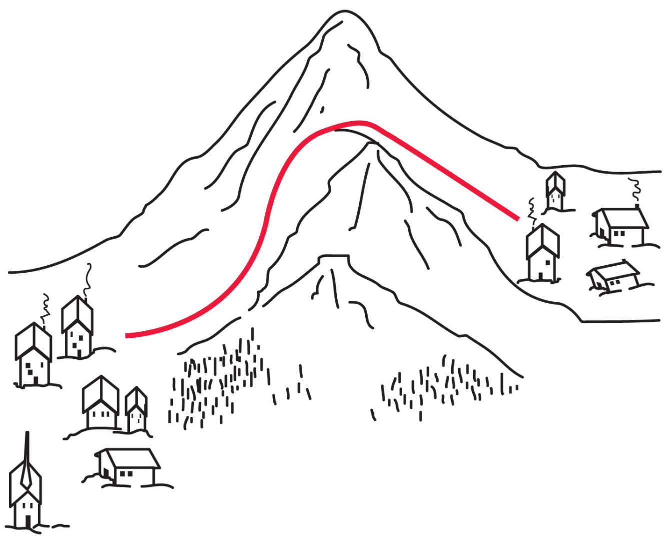
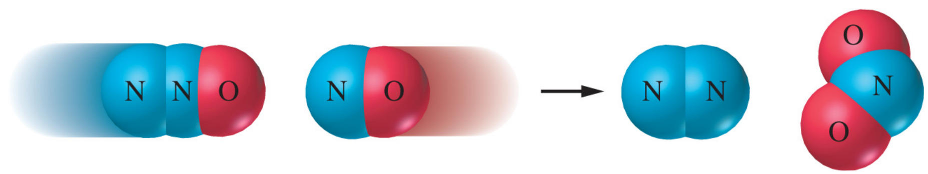
Chapter 14: Chemical Kinetics





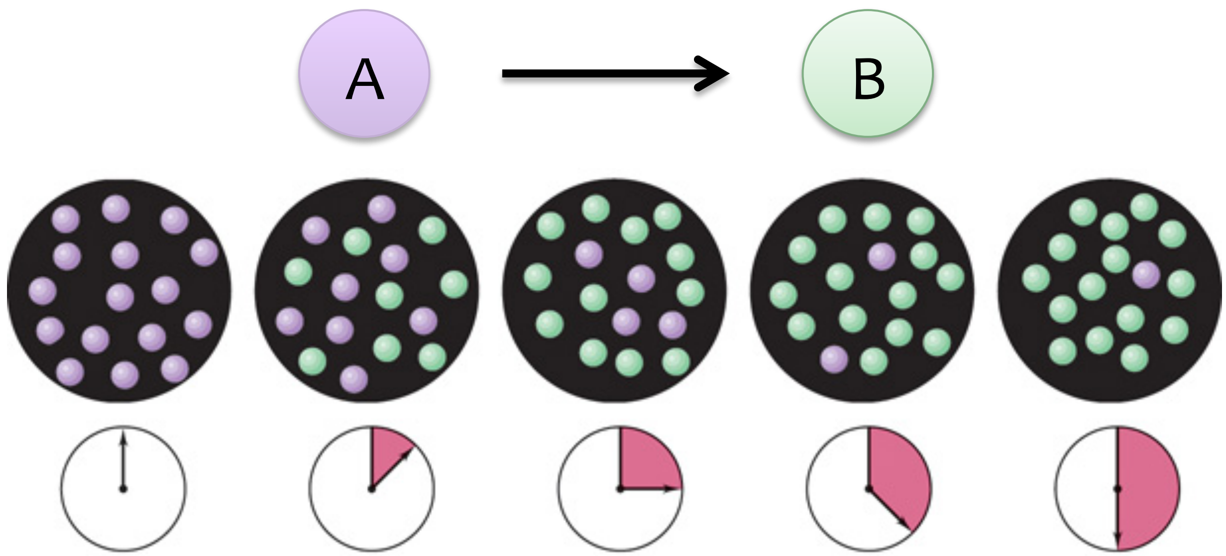
$$k = Ae^{-E_a/RT}$$

Chemical Kinetics

- We can use **ΔH** to tell if a reaction is energetically possible or not
- We can use **K** to tell if a reaction is product or reactant favoured.
- But this gives us no information on *<u>how fast</u>* the reaction goes from reactants to products.
- **KINETICS** — the study of REACTION RATES and their relation to the way the reaction proceeds, i.e., its MECHANISM.

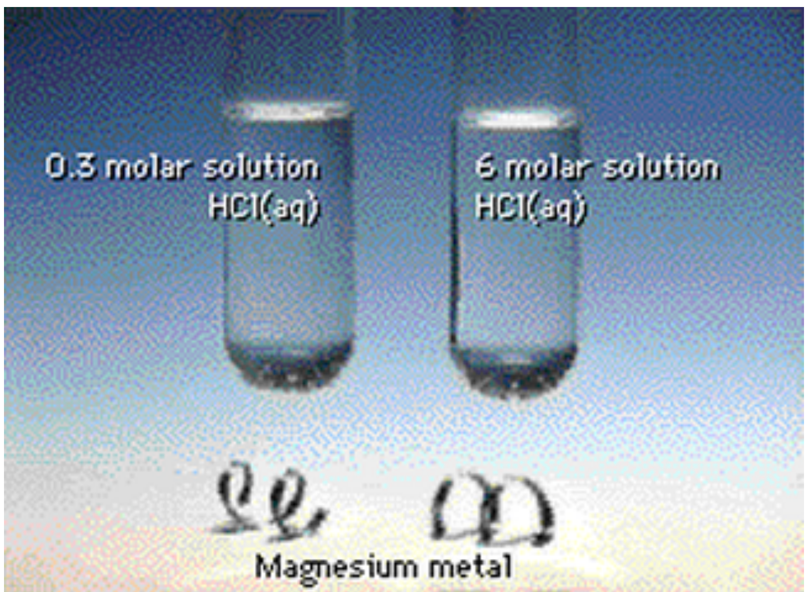
Reaction Rates

- chemical kinetics concerns how rates of chemical reactions are measured
- the rate of a reaction describes how the concentration of a reactant or product changes with time (in **M/s**)



Factors Affecting Rates

1. Concentrations of reactants
2. Contact surface between reactants
3. Temperature
4. Addition of Catalyst*

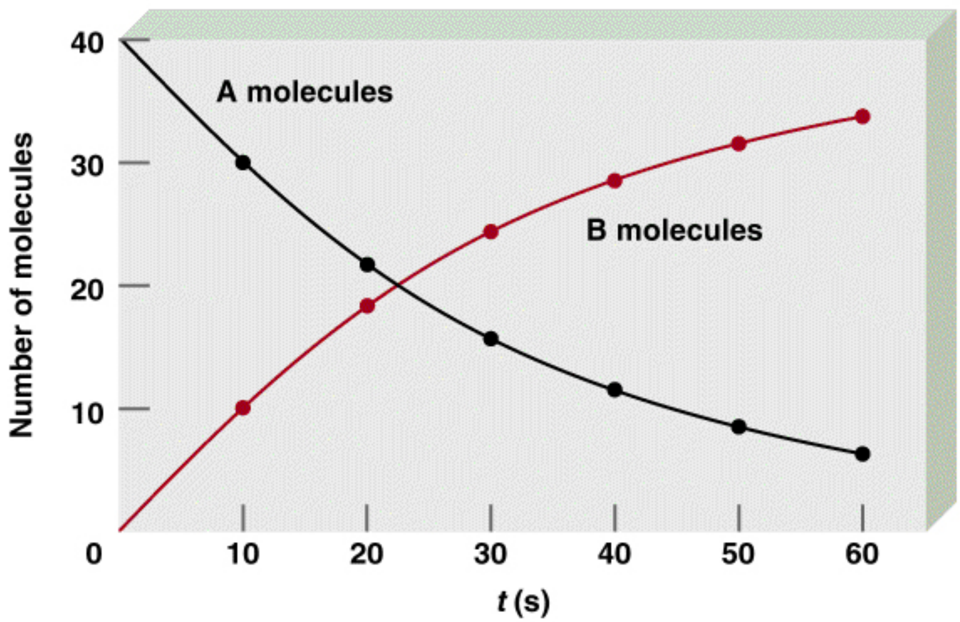


54°C Bleaching food dye 22°C

Determining a Reaction Rate

for the reaction $A \rightarrow B$:

$$\text{rate} = \frac{M}{s} = -\frac{\Delta[A]}{\Delta t} = +\frac{\Delta[B]}{\Delta t}$$



- we want the rate to be positive, so, for reactants, the sign is negative, since:

$$\frac{\Delta[A]}{\Delta t} < 0$$

General Rate of Reaction

- for the general reaction:

$$a\,A + b\,B \rightarrow c\,C + d\,D$$

reaction rate = rate of ______________ of reactants

$$= -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t}$$

= rate of ______________ of products

$$= +\frac{1}{c}\frac{\Delta[C]}{\Delta t} = +\frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

Example: Expressing the Rate of a Reaction

What are the 4 rate expressions for the reaction:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

Your Turn…

For the following reaction,

$$2NO_2Br(g) \longrightarrow 2NO_2(g) + Br_2(g)$$

the rate can be expressed as

$$\text{rate} = +\frac{d[Br_2]}{dt}$$

<u>Equivalent</u> expressions are…

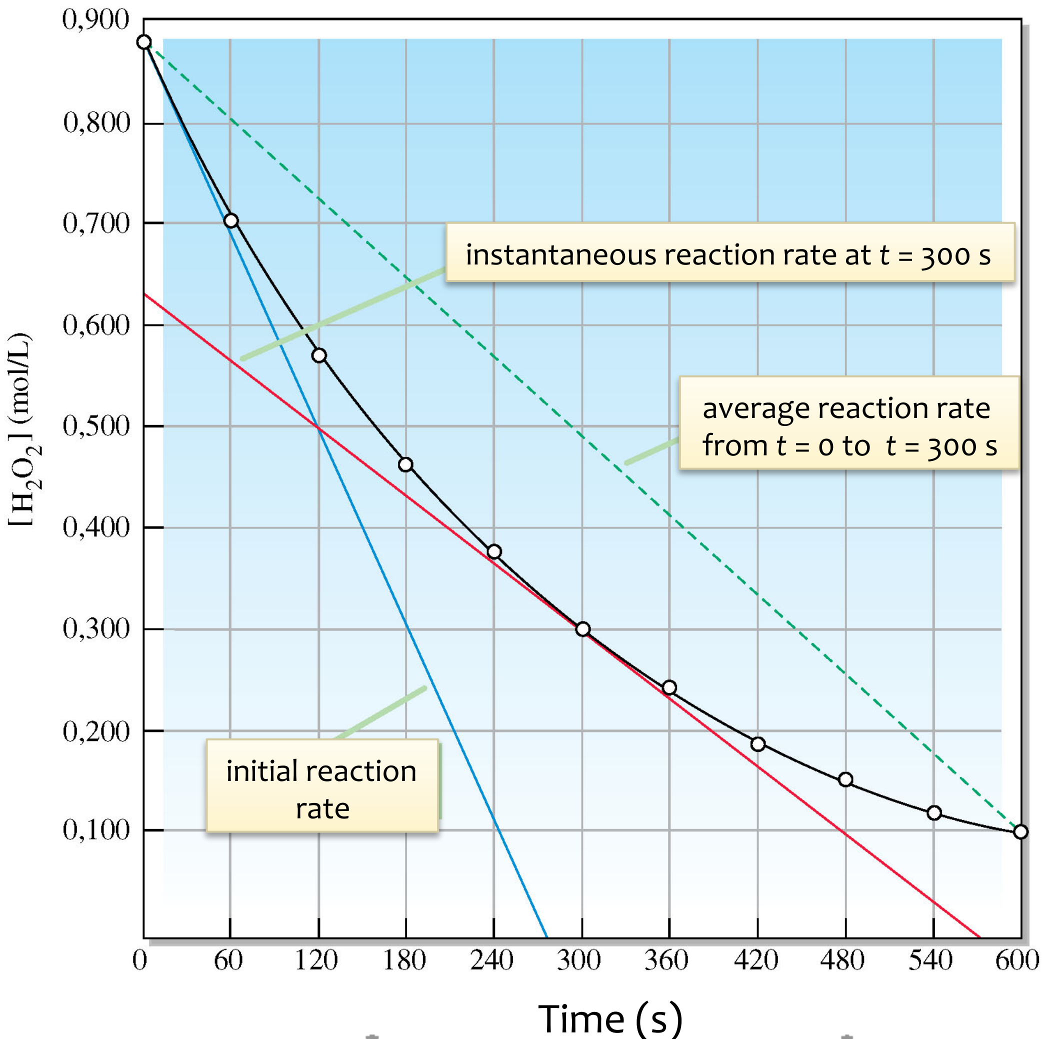
A. $\text{rate} = +\frac{d[NO_2]}{dt} = +\frac{d[NO_2Br]}{dt}$

B. $\text{rate} = +\frac{1}{2}\cdot\frac{d[NO_2]}{dt} = +\frac{1}{2}\cdot\frac{d[NO_2Br]}{dt}$

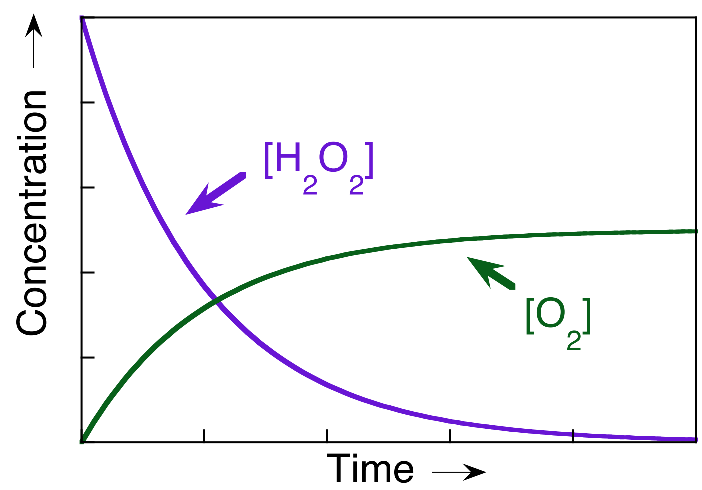
C. $\text{rate} = -\frac{1}{2}\cdot\frac{d[NO_2]}{dt} = +\frac{1}{2}\cdot\frac{d[NO_2Br]}{dt}$

D. $\text{rate} = +\frac{1}{2}\cdot\frac{d[NO_2]}{dt} = -\frac{1}{2}\cdot\frac{d[NO_2Br]}{dt}$

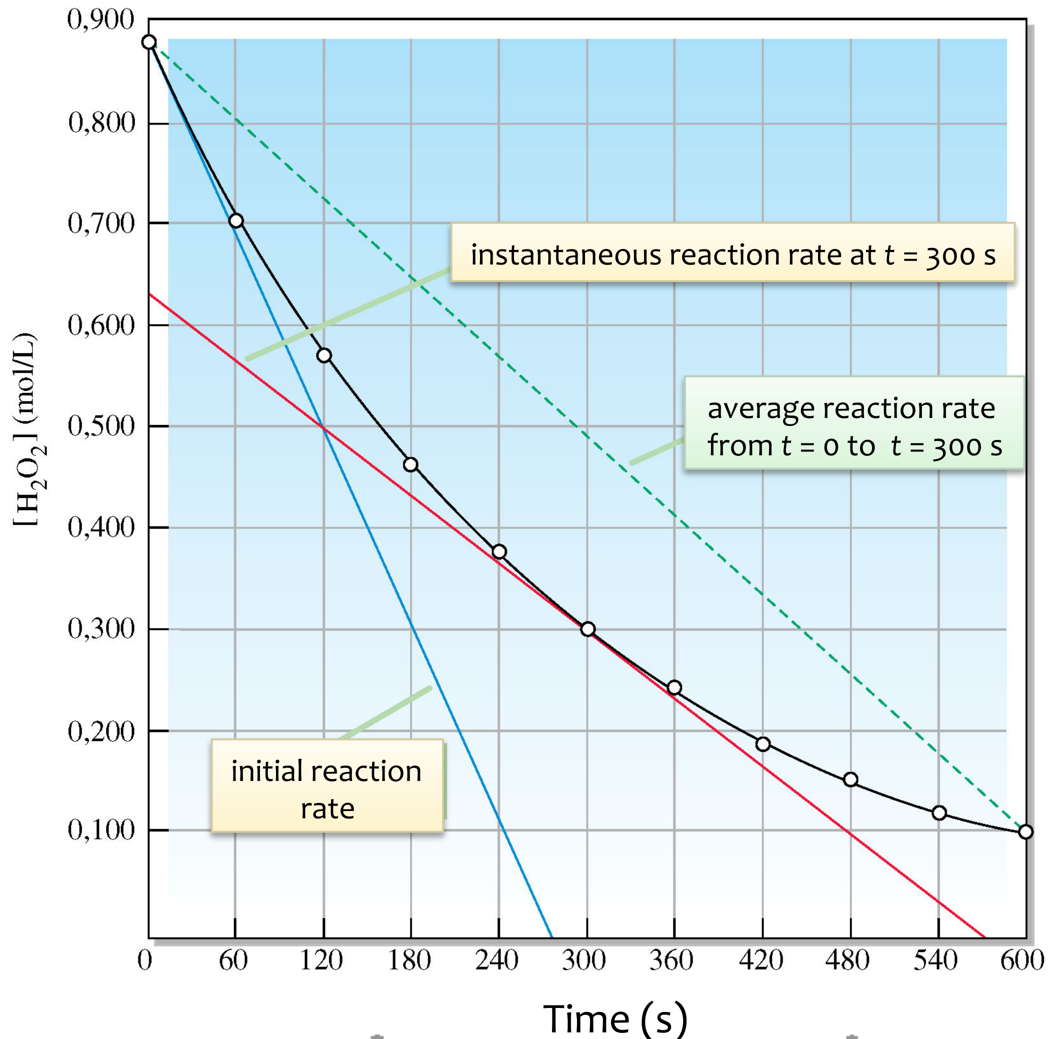
Reaction Rates



$$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$$



Reaction Rates



$$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$$

- average reaction rate:

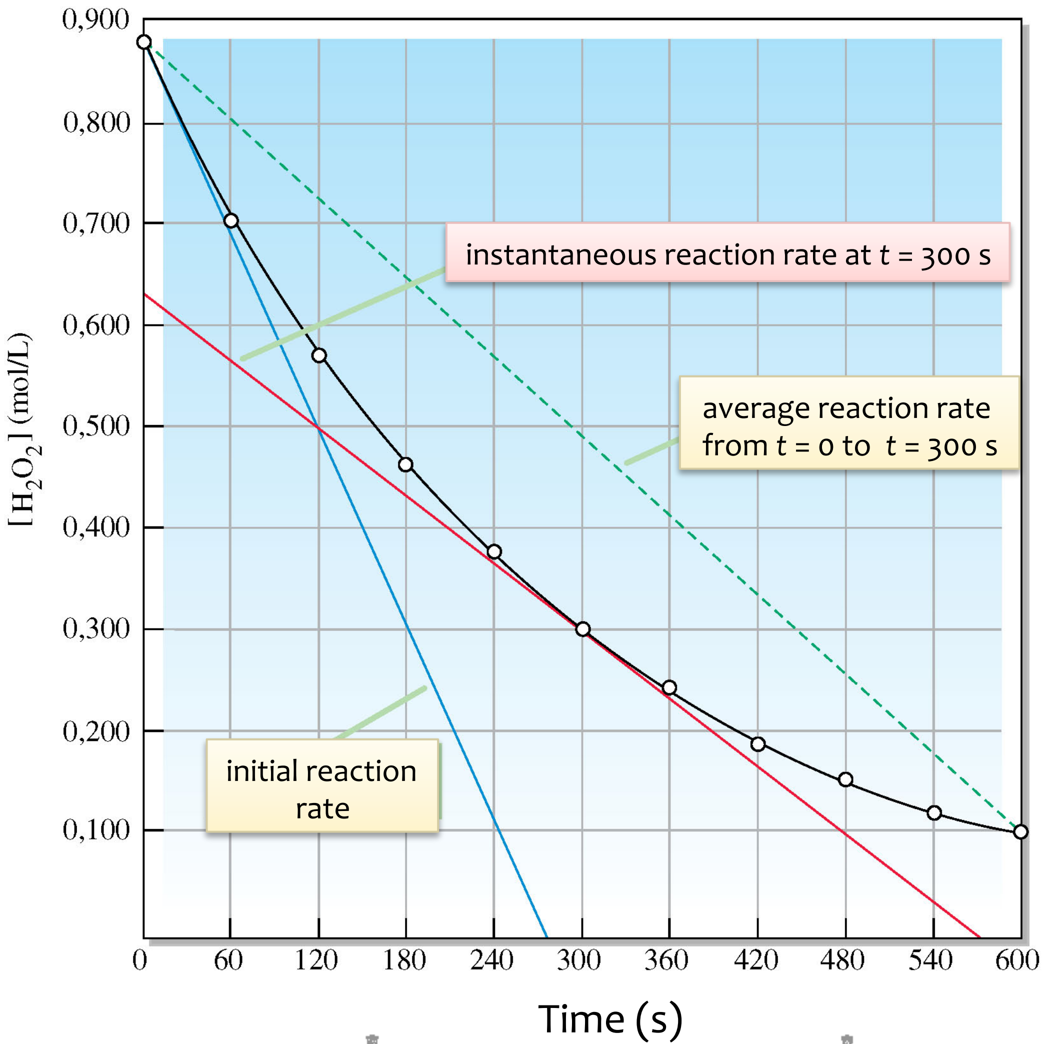
$$\text{rate} = -\frac{\Delta[H_2O_2]}{\Delta t}$$

$$= -\frac{[H_2O_2]_2 - [H_2O_2]_1}{t_2 - t_1}$$

$$= -\frac{0.094\ M - 0.882\ M}{600\ s - 0\ s}$$

$$= 0.00131\ M/s$$

Reaction Rates



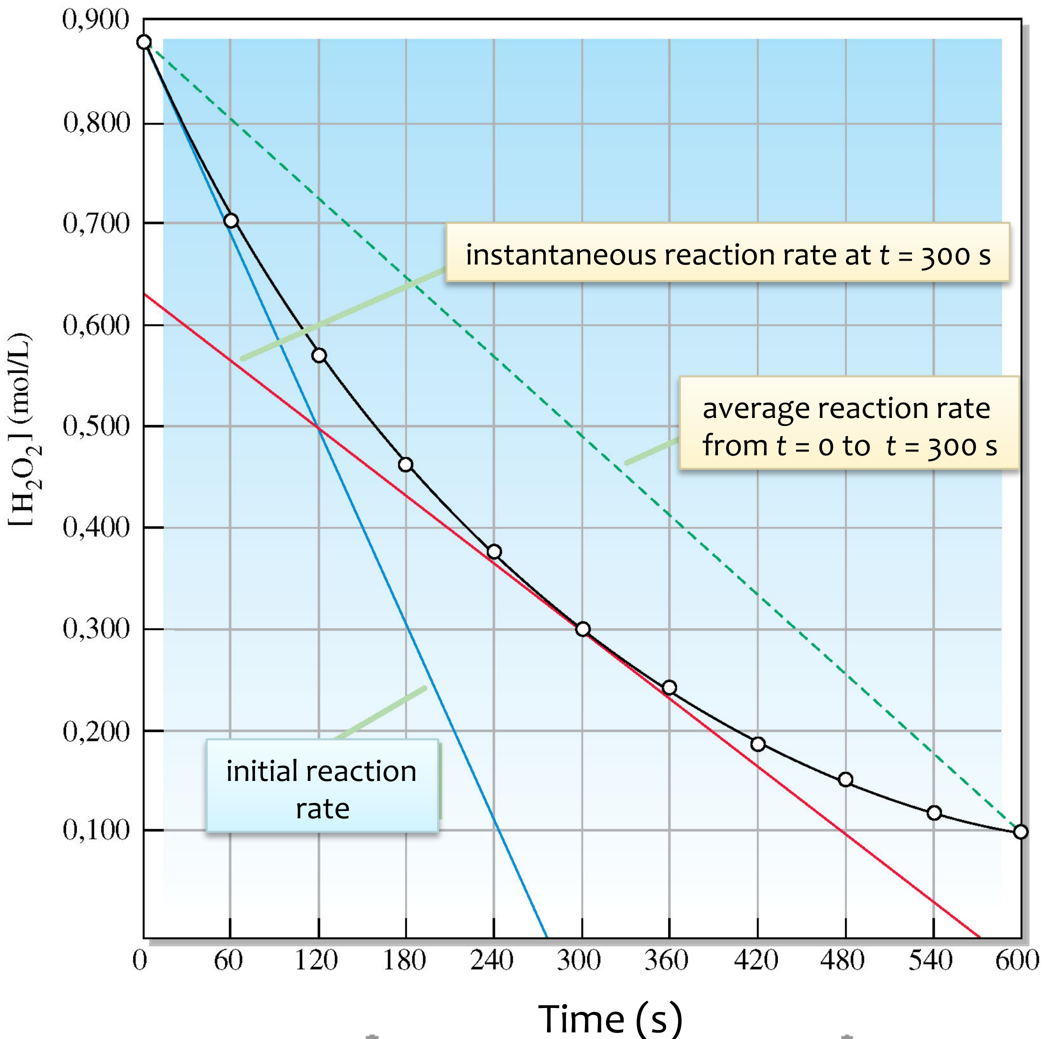
- instantaneous reaction rate:

$$\text{rate} = -\frac{\Delta[H_2O_2]}{\Delta t}$$

where $t \rightarrow 0$

$$\begin{aligned}\text{rate} &= -\frac{d[H_2O_2]}{dt} \\ &= -\text{ slope of tangent} \\ &= -\frac{[H_2O_2]_2 - [H_2O_2]_1}{t_2 - t_1} \\ &= -\frac{0\text{ M} - 0.630\text{ M}}{570\text{ s} - 0\text{ s}} \\ &= 0.00111\text{ M/s}\end{aligned}$$

Reaction Rates



- initial reaction rate:

$$\text{rate} = -\frac{\Delta[H_2O_2]}{\Delta t}$$

where $t \rightarrow 0$

$$\text{rate} = -\frac{d[H_2O_2]}{dt}$$

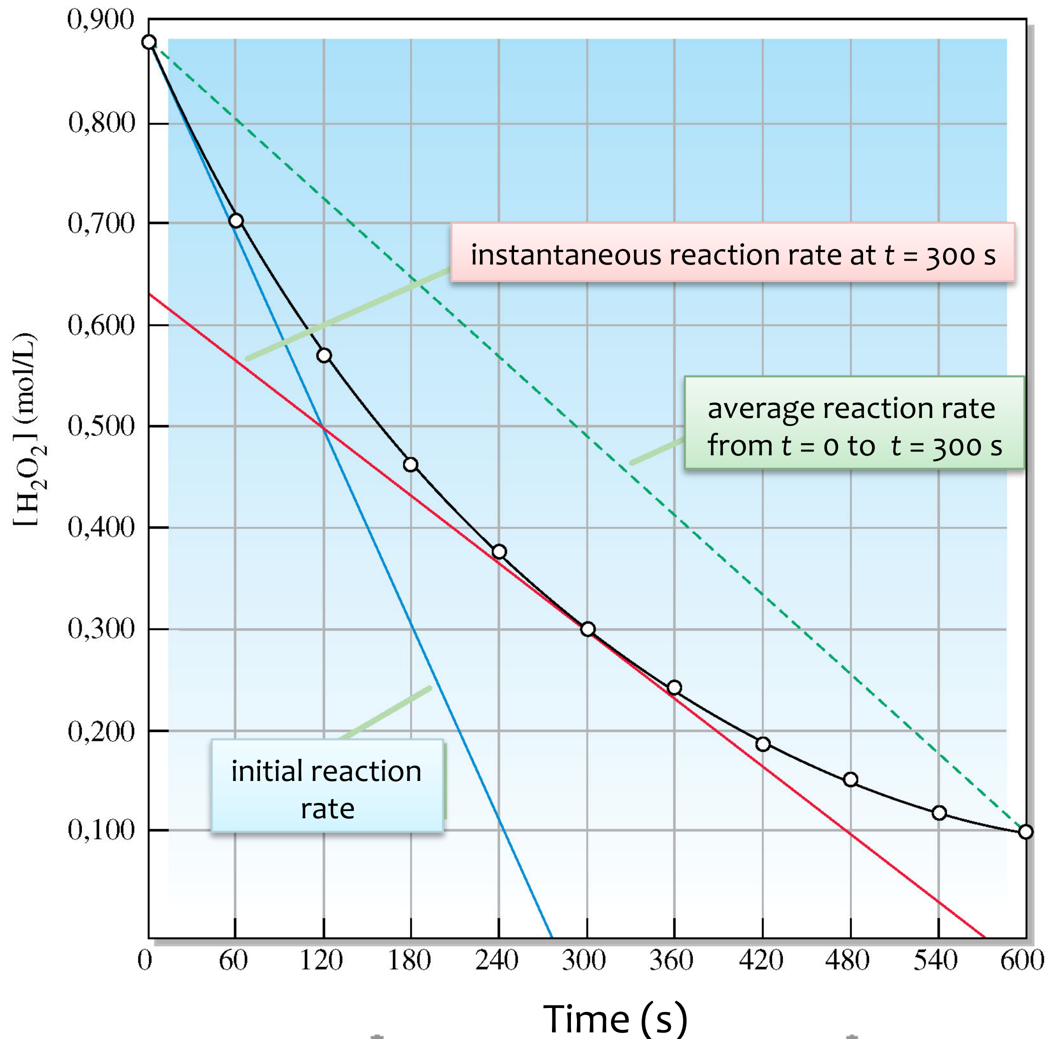
$$= -\ \text{slope of tangent}$$

$$= -\frac{[H_2O_2]_2 - [H_2O_2]_1}{t_2 - t_1}$$

$$= -\frac{0\ \text{M} - 0.882\ \text{M}}{275\ \text{s} - 0\ \text{s}}$$

$$= 0.00321\ \text{M/s}$$

Reaction Rates



- average reaction rate:

  0.00131 M/s
- instantaneous reaction rate:

  0.00111 M/s
- initial reaction rate:

  0.00321 M/s

Rate Laws

- for the general reaction:

$$aA + bB \rightarrow cC + dD$$

$$\text{rate} = k[A]^x[B]^y$$

- NOTE:

$$x \neq a, \quad y \neq b$$

- x and y must be determined experimentally!
- x and y can be positive, negative, or fractional values!

Rate Laws

$$aA + bB \rightarrow cC + dD$$

$$\text{rate} = k[A]^x[B]^y$$

- k is the rate constant
- the **VALUE** of k depends on:
  - (1) the reaction
  - (2) the temperature
  - (3) the presence of a catalyst.
- the **UNIT** of k depends on the overall order of the reaction:
  - the sum of all exponents in the rate law (in this example, x + y)
  - in this example, the reaction is said to be

"x order in A" and "y order in B"

Determining Rate Laws

1. Method of Initial Rates
   – good for slow reactions
2. Graphical method
   – good for fast reactions

The Method of Initial Rates

- **IDEA:** vary the concentration of a reagent and observe its effect on the initial rate

$$F_2(g) + 2\ ClO_2(g) \rightarrow 2\ FClO_2(g)$$

$[F_2]$ initial (M)	$[ClO_2]$ initial (M)	initial rate (M/s)
0.10	0.010	0.0012
0.10	0.040	0.0048
0.20	0.010	0.0024

The method of initial rates

$$\text{rate} \propto [\text{F}_2][\text{ClO}_2]$$

$$\text{rate} = \text{k}[\text{F}_2][\text{ClO}_2]$$

- we can use the data from any of the three trials to find the value of the rate constant, k
- if we take the first trial:

$$\text{rate} = \text{k}[\text{F}_2][\text{ClO}_2]$$

$$\text{k} = \frac{\text{rate}}{[\text{F}_2][\text{ClO}_2]} = \frac{0.0012\ \text{M/s}}{(0.10\ \text{M})(0.01\ \text{M})} = 1.2\ \text{M}^{-1}\text{s}^{-1}$$

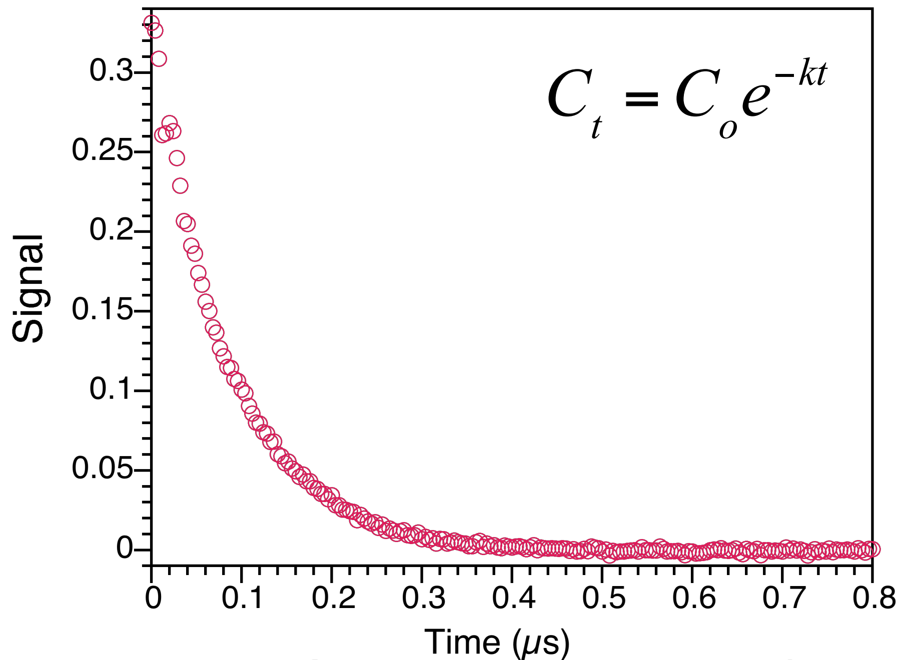
Example: Deriving Rate Laws

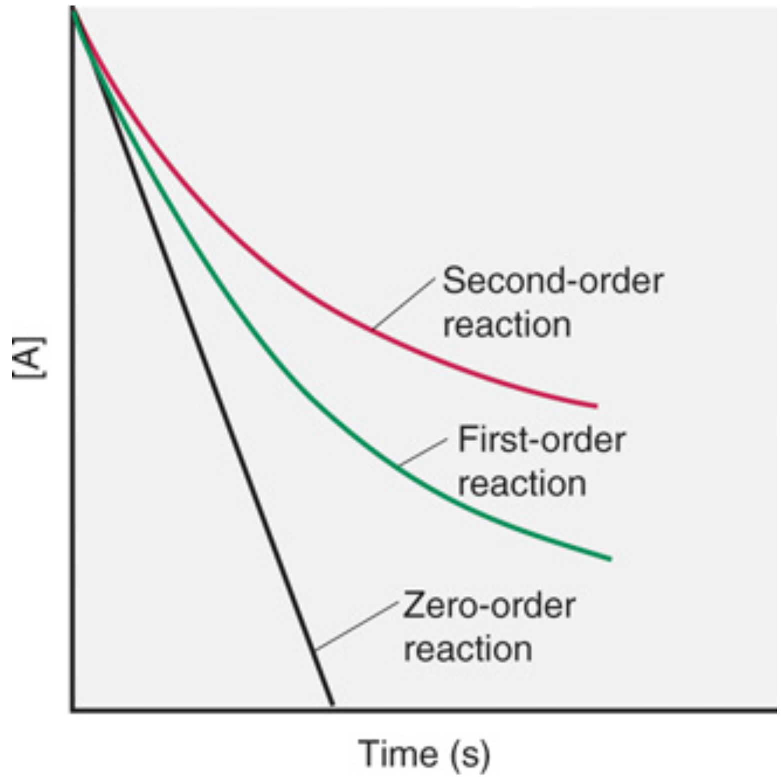
The initial rates of the reaction A + 2 B → C are followed at 25°C. Using the data below, derive the rate law for the reaction and the value of the rate constant.

Trial	initial [A]	initial [B]	initial rate (M/s)
1	0.100	0.100	1.74×10^{-5}
2	0.200	0.100	6.96×10^{-5}
3	0.400	0.200	3.94×10^{-4}

Graphical Method

- follow the concentration of reactant (or product) as a function of time
- mathematically fit results



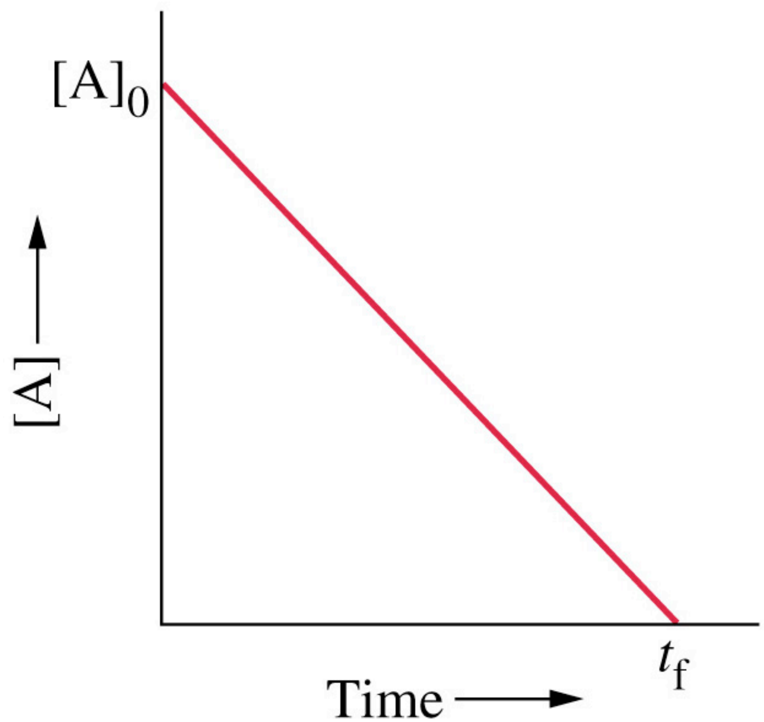


Concentrations as a function of time

- the rate laws allow us to determine the rate of the reaction at any point in the reaction
- to determine an equation that will link the concentration of a reactant at any point in time ($[A]_t$) to the initial concentration ($[A]_o$), k and the time (t), we must integrate the rate law
- now, let's examine in detail:
  - zero order reactions
  - first order reactions
  - second order reactions

Zero Order Reactions

- the sum of exponents is zero (x + y + ... = 0)
- the graph of [A] as a function of time is a straight line



A → products

rate = k $[A]^0$

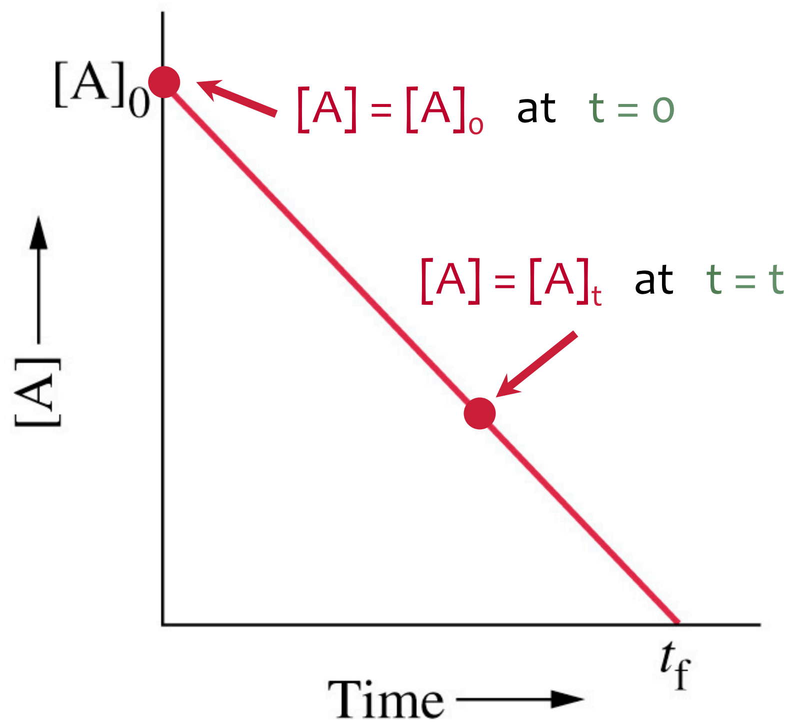
rate = k

value of k = – slope

units of k = mol L^{-1} s^{-1}

Zero Order Reactions

- Integrating the rate law from time = 0 to time = t :



$$\text{rate} = -\frac{d[\mathrm{A}]}{dt} = k$$

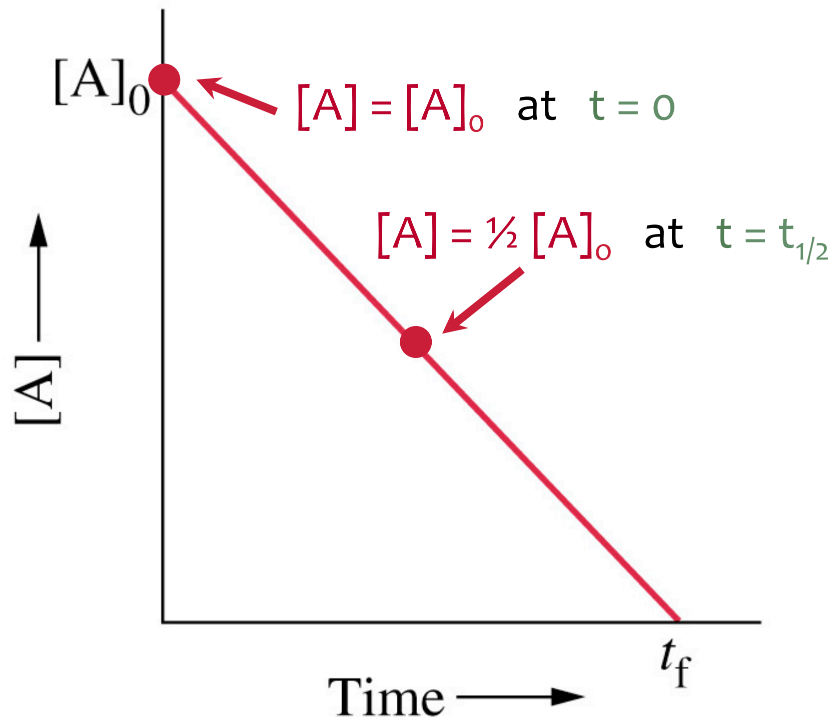
$$-\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} d[\mathrm{A}] = \int_0^t k\,dt$$

$$-[\mathrm{A}]_t + [\mathrm{A}]_0 = kt$$

$$[\mathrm{A}]_t = [\mathrm{A}]_0 - kt$$

Zero Order Half-Life

- the half-life of a reaction, $t_{1/2}$, is the time needed for the concentration of a reactant to *decrease by half*



- for a zero order reaction:

$$t = \frac{[A]_o - [A]_t}{k}$$

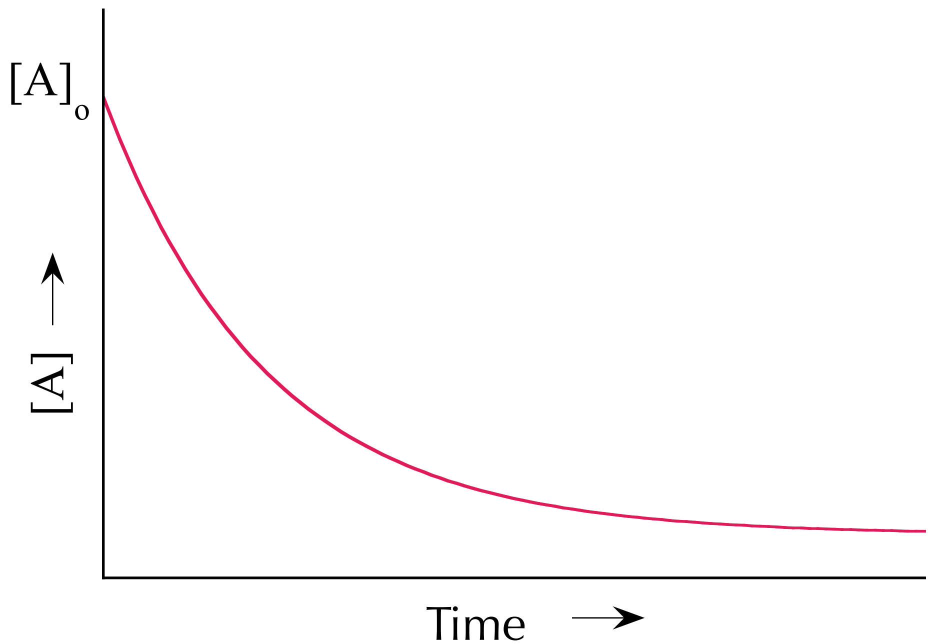
$$\text{at } t_{1/2} \qquad [A]_t = \frac{1}{2}[A]_o$$

$$\text{therefore} \qquad t_{1/2} = \frac{[A]_o}{2k}$$

- for zero order reactions, the half-life is dependent on the concentration

First Order Reactions

- the sum of exponents is one (x + y + … = 1)
- the graph of [A] as a function of time is a monoexponential curve



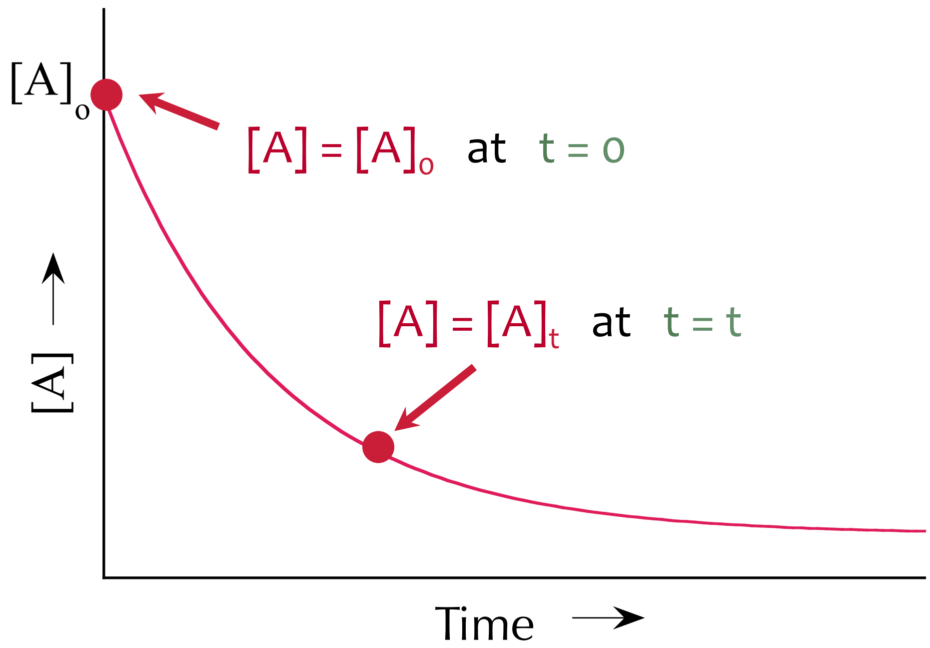
$$A \longrightarrow \text{products}$$

$$\text{rate} = k\,[A]^1$$

$$\text{units of } k = s^{-1}$$

First Order Reactions

- Integrating the rate law from time = 0 to time = t :



$$\text{rate} = -\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]$$

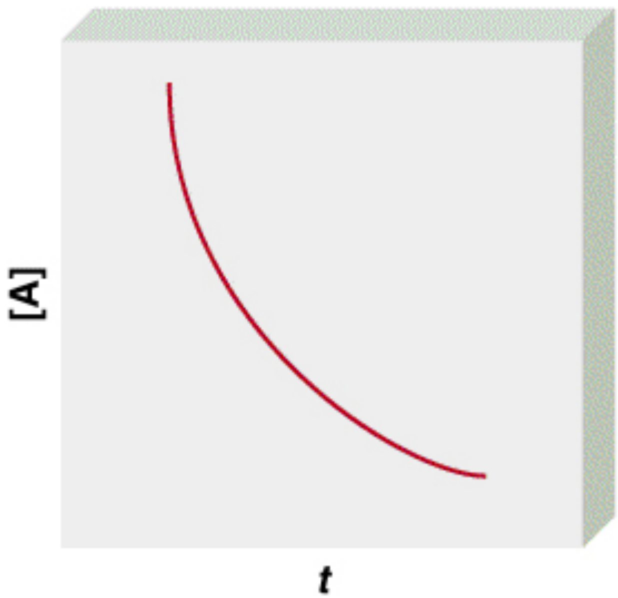
$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} \frac{1}{[\mathrm{A}]}\, d[\mathrm{A}] = -\int_0^t k\, dt$$

$$\ln\left(\frac{[\mathrm{A}]_t}{[\mathrm{A}]_0}\right) = -kt$$

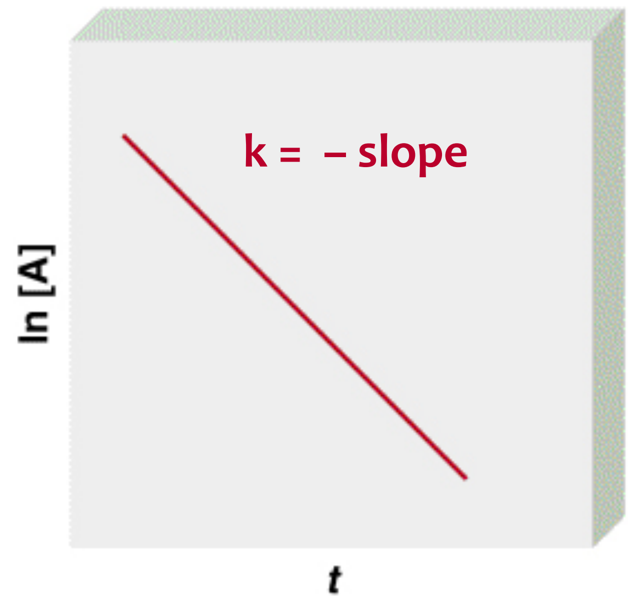
$$\ln[\mathrm{A}]_t = \ln[\mathrm{A}]_0 - kt$$

First Order Reactions

[A] vs t = CURVE



ln [A] vs t = STRAIGHT LINE



$$\ln[\mathrm{A}]_t = \ln[\mathrm{A}]_0 - kt$$

Example 1: First order reactions

For the natural decomposition of sucrose, the rate law is

$$\text{rate} = k\,[\text{sucrose}]$$

where $k = 0.21\ \text{hr}^{-1}$. If $[\text{sucrose}]_0 = 0.010\ M$, how long will it take for the concentration to drop by 90%?

Example 2: First order reactions

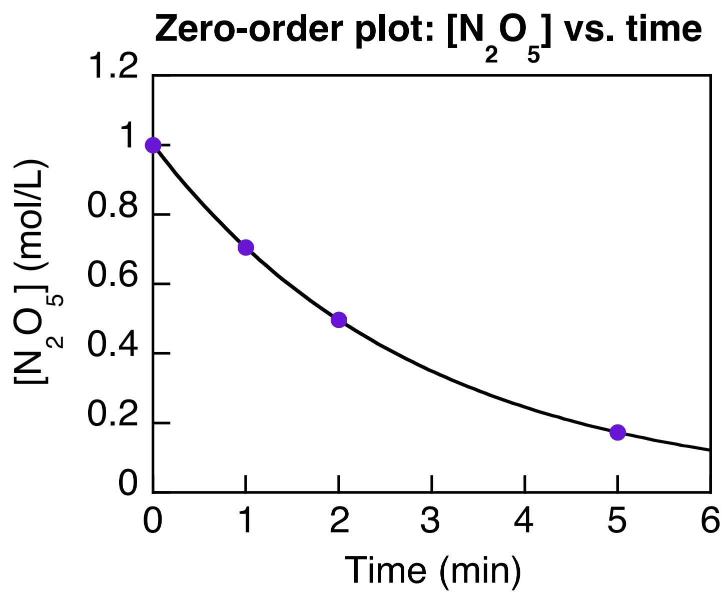
Using the data below, is the following reaction first order in N_2O_5?

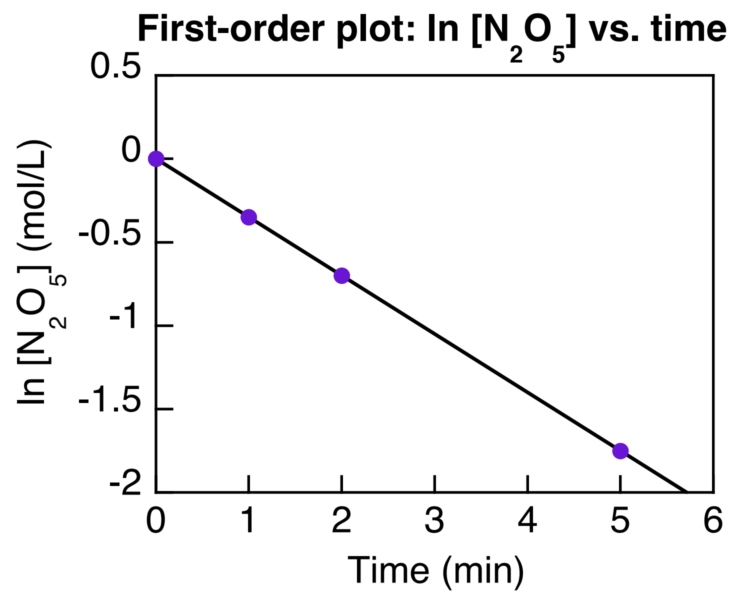
$$2\ N_2O_5(g) \rightarrow 4\ NO_2(g)\ +\ O_2(g)$$

Time (min)	$[N_2O_5]_0$ (mol/L)
0	1.00
1.0	0.705
2.0	0.497
5.0	0.173

Example 2: First order reactions

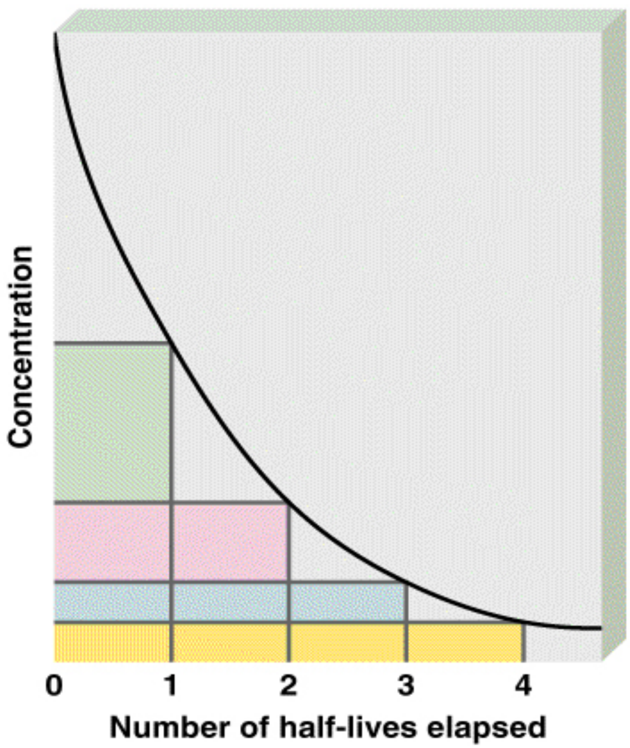
$$2\,N_2O_5(g) \rightarrow 4\,NO_2(g) + O_2(g)$$





First Order Half-Life

- the half-life of a reaction, $t_{1/2}$, is the time needed for the concentration of a reactant to *decrease by half*



- for a first order reaction:

$$t = \frac{\ln \frac{[A]_o}{[A]_t}}{k}$$

$$\text{at } t_{1/2} \quad [A]_t = \frac{1}{2}[A]_o$$

$$\text{therefore} \qquad t_{1/2} = \frac{\ln 2}{k}$$

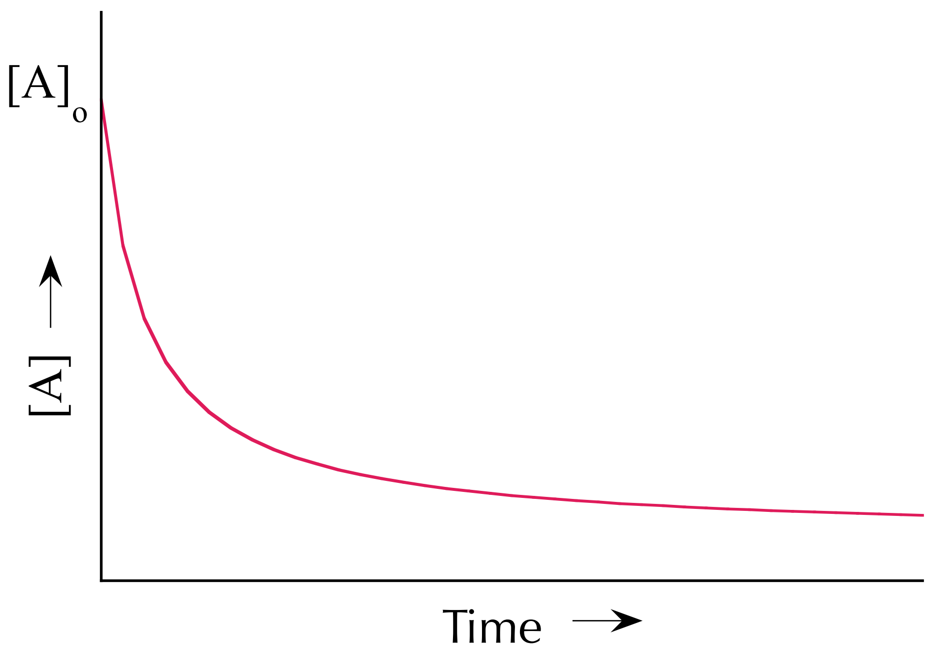
- for first order reactions, the half-life is independent of the concentration

Example: Half-life of a first order reaction

The half-life of a first order reaction is 84.1 min. Calculate the rate constant for the reaction.

Second Order Reactions

- the sum of exponents is two (x + y + … = 2)
- the graph of [A] as a function of time is a biexponential curve



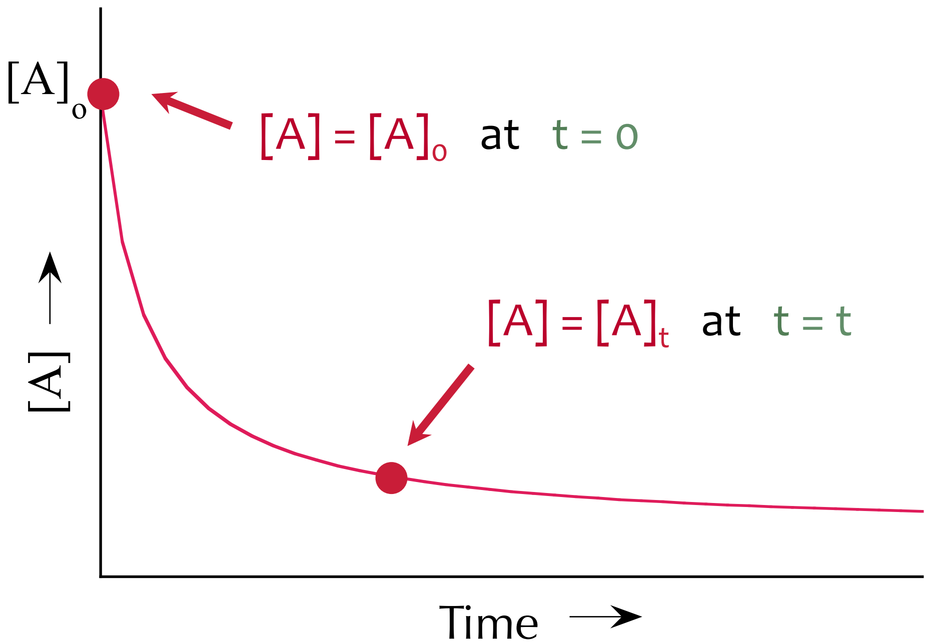
$$A \longrightarrow \text{products}$$

$$\text{rate} = k\,[A]^2$$

$$\text{units of } k = M^{-1}\,s^{-1}$$

Second Order Reactions

- Integrating the rate law from time = 0 to time = t :



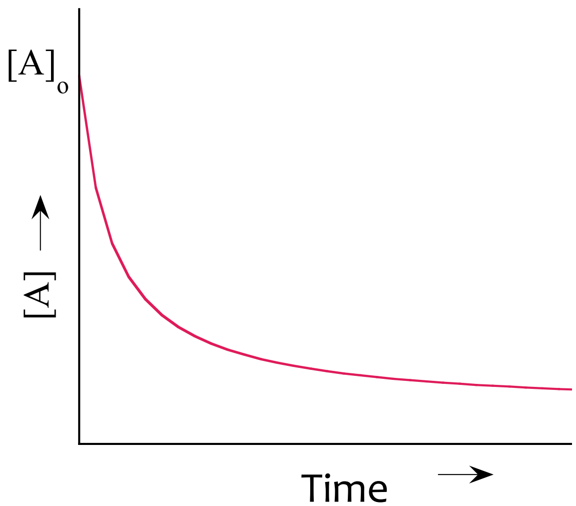
$$\text{rate} = -\frac{d[\text{A}]}{dt} = k[\text{A}]^2$$

$$\int_{[\text{A}]_0}^{[\text{A}]_t} \frac{1}{[\text{A}]^2}\, d[\text{A}] = -\int_0^t k\, dt$$

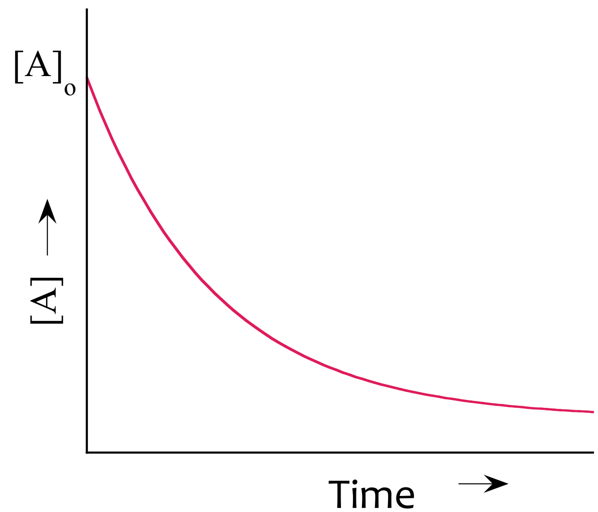
$$\frac{1}{[\text{A}]_t} = \frac{1}{[\text{A}]_0} + kt$$

Second Order Reactions

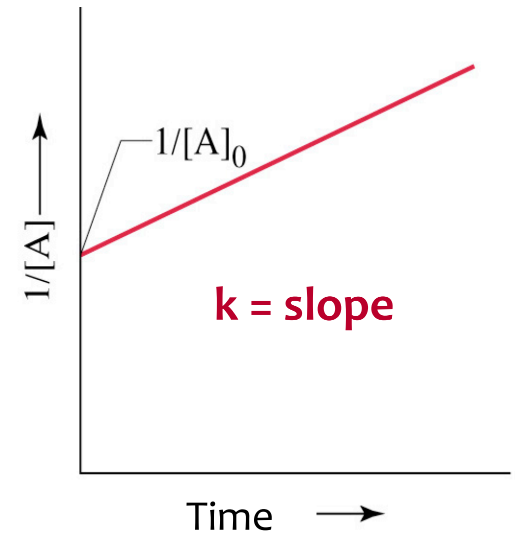
[A] vs t = CURVE



ln [A] vs t = CURVE



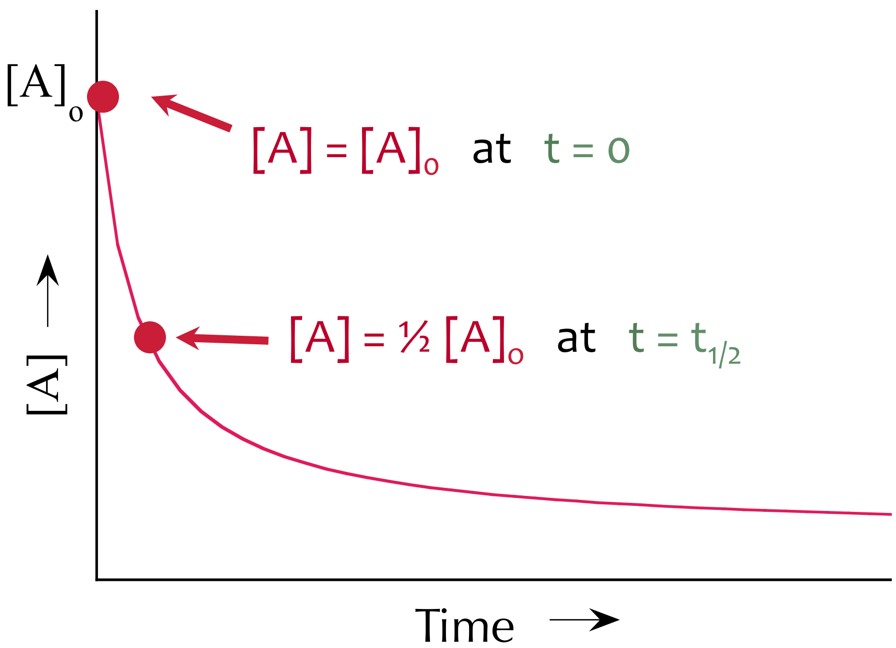
1/[A] vs t = STRAIGHT LINE



$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$$

Second Order Half-Life

- the half-life of a reaction, $t_{1/2}$, is the time needed for the concentration of a reactant to *decrease by half*



- for a second order reaction:

$$\frac{1}{[A]_t} = \frac{1}{[A]_o} + kt$$

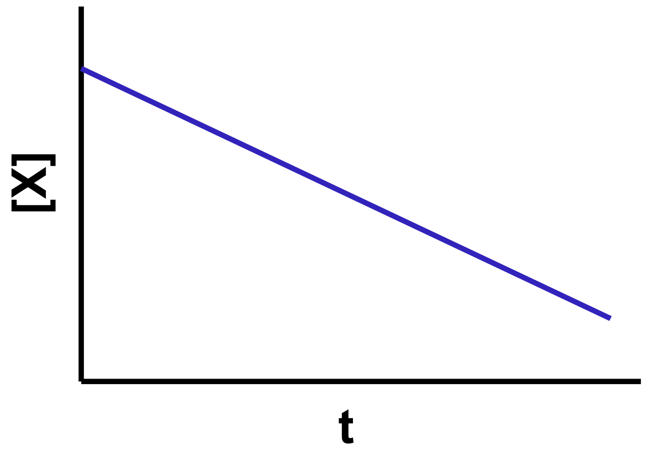
$$\text{at } t_{1/2} \quad [A]_t = \frac{1}{2}[A]_o$$

$$\text{therefore} \qquad t_{1/2} = \frac{1}{[A]_o k}$$

- for second order reactions, the half-life is dependent on the concentration

Your Turn…

Reaction A has a rate constant which is equal to 16.2 L mol^{-1} s^{-1}. A plot relating the concentrations of the reactant with time is plotted for *Reaction B* to the right.



Enter the numerical order for Reactions A and B, respectively.

For example, if you wish to answer "Reaction A is zero-order and Reaction B is second-order, please enter "02"

Pseudo-1st order reactions

- reaction involving 2 different reactants
- concentration of one reactant is in MAJOR EXCESS

$$A + B \rightarrow \text{products}$$

$$\text{rate} = k\,[A][B]$$

$$[B] >>> [A]$$

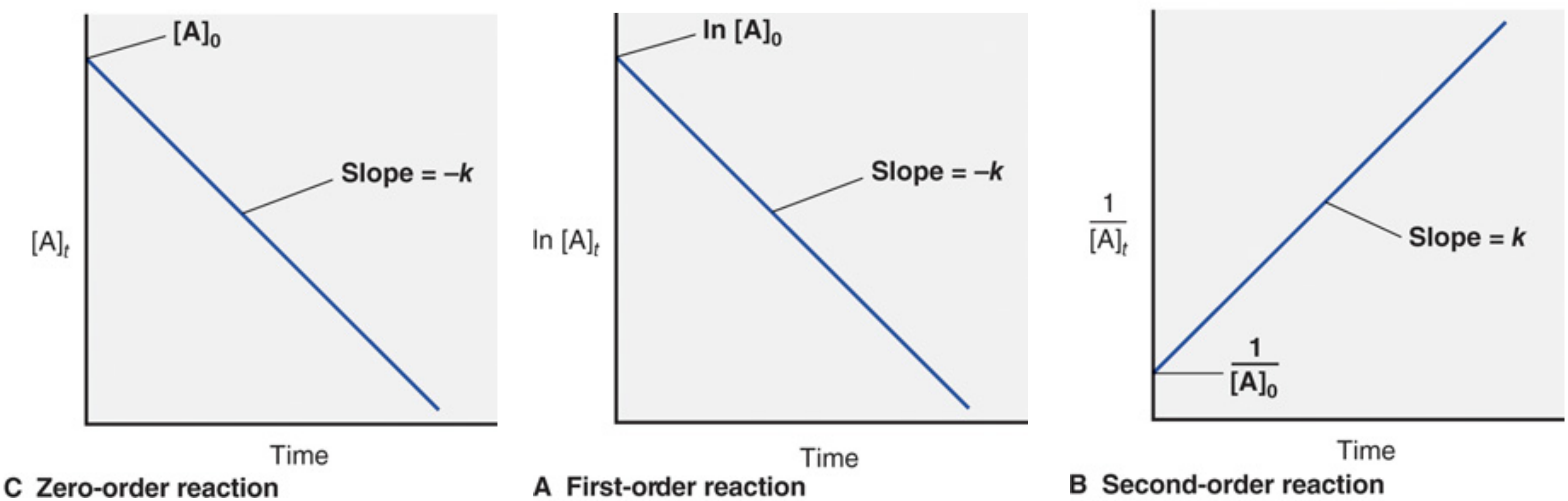
$$\text{Define a new rate constant:} \quad k' = k[B]$$

$$\text{rate} = k'[A]$$

$$\text{units of } k = s^{-1}$$

Back to the Graphical Method…

- collect data (concentration with time)
- make the following graphs:



Summary Table

	Zero Order	1st Order	2nd Order
Rate expression	$\text{rate} = k[A]^0$		
Rate Law	$\text{rate} = -\frac{d[A]}{dt} = k$		
Integrated Rate Law	$[A]_t = [A]_0 - kt$		
Units of k	$M\ s^{-1}$		
Plot to get k	[A] vs. t		
Half-life	$t_{1/2} = \frac{[A]_o}{2k}$		

Theoretical Models for Chemical Kinetics

- How are reactants converted to products at the molecular level?

- We want to connect the

RATE LAW → MECHANISM

Kinetic Molecular Theory… again

- KMT can be used to calculate collision density
- For example:
  - gases undergo 10^{32} collisions/L•s
  - IF every collision yielded product, then

theoretical rate = 10^{6} M/s

  - ACTUAL rates are several orders of magnitude less

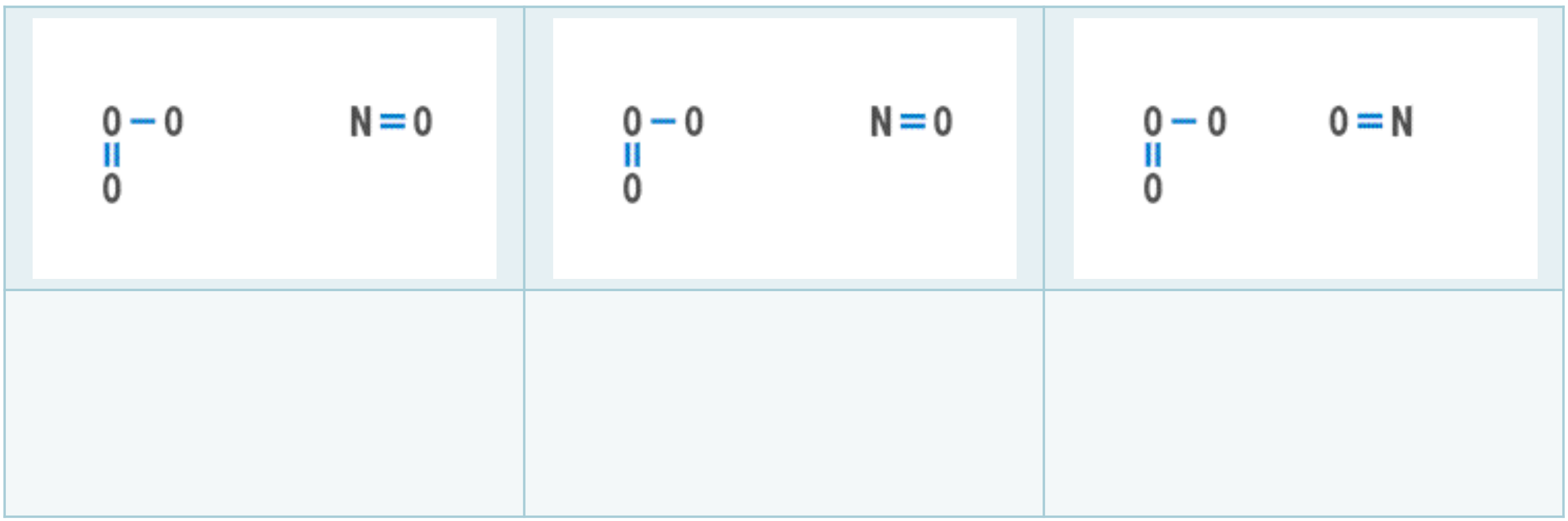
typical actual rate = 10^{-4} M/s

- CONCLUSION: Only a fraction of collisions yield a reaction!

Collision Theory

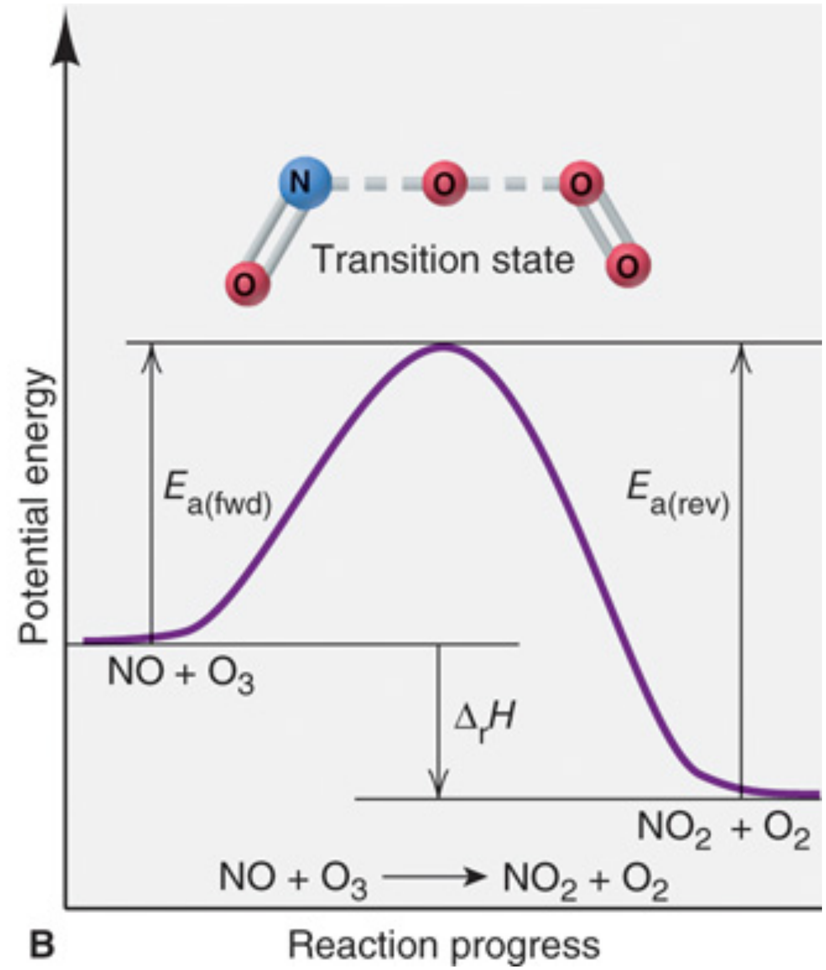
- Reactions require:
  - activation energy
  - correct geometry

$$O_3(g) + NO(g) \rightarrow O_2(g) + NO_2(g)$$



Transition State Theory

- The activated complex is a hypothetical species lying between reactants and products at a point on the reaction profile called the transition state.
- Reaction profile = diagram of the energy versus reaction progress



Your Turn…

A particular reaction was found to have forward and reverse activation energies of 60 and 140 kJ mol^{-1}, respectively. The enthalpy change for the reaction is, (do not use a calculator)

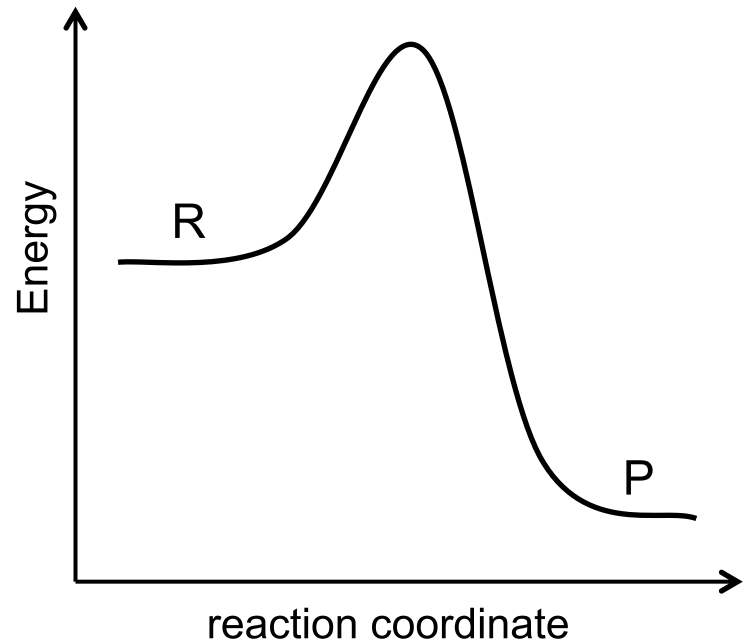
A. $\Delta H = 60$ kJ mol^{-1}

B. $\Delta H = -60$ kJ mol^{-1}

C. $\Delta H = 80$ kJ mol^{-1}

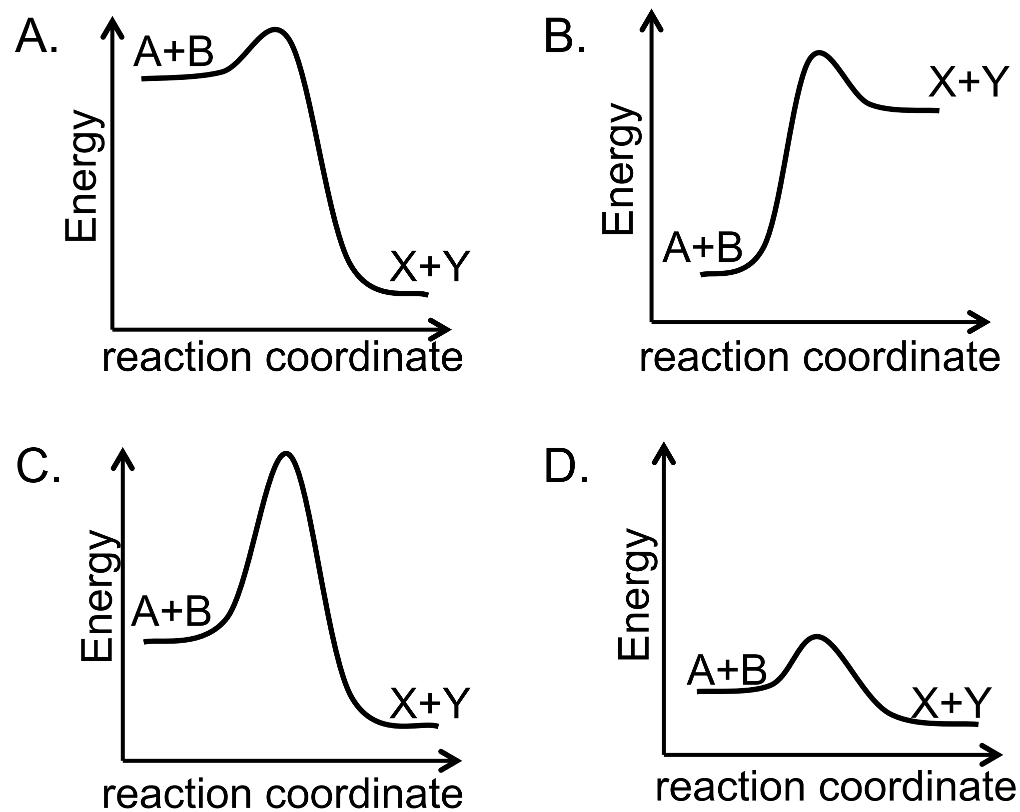
D. $\Delta H = -80$ kJ mol^{-1}

E. I'm not sure



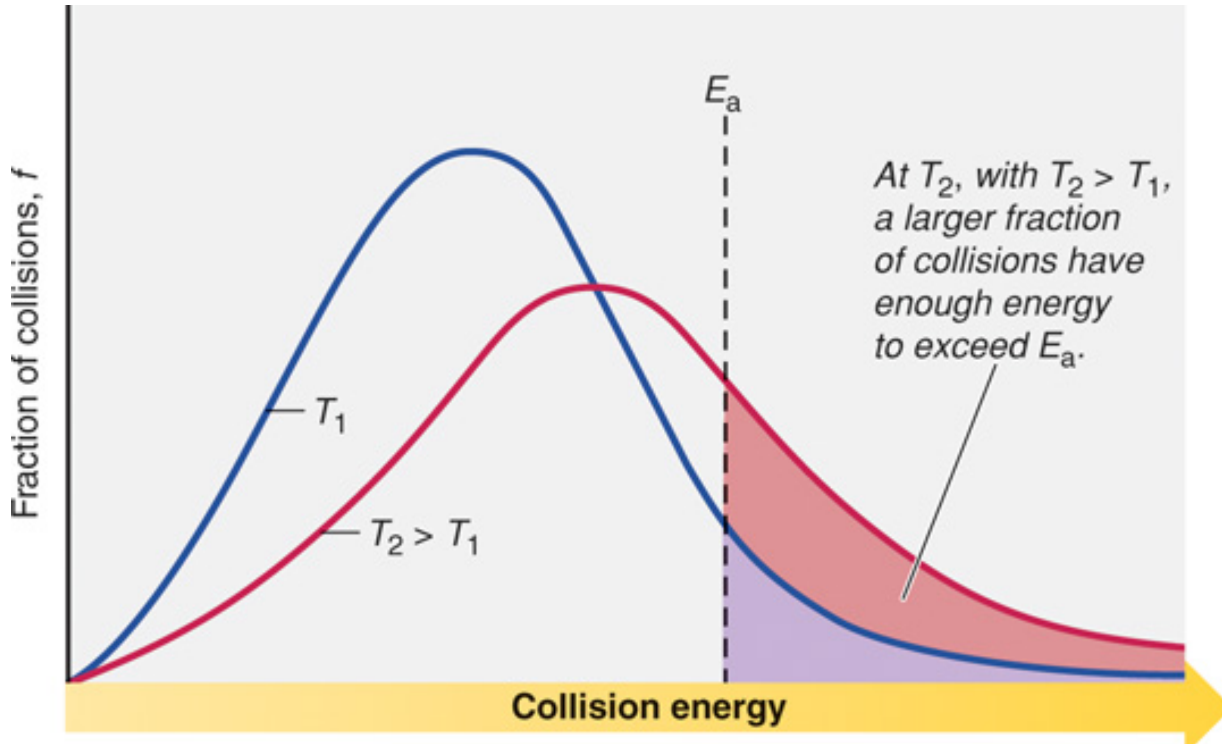
Your Turn…

The reaction between A and B is determined to be a fairly **fast** reaction and **slightly exothermic**. Which of the following potential energy surfaces fit this description?



Average Kinetic Energy and T

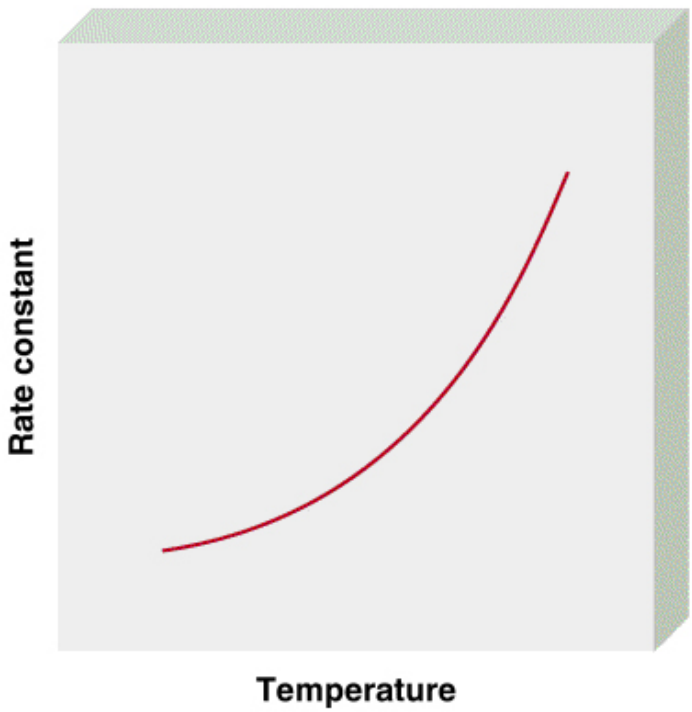
Recall from kinetic molecular theory:



If activation barrier is high, only a few molecules have sufficient kinetic energy and the reaction is slower.

As temperature increases, reaction rate increases.

Effect of Temperature on Rate Constants



- reaction rates, and thus rate constants, increase when the temperature is increased
- there are very few exceptions to this rule!
  - for example, an enzyme-catalyzed reaction can begin to slow down as the temperature is decreased, since the enzyme can become denatured at high T

Effect of Temperature on Reaction Rates

- Arrhenius demonstrated that many rate constants vary with temperature according to the equation:

$$k = Ae^{-E_a/RT}$$

taking the ln of both sides:

$$\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$$

Temperature Dependence of k

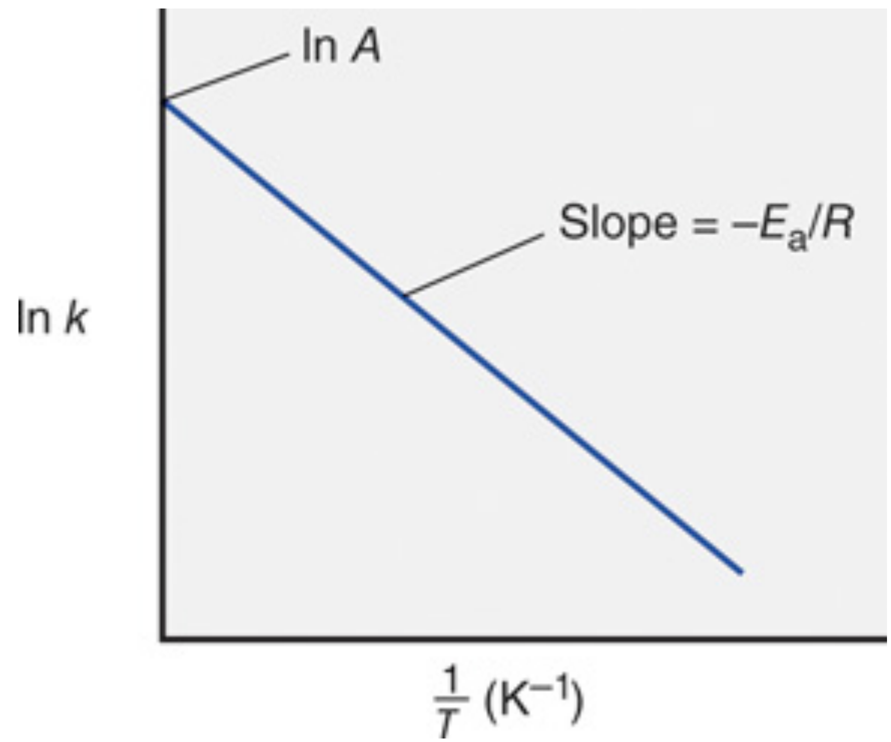
For graphs of ln k versus 1/T:

$$\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$$

$y = mx + b$

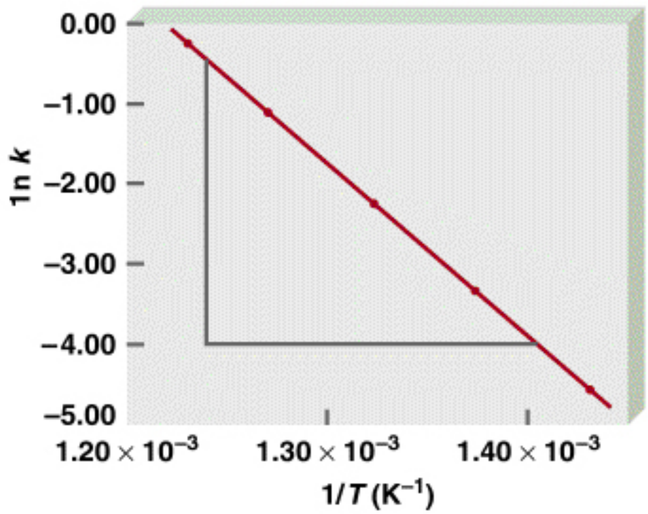
slope =

y-intercept =



The Arrhenius Equation

- it is possible to determine the activation energy from two rate constants, k_1 and k_2, measured at two temperatures, T_1 and T_2



k ($1/M^{\frac{1}{2}} \cdot s$)	T (K)
0.011	700
0.035	730
0.105	760
0.343	790
0.789	810

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

- subtracting the first equation from the second gives:

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Reaction Mechanisms

- **MECHANISM**: A step-by-step description of a chemical reaction.
- Each step is called an **ELEMENTARY PROCESS**
  - Any molecular event that significantly alters a molecules energy of geometry or produces a new molecule.
- Reaction mechanism must be consistent with:
  - Stoichiometry for the overall reaction
  - The experimentally determined rate law

Elementary Processes

1. Can be unimolecular or bimolecular
2. Exponents for concentration terms are the same as the stoichiometric factors for the elementary process
3. Elementary processes are reversible
4. Intermediates are produced in one elementary process and consumed in another
5. One elementary step is usually slower than all the others and is known as the RATE DETERMINING STEP, RDS

MECHANISMS

- The O_3 + NO reaction examined previously occurs in a *single ELEMENTARY step*

$$O_3 + NO \rightarrow O_2 + NO_2$$

- HOWEVER: Many reactions involve a sequence of elementary steps

The sum of the elementary steps gives the ________________

Link between Molecularity and Order

TABLE 14.7 Rate Laws for General Elementary Steps

Elementary Step	Molecularity	Rate Law
$A \longrightarrow$ product	Unimolecular	Rate $= k[A]$
$2A \longrightarrow$ product	Bimolecular	Rate $= k[A]^2$
$A + B \longrightarrow$ product	Bimolecular	Rate $= k[A][B]$
$2A + B \longrightarrow$ product	Termolecular	Rate $= k[A]^2[B]$

Example: Decomposition of Ozone

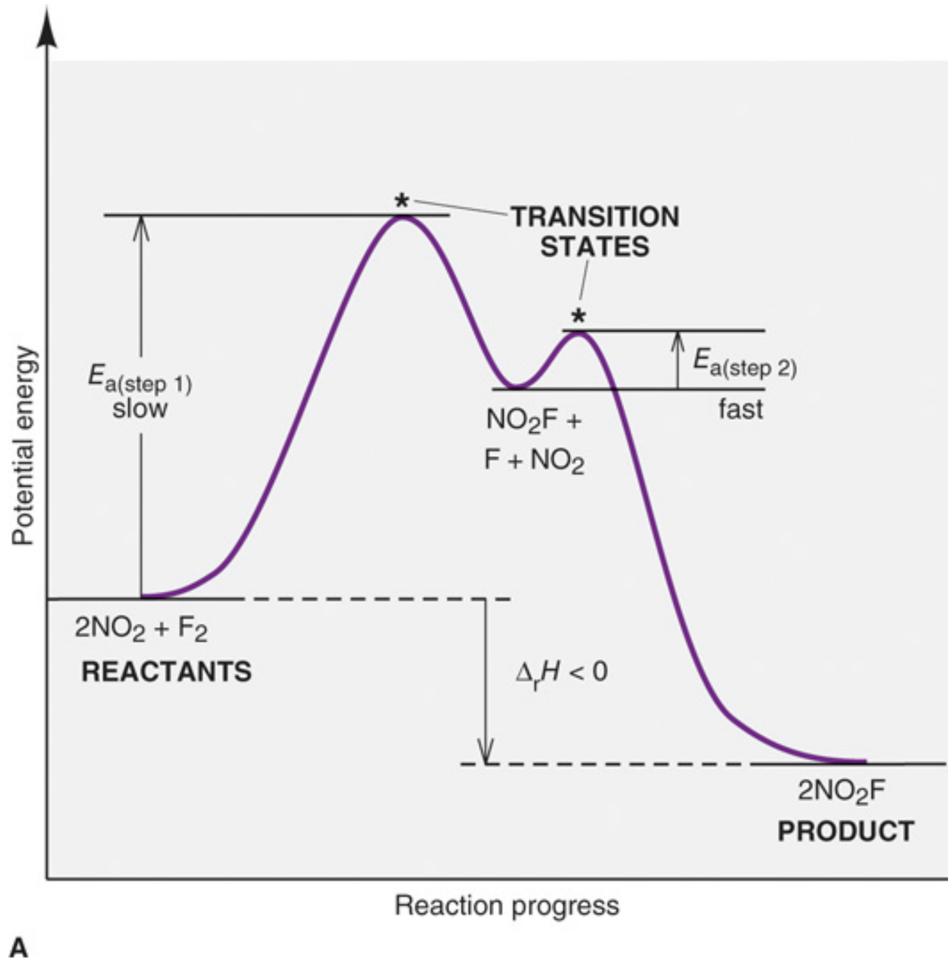
- Overall reaction: $2\ O_3 \xrightarrow{\text{UV}} 3\ O_2$

Examples: Postulating a mechanism

Postulate a plausible mechanism for the following reactions.

Overall Reaction	Experimental Data
$H_2(g) + 2\ ICl(g) \rightarrow I_2(g) + 2\ HCl(g)$	HI is an intermediate $\text{rate} = k_{obs}[H_2][ICl]$
$NO_2(g) + CO(g) \rightarrow CO_2(g) + NO(g)$	$\text{rate} = k_{obs}[NO_2]^2$
$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$	$\text{rate} = k_{obs}[NO_2][F_2]$

Reaction profile for this mechanism: A Slow Step Followed by a Fast Step



Example: Postulating a mechanism

Postulate a plausible mechanism for the following reaction.

$$2NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

Experimental investigation shows that NO_3 is a reaction intermediate that forms in a fast equilibrium and the rate law is:

$$\text{rate} = k_{obs}[NO]^2[O_2]$$

Your Turn…

What is the correct expected rate law for the overall reaction, based on the following proposed mechanism and experimental data?

$$A + B \rightarrow X$$
$$X \rightarrow C$$
$$C + A \rightarrow D$$

$$k_1 <<< k_2 < k_3$$

A. rate = k[A][C]

B. rate = $k[A]^2[C]$

C. rate = k[A][B]

D. rate = k[X]

The Steady State Approximation

- used to eliminate intermediates from rate laws

$$A \rightarrow X \rightarrow C$$

rate of formation of X = rate of disappearance of X

- or:

Example: Postulating a mechanism

Postulate a plausible mechanism for the following reaction.

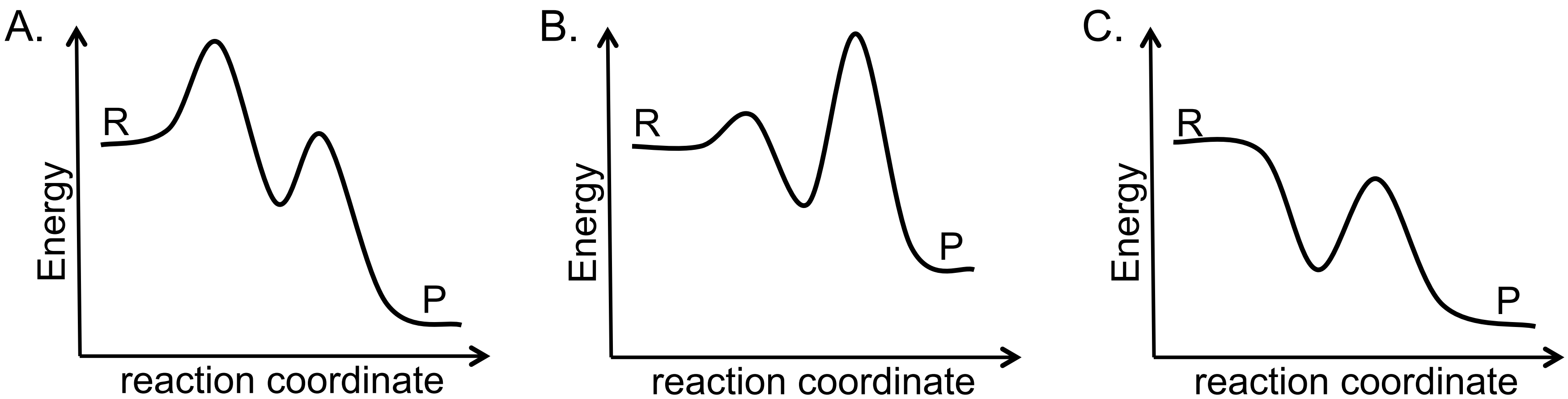
$$2NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

Experimental investigation shows that NO_3 is a reaction intermediate that forms in an equilibrium and the rate law is:

$$\text{rate} = k_{obs}[NO]^2[O_2]$$

Your Turn…

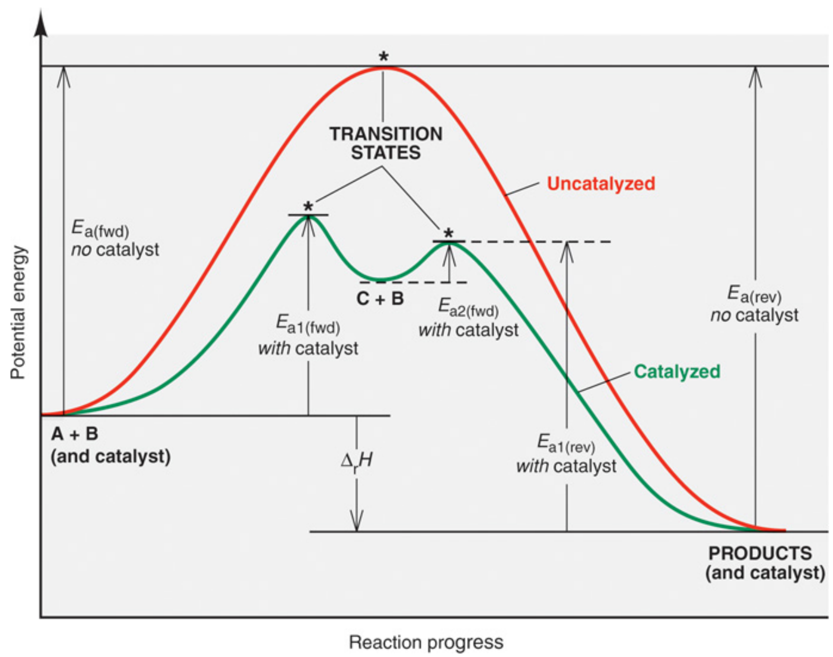
The exothermic decomposition of peroxide was determined to occur via two separate steps in which the first step is the rate determining step. Which of the following three potential energy diagrams best summarizes these findings.



CATALYSIS

- Catalysts speed up reactions by altering the mechanism to lower the activation energy barrier.

Catalysis



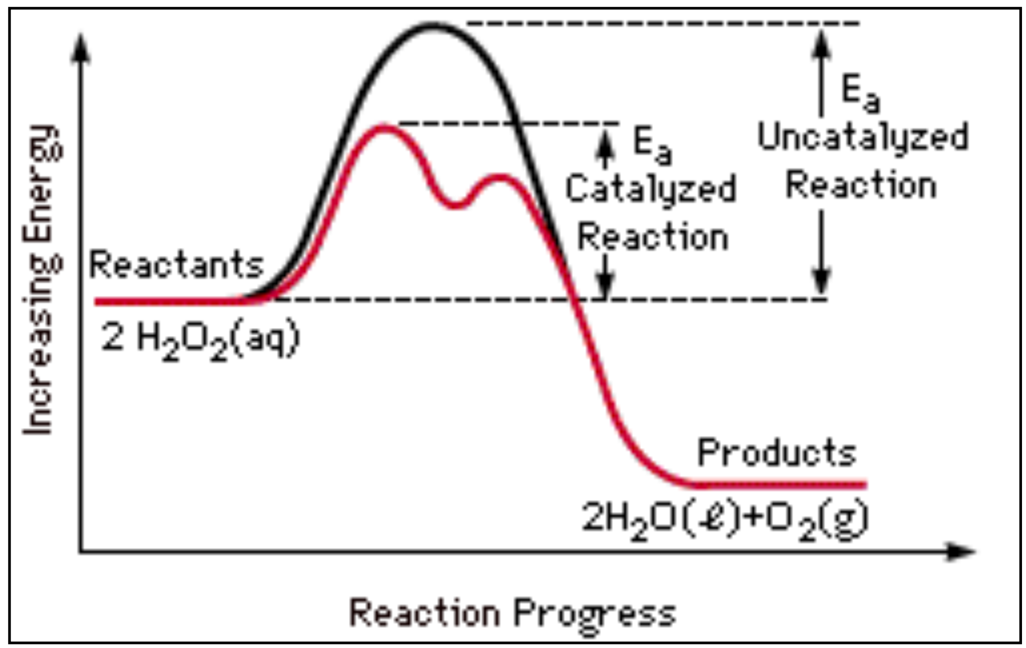
- speed up reactions by altering the mechanism to lower the E_a barrier
- the catalyst does **not** affect the difference in energy between the reactants and products
- the catalyst also increases the rate of the reverse reaction

$$k = Ae^{-E_a/RT}$$

Catalysis and Activation Energy

- Example: MnO_2 catalyzed decomposition of H_2O_2

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$$



Uncatalyzed reaction

Catalyzed reaction

Chapter 14: Key Concepts

1. Reaction rate expression
2. Measuring reaction rates
3. The rate law
4. Zero, first, and second order reactions
5. Reaction profiles and activation energy
6. The Arrhenius equation
7. Catalysis (*no enzyme catalysis)

Chapter 14: Suggested Problems

14.2, 14.3, 14.5, 14.14, 14.18, 14.22,
14.25, 14.26, 14.28, 14.34, 14.38, 14.41,
14.43, 14.52, 14.54, 14.59, 14.64, 14.67,
14.69, 14.72, 14.74, 14.77, 14.83, 14.85,
14.89, 14.92, 14.96, 14.98, 14.99,
14.110, 14.114, 14.125