# CHEMICAL KINETICS

## **Chemical Kinetics:**

- The study of the ***Rates of Chemical Reactions***: how fast do chemical reactions proceed to form products
- The study of ***Reaction Mechanisms***: the steps involved in the change from reactants to products.

## **Rates of Reactions**

- Factors affecting Reaction Rates:

| | |
|---|---|
| 1. Concentration of Reactants: | Rate $\alpha$ Concentration of Reactants |
| 2. Presence of a Catalyst: | A catalyst is a substance that increases the Reaction Rate without being consumed |
| 3. Temperature: | Rate $\alpha$ Temperature |
| 4. Surface Area of Reactants: | Rate $\alpha$ Surface Area of Reactants |

## **Definition of Reaction Reaction Rate**

$$H_2\,(g) + I_2\,(g) \rightarrow 2\,HI\,(g)$$

Reaction Rate:

- increase in the molar concentration of a product per unit time

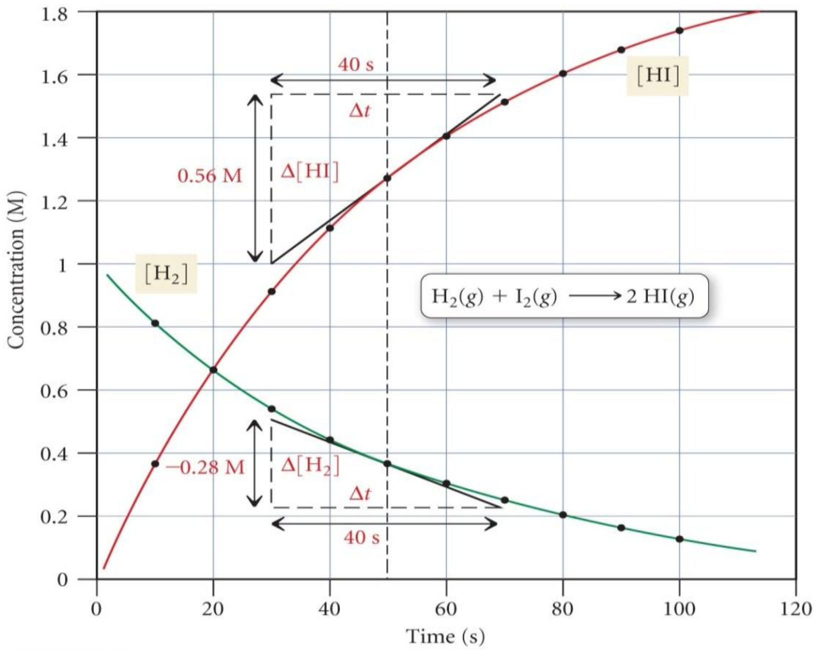
OR

- decrease in the molar concentration of reactant per unit time

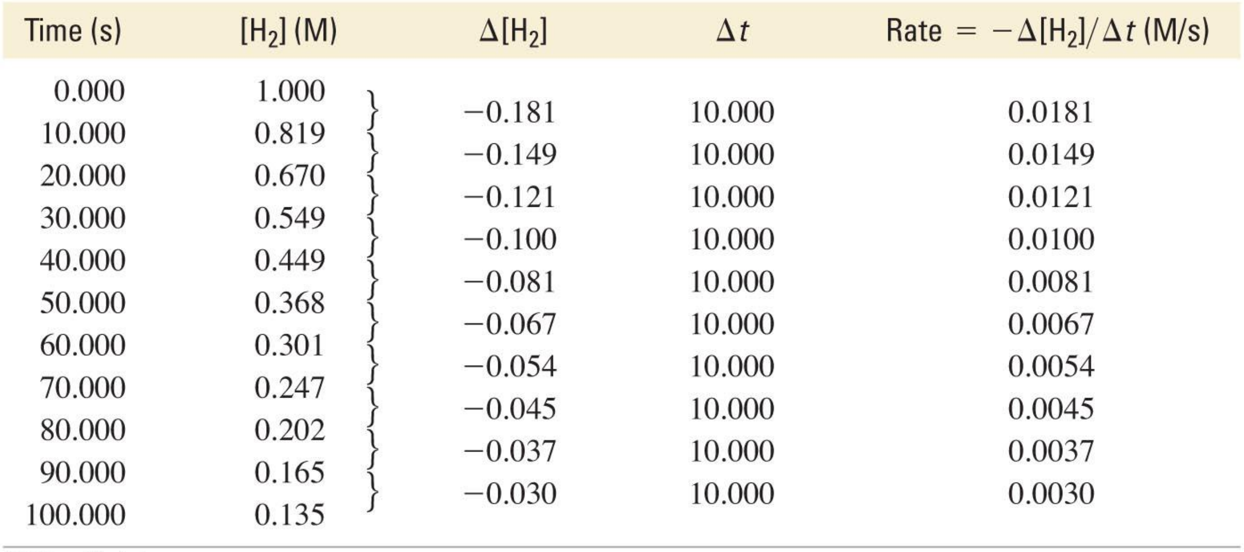
$$\text{Rate of disappearance of } H_2 = \frac{\Delta[\,H_2]}{\Delta\, t} = \frac{\text{decrease in the molar conc. of } H_2}{\text{time interval}}$$

- The expression above is referred to as: Average Rate over the time interval $\Delta t$

# REACTION RATES



- Reactant concentration decreases with time, while product concentration increases with time.



| Time (s) | $[H_2]$ (M) | $\Delta[H_2]$ | $\Delta t$ | Rate $= -\Delta[H_2]/\Delta t$ (M/s) |
|---|---|---|---|---|
| 0.000 | 1.000 | −0.181 | 10.000 | 0.0181 |
| 10.000 | 0.819 | −0.149 | 10.000 | 0.0149 |
| 20.000 | 0.670 | −0.121 | 10.000 | 0.0121 |
| 30.000 | 0.549 | −0.100 | 10.000 | 0.0100 |
| 40.000 | 0.449 | −0.081 | 10.000 | 0.0081 |
| 50.000 | 0.368 | −0.067 | 10.000 | 0.0067 |
| 60.000 | 0.301 | −0.054 | 10.000 | 0.0054 |
| 70.000 | 0.247 | −0.045 | 10.000 | 0.0045 |
| 80.000 | 0.202 | −0.037 | 10.000 | 0.0037 |
| 90.000 | 0.165 | −0.030 | 10.000 | 0.0030 |
| 100.000 | 0.135 | | | |

# REACTION RATES

- The Reaction Rate decreases as the reaction proceeds.
  Reason: the concentration of reactants decreases

- Any substance in the reaction can be used to express the Rxn. Rate

$$H_2\,(g) + I_2\,(g) \rightarrow 2\,HI\,(g)$$

$$\text{Rate of disappearance of } H_2 = \frac{\Delta[\,H_2]}{\Delta t} = \frac{\text{decrease in the molar conc. of } H_2}{\text{time interval}}$$

$$\text{Rate of disappearance of } I_2 = \frac{\Delta[I_2]}{\Delta t} = \frac{\text{decrease in the molar conc. of } I_2}{\text{time interval}}$$

$$\text{Rate of formation of HI} = \frac{\Delta[HI]}{\Delta t} = \frac{\text{increase in the molar conc. of HI}}{\text{time interval}}$$

- Reaction Rate is always positive

$$\text{(a) Rate of formation of a product} = \frac{\Delta[\text{increase in concentration of product}]}{\Delta t}$$

$$\text{(b) Rate of decomposition of a reactant} = -\frac{\Delta[\text{decrease in concentration of reactant}]}{\Delta t}$$

Since: Δ[decrease in concentration of reactant] has a negative value the Reaction Rate will be positive

**<u>Reaction Rate in terms of stoichiometry</u>**

$$H_2\,(g) + I_2\,(g) \rightarrow 2\,HI\,(g)$$

$$\text{Rate of increase of HI} = 2 \times \text{Rate of decrease of } H_2$$

OR

$$\frac{\text{Rate of increase of HI}}{2} = \text{Rate of decrease of } H_2$$

Reason: 2 moles of HI are formed from reaction of 1 mole of $H_2$

# REACTION RATES

**Examples:**

1. For the hypothetical reaction shown below, write a rate expression based on each reactant and product:

$$3\,A + B \rightarrow 2\,C + 4\,D$$

Rate based on A =

Rate based on C =

Rate based on B =

Rate based on D =

Rate =

2. Consider the following reaction:

$$H_2O_2\,(aq) + 3\,I^-\,(aq) + 2\,H^+\,(aq) \rightarrow I_3^-\,(aq) + 2\,H_2O\,(l)$$

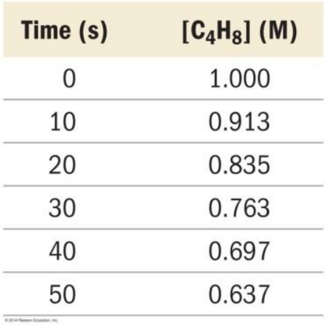
In the first 10.0 seconds of the reaction, the concentration of $I^-$ dropped from 1.000 M to 0.868 M.

a) Calculate the average rate of this reaction in this time interval.

b) Predict the rate of change in concentration of $H^+$ during this time interval.

**Examples (cont'd):**

3. The following data was collected for the reaction shown below:



| Time (s) | $[C_4H_8]$ (M) |
|---|---|
| 0 | 1.000 |
| 10 | 0.913 |
| 20 | 0.835 |
| 30 | 0.763 |
| 40 | 0.697 |
| 50 | 0.637 |

$$C_4H_8\ (g) \rightarrow 2\ C_2H_4\ (g)$$

a) What is the average rate of reaction between 0 and 10 seconds?

b) What is the rate of formation of $C_2H_4$ between 20 and 30 seconds?

4. For the reaction A + 2B $\rightarrow$ C, the initial rate is 0.100 M/s, at a given condition. What is $\Delta[B]/\Delta t$ under the same conditions?

   a) –0.0500 M/s

   b) –0.100 M/s

   c) –0.200 M/s

# RATE DETERMINATION

- Rate determination is done by monitoring the change in concentration of reactant or product over time.

**Method**:

- Withdraw samples from the reaction vessel at various times and analyze some of their physical or chemical properties that give information on the concentrations present.

**Properties appropriate and easy to monitor**

- Color (if product or reactant absorbs light); a spectrophotometer (shown on bottom of page) can be used to quantify the difference in color difference of reactants and products.

- Volume, at constant P and T; useful if gaseous substances are present, and
  # of mol of gaseous reactants ≠ # of mol of gaseous products

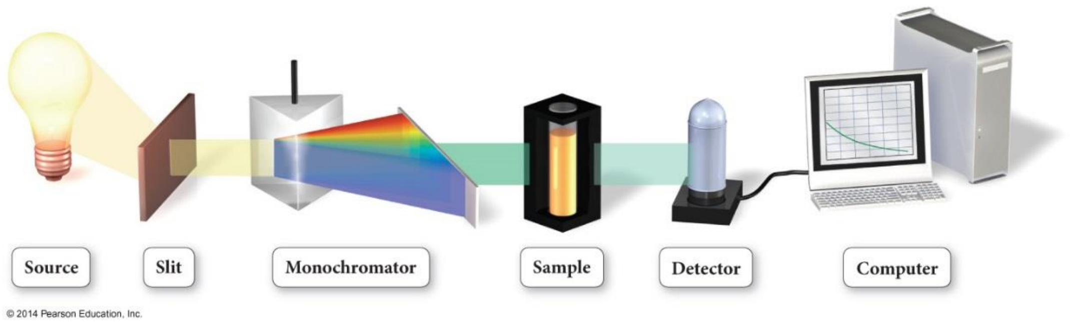
- Pressure at constant V and T; useful if gaseous substances are present, and
  # of mol of gaseous reactants ≠ # of mol of gaseous products

- Density; useful is density of reactants ≠ density of products

**Properties not appropriate to monitor**

- Flammability (difficult to measure quantitatively)

- Mass (mass is conserved in a chemical reaction)



# RATE LAW

- The Rate of Reaction depends on the concentration of one or more of the reactants and, for the simple reaction (A → products) it can be written as:

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

- The relationship above is called the ***Rate Law***, where ***k*** is a constant of proportionality called the ***rate constant*** and ***n*** is the ***reaction order***. This relationship describes how the rate of a reaction changes with respect to the concentration of a reactant.

- For a more general reaction with general equation of the form:

$$\mathbf{aA + bB \xrightarrow{C} dD + eE}$$

the Rate Law has the form: $\text{Rate} = k\,[A]^m[B]^n[C]^p$

where,

**m, n, and p**

- ➢ are reaction orders with respect to each reactant or the catalyst,
- ➢ are frequently, but not always integers
- ➢ are determined experimentally
- ➢ are **<u>not</u>** the coefficients in the balanced chemical equation

and

**k**

- ➢ is the Rate Constant
- ➢ with its units depending upon the form of Rate Law
- ➢ and its value depending on temperature

# REACTION ORDER

- Reaction Order is the exponent (n) of the concentration of that species in the Rate Law, as determined experimentally.

- When $n = 0$, the reaction is zero order, when $n = 1$, the reaction is first order and when $n = 2$, the reaction is second order.

- Although other orders are possible, including fractional or negative orders, they are not common.

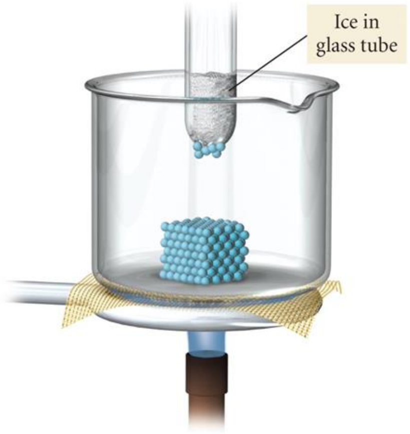
**Zero-Order Reaction:**

- In a zero-order reaction, the rate of the reaction is independent of the reactant concentration.

$$\text{Rate} = k\,[A]^0 = k$$

- Zero-order reactions occur under conditions where the actual amount of reactant available for a reaction does not change as the overall amount of reactant changes.

- For example, sublimation is usually zero order, since the amount of substance on the surface available to sublime does not change as the substance sublimes.



**First-Order Reaction:**

- In a first-order reaction, the rate of a reaction is directly proportional to the concentration of the reactant.

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

- Therefore, the rate of a first-order reaction slows down as the reaction proceeds because the concentration of the reactant decreases.

- Furthermore, the rate of the reaction increases with the same change factor in concentration of the reactant. For example, doubling the concentration of a reactant in a first-order reaction, doubles the rate of reaction.

**Second-Order Reaction:**

- In a second-order reaction, the rate of a reaction is proportional to square of the concentration of the reactant.

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

- Therefore, the rate of a second-order reaction is more sensitive to the concentration of the reactant. Furthermore, since the rate of the reactant increases with the square of the change factor in concentration of the reactant, doubling the concentration of a reactant in a second-order reaction, quadruples the rate of reaction.

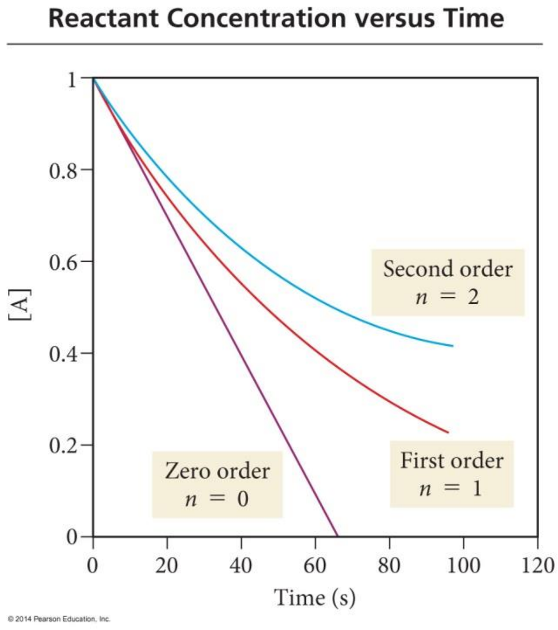
# REACTION ORDER

- Effect of concentration change on reaction rates and orders can be summarized as:

| Order | Effect of Doubling Concentration | Rate |
|---|---|---|
| **Zero** | $2^0$ | **No Effect** |
| **First** | $2^1$ | **x 2** |
| **Second** | $2^2$ | **x 4** |
| **Negative** | $2^{-1}$ | **x ½** |
| **Half** | $2^{1/2}$ | $\sqrt{2}$ |

- Diagram A below shows how the concentration of reactant changes with time for the three common reaction orders, with identical rate constant (k) and initial concentrations.

- Diagram B shows how the rate of reaction changes as a function of reactant concentration.



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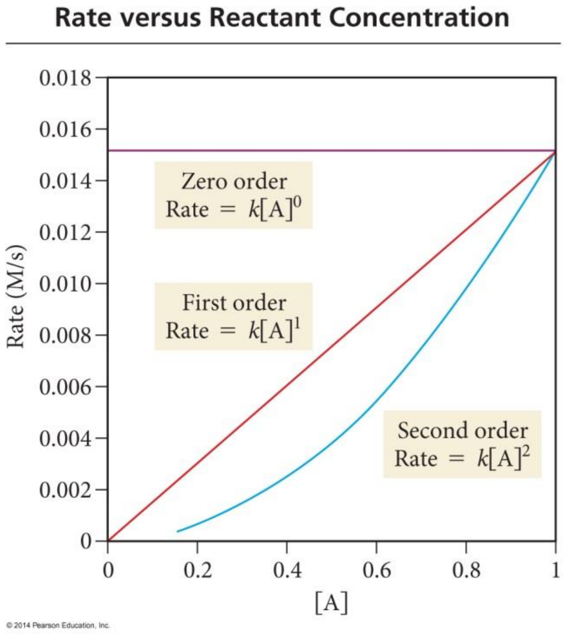
**A**



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**B**

# EXPERIMENTAL DETERMINATION OF RATE LAW

- In determining the rate law for a reaction, first the order of reaction with respect to each reactant and catalyst must be found.

- Commonly a series of experiments are done in which the initial concentrations of reactants are varied (usually doubled).

- The results of these experiments will yield the respective orders of reaction.

Example: $2\ N_2O_5\,(g) \longrightarrow 4\ NO_2\,(g) + O_2\,(g)$

| | **Initial $N_2O_5$ Conc. (M)** | **Initial Rate of Disappearance of $N_2O_5$ (M/s)** |
|---|---|---|
| Experiment 1 | $1.0\text{x}10^{-2}$ | $4.8\text{x}10^{-6}$ |
| Experiment 2 | $2.0\text{x}10^{-2}$ | $9.6\text{x}10^{-6}$ |

**Rate = k $[N_2O_5]^m$** m = ? (must be determined from experimental data)

$$\frac{\text{Rate Exp. 2}}{\text{Rate Exp. 1}} = \frac{k\,(2)^m}{k(1)^m} = \frac{9.6\text{x}10^{-6}}{4.8\text{x}10^{-6}} = 2$$

**Experimental:** ➢ Doubling $[N_2O_5]$ doubled the rate of reaction

**It follows:** ➢ m = 1 ($2^1 = 2$)

**The Reaction is:** ➢ First order in $N_2O_5$
➢ First order overall

$\boxed{\textbf{Rate} = k\,[N_2O_5]^1}$ $\boxed{\textbf{Rate} = k\,[N_2O_5]}$

**Examples:**

1. Use the rate data below to
   A) determine the reaction orders with respect to $[H_2O_2]$, $[I^-]$ and $[H^+]$ and
   B) find the rate constant k for the reaction shown below:

$$H_2O_2\,(aq) + 3\,I^-(aq) + 2\,H^+(aq) \longrightarrow I_3^-(aq) + 2\,H_2O\,(l)$$

| | Initial Concentrations (M) | | | Initial Rate (M/s) |
|---|---|---|---|---|
| | **$[H_2O_2]$** | **$[I^-]$** | **$[H^+]$** | |
| Experiment 1 | 0.010 | 0.010 | 0.00050 | $1.15 \times 10^{-6}$ |
| Experiment 2 | 0.020 | 0.010 | 0.00050 | $2.3 \times 10^{-6}$ |
| Experiment 3 | 0.010 | 0.020 | 0.00050 | $2.30 \times 10^{-6}$ |
| Experiment 4 | 0.010 | 0.010 | 0.00100 | $1.15 \times 10^{-6}$ |

**Solution**

A) Compare two rate experiments in which all concentrations of reactants but one are held constant:

**$[H_2O_2]$** : Compare **Experiment 1** and **Experiment 2**
**When $[H_2O_2]$ is doubled**, the **Rate is doubled**
It follows: $2^m = 2$ $m = 1$ **1st order in $[H_2O_2]$**

**$[I^-]$** : Compare **Experiment** 1 and **Experiment 3**
**When $[I^-]$ is doubled**, the **Rate is doubled**
It follows: $2^n = 2$ $n = 1$ **1st order in $[I^-]$**

**$[H^+]$:** Compare Experiment 1 and Experiment 4
When **$[H^+]$ is doubled**, **the Rate does not change**
It follows: $2^p = 1$ $p = 0$ **0 order in $[H^+]$**

$$H_2O_2\,(aq) + 3\,I^-(aq) + 2\,H^+(aq) \longrightarrow I_3^-(aq) + 2\,H_2O(l)$$

**Summary**:

| | |
|---|---|
| 1st order in | $[H_2O_2]$ |
| 1st order in | $[I^-]$ |
| 0 order in | $[H^+]$ |

$$\text{RATE} = k\,[H_2O_2]^1\,[I^-]^1\,[H^+]^0$$

commonly written : $\boxed{\text{RATE} = k\,[H_2O_2]\,[I^-]}$

**NOTE**: Reaction Orders are **not** related to the coefficients of the overall equation

**Examples (cont'd):**

B) Find the Rate Constant, k

From Experiment 1: (any other experiment could be used)

$[H_2O_2] = 0.010$ M
$[I^-] = 0.010$ M
Rate = $1.15 \times 10^{-6}$ M/s
k = ?

$$\text{RATE} = k\,[H_2O_2]\,[I^-] \qquad k = \frac{\text{Rate}}{[H_2O_2][I^-]} = \frac{1.15\text{x}10^{-6}\ \text{M/s}}{(0.010\ \text{M})(0.010\ \text{M})} = 1.2\text{x}10^{-2}\ \text{M}^{-1}\text{s}^{-1}$$

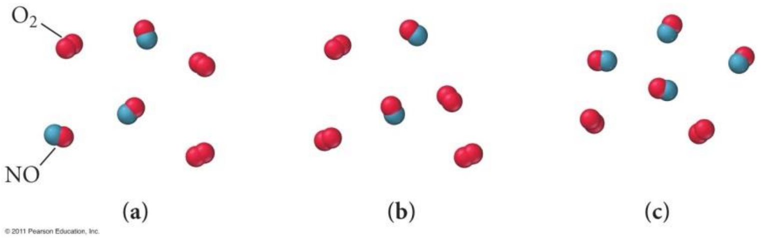
2. Use the rate data below to
   A) determine the rate law for the reaction A + B → C, and
   B) calculate the rate constant k, and
   C) calculate the rate of reaction for experiment 4

| **Experiment Number** | **[A] (M)** | **[B] (M)** | **Initial Rate (M/s)** |
|---|---|---|---|
| 1 | 0.100 | 0.100 | $4.0\text{x}10^{-5}$ |
| 2 | 0.100 | 0.200 | $4.0\text{x}10^{-5}$ |
| 3 | 0.200 | 0.100 | $16.0\text{x}10^{-5}$ |
| 4 | 0.050 | 0.100 | ???? |

**Examples (cont'd):**

1. The reaction below was experimentally determined to be 1st order with respect to $O_2$ and 2nd order with respect to NO. Which mixture in the diagram below has the fastest initial rate?

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



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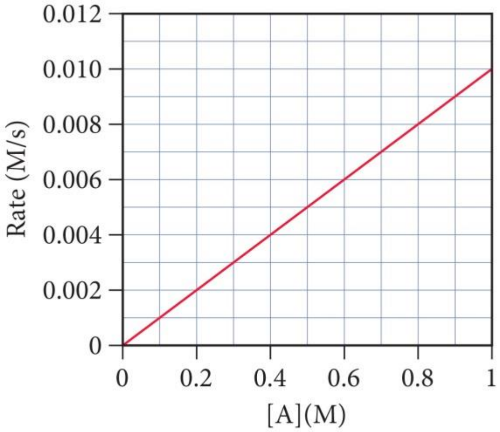
2. The graph below shows a plot of the rate of reaction versus the concentration of the reactant A for the reaction A → products.



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   a. What is the order of the reaction with respect to A?

   b. Write the rate law for the reaction and determine the value of k.

# INTEGRATED RATE LAW (1$^{ST}$ ORDER REACTION)

- The rate laws discussed earlier examine the relationship between concentration of a reactant and the rate of a reaction. But often, the relationship between the concentration of a reactant and time is of interest.

- The integrated rate law for a reaction is a relationship between the concentrations of the reactants and time. For example, consider a simple first order decomposition reaction shown below:

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

Rate Law: $\text{Rate} = k[A]$

- Since Rate = $-\Delta[A]/\Delta t$, the following can be written:

**Differential Rate Law** $$-\frac{\Delta [A]}{\Delta t} = k [A]$$

- Calculus can be used to integrate the differential rate law and obtain the 1st order integrated rate law:

**Integrated Rate Law** $$\ln\frac{[A]_t}{[A]_0} = -kt$$

- The integrated rate law can be used to calculate the concentration of reactant at any time during the reaction.

**Examples:**

1. Sulfuryl chloride, $SO_2Cl_2$, decomposes when heated:

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

In an experiment, the initial concentration of $SO_2Cl_2$ was 0.0248 M. If the reaction is first order with the Rate Constant of $2.2 \times 10^{-5}\ s^{-1}$, what is the concentration of $SO_2Cl_2$ after 2.5 hours?

$[A]_0 = 0.0248$ M $k = 2.2 \times 10^{-5}\ s^{-1}$ $t = 2.5\ h\ (9\underline{0}00\ s)$

$$\ln\frac{[A]_t}{[A]_0} = -kt \qquad \ln\frac{[A]_t}{0.0248} = -(2.2\times10^{-5}\ s^{-1})(9\underline{0}00\ s) = -0.1\underline{9}8$$

Taking antilog of both sides,

$$\frac{[A]_t}{0.0248} = e^{-0.1\underline{9}8} = 0.82 \qquad [A]t = (0.0248)(0.82) = 2.0\times10^{-2}\ M$$

**Examples (cont'd):**

2. Cyclobutane, $C_4H_8$ decomposes, when heated to give ethylene:

$$C_4H_8\,(g) \longrightarrow 2\,C_2H_4\,(g)$$

The reaction is first order. In an experiment, the initial $[C_4H_8] = 0.00150$ M.
After heating at 450°C for 455 seconds, $[C_4H_8] = 0.00119$ M. Based on this information, determine the rate constant for this reaction at this temperature.

$[C_4H_8]_0 = 0.00150$ M $\qquad$ $[C_4H_8]_{455} = 0.00119$ M

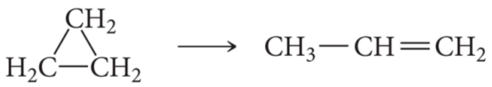
$$\ln\frac{[C_4H_8]_{455}}{[C_4H_8]_0} = \ln\frac{0.00119\text{ M}}{0.00150\text{ M}} = -\,k\,(455\text{ s})$$

$$\ln 0.79\underline{3}3 = -455\,\mathbf{k}$$

$$-0.23\underline{1}6 = -455\,\mathbf{k}$$

$$\mathbf{k} = 5.09 \times 10^{-4}\text{ s}^{-1}$$

3. Cyclopropane rearranges to form propene in the gas phase:



The reaction is first order and has a rate constant of $3.36\text{x}10^{-5}\text{ s}^{-1}$ at 720 K. If the initial concentration of cyclopropane is 0.0445 M, what will the cyclopropane concentration be after 235.0 min?

# HALF-LIFE ($t_{1/2}$) OF A FIRST ORDER REACTION

- Half-life is the time it takes for the reactant concentration to decrease to one-half of its initial value.

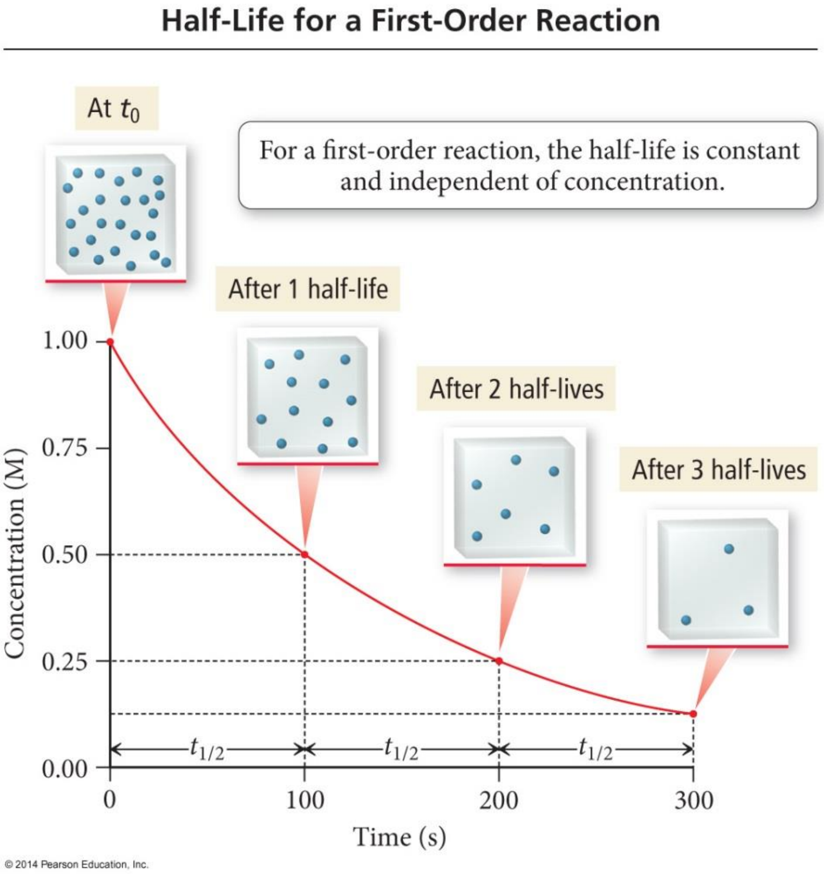
$$\ln \frac{[A]_t}{[A]_0} = -kt$$

In one half-life ($t_{1/2}$): $[A]_t = \frac{1}{2}[A]_0 \Longrightarrow \ln \frac{\frac{1}{2}[A]_0}{[A]_0} = -k(t_{1/2})$

$$-0.693 = -k(t_{1/2}) \Longrightarrow \boxed{t_{1/2} = \frac{0.693}{k}}$$

**NOTES:**

- Half-Life does not depend on the initial concentration, $[A]_0$



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**Example:**

1. Dinitrogen pentoxide, decomposes when heated in carbon tetrachloride solvent:

$$N_2O_5\,(g) \longrightarrow 2\,NO_2\,(g) + \tfrac{1}{2}\,O_2\,(g)$$

The rate law is first order in $N_2O_5$ with a rate constant of $6.2\text{x}10^{-4}\ \text{min}^{-1}$. What is the half-life for this reaction?

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{6.2\text{x}10^{-4}\ \text{min}^{-1}} = 1118\ \text{min} = 1.1\text{x}10^{3}\ \text{min}$$

2. A first order reaction has a half-life of 26.4 seconds. How long does it take for the concentration of the reactant to fall to 1/8 of its initial value?

3. The radioactive decay of U-238 is first order with a half-life of $4.5\text{x}10^{9}$ years. How long would it take for 10% of the U-238 atoms in a sample to U-238 to decay?

# GRAPHING FIRST ORDER REACTIONS

- The order of a reaction can be determined by graphing the experimental data. For a first order reaction, the integrated rate law can be written as:

- First order Rate Law: $\ln \frac{[A]_t}{[A]_0} = -kt$

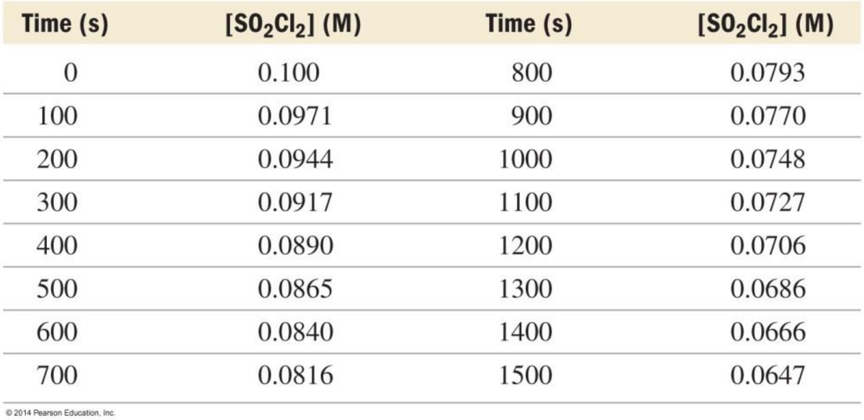
- This equation may be rewritten:

$\ln [A]_t = -kt + \ln [A]_0$ (This is the equation of a straight line, y = mx + b)

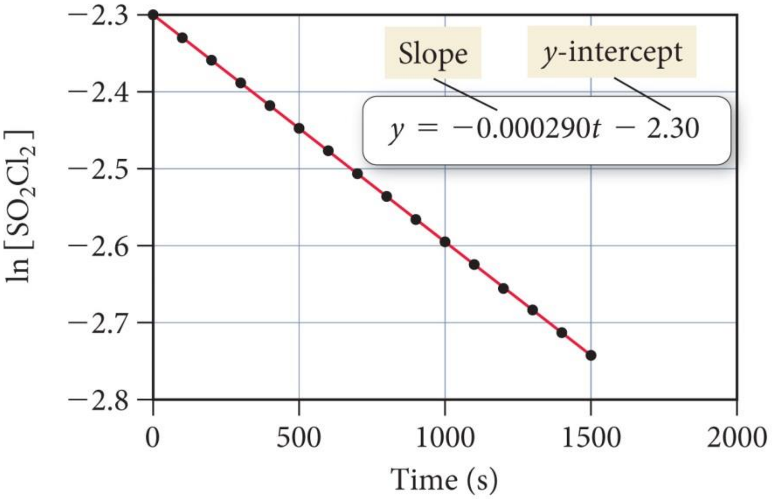
- A plot of ***ln [A] (y)*** versus ***time (x)*** should give a straight line for a first order reaction with a slope of ***–k*** and a y-intercept of ***ln[A]₀***.

- For example, for the decomposition of $SO_2Cl_2$ (shown below), the concentration vs. time data can be graphed to show that the reaction is first order.

$$SO_2Cl_2\ (g) \longrightarrow SO_2\ (g) + Cl_2\ (g)$$



| Time (s) | $[SO_2Cl_2]$ (M) | Time (s) | $[SO_2Cl_2]$ (M) |
|---|---|---|---|
| 0 | 0.100 | 800 | 0.0793 |
| 100 | 0.0971 | 900 | 0.0770 |
| 200 | 0.0944 | 1000 | 0.0748 |
| 300 | 0.0917 | 1100 | 0.0727 |
| 400 | 0.0890 | 1200 | 0.0706 |
| 500 | 0.0865 | 1300 | 0.0686 |
| 600 | 0.0840 | 1400 | 0.0666 |
| 700 | 0.0816 | 1500 | 0.0647 |

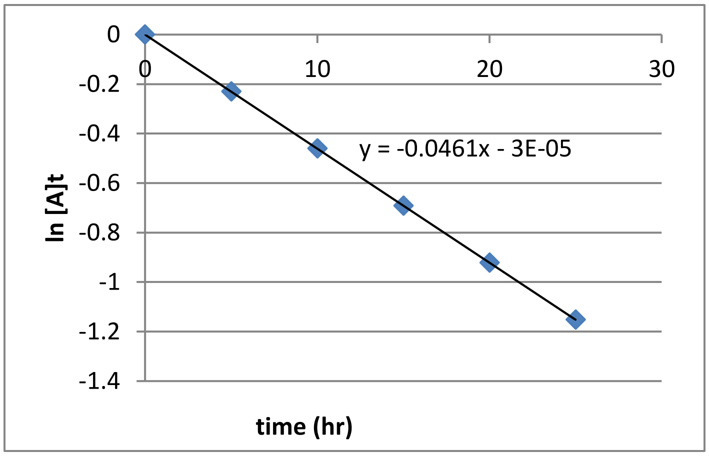


# GRAPHING FIRST ORDER REACTIONS

**Example:**

1. Use the graph provided on the previous page to determine the concentration of $SO_2Cl_2$ at 1900 s. (Round to 3 significant figures)

2. Shown below is a graph of concentration vs. time for decomposition of $CH_3CN$. Determine the order of the reaction and the value of rate constant at this temperature.



# INTEGRATED RATE LAW ($2^{ND}$ ORDER REACTION)

$$a\,A \longrightarrow \text{Products}$$

$$\text{Rate} = -\frac{\Delta\,[A]}{\Delta t} = k\,[A]^2 \longleftarrow$$

**Differential Rate Law**

By using calculus:

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

**Integrated Rate Law**

**<u>Example</u>:**

1. For the reaction

$$2\,NO_2\,(g) \longrightarrow 2\,NO\,(g) + O_2\,(g)$$

At 330 K:

$k = 0.775\ M^{-1}s^{-1}$ $[A]_0 = 0.0030\ M$ **$[A]_{645}$** = ?

$$\frac{1}{[A]_t} = (0.775\ M^{-1}s^{-1})(645\ s) + \frac{1}{0.0030\ M}$$

$$\frac{1}{[A]_t} = (49\underline{9}.9\ M^{-1}) + (3\underline{3}3.3\ M^{-1}) = 8.3\text{x}10^2\ M^{-1}$$

$$\mathbf{[A]_t = 0.0012\ M}$$

# HALF-LIFE ($t_{1/2}$) OF A 2$^{ND}$ ORDER REACTION

- Half-life is the time it takes for the reactant concentration to decrease to one-half of its initial value.

For a second order reaction: $\text{Rate} = k\,[A]^2$ and $\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$

In one half-life ($t_{1/2}$): $[A]_t = \dfrac{1}{2}[A]_0 \Longrightarrow \dfrac{1}{0.5[A]_0} = kt + \dfrac{1}{[A]_0}$

$$kt_{1/2} = \frac{1}{0.5[A]_0} - \frac{1}{[A]_0} = \frac{1}{[A]_0} \Longrightarrow \boxed{t_{1/2} = \frac{1}{k\,[A]_0}}$$

**NOTES:**

- Half-Life depends on the initial concentration, $[A]_0$
- Half-Life increases as reaction progresses

**Example:**

1. For a particular 2nd order reaction $k = 0.775\ M^{-1}s^{-1}$.

a) How long does it take to the concentration to decrease from 0.0030 M to 0.0015?

For concentration to drop to half of its original value, t = half-life

$$t_{1/2} = \frac{1}{k\,[A]_0} = \frac{1}{(0.775\ M^{-1}s^{-1})(0.0030\ M)} = 430\ s$$

b) How long does it take for the concentration to be halved again?

$$t_{1/2} = \frac{1}{k\,[A]_0} = \frac{1}{(0.775\ M^{-1}s^{-1})(0.0015\ M)} = 860\ s \longleftarrow$$

**Twice as long**

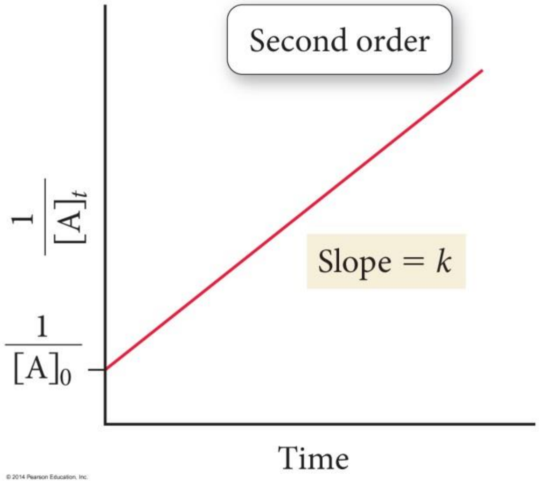
# GRAPHING 2$^{ND}$ ORDER REACTIONS

- The second order integrated rate law is in the form of a an equation for a straight line.

$$\frac{1}{[A]_t} = k \quad t \quad + \frac{1}{[A]_0}$$

$$y \quad = \quad m \;\; x \quad + \quad b$$

- A plot of **$1/[A]_t$ (y)** versus **time (s)** should give a straight line for a second order reaction with a slope of **k** and y-intercept of **$1/[A]_0$.**



Summary:

To determine the order of a reaction,

1. Collect time vs. concentration data for the reaction.
2. Assuming 1st order, plot ln [A] vs. time.
3. If a linear graph is obtained, then it is 1st order.
4. If no linear graph, then plot 1/[A] vs. time.
5. If a linear graph is obtained, then it is 2nd order.

**Example:**

1. Given the experimental data listed on the right, determine if the reaction shown below is 1st or 2nd order, and determine the rate constant (k) for the reaction shown below:

$$NO_2\,(g) \longrightarrow NO(g) + O\,(g)$$

| Time (s) | $[NO_2]$ (M) |
|---|---|
| 0 | 0.01000 |
| 50 | 0.00887 |
| 100 | 0.00797 |
| 150 | 0.00723 |
| 200 | 0.00662 |
| 250 | 0.00611 |
| 300 | 0.00567 |
| 350 | 0.00528 |
| 400 | 0.00495 |
| 450 | 0.00466 |
| 500 | 0.00440 |
| 550 | 0.00416 |
| 600 | 0.00395 |
| 650 | 0.00376 |
| 700 | 0.00359 |
| 750 | 0.00343 |
| 800 | 0.00329 |
| 850 | 0.00316 |
| 900 | 0.00303 |
| 950 | 0.00292 |
| 1000 | 0.00282 |

Strategy:

- We must first see if the data fits the Rate Law for 1st Order Reactions. If it does, the reaction is of the 1st order
- If it does not, we must see if the data fits the Rate Law for 2nd Order If it does, the reaction is of the 2nd order

First Order Rate Law:

$$\ln [A]_t = -k\,t + \ln [A]_0$$

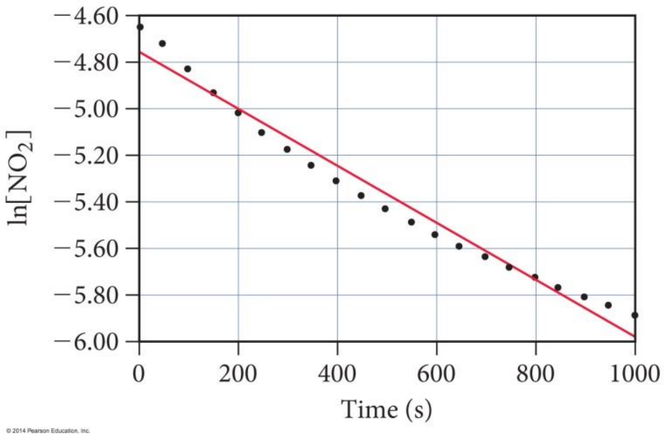
Plot ln $[A]_t$ as a function of t

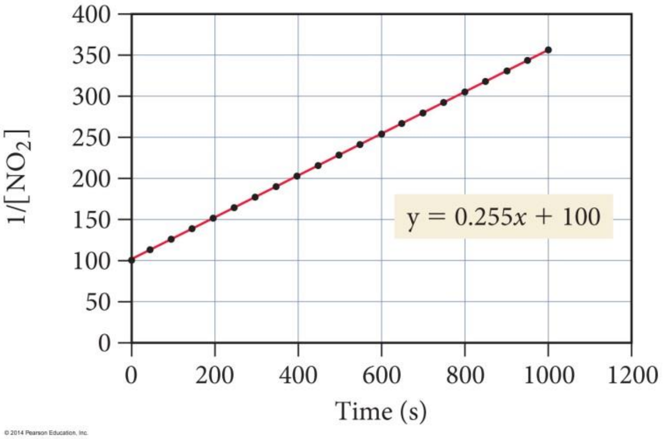
$$\boxed{y = m\,x + b}$$

Second order Rate Law

$$\frac{1}{[A]_t} = k\,t + \frac{1}{[A]_0}$$

Plot $1/[A]_t$ as a function of t



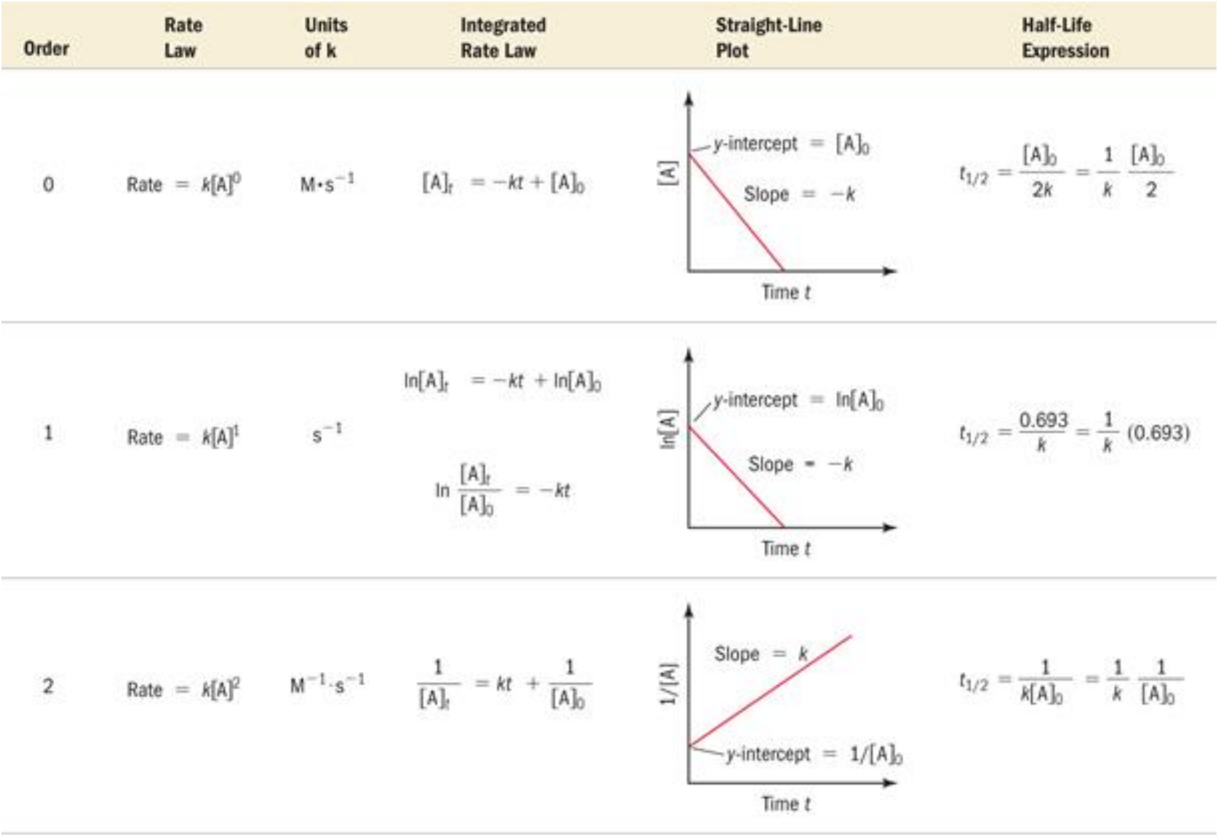


- Not a straight line
- Reaction is not of 1st Order

- A straight line is obtained
- **Reaction is of 2nd Order**

k = slope = 0.255 $M^{-1}s^{-1}$

# SUMMARY OF KINETICS EQUATIONS

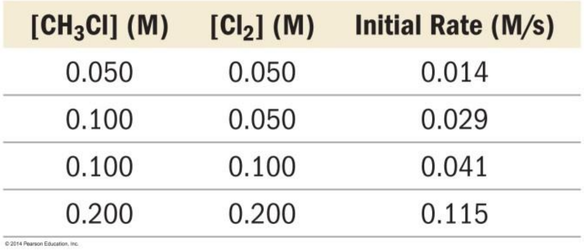


| Order | Rate Law | Units of k | Integrated Rate Law | Straight-Line Plot | Half-Life Expression |
|---|---|---|---|---|---|
| 0 | Rate = $k[A]^0$ | $M \cdot s^{-1}$ | $[A]_t = -kt + [A]_0$ | [A]<br>y-intercept = $[A]_0$<br>Slope = $-k$<br>Time $t$ | $t_{1/2} = \frac{[A]_0}{2k} = \frac{1}{k}\frac{[A]_0}{2}$ |
| 1 | Rate = $k[A]^1$ | $s^{-1}$ | $\ln[A]_t = -kt + \ln[A]_0$<br>$\ln\frac{[A]_t}{[A]_0} = -kt$ | ln[A]<br>y-intercept = $\ln[A]_0$<br>Slope = $-k$<br>Time $t$ | $t_{1/2} = \frac{0.693}{k} = \frac{1}{k}(0.693)$ |
| 2 | Rate = $k[A]^2$ | $M^{-1} \cdot s^{-1}$ | $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$ | 1/[A]<br>Slope = $k$<br>y-intercept = $1/[A]_0$<br>Time $t$ | $t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{k}\frac{1}{[A]_0}$ |

**Examples:**

1. The data shown below was collected for the reaction:

$$CH_3Cl\ (g) + 3\ Cl_2\ (g) \longrightarrow CCl_4\ (g) + 3\ HCl\ (g)$$



| $[CH_3Cl]$ (M) | $[Cl_2]$ (M) | Initial Rate (M/s) |
|---|---|---|
| 0.050 | 0.050 | 0.014 |
| 0.100 | 0.050 | 0.029 |
| 0.100 | 0.100 | 0.041 |
| 0.200 | 0.200 | 0.115 |

Write the rate law and calculate the rate constant for this reaction.

Rate =

k =

**Examples (cont'd):**

2. The reaction shown below is found to be first order with respect to A, second order with respect to B and zero order with respect to C. Answer the following questions based on this information.

$$A + B + C \rightarrow \text{product}$$

a) Write a rate law for this reaction.

b) By what factor does the reaction rate change if the concentrations of all the three reactants double?

c) By what factor does the reaction rate change if the concentration of A is doubled and concentration of B is halved?

3. In a kinetic study of the reaction shown below, the following data were obtained for the initial rates of disappearance of A and B

$$A + 2B \longrightarrow C$$

| **Exp.** | **[A] (M)** | **[B] (M)** | **Initial Rate (M/s)** |
|---|---|---|---|
| 1 | 0.010 | 0.010 | $1.5 \text{ x} 10^{-6}$ |
| 2 | 0.030 | 0.010 | $4.5 \text{ x } 10^{-6}$ |
| 3 | 0.020 | 0.020 | $1.2 \text{ x } 10^{-5}$ |

Write the rate law and calculate the rate constant for this reaction.

Rate =

k =

4. In the presence of excess thiocyanate ion ($SCN^-$) the following reaction is 1st order with respect to $Fe^{3+}$ with a rate constant of $1.27\ s^{-1}$.

$$Fe^{3+}(aq) + SCN^-(aq) \longrightarrow Fe(SCN)^{2+}(aq)$$

   a) What is the Half-Life in seconds?

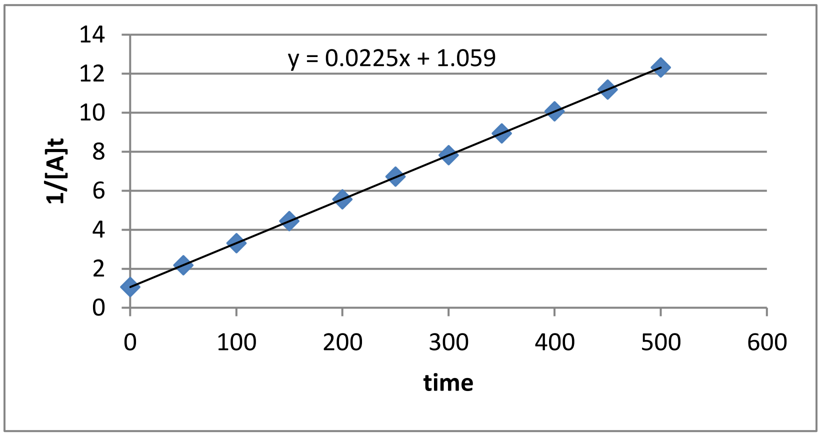
      $t_{1/2} =$

   b) How many seconds would be required for the initial concentration of $Fe^{3+}$ to decrease to each of the following values? (25.0 % and 12.5 %)

   c) How many seconds are required for 90.0% of reaction to be completed?

5. The graph below was prepared for the reaction:

$$AB(g) \longrightarrow A(g) + B(g)$$



   a) Determine the order of the reaction and the value of the rate constant.

   b) Predict the concentration of AB at 25 seconds.

   c) Determine the rate of the reaction when the concentration of AB is 0.10 M?

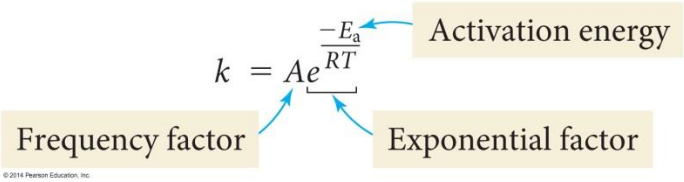
# TEMPERATURE AND RATE

- The rate of reaction depends on temperature, and the rate law for a reaction can be expressed as:

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

- The temperature dependence of the rate is contained in the rate constant (k), which is a constant only when the temperature remains constant.

- An increase in temperature generally results in an increase in k, which results in a faster rate. This relationship is expressed in the Arrhenius equation, which relates the rate constant (k) to the temperature in Kelvin.



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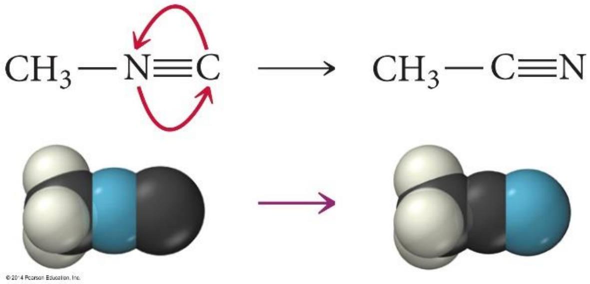
- In this equation,
  - **R** = gas constant (8.314 J/molK)
  - **$E_a$** = Activation energy (energy barrier)
  - **A** = frequency factor (the number of times reactants approach the activation barrier per unit time)

To better understand these factors, we examine the reaction in which $CH_3NC$ (methyl isonitrile) rearranges to form $CH_3CN$ (acetonitrile):



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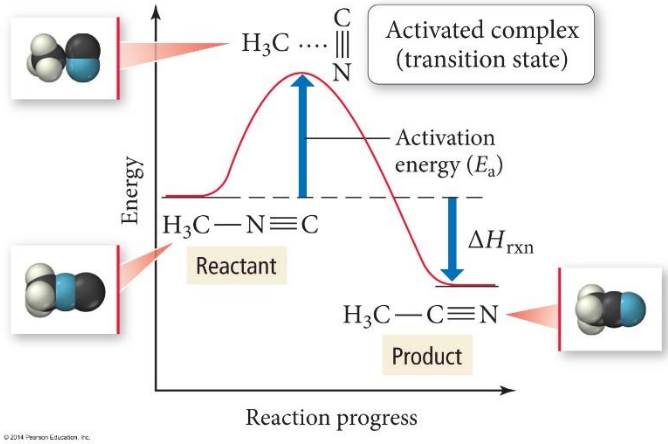
# TEMPERATURE AND RATE

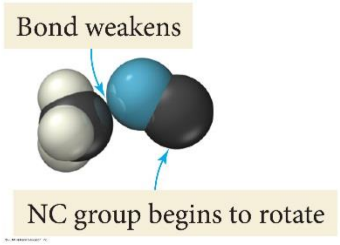
## Activation Energy:

- Activation energy ($E_a$) is defined as the energy barrier that must be overcome for reactants to transform into products.

- To get from reactants to products, the molecule must go through a high energy intermediate state called the ***activated complex*** or ***transition state***.



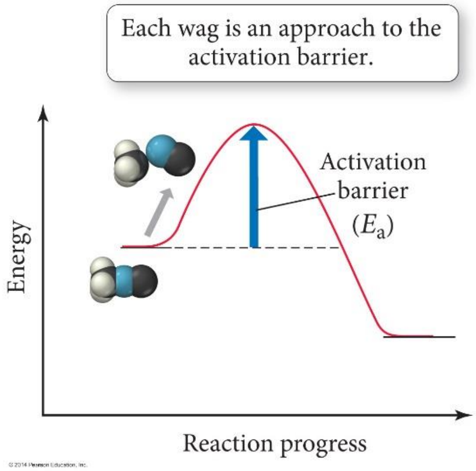
- For transformation of $CH_3NC$ to $CH_3CN$, even though the overall reaction is energetically downhill (exothermic), it must first go uphill (endothermic) to reach the activated complex, because energy is required to initially weaken the $H_3C$–N bond to allow rotation.



## Frequency Factor:

- For this reaction, the frequency factor represents each time the NC part of the molecule begins to rotate (wags) and approaches the activation barrier.

- Note that approaching the activation barrier is not equivalent to overcoming the barrier. Most of the approaches do not have enough energy to overcome the barrier.



# TEMPERATURE AND RATE

## Exponential Factor:

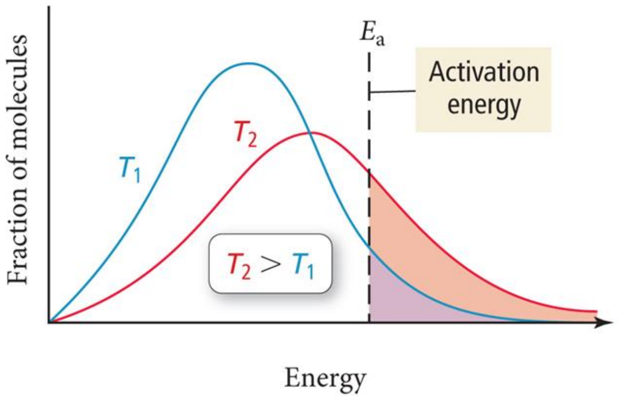
- The exponential factor is a number between 0 and 1 that represents the fraction of molecules that possess enough energy to overcome the activation barrier. The exponential factor is the fraction of approaches that are actually successful and result in the product.

- The exponential factor depends on both the temperature (T) and the activation energy ($E_a$) of the reaction:

$$\text{Exponential factor} = e^{-E_a/RT}$$

- A low activation energy and a high temperature make the negative exponent small, so the exponential factor approaches 1. A high activation energy and a low temperature make the exponent a very large negative number, so the exponential factor becomes small.

- The effect of increase in temperature on the energy of the particles is shown in the diagram below. As the temperature increases, the fraction of molecules with enough energy to surmount the activation energy increases.



## Summarizing Temperature and Reaction Rates:

- ➢ The frequency factor is the number of times the reactants approach the activation barrier per unit time.

- ➢ The exponential factor is the fraction of approaches that are successful in surmounting the activation barrier and forming products.

- ➢ The exponential factor increases with increasing temperature but decreases with increasing activation energy.

# ARRHENIUS PLOTS: DETERMINATION OF A & $E_a$

- The frequency factor (A) and the activation energy ($E_a$) are important quantities in understanding the kinetics of any reaction. These factors can be measured in the laboratory by manipulating and rearranging the Arrhenius equation as shown below:

$$k = A\,e^{-E_a/RT}$$

- Taking natural log of both sides of the equation above,

$$\ln k = \ln (A\,e^{-E_a/RT})$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

- Rearranging the last equation above we can obtain:

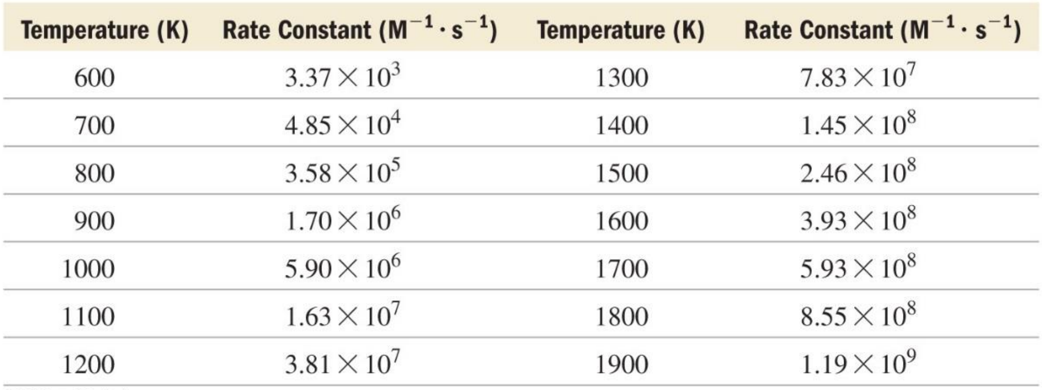
$$\mathbf{\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A}$$

- The equation above is in the form of a straight line. A plot of ***ln k*** vs ***1/T*** (in Kelvin) results a straight line with slope equal to ***–$E_a$/R***. Such plot is called the ***Arrhenius plot*** and is commonly used in the analysis of kinetic data.

**<u>Examples:</u>**

1. The kinetic data, shown below, was collected for the decomposition of ozone. Determine the frequency factor and the activation energy (in kJ/mol) for this reaction.

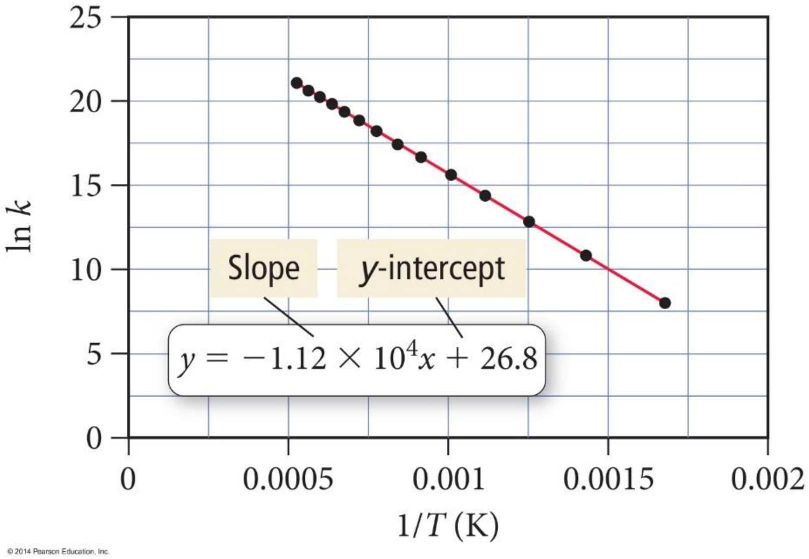
$$O_3\,(g) \rightarrow O_2\,(g) + O\,(g)$$



| Temperature (K) | Rate Constant ($M^{-1} \cdot s^{-1}$) | Temperature (K) | Rate Constant ($M^{-1} \cdot s^{-1}$) |
|---|---|---|---|
| 600 | $3.37 \times 10^3$ | 1300 | $7.83 \times 10^7$ |
| 700 | $4.85 \times 10^4$ | 1400 | $1.45 \times 10^8$ |
| 800 | $3.58 \times 10^5$ | 1500 | $2.46 \times 10^8$ |
| 900 | $1.70 \times 10^6$ | 1600 | $3.93 \times 10^8$ |
| 1000 | $5.90 \times 10^6$ | 1700 | $5.93 \times 10^8$ |
| 1100 | $1.63 \times 10^7$ | 1800 | $8.55 \times 10^8$ |
| 1200 | $3.81 \times 10^7$ | 1900 | $1.19 \times 10^9$ |

**Examples (cont'd):**

To determine A and $E_a$, a plot of ln k vs 1/T is prepared, using the data above.



Activation energy can be calculated from the slope:

$$m = \frac{-E_a}{R} = -1.12\text{x}10^4 \text{ K}$$

$$E_a = -(-1.12\text{x}10^4 \text{ K})(8.314 \text{ J/molK}) = 9.31\text{x}10^4 \text{ J/mol} = 93.1 \text{ kJ/mol}$$

The frequency factor can be determined from the y-intercept:

$$\ln A = 26.8$$

$$A = e^{26.8} = 4.36\text{x}10^{11}$$

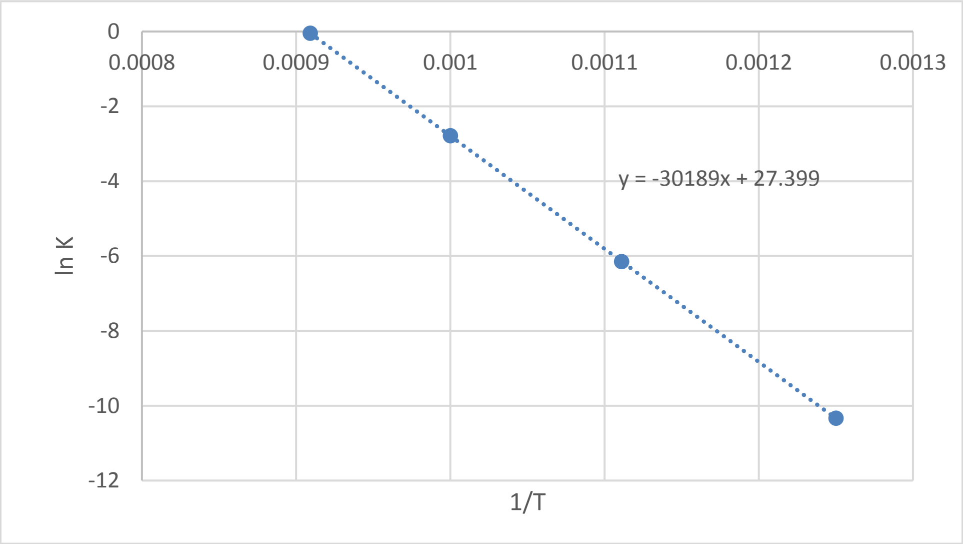
2. Use the results obtained in problem above to determine the rate constant at 298 K for the decomposition of ozone.

**Examples (cont'd):**

3. Reaction A and reaction B have identical frequency factors. However, reaction B has a higher activation energy than reaction A. Which reaction has a greater rate constant at room temperature?

4. Use the Arrhenius plot shown below to determine the frequency factor (A) and activation energy ($E_a$, in kJ/mol) for the first order decomposition of $N_2O$:

$$N_2O\ (g) \rightarrow N_2\ (g) + O\ (g)$$



# COLLISION THEORY

- Earlier we discussed the frequency factor as representing the number of approaches to the activation barrier per unit time. Let's now apply this to a reaction involving two gas-phase reactants:

$$A\ (g) + B\ (g) \rightarrow \text{products}$$

- Based on ***collision theory***, a chemical reaction occurs after a sufficiently energetic collision between two reactant molecules.

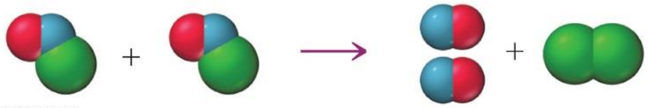
- Furthermore, collision theory separates the frequency factor (A) into two distinct parts, as shown in the equations below:

$$\begin{aligned} k &= Ae^{\frac{-E_a}{RT}} \\ &= \underbrace{p}_{\text{Orientation factor}}\underbrace{z}_{\text{Collision frequency}}e^{\frac{-E_a}{RT}} \end{aligned}$$

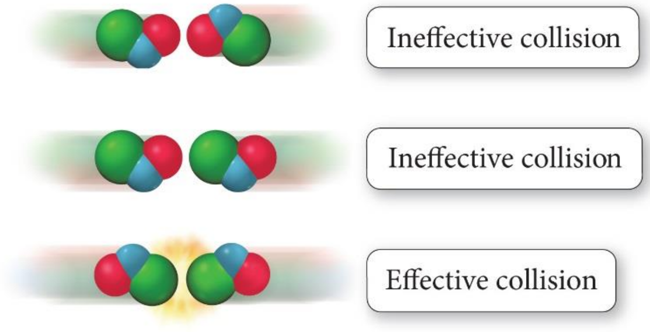
- The collision frequency (z) is the number of collisions that occur per unit time, which can be calculated from the pressure of the gases and the reaction temperature. The orientation factor (p) represents the fraction of the collisions with orientation that allows the reaction to occur.

- The orientation factor can be better understood by considering the reaction shown below:

$$\text{NOCl}(g) + \text{NOCl}(g) \longrightarrow 2\,\text{NO}(g) + \text{Cl}_2(g)$$



- In order for the above reaction to occur, two molecules of sufficient energy and proper orientation must collide. Therefore, as shown below, not all collisions of sufficient energy will lead to products, since they do not possess proper orientation.



# COLLISION THEORY

- Some reactions have orientation factors that are much smaller than one. This indicates that the orientation requirements for these reactions are very stringent, and molecules must be aligned in a very specific way for the reaction to occur. One such example is shown below:

$$H_2\,(g) + CH_2 = CH_2\,(g) \rightarrow CH_3 - CH_3\,(g) \qquad p = 1.7\text{x}10^{-6}$$

- Reactions between atoms usually have orientation factors of approximately 1 because atoms are spherical and thus any orientation will lead to the formation of product.

**Examples:**

1. Which reaction below would you expect to have the smallest orientation factor? Explain.

    a) $H\,(g) + I\,(g) \rightarrow HI\,(g)$

    b) $H_2\,(g) + I_2\,(g) \rightarrow 2\,HI\,(g)$

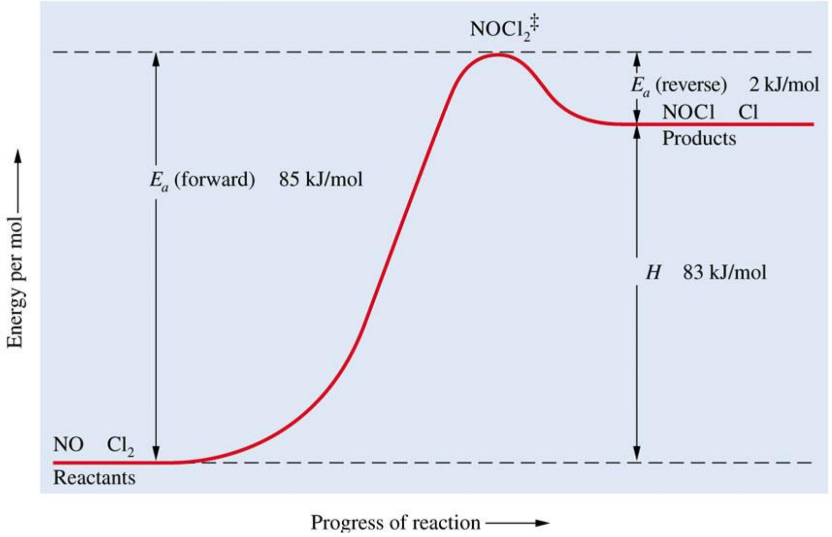
    c) $HCl\,(g) + HCl\,(g) \rightarrow H_2\,(g) + Cl_2\,(g)$

2.

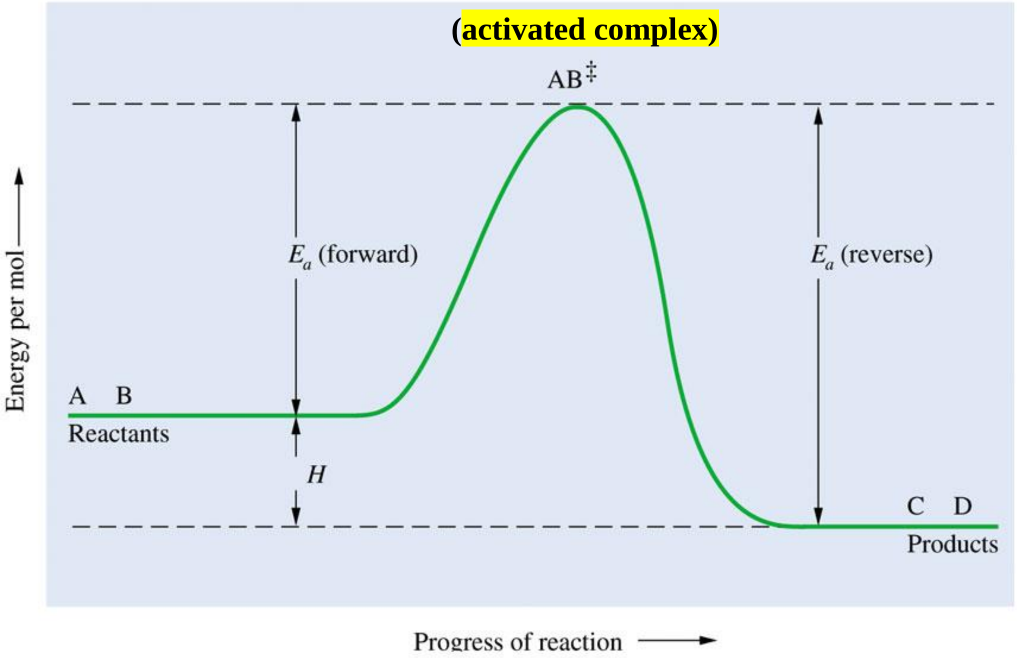
# POTENTIAL – ENERGY DIAGRAMS FOR REACTIONS

- A potential energy diagram shows how the energy of the reactants, activated complex and products are related for an endothermic and for an exothermic reaction.

## ***Endothermic Reactions***

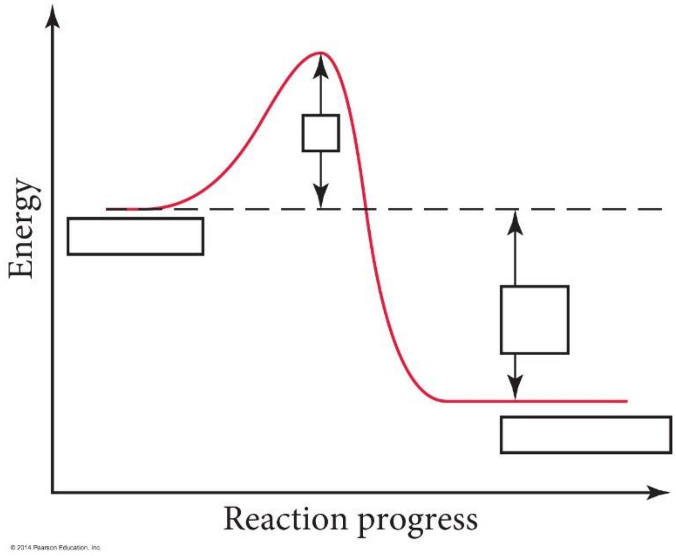

**(activated complex)**

## ***Exothermic Reactions***


**(activated complex)**

**Examples:**

1. The diagram below shows the energy of a reaction as the reaction progresses. Label each blank box in the diagram.



2. Sketch a potential energy diagram for the decomposition of nitrous oxide:

$$2\ N_2O\ (g) \rightarrow 2\ N_2\ (g) + O_2\ (g)$$

The activation energy for the forward reaction is 251 kJ; the ΔH° is +167 kJ. What is the activation energy for the reverse reaction? Label the diagram appropriately.

# REACTION MECHANISMS

- Reaction Mechanisms show the steps involved in the change from Reactants to Products
- Mechanisms consist of a set of "**Elementary Reactions**" whose overall effect is the Net Chemical Equation.

## Elementary Reactions:

- **Elementary reactions** are single molecular events that result in a reaction and are caused by molecular collisions

$NO_2\,(g) + CO\,(g) \longrightarrow NO\,(g) + CO_2\,(g)$ Net Chemical Equation

Below 500K, this reaction takes place in 2 steps:

Elementary Reaction 1: $NO_2 + NO_2 \longrightarrow \underset{\text{Reaction intermediate (short-lived)}}{NO_3} + NO$

Elementary Reaction 2: $NO_3 + CO \longrightarrow NO_2 + CO_2$

- Adding the steps (Elementary Reactions) yields the Overall Equation:

$$\begin{array}{l} \cancel{NO_2}\text{-} + NO_2 \longrightarrow \cancel{NO_3} + NO \\ \cancel{NO_3} + CO \longrightarrow \cancel{NO_2} + CO_2 \\ \hline NO_2 + CO \longrightarrow NO + CO_2 \end{array}$$

Overall Equation

## Examples:

1. The decomposition of Ozone ($O_3$) is believed to occur in 2 steps:

Elementary Reaction 1: $O_3 \rightleftharpoons O_2 + O$

Elementary Reaction 2: $O_3 + O \longrightarrow 2O_2$

Identify any Reaction Intermediate:
What is the Overall equation?

**Examples (cont'd):**

2. Sodium hydrogen carbonate (**$NaHCO_3$**), also called sodium bicarbonate can been synthesized through a sequence of 3 elementary steps:

$$CO_2\ g) \quad + \quad H_2O \rightleftharpoons H_2CO_3\ (aq)$$

$$H_2CO_3\ (aq) \quad + \quad NH_4OH \longrightarrow NH_4HCO_3\ (aq) + H_2O\ (l)$$

$$NH_4HCO_3\ (aq) + NaCl\ (aq) \longrightarrow \mathbf{NaHCO_3\ (s)} + NH_4Cl\ (aq)$$

Identify the Reaction Intermediates:

Write the Overall Equation:

$$CO_2\ g) \quad + \quad H_2O\ (l) \rightleftharpoons H_2CO_3\ (aq)$$

$$H_2CO_3\ (aq) \quad + \quad NH_4OH \longrightarrow NH_4HCO_3\ (aq) + H_2O\ (l)$$

$$NH_4HCO_3\ (aq) + NaCl\ (aq) \longrightarrow \mathbf{NaHCO_3\ (s)} + NH_4Cl\ (aq)$$

# MOLECULARITY

- **Molecularity** is the number of molecules on the reactant side of an Elementary Reaction.

**Unimolecular Reactions:**

- ***Unimolecular*** reactions are Elementary Reactions that involve ***one*** reactant molecule.
- These are commonly the decomposition reactions of unstable species.

$$\underset{\text{excited molecule}}{O_3^*} \longrightarrow O_2 + O$$

**Bimolecular Reactions:**

- ***Bimolecular*** reactions are Elementary Reactions that involve ***two*** reactant molecules.
- These are very common reactions.

$$O{=}N + Cl{-}Cl \longrightarrow O{=}N{-}Cl + Cl$$

**Termolecular Reactions:**

- ***Termolecular*** reactions are Elementary Reactions that involve ***three*** reactant molecules.
- These are less common because the chance of three molecules coming together with the right orientation is unlikely.

**Examples:**

1. What is the molecularity of each of the following elementary reactions?

$O + O_2 + N_2 \longrightarrow O_3 + N_2^*$

$NO_2Cl + Cl \longrightarrow NO_2 + Cl_2$

$Cl + H_2 \longrightarrow HCl + H$

$CS_2 \longrightarrow CS + S$

## Rate Equation for an Elementary Reaction

I. For an Overall Reaction, the Rate Law cannot be predicted by the Overall Equation

Reasons:

- The majority of reactions consist of several elementary steps.
- The Rate Law is the combined result of the elementary steps
- The rate of all the elementary reactions must be known in order to predict the rate law for the overall equation.

II. For an Elementary Reaction, the Rate Law can be written directly from the Elementary Equations

- The rate of an elementary reaction is proportional to the product of the concentrations of each reactant molecule.

1. Unimolecular Elementary Reactions

$A \longrightarrow B + C$ Rate = k [A]

2. Bimolecular Elementary Reactions

$A + B \longrightarrow C + D$ Rate = k [A] [B]

Reason:

- The frequency of collisions is proportional to the number of A molecules ($n_A$) and the number of B molecules ($n_B$)

3. Termolecular Elementary Reactions

$A + B + C \longrightarrow D + E$ Rate = k [A] [B] [C]

**Examples:**

Write Rate Equations for each of the elementary reactions shown below:

1) $O_3 + NO \longrightarrow O_2 + NO_2$

Rate =

2) $CS_2 \longrightarrow CS + S$

Rate =

3) $2NO_2 \longrightarrow N_2O_4$

Rate =

**NOTE:**

- For elementary reactions **ONLY,** the coefficients of the balanced chemical elementary reaction are the exponents to which the concentrations of the reactants are raised.

# THE RATE LAW AND THE MECHANISM

- The Suggested Mechanism for a particular reaction:
  - cannot be observed directly,
  - is a rationalized explanation based on experimental data,
  - is accepted provisionally, and may be replaced by another suggested mechanism based on further experimentation.

- A Suggested Mechanism
  - Is considered **correct** if it **agrees** with the experimentally determined Rate Law
  - Is considered **incorrect** if it **does not agree** with the experimentally determined Rate Law

**Example 1:**

Overall Equation: $2\ NO_2\,(g) + F_2\,(g) \longrightarrow 2\ NO_2F\ (g)$

Experimental Rate Law: Rate = k $[NO_2]\,[F_2]$

NOTE: 1st order with respect to $NO_2$

1st order with respect to $F_2$

2nd order Overall

**Predicted Possible Mechanisms:**

1. One Single Elementary Reaction

$NO_2 + NO_2 + F_2 \longrightarrow 2\ NO_2F$ (Termolecular)

Predicted Rate Law: Rate: k $[NO_2]^2\,[F_2]$

NOTE: 2nd order with respect to $NO_2$

1st order with respect to $F_2$

3rd order overall

- The predicted Rate Law does not agree with the experimental Rate Law

- This mechanism must be incorrect.

## 2. Two Single Elementary Reactions

$$NO_2 + F_2 \xrightarrow{k_1} NO_2F + F \qquad \text{(slow step)}$$

$$NO_2 + F \xrightarrow{k_2} NO_2F \qquad \text{(fast step)}$$

Overall: $2\ NO_2 + F_2 \longrightarrow 2\ NO_2F$

Reaction Intermediate: F

**NOTE:**

- The Rate Law is determined by the slow step
- **THE SLOWEST STEP ——> THE RATE DETERMINING STEP**
- Predicted Rate Law = RATE (rate-determining-step) = $k_1[NO_2]\ [F_2]$

**NOTE:**
1st order with respect to $NO_2$
1st order with respect to $F_2$
2nd order overall

- The predicted Rate Law agrees with the experimental Rate Law
- This mechanism must be correct.

| Predicted Rate Law | Experimental Rate Law |
|---|---|
| Rate $= k_1[NO_2]\ [F_2]$ | Rate $= k\,[NO_2]\ [F_2]$ |

The two Rate Laws are identical if: $k_1 = k$

**Example 2:**

The following mechanism has been proposed for decomposition of ozone to oxygen gas:

$$O_3 \xrightleftharpoons[k_{-1}]{k_1} O_2 + O \qquad \text{(fast equilibrium)}$$

$$O_3 + O \xrightarrow{k_2} 2\ O_2 \qquad \text{(slow)}$$

Determine the Rate Law based on this mechanism.

# CATALYSIS

- Earlier we learned that reaction rates can be increased by various factors, such as increasing concentration or increasing temperature. But sometimes these methods are not feasible. Alternately, reaction rates can also be increased by use of a catalyst.

- A **catalyst** is a substance that speeds up a reaction without being consumed. In theory the catalyst may be used over and over again. In practice, however, there is some loss of catalyst through other reactions that occur at the same time (side-reactions).

- A catalyst works by providing an ***alternate mechanism*** for the reaction–one in which the ***rate-determining step*** has a ***lower activation energy***. For example, consider the noncatalytic destruction of ozone in the upper atmosphere:

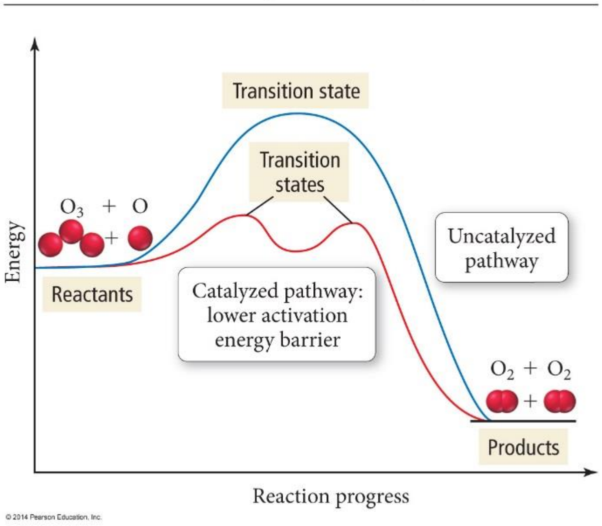
$$O_3\,(g) + O\,(g) \longrightarrow 2\,O_2\,(g)$$

- In this reaction, ozone reacts with an oxygen atom to produce two oxygen molecules. This reaction is slow due to its high activation energy, and therefore proceeds at a fairly slow speed.

- However, the addition of Cl atoms (caused by photodissociation of man-made chlorofluorocarbons) in the upper atmosphere, provide an alternate pathway by which $O_3$ can be destroyed.

- Since this alternate pathway has a lower activation energy than the uncatalyzed pathway, it occurs at a much faster rate.

Energy Diagram for Catalyzed and Uncatalyzed Pathways



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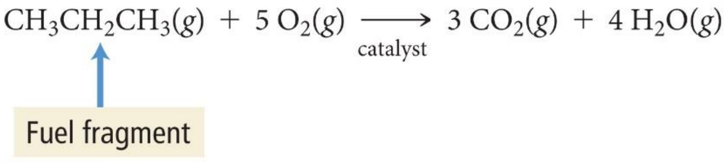
- Although the reaction described above is an undesirable use of a catalyst, many catalysts are used to speed up desirable reactions. For example, the catalytic converter in your car is used to convert harmful exhaust pollutants such as nitrogen monoxide and carbon monoxide into less harmful substances:

$$2\,NO\,(g) + 2\,CO\,(g) \xrightarrow{\text{catalyst}} N_2\,(g) + 2\,CO_2\,(g)$$

- The catalytic converter also promotes the complete combustion of any fuel fragments present in the exhaust, preventing potential formation of air pollutants in the atmosphere.



$$CH_3CH_2CH_3(g) + 5\,O_2(g) \xrightarrow[\text{catalyst}]{} 3\,CO_2(g) + 4\,H_2O(g)$$

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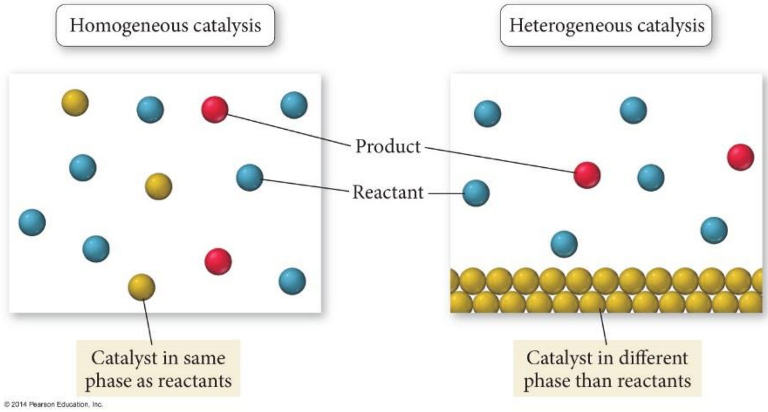
# HOMOGENEOUS & HETEROGENEOUS CATALYSIS

- Catalysts can be categorized into two types: homogeneous and heterogeneous.

- In **homogeneous catalysis** the catalyst exists in the same phase (state) as the reactants. The catalyzed destruction of ozone by Cl is an example of this type of catalysis.

- In **heterogeneous catalysis** the catalyst exists in a different phase than the reactants. The solid catalysts used in the automobile catalytic converters is an example of this type of catalysis.



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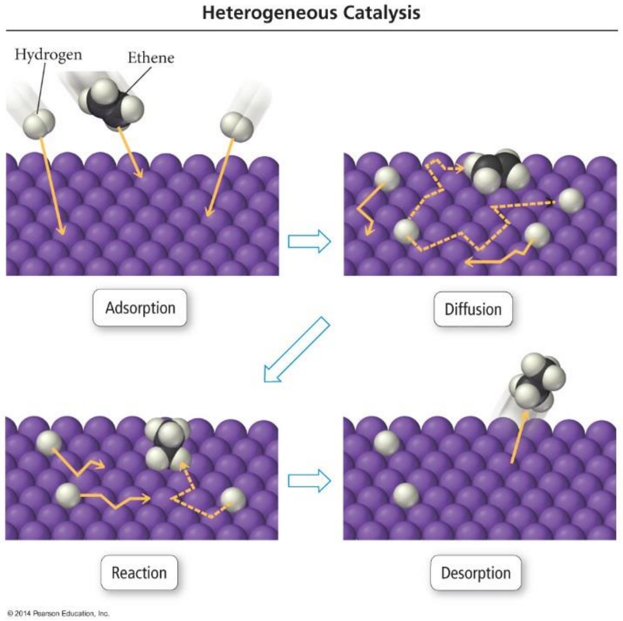
- Another example of heterogeneous catalysis is the ***hydrogenation*** of double bonds in alkenes. For example, the reaction between ethene and hydrogen is a relatively slow reaction at normal temperatures:

$$H_2C = CH_2\ (g)\ +\ H_2\ (g) \longrightarrow H_3C - CH_3\ (g)$$

- However, in presence of a catalyst, the reaction occurs rapidly. The catalysis occurs by the four-step process shown below.

- The large activation energy of the hydrogenation reaction–due primarily to the strength of the hydrogen-hydrogen bond in $H_2$– is greatly lowered when the reactants adsorb onto the surface of the catalyst.



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# ENZYME CATALYSIS

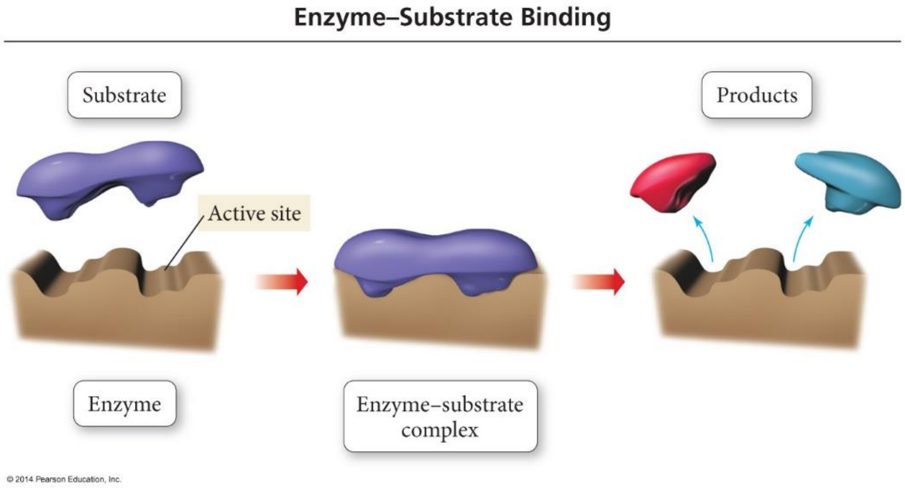
- ***Enzymes*** are the catalysts of biological organisms.

- Enzymes are large protein molecules that are ***highly specific*** sites in their structure, called ***active sites***. The properties and shape of the active site is just right to bind the reactant molecule, called the ***substrate***.

- The general mechanism by which an enzyme (E) binds a substrate (S) and then reacts to form the products (P) is:

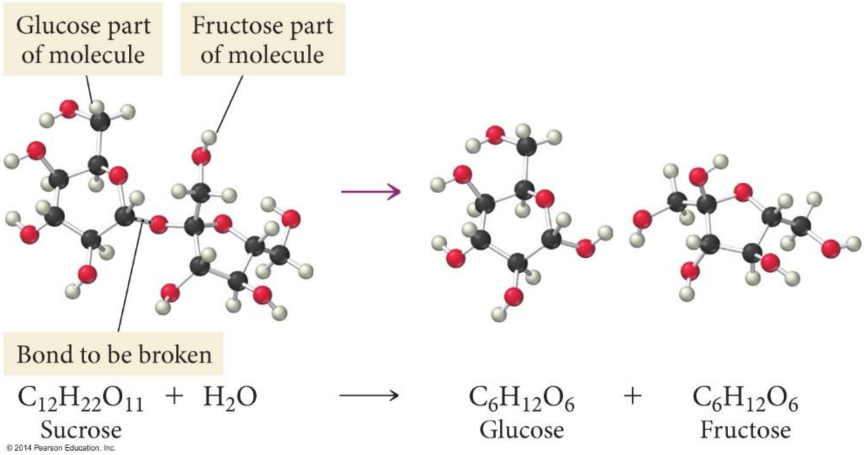
$$E + S \rightleftharpoons ES \qquad \text{Fast}$$

$$ES \longrightarrow E + P \qquad \text{Slow, rate determining}$$



Enzyme–Substrate Binding

- Breakdown of sucrose (table sugar) into glucose and fructose in the body, a slow reaction at normal body temperatures, is facilitated by the catalysis with the enzyme sucrase.



$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

## Answers to In-Chapter Problems:

| ***Page*** | ***Example No.*** | ***Answer*** |
|---|---|---|
| 4 | 1 | $\text{Rate} = -\frac{1}{3}\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{\Delta t} = \frac{1}{2}\frac{\Delta[C]}{\Delta t} = \frac{1}{4}\frac{\Delta[D]}{\Delta t}$ |
| | 2 | a) $4.40\text{x}10^{-3}$ M/s b) $-8.80\text{x}10^{-3}$ M/s |
| 5 | 4 | $8.7\text{x}10^{-3}$ M/s b) $1.4\text{x}10^{-2}$ M/s |
| | 5 | c |
| 12 | 2A | Rate = $k[A]^2$ |
| | 2B | $k = 4.0\text{x}10^{-3}$ $M^{-1}s^{-1}$ |
| | 2C | Rate (4) = $1.0\text{x}10^{-5}$ M/s |
| 13 | 3 | c |
| | 4 | a) First order b) $k = 0.010\ s^{-1}$ |
| 15 | 3 | 0.0277 M |
| 17 | 2 | 79.2 s |
| | 3 | $6.8\text{x}10^{8}$ yrs |
| 19 | 1 | $5.78\text{x}10^{-2}$ M |
| | 2 | 1st order $k=0.0461\ hr^{-1}$ |
| 24 | 1 | Rate = $k[CH_3Cl][Cl_2]^{1/2}$ $k = 1.3\ M^{-1/2}\ s^{-1}$ |
| 25 | 2 | a) Rate = $k[A][B]^2$ b) 8 c) ½ |
| | 3 | Rate = $k[A][B]^2$ ; $k = 1.5\ M^{-2}s^{-1}$ |
| 26 | 4 | a) $t_{1/2} = 0.546$ s b) t = 1.09 s (25%); 1.64 s (12.5%)<br>c) t = 1.81 s |
| | 5 | a) 2nd order; $k = 2.25\text{x}10^{-2}\ M^{-1}s^{-1}$ b) [AB]= 0.617 M<br>c) $2.25\text{x}10^{-4}$ M/s |
| 31 | 2 | $2.09\text{x}10^{-5}\ M^{-1}s^{-1}$ |
| 32 | 3 | Reaction A is faster and therefore has a larger rate constant |
| | 4 | $E_a = 251$ kJ/mol A= $7.93\text{x}10^{11}$ |
| 34 | 1 | c |
| 36 | 2 | $E_a$ (reverse rxn) = 84 kJ |