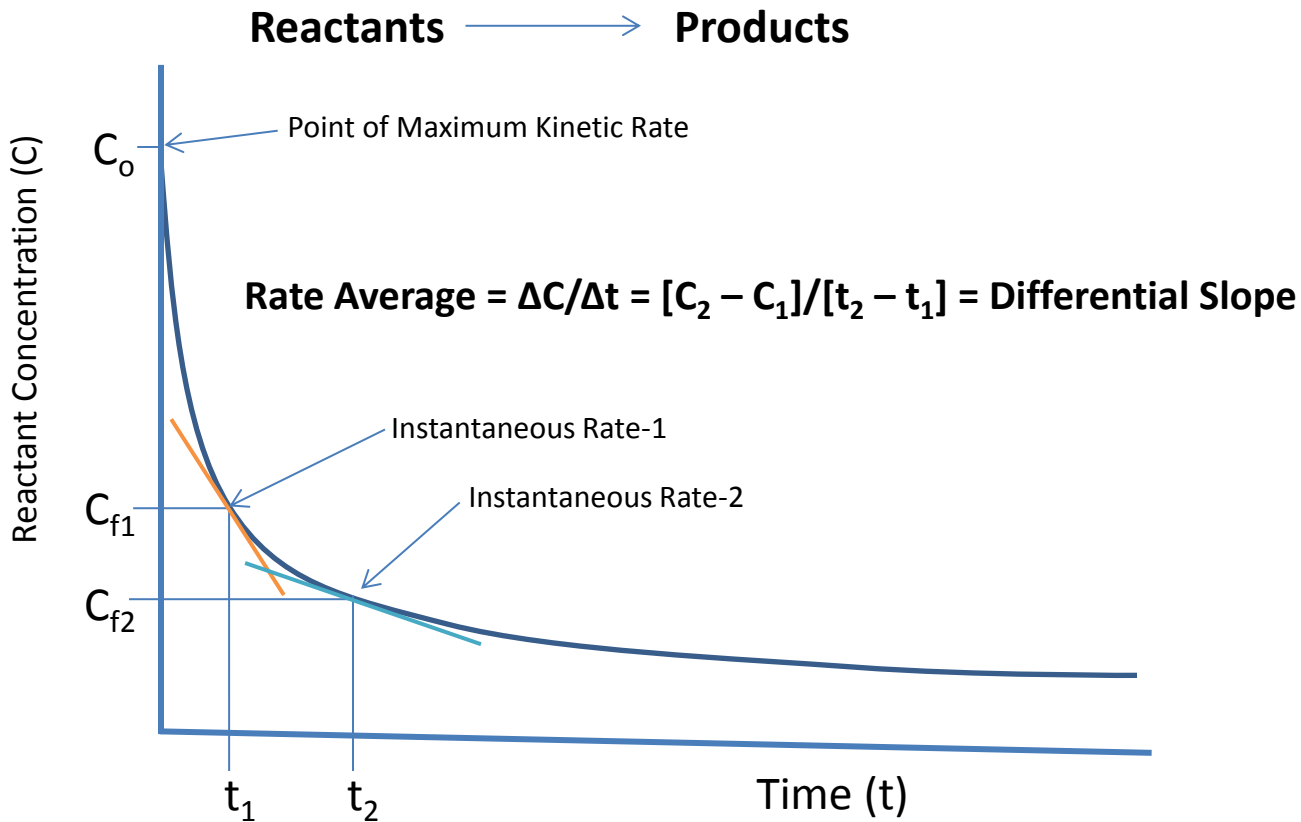
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# Rate $\propto$ f(concentration)

- Four types of problems
  - Rate Averaging
  - Rate  $\propto$  f(Equation Coefficients)
  - Experimental Rate Laws
  - Decay Process and Half Life

# Rate $\propto f(\text{concentration})$

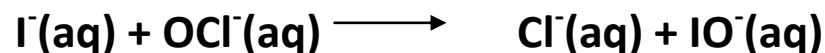
## Rate Averaging or, Instantaneous Rxn Rate



# Rate $\propto$ f(concentration)

## Rate Averaging or, Instantaneous Rxn Rate

- Iodide ion ( $I^-$ ) is oxidized by the hypochlorite ion ( $OCl^-$ ) in a basic solution according to the following reaction in aqueous media:



Determine the 'Rate Average' if in a 1.00 Molar NaOH(aq) solution at 25°C, the Iodide concentration at different times are as follows:

Time(sec)	$[I^-(aq)]$	Rate (avg)
2	0.00169	$1.13 \times 10^{-3} \text{ M/s}$
8	0.00101	

# Rate $\propto$ f(concentration)

Rate as a Function of Equation Coefficients

Calculate rate of formation of NO(g) and the rate of disappearance of NH<sub>3</sub>(g) for reaction when the rate of formation of water is 0.040 M/s.



# Rate $\propto$ f(concentration)

## Experimental Rate Laws

Consider the general reaction:



The 'empirical' rate law is:

$$\text{Rate} = k[A]^x$$

$k$  = rate constant (relative speed of reaction)

$[A]$  = molar concentration of compound A

$x$  = order of reaction (rate trend)

# Rate $\propto$ f(concentration)

## Experimental Rate Laws

- For  $A \longrightarrow$  Products
- Rate =  $k[A]^x$ 
  - What if  $x = 0$ , What would be the rate trend for a 'zero' order rxn?
  - What if  $x = 1$ , What would be the rate trend for a '1<sup>st</sup> order rxn?
  - What if  $x = 2$ , What would be the rate trend for a '2<sup>nd</sup> order rxn?
- What is the overall order of a chemical rxn with multiple reactant components?



# Rate $\propto$ f(concentration)

## Experimental Rate Laws

For  $A \longrightarrow$  Products  $\Rightarrow$  Empirical Rate Law  $\Rightarrow$  Rate =  $k[A]^x$

	Molar Concentration [A]				
Order of Reaction	[A] = a Reference Concentration	[A] = 2a	[A] = 3a	[A] = 4a	[A] = 5a
0	$k(a)^0$ =k	$k(2a)^0$ =k	$k(3a)^0$ =k	$k(4a)^0$ =k	$k(5a)^0$ =k
1	$k(a)^1$ = ka	$k(2a)^1$ =2ka	$k(3a)^1$ =3ka	$k(4a)^1$ =4ka	$k(5a)^1$ =5ka
2	$k(a)^2$ = ka <sup>2</sup>	$k(2a)^2$ =4ka <sup>2</sup>	$k(3a)^2$ =9ka <sup>2</sup>	$k(4a)^2$ =16ka <sup>2</sup>	$k(5a)^2$ =25ka <sup>2</sup>
3	$k(a)^3$ =ka <sup>3</sup>	$k(2a)^3$ =8ka <sup>3</sup>	$k(3a)^3$ =27ka <sup>3</sup>	$k(4a)^3$ =256ka <sup>3</sup>	$k(5a)^3$ =625ka <sup>3</sup>

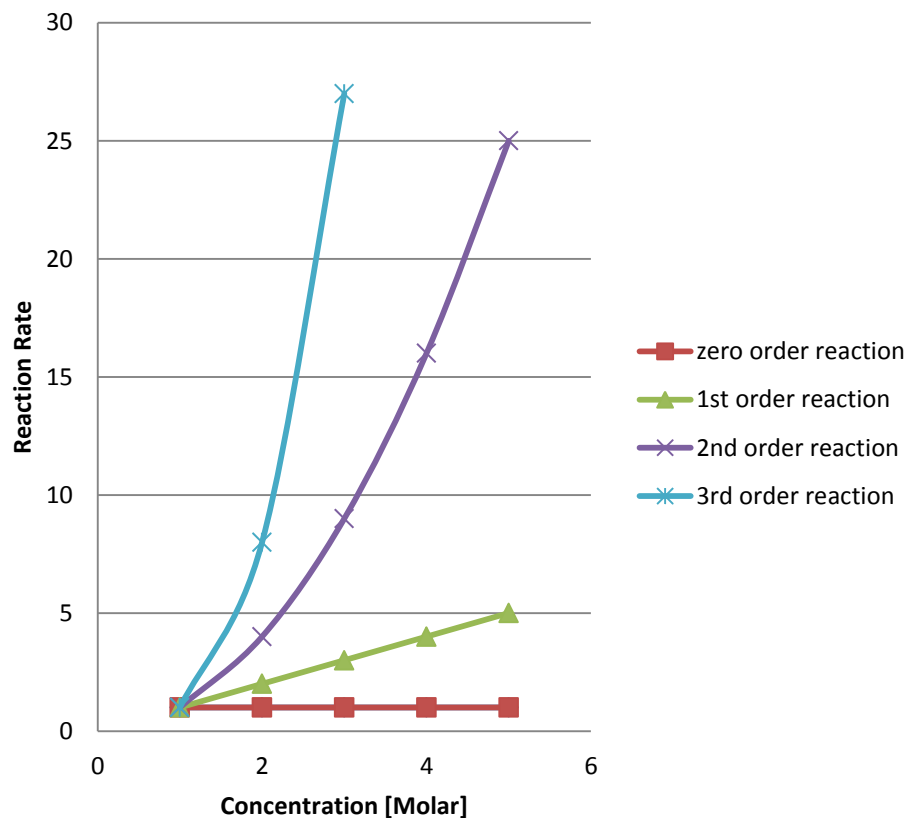
# Experimental Rate Laws

## Rate as a Function of Reaction Order

For Rxn  $A \rightarrow$  Products

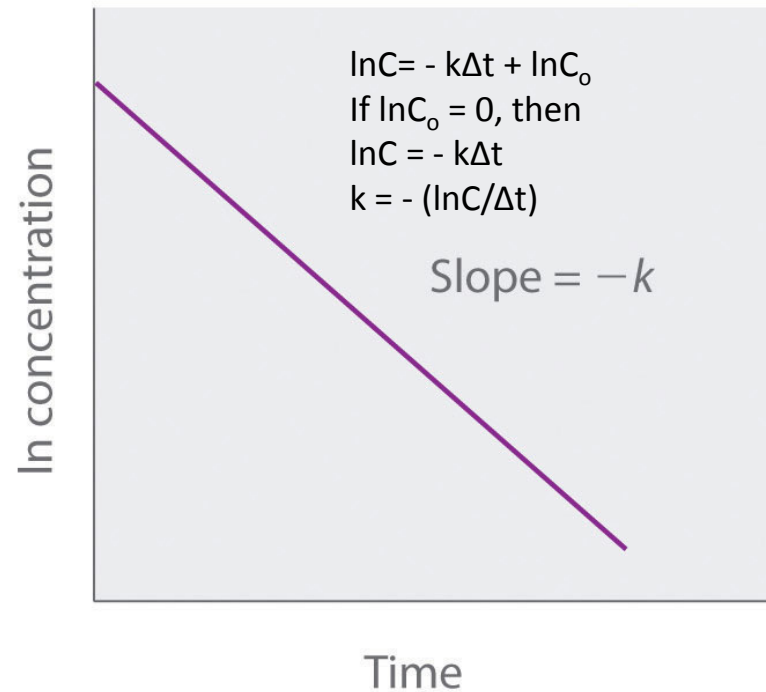
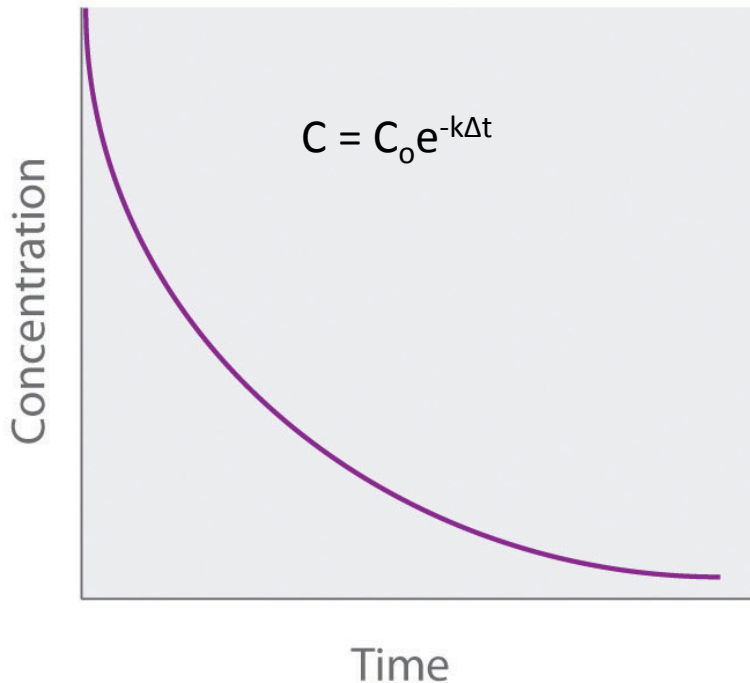
For Rate = $k[A]^x$ and let $k=1$ & $a = 1$				
[A]	$k[A]^0$	$k[A]^1$	$k[A]^2$	$k[A]^3$
1	1	1	1	1
2	1	2	4	8
3	1	3	9	27
4	1	4	16	256
5	1	5	25	625

Rate as Function of Rxn Order



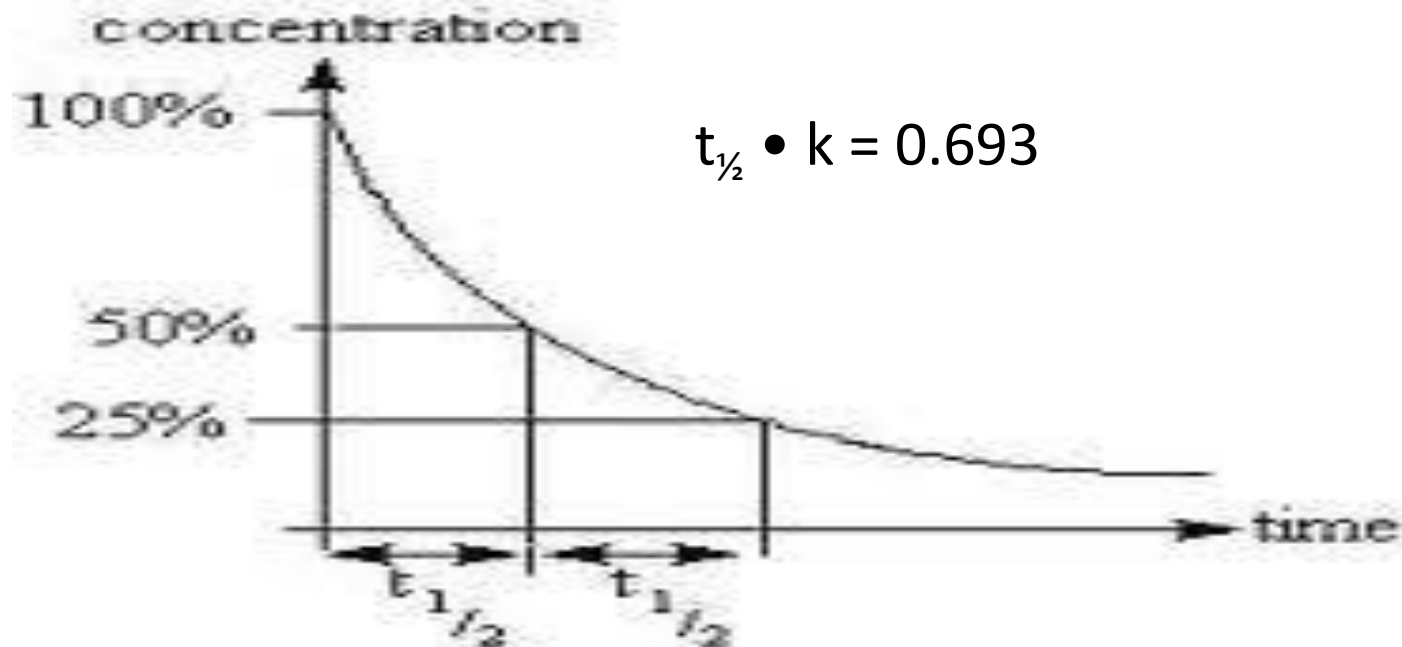
# The Decay Process

- For 1<sup>st</sup> order reaction decay, the change in concentration as a function of time is graphically defined by the following trend:



# The Decay Process – Half Life

- Half Life is the time needed to reduce initial concentration of reactant to one-half of its original value.
- The 'half-life equation' is:
- For a 1<sup>st</sup> order reaction process, half-life is constant



# The Decay Process – Decay Problems

- Calculate
- Final Concentration
- Half Life
- Time of Decay to Final Concentration

Calculate	Equation
Final Concentration	$C = C_0 e^{-kt}$
Half Life	$kt_{1/2} = 0.693$
Decay Time to Final Concentration	$t = [\ln(C/C_0)]/-k$

C = Final Concentration  
C<sub>0</sub> = Initial Concentration  
k = Rate Constant  
t = Time  
t<sub>1/2</sub> = Half Life  
e = Base of Natural Logarithm

# Chemical Kinetics – The Collision Theory

- For any reaction to proceed from reactants to products, four reaction events must occur simultaneously ... These are:
  - The reactants must be in sufficient concentration so as to effectively interact by collision,
  - Effective collisions must occur such that particles interact in specific orientations,
  - Reagents must be naturally reactive, and
  - Internal positional energy of reacting particles must be at or above a critical activation energy in order to achieve product.

# Chemical Kinetics – The Collision Theory

- C – Concentration
- E – Effective Collisions
- N – Naturally Reactive Substances
- T – Temperature ( Internal Energy Content )
  
- Related in Arrhenius Equation

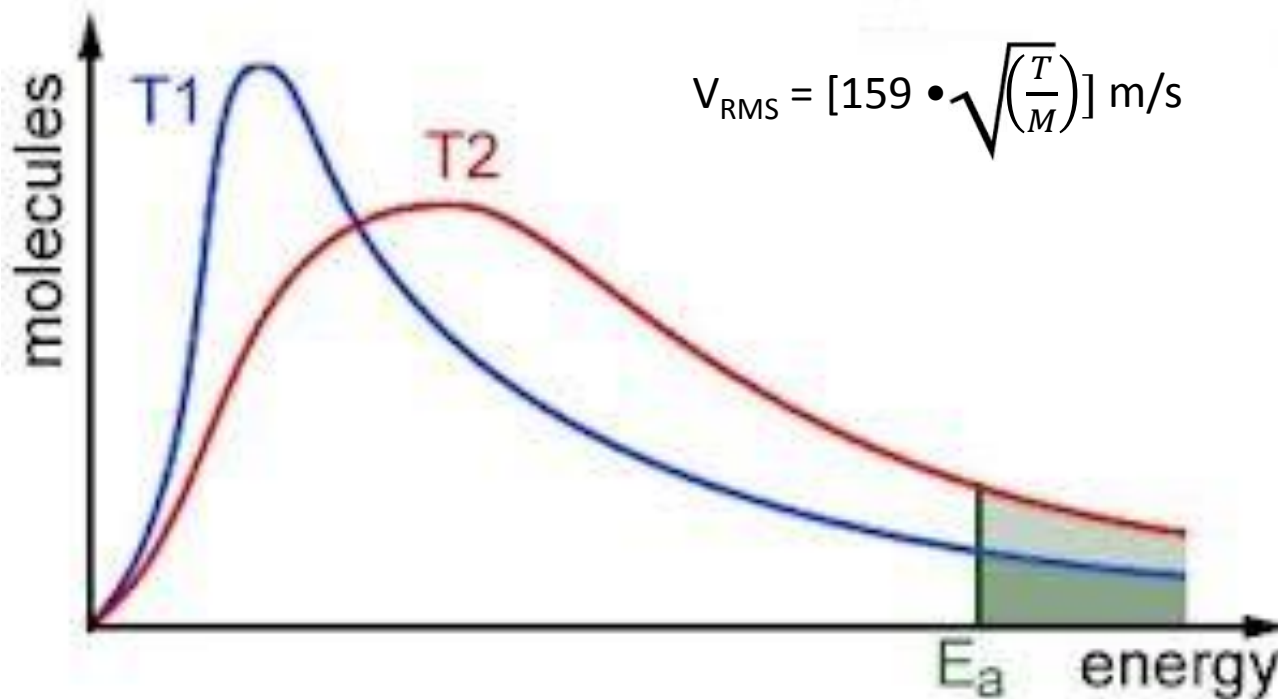
$$k = Ae^{-(\Delta H/RT)}$$

$$\ln(k_2/k_1) = [\Delta E_a/R(1/T_1 - 1/T_2)]$$

# Collision Theory

- **Maxwell – Boltzmann Distribution Curves**

Average Particle Velocity, or Root Mean Square Velocity is directly proportional to Kinetic Energy

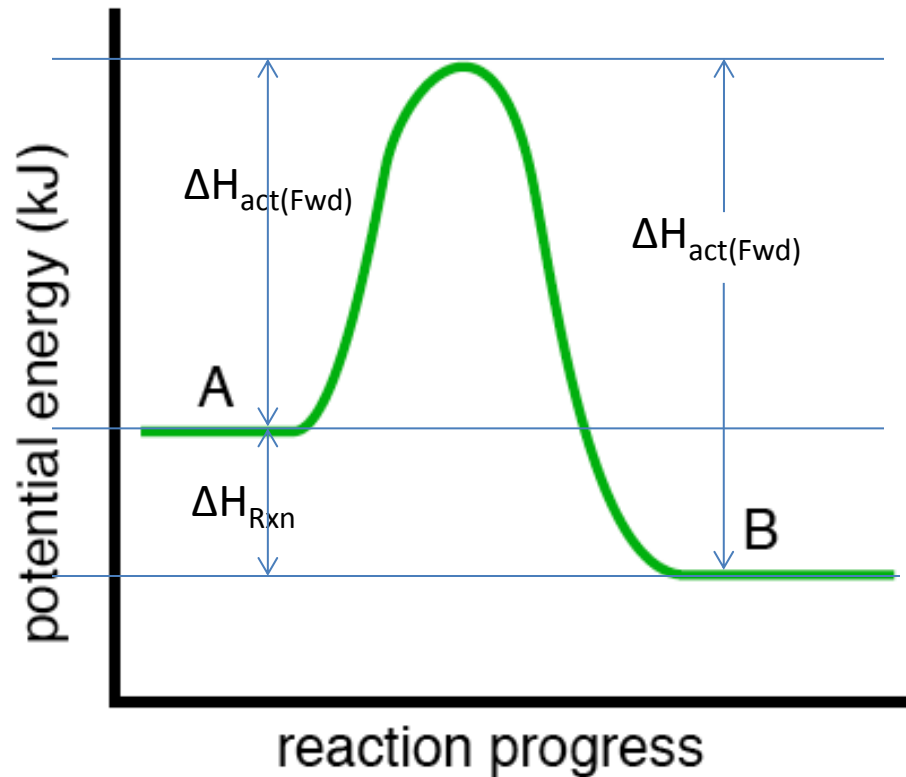


$$V_{\text{RMS}} = [159 \cdot \sqrt{\left(\frac{T}{M}\right)}] \text{ m/s}$$



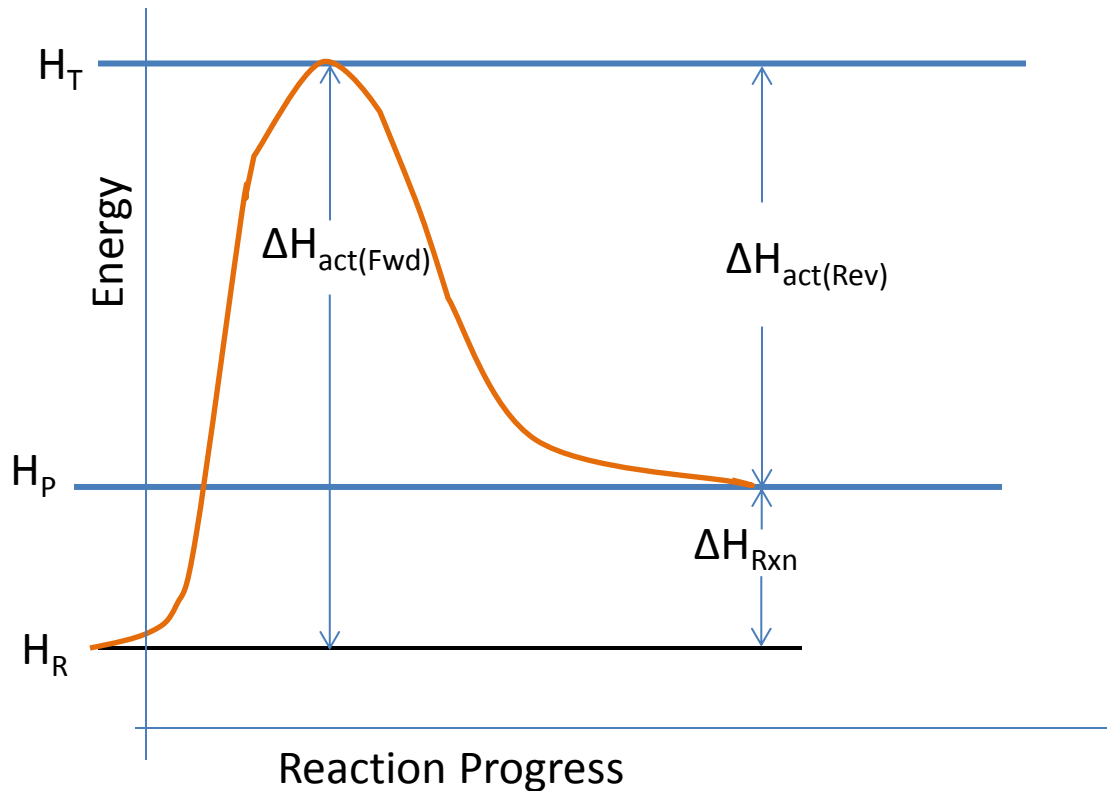
# Transition State Theory

- Potential Energy Diagrams – Exothermic Rxn



# Transition State Theory

## Potential Energy Diagrams – Endothermic Rxn



# Transition State Theory

- Potential Energy Diagrams – Model Problems
  - Draw and label the potential-energy diagram for the reaction  $\text{N}_2\text{O}_4(\text{g}) \ggg 2\text{NO}_2(\text{g})$ ;  $\Delta E_{\text{Rxn}} = 57\text{Kj}$ . The activation energy for the reverse reaction ( $\Delta E_{\text{act (rev)}}$ ) = 23Kj. What is the activation energy for the forward reaction ( $\Delta E_{\text{act (fwd)}}$ )?

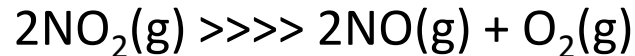
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- For the formation of 1 mol of nitrosyl chloride at a given temperature,  $\Delta E_{\text{act (fwd)}} = -44 \text{ kJ}$ .  
 $\text{NO}(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g}) \ggg \text{NOCl}(\text{g})$   
The activation energy for this reaction is 65Kj.  
What is the activation energy for the reverse reaction  $\Delta E_{\text{act (fwd)}}$  ?

# Transition State Theory

- The Arrhenius Equation – Model Exam Problems

- The decomposition of nitrogen dioxide is experimentally determined to be 1<sup>st</sup> order in NO<sub>2</sub>(g) for reaction:



If the process has a rate constant of 0.498 M/s at 319°C and a rate constant of 1.81 M/s at 345°C. What is the value of the activation energy for this reaction? What is the rate constant at 420°C? (Ans:  $\Delta E_a = 114 \text{ KJ/mol}$ ;  $k @ 420^\circ\text{C} = 14 \text{ M/s}$ )

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- A second-order reaction has a rate constant of  $8.7 \times 10^{-4}/(\text{M}\cdot\text{s})$  at 30°C. At 40°C, the rate constant is  $1.8 \times 10^{-3}/(\text{M}\cdot\text{s})$ . What is the activation energy for this reaction and predict the value of the rate constant at 45°C. (Ans:  $\Delta E_a = 57 \text{ KJ/mol}$ ,  $k@45^\circ\text{C} = 14 \text{ M/s}$ )