

Unit 5: CHEMICAL KINETICS AND EQUILIBRIA

Chapter 13: Chemical Kinetics

13.1: The Rate of a Reaction

Chemical Kinetics: - the branch of chemistry that studies the how fast reaction proceeds.

Reaction Rates: - the speed of which the concentration of a reactant or product changes per unit of time.
 - unit is in **mol/(L • s)** or **mol/(L • min)**

$$\text{Rate} = \frac{\Delta[A]}{\Delta t} = \frac{\text{Concentration A at } t_2 - \text{Concentration A at } t_1}{t_2 - t_1}$$

Average Rate: - like average speed, it is the change in concentration per interval of time.

Instantaneous Rate: - like instantaneous speed, it is the change in concentration at a particular time.

Example 1: The concentrations of the reactant and product of the reaction, $A \rightarrow 2 B$, are recorded below.

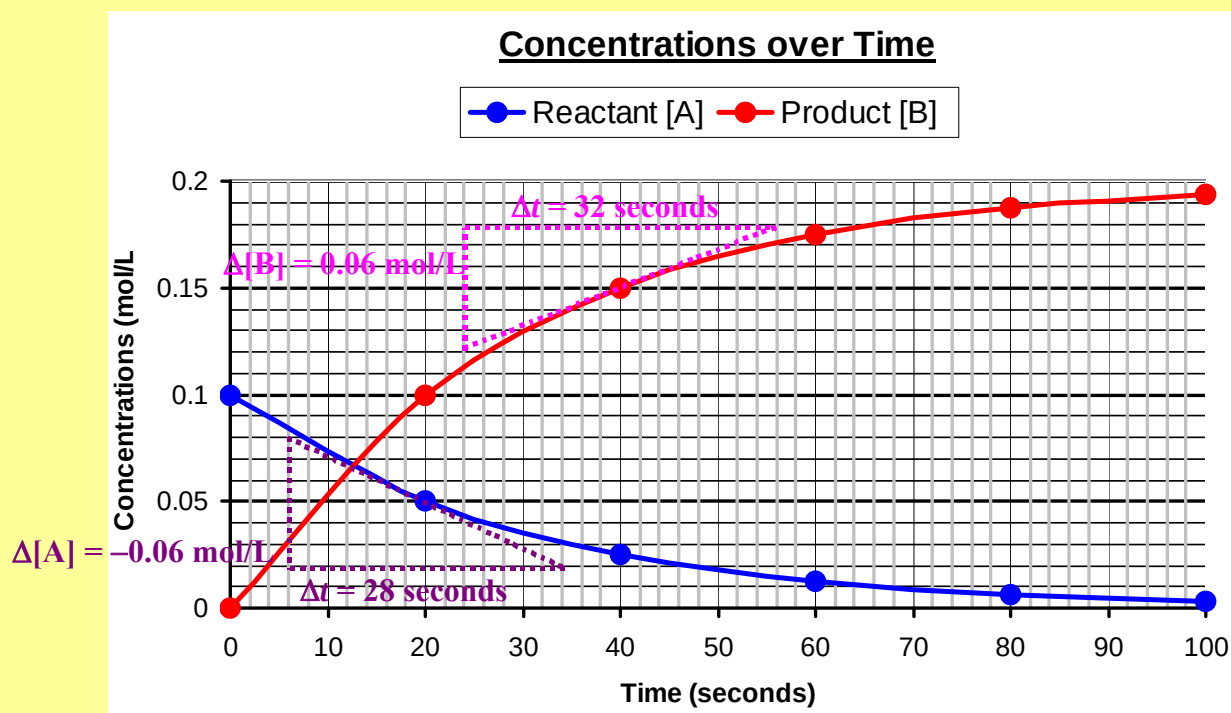
- Determine the average reaction rates for each time interval.
- Graph concentrations versus time for both reactant and product.
- Find the instantaneous reaction rates of reactant A at 20 seconds and product B at 40 seconds.

Time (seconds)	Reactant [A]	Product [B]
0	0.1	0
20	0.05	0.1
40	0.025	0.15
60	0.0125	0.175
80	0.0063	0.1875
100	0.0031	0.1938

a. Average Reaction Rates (Note: Reactant Rate is Negative because A is consumed.)

Time Intervals (seconds)	Reactant Rate = $\frac{\Delta[A]}{\Delta t}$ (mol/(L • s))	Product Rate = $\frac{\Delta[B]}{\Delta t}$ (mol/(L • s))
0.00 to 20.00	$\frac{(0.05 - 0.1) \text{ mol/L}}{(20.00 - 0.00) \text{ s}} = -0.002500$	$\frac{(0.1 - 0) \text{ mol/L}}{(20.00 - 0.00) \text{ s}} = 0.005000$
20.00 to 40.00	$\frac{(0.025 - 0.05) \text{ mol/L}}{(40.00 - 20.00) \text{ s}} = -0.001250$	$\frac{(0.15 - 0.1) \text{ mol/L}}{(40.00 - 20.00) \text{ s}} = 0.002500$
40.00 to 60.00	$\frac{(0.0125 - 0.025) \text{ mol/L}}{(60.00 - 40.00) \text{ s}} = -0.000625$	$\frac{(0.175 - 0.15) \text{ mol/L}}{(60.00 - 40.00) \text{ s}} = 0.001250$
60.00 to 80.00	$\frac{(0.0063 - 0.0125) \text{ mol/L}}{(80.00 - 60.00) \text{ s}} = -0.000310$	$\frac{(0.1875 - 0.175) \text{ mol/L}}{(80.00 - 60.00) \text{ s}} = 0.000625$
80.00 to 100.00	$\frac{(0.0031 - 0.0063) \text{ mol/L}}{(100.00 - 80.00) \text{ s}} = -0.000160$	$\frac{(0.1938 - 0.1875) \text{ mol/L}}{(100.00 - 80.00) \text{ s}} = 0.000315$

b. Concentrations versus Time Graph.



c. Instantaneous Rates

$$\text{Reactant Rate} = \frac{\Delta[A]}{\Delta t} = \frac{-0.06 \text{ mol/L}}{28 \text{ s}}$$

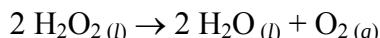
$$\text{Reactant [A] Rate} = -0.002143 \text{ mol/(L} \cdot \text{s)}$$

$$\text{Product Rate} = \frac{\Delta[B]}{\Delta t} = \frac{0.06 \text{ mol/L}}{32 \text{ s}}$$

$$\text{Product [B] Rate} = 0.001875 \text{ mol/(L} \cdot \text{s)}$$

Determining Rates Using Pressure

If a reaction starts from a solid or a liquid were to generate a gas, we can determine the rate of the reaction by measuring pressures instead of concentrations at various times. Consider the decomposition of $\text{H}_2\text{O}_2(l)$



We can measure the pressure of $\text{O}_2(g)$ generated to find the rate by using the Ideal Gas Law, $PV = nRT$.

$$P = \frac{n}{V} RT \rightarrow P_{\text{oxygen}} = [\text{O}_2]RT \rightarrow [\text{O}_2] = \frac{P_{\text{O}_2}}{RT}$$

$$\text{Rate} = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{RT} \left(\frac{\Delta P_{\text{O}_2}}{\Delta t} \right)$$

Rate Constant (k): - a constant of proportionality between reaction rate and the concentration of reactant.

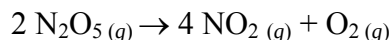
- as the concentration of reactant increases, the reaction rate increases due to more chances for collisions to occur between reactants and hence the speed of the reaction increases. However, rate constant will remain the same.
- the unit of the rate constant depends on the overall order of the reaction (explains in next section).

For a reaction: $A \rightarrow B$

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

$$\text{Rate} = kP_A$$

$$k = \text{rate constant} \quad k = \frac{\text{Rate}}{[A]} \quad k = \frac{\text{Rate}}{P_A}$$

*(Note: Both reaction rates are positive because they are net consumption rates.)**(The Rate Equation can follow many different form – more explanations in the next section)***Example 2:** Dinitrogen pentaoxide decomposes into nitrogen dioxide and oxygen gases as follows.

An experiment was conducted at different initial concentrations and the rate after 1.00 minute was calculated from the final concentration as shown below. Determine the rate constant of this reaction.

	Initial $[\text{N}_2\text{O}_5]$	Rate (mol/L • s)
Trial 1	0.100 mol/L	2.3×10^{-4}
Trial 2	0.050 mol/L	1.2×10^{-4}
Trial 3	0.025 mol/L	5.9×10^{-5}

$$\begin{aligned}
 \text{Trial 1: } k_1 &= \frac{\text{Rate}_1}{[\text{N}_2\text{O}_5]_{0,1}} = \frac{2.3 \times 10^{-4} \text{ mol/(L} \cdot \text{s)}}{0.100 \text{ mol/L}} & k_1 &= 2.3 \times 10^{-3} \text{ s}^{-1} \\
 \text{Trial 2: } k_2 &= \frac{\text{Rate}_2}{[\text{N}_2\text{O}_5]_{0,2}} = \frac{1.2 \times 10^{-4} \text{ mol/(L} \cdot \text{s)}}{0.050 \text{ mol/L}} & k_2 &= 2.4 \times 10^{-3} \text{ s}^{-1} \\
 \text{Trial 3: } k_3 &= \frac{\text{Rate}_3}{[\text{N}_2\text{O}_5]_{0,3}} = \frac{5.9 \times 10^{-4} \text{ mol/(L} \cdot \text{s)}}{0.025 \text{ mol/L}} & k_3 &= 2.4 \times 10^{-3} \text{ s}^{-1}
 \end{aligned}
 \left. \vphantom{\begin{aligned} \text{Trial 1: } k_1 \\ \text{Trial 2: } k_2 \\ \text{Trial 3: } k_3 \end{aligned}} \right\} k_{\text{avg}} = 2.4 \times 10^{-3} \text{ s}^{-1}$$

Note that the $k_1 \approx k_2 \approx k_3$. For other reactions, k would be calculated in a similar but slightly different way depending on the order of the reaction (explains in next section).**Relationship between Molar Quantities and Reaction Rates**For any chemical equation, $aA + bB \rightarrow cC + dD$,

$$\text{Rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

Example 3: For the reaction $\text{N}_2 (g) + 3 \text{Cl}_2 (g) \rightarrow 2 \text{NCl}_3 (g)$, what is the rate of consumption of N_2 and Cl_2 if the rate of production of NCl_3 is $0.453 \text{ mol/(L} \cdot \text{s)}$?

$$\begin{aligned}
 \text{Rate of } \text{N}_2 &= \frac{\Delta[\text{N}_2]}{\Delta t} = -\frac{\Delta[\text{N}_2]}{\Delta t} = -\frac{1}{3} \frac{\Delta[\text{Cl}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NCl}_3]}{\Delta t} \\
 \text{Rate of } \text{Cl}_2 &= \frac{\Delta[\text{Cl}_2]}{\Delta t} = \frac{\Delta[\text{N}_2]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{NCl}_3]}{\Delta t} = -\frac{1}{2} (0.453 \text{ mol/(L} \cdot \text{s)}) \\
 \text{Rate of } \text{NCl}_3 &= \frac{\Delta[\text{NCl}_3]}{\Delta t} = \frac{\Delta[\text{Cl}_2]}{\Delta t} = -\frac{3}{2} \frac{\Delta[\text{NCl}_3]}{\Delta t} = -\frac{3}{2} (0.453 \text{ mol/(L} \cdot \text{s)})
 \end{aligned}$$

Rate of $\text{N}_2 = 0.227 \text{ mol/(L} \cdot \text{s)}$
 Rate of $\text{Cl}_2 = 0.680 \text{ mol/(L} \cdot \text{s)}$

Assignment**13.1 pg. 589 #1 to 3, 5 to 8**

13.2: The Rate Law

Rate Law: - a reaction rate where it is depended solely on the concentrations of the reactants with the assumption that it is an irreversible reaction.

Two Kinds of Rate Laws:

1. **Differential Rate Law:** - sometimes called rate law, which relates the reaction rate on reactants' concentrations only.
2. **Integrated Rate Law:** - the rate law that relates the concentration of the chemical species with time.
- it is derived by integrating the differential rate law with respect of concentration and time (explains in the next section).

Order (n): - the rational exponent of the reactant's concentration in the rate law as determined by experimentation. **(It is NOT the coefficient of the chemicals.)**

Rate Laws

Single Reactant: $Rate = k[A]^n$
Multiple Reactants: $Rate = k[A]^n[B]^m$

k = rate constant n and m = order of a particular reactant
(Note: Both reaction rates are positive because they are net consumption rates.)

Overall Rate Order: - the sum of all orders of all reactants.

Example 1: For the following rate laws, determine their overall rate order and the unit of the rate constant.

a. $Rate = k[A]$

$n = 1$ (First order)

$$k = \frac{Rate}{[A]} = \frac{\text{mol}/(\text{L} \cdot \text{s})}{\text{mol}/\text{L}} = \text{s}^{-1}$$

b. $Rate = k[A]^2$

$n = 2$ (Second order)

$$k = \frac{Rate}{[A]^2} = \frac{\text{mol}/(\text{L} \cdot \text{s})}{(\text{mol}/\text{L})^2} = \text{L}/(\text{mol} \cdot \text{s})$$

c. $Rate = k[A][B]$

$n + m = 1 + 1 = 2$
 (Second order)

$$k = \frac{Rate}{[A][B]} = \frac{\text{mol}/(\text{L} \cdot \text{s})}{(\text{mol}/\text{L})^2}$$

$$k = \text{L}/(\text{mol} \cdot \text{s})$$

d. $Rate = k[A]^2[B]$

$n + m = 2 + 1 = 3$
 (Third order)

$$k = \frac{Rate}{[A]^2[B]} = \frac{\text{mol}/(\text{L} \cdot \text{s})}{(\text{mol}/\text{L})^2(\text{mol}/\text{L})}$$

$$k = \text{L}^2/(\text{mol}^2 \cdot \text{s})$$

e. $Rate = k$

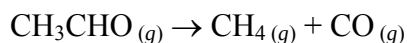
$n = 0$ (Zero order)
 $k = \text{mol}/(\text{L} \cdot \text{s})$

Initial Rate ($[A]_0$): - the instantaneous reaction rate at the beginning instant ($t = 0$) of the reaction.
 - for a single reactant, its order can be found by the instantaneous reaction rates and its concentrations at two different times.

Determining Rate Law of a Single Reactant using Instantaneous Rates

$$\frac{Rate\ 2}{Rate\ 1} = \frac{k[A]_{t_2}^n}{k[A]_{t_1}^n} = \left(\frac{[A]_{t_2}}{[A]_{t_1}} \right)^n$$

Example 2: The decomposition of acetaldehyde (ethanal) at 298 K yields the following kinetic data.



Time (seconds)	$[\text{CH}_3\text{CHO}_{(g)}]$ (mol/L)	Instantaneous Rate (mol/(L • s))
0.000	0.400	1.4
0.095	0.300	0.79
0.286	0.200	0.35
0.857	0.100	0.088

- Determine the rate law and the rate constant.
- Graph the concentration versus time plot for the decomposition of $\text{CH}_3\text{CHO}_{(g)}$.
- Calculate the reaction rate when the concentration of acetaldehyde is 0.250 mol/L.

a. To find Rate Law, pick any two concentrations and rates

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k[\text{CH}_3\text{CHO}]_{0,t_2}^n}{k[\text{CH}_3\text{CHO}]_{0,t_1}^n} \quad \frac{0.79}{1.4} = \frac{k(0.300)^n}{k(0.400)^n}$$

$$0.5642857143 = (0.75)^n$$

$$\log(0.5642857143) = n \log(0.75)$$

$$\frac{\log(0.5642857143)}{\log(0.75)} = n$$

$$n = 1.98898237 \approx 2$$

$$\text{Rate} = k[\text{CH}_3\text{CHO}]^2 \quad (\text{Overall } 2^{\text{nd}} \text{ Order})$$

To calculate the Rate Constant, pick any one of the concentrations and rates.

$$\text{Rate} = k[\text{CH}_3\text{CHO}]^2$$

$$1.4 = k(0.400 \text{ mol/L})^2$$

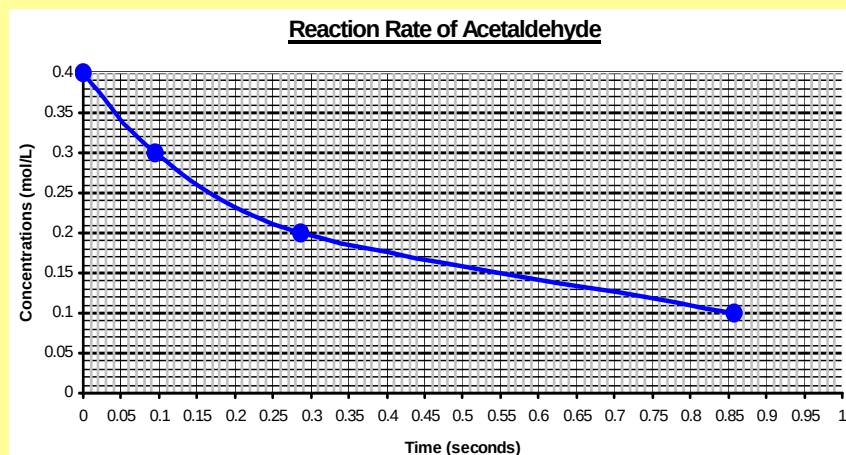
$$\frac{1.4 \text{ mol/(L} \cdot \text{s)}}{(0.400 \text{ mol/L})^2} = k$$

$$k = 8.75 \text{ L/(mol} \cdot \text{s)}$$

$$\text{Rate} = (8.75 \text{ L/(mol} \cdot \text{s)})[\text{CH}_3\text{CHO}]^2$$

(The negative sign in k is dropped because we know reactant rate is one of consumption.)

b. Concentration versus Time Graph



c. When $[\text{CH}_3\text{CHO}_{(g)}] = 0.250 \text{ mol/L}$,

$$\text{Rate} = (8.75 \text{ L/(mol} \cdot \text{s)})[\text{CH}_3\text{CHO}]^2$$

$$\text{Rate} = (8.75 \text{ L/(mol} \cdot \text{s)})(0.250)^2 \text{ mol}^2/\text{L}^2$$

$$\text{Rate} = 0.547 \text{ mol/(L} \cdot \text{s)}$$

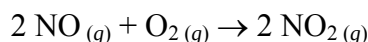
- Method of Initial Rates:** - the use of initial rate(s) to determine the overall rate order of the reaction.
- for x number of reactants, we will need at least $(x + 1)$ number of experiments with various initial rates and initial concentrations.
 - the order of a particular reactant is determined by dividing the initial rates of the two experiments with different initial concentrations of that particular reactant, while having the same initial concentrations of other reactants.

Determining Rate Law of Multiple Reactants using Initial Rates

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k[A]_{0, \text{exp 2}}^n [B]_{0, \text{exp 2}}^m}{k[A]_{0, \text{exp 1}}^n [B]_{0, \text{exp 1}}^m} = \left(\frac{[A]_{0, \text{exp 2}}}{[A]_{0, \text{exp 1}}} \right)^n \quad \text{where } [B]_{0, \text{exp 1}} = [B]_{0, \text{exp 2}}$$

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{k[A]_{0, \text{exp 3}}^n [B]_{0, \text{exp 3}}^m}{k[A]_{0, \text{exp 1}}^n [B]_{0, \text{exp 1}}^m} = \left(\frac{[B]_{0, \text{exp 3}}}{[B]_{0, \text{exp 1}}} \right)^m \quad \text{where } [A]_{0, \text{exp 3}} = [A]_{0, \text{exp 1}}$$

Example 3: The formation of nitrogen dioxide from the combustion of nitrogen monoxide at 660 K gives the following kinetic data. Determine the rate law and the rate constant.



Experiment	[NO _(g)] (mol/L)	[O _{2(g)}] (mol/L)	Measured Initial Rate (mol/(L • s))
1	0.010	0.010	2.5×10^{-5}
2	0.020	0.010	1.0×10^{-4}
3	0.010	0.020	5.0×10^{-5}

To find Rate Law, we first have to pick the two concentrations and rates where [O₂] stays constant.

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k[\text{NO}]_{0, \text{exp 2}}^n [\text{O}_2]_{0, \text{exp 2}}^m}{k[\text{NO}]_{0, \text{exp 1}}^n [\text{O}_2]_{0, \text{exp 1}}^m} \quad \frac{1.0 \times 10^{-4}}{2.5 \times 10^{-5}} = \frac{k(0.020 \text{ mol/L})^n (0.010 \text{ mol/L})^m}{k(0.010 \text{ mol/L})^n (0.010 \text{ mol/L})^m}$$

$$4 = (2)^n \quad n = 2$$

Then, we have to pick the two concentrations and rates where [NO] stays constant.

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{k[\text{NO}]_{0, \text{exp 3}}^n [\text{O}_2]_{0, \text{exp 3}}^m}{k[\text{NO}]_{0, \text{exp 1}}^n [\text{O}_2]_{0, \text{exp 1}}^m} \quad \frac{5.0 \times 10^{-5}}{2.5 \times 10^{-5}} = \frac{k(0.010 \text{ mol/L})^n (0.020 \text{ mol/L})^m}{k(0.010 \text{ mol/L})^n (0.010 \text{ mol/L})^m}$$

$$2 = (2)^m \quad m = 1$$

$$\text{Rate} = k[\text{NO}]^2[\text{O}_2] \quad (\text{Overall 3}^{\text{rd}} \text{ Order})$$

To calculate the Rate Constant, we can pick the concentration and rate from any experiment.

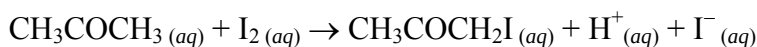
$$\text{Rate} = k[\text{NO}]^2[\text{O}_2]$$

$$2.5 \times 10^{-5} \text{ mol/(L} \cdot \text{s)} = k(0.010 \text{ mol/L})^2(0.010 \text{ mol/L})$$

$$\frac{2.5 \times 10^{-5} \text{ mol/(L} \cdot \text{s)}}{(0.010 \text{ mol/L})^2(0.010 \text{ mol/L})} = k \quad k = 25 \text{ L}^2/(\text{mol}^2 \cdot \text{s)}$$

$$\text{Rate} = (25 \text{ L}^2/(\text{mol}^2 \cdot \text{s}))[\text{NO}]^2[\text{O}_2]$$

Example 4: The reaction rate of the acetone iodination not only depends on the concentrations of the reactants, but it also relates to the concentration of the $\text{H}^+_{(\text{aq})}$ ion. The rate law has a format of $\text{Rate} = k[\text{CH}_3\text{COCH}_3]^n[\text{I}_2]^m[\text{H}^+]^p$. Several experiments were done at 298 K and the initial rates of the reaction are measured. Using the data below, find the final rate law and the rate constant.



Experiment	$[\text{CH}_3\text{COCH}_3_{(\text{aq})}]$	$[\text{I}_{2(\text{aq})}]$	$[\text{H}^+_{(\text{aq})}]$	Measured Initial Rate (mol/(L • s))
1	0.80 mol/L	0.001 mol/L	0.20 mol/L	4.2×10^{-6}
2	1.6 mol/L	0.001 mol/L	0.20 mol/L	8.4×10^{-6}
3	0.80 mol/L	0.001 mol/L	0.40 mol/L	8.4×10^{-6}
4	0.80 mol/L	0.0005 mol/L	0.20 mol/L	4.2×10^{-6}

To find Rate Law, we first have to pick the two concentrations and rates where $[\text{I}_2]$ and $[\text{H}^+]$ stay constant.

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k[\text{CH}_3\text{COCH}_3]_{0, \text{exp 2}}^n [\text{I}_2]_{0, \text{exp 2}}^m [\text{H}^+]_{0, \text{exp 2}}^p}{k[\text{CH}_3\text{COCH}_3]_{0, \text{exp 1}}^n [\text{I}_2]_{0, \text{exp 1}}^m [\text{H}^+]_{0, \text{exp 1}}^p} = \frac{8.4 \times 10^{-6}}{4.2 \times 10^{-6}} = \frac{k(1.6 \text{ mol/L})^n (0.001 \text{ mol/L})^m (0.20 \text{ mol/L})^p}{k(0.80 \text{ mol/L})^n (0.001 \text{ mol/L})^m (0.20 \text{ mol/L})^p}$$

$$2 = (2)^n \quad n = 1$$

To find Rate Law, we first have to pick the two concentrations and rates where $[\text{CH}_3\text{COCH}_3]$ and $[\text{H}^+]$ stay constant.

$$\frac{\text{Rate 4}}{\text{Rate 1}} = \frac{k[\text{CH}_3\text{COCH}_3]_{0, \text{exp 4}}^n [\text{I}_2]_{0, \text{exp 4}}^m [\text{H}^+]_{0, \text{exp 4}}^p}{k[\text{CH}_3\text{COCH}_3]_{0, \text{exp 1}}^n [\text{I}_2]_{0, \text{exp 1}}^m [\text{H}^+]_{0, \text{exp 1}}^p} = \frac{4.2 \times 10^{-6}}{4.2 \times 10^{-6}} = \frac{k(0.80 \text{ mol/L})^n (0.0005 \text{ mol/L})^m (0.20 \text{ mol/L})^p}{k(0.80 \text{ mol/L})^n (0.001 \text{ mol/L})^m (0.20 \text{ mol/L})^p}$$

$$1 = (0.5)^m \quad m = 0$$

To find Rate Law, we first have to pick the two concentrations and rates where $[\text{I}_2]$ and $[\text{CH}_3\text{COCH}_3]$ stay constant.

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{k[\text{CH}_3\text{COCH}_3]_{0, \text{exp 3}}^n [\text{I}_2]_{0, \text{exp 3}}^m [\text{H}^+]_{0, \text{exp 3}}^p}{k[\text{CH}_3\text{COCH}_3]_{0, \text{exp 1}}^n [\text{I}_2]_{0, \text{exp 1}}^m [\text{H}^+]_{0, \text{exp 1}}^p} = \frac{8.4 \times 10^{-6}}{4.2 \times 10^{-6}} = \frac{k(0.80 \text{ mol/L})^n (0.001 \text{ mol/L})^m (0.40 \text{ mol/L})^p}{k(0.80 \text{ mol/L})^n (0.001 \text{ mol/L})^m (0.20 \text{ mol/L})^p}$$

$$2 = (2)^p \quad p = 1$$

$$\text{Rate} = k[\text{CH}_3\text{COCH}_3]^1 [\text{I}_2]^0 [\text{H}^+]^1$$

$$\text{Rate} = k[\text{CH}_3\text{COCH}_3][\text{H}^+] \quad (\text{Overall 2}^{\text{nd}} \text{ Order})$$

To calculate the Rate Constant, we can pick the concentration and rate from any experiment.

$$\begin{aligned} \text{Rate} &= k[\text{CH}_3\text{COCH}_3][\text{H}^+] \\ 4.2 \times 10^{-6} \text{ mol/(L} \cdot \text{s)} &= k(0.80 \text{ mol/L})(0.20 \text{ mol/L}) \\ \frac{4.2 \times 10^{-6} \text{ mol/(L} \cdot \text{s)}}{(0.80 \text{ mol/L})(0.20 \text{ mol/L})} &= k \end{aligned}$$

$$k = 2.625 \times 10^{-5} \text{ L/(mol} \cdot \text{s)}$$

$$\text{Rate} = (2.625 \times 10^{-5} \text{ L/(mol} \cdot \text{s)})[\text{CH}_3\text{COCH}_3][\text{H}^+]$$

Assignment

13.2 pg. 589–590 #9 to 22; pg. 593–594 #72 and 87

13.3: The Relationship Between Reactant Concentration and Time (Integrated Rate Law)**1. Integrated First-Order Rate Law for Single Reactant**

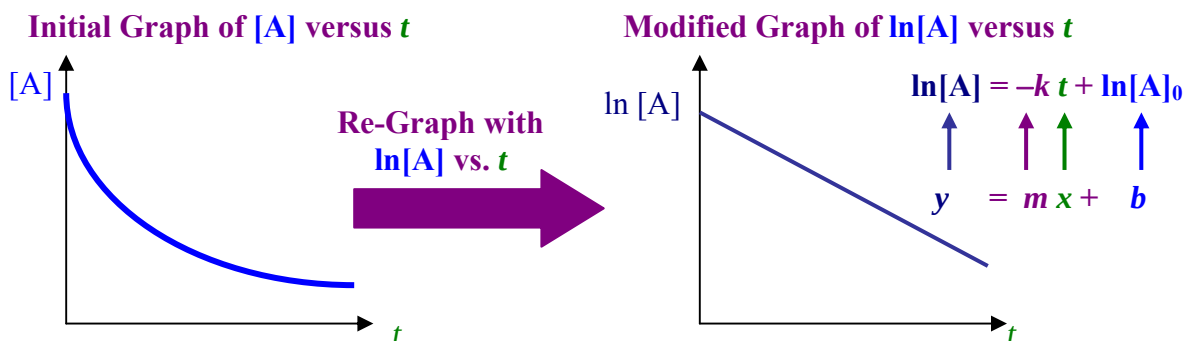
$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A] \quad (\text{Starting from First-Order Rate Law})$$

$$\frac{1}{[A]} \Delta[A] = -k \Delta t \quad (\text{Rearrange Equation for Integration})$$

$$\int_{[A]_0}^{[A]} \frac{1}{[A]} d[A] = -k \int_0^t dt \quad (\Delta t = dt \text{ and } \Delta[A] = d[A]; \text{ Integrate Both Sides: } \int \frac{1}{x} dx = \ln x)$$

$$\ln [A] - \ln [A]_0 = -kt \quad (\text{Apply one of the Logarithm Laws: } \log A - \log B = \log \left(\frac{A}{B} \right))$$

$$\ln \left(\frac{[A]}{[A]_0} \right) = -kt \quad (\text{Integrated First Order Rate Laws – Two Versions})$$

Graphing Integrated First-Order Rate Law for Single Reactant

If $\ln [A]$ versus t graph is a linear relation, then it is a First Order Reaction with $-k = \text{slope}$ and $\ln [A]_0 = y\text{-intercept}$.

Half-Life ($t_{1/2}$): - the amount of time it takes to half the original reactant's concentration.

- at half-life, $t_{1/2}$, the reactant's concentration is $\frac{1}{2}[A]_0 = [A]$:

$$\ln \left(\frac{[A]}{[A]_0} \right) = -kt \Rightarrow \ln \left(\frac{\left(\frac{1}{2} [A]_0 \right)}{[A]_0} \right) = -k t_{1/2} \Rightarrow \ln (1/2) = -k t_{1/2} \quad (\text{Since } \ln(1/2) = -\ln(2))$$

$$\Rightarrow \ln (2) = k t_{1/2}$$

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

Integrated First Order Rate Laws for Single Reactant

$$\ln [A] = -kt + \ln [A]_0 \quad \ln \left(\frac{[A]}{[A]_0} \right) = -kt \quad t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

$[A]$ = Concentration of Reactant at time t

$[A]_0$ = Concentration of Reactant at time 0

k = Rate Constant

t = time $t_{1/2}$ = half-life

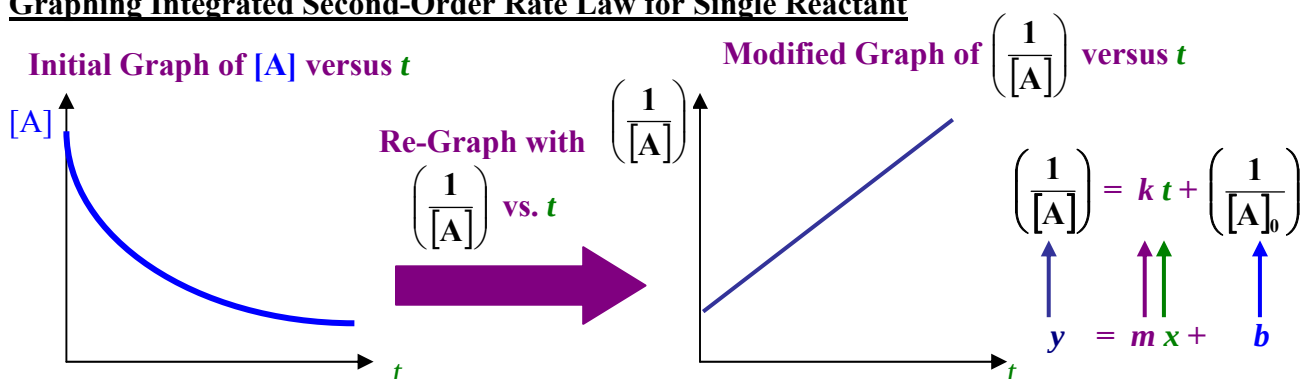
2. Integrated Second-Order Rate Law for Single Reactant

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2 \quad (\text{Starting from Second-Order Rate Law})$$

$$-\frac{1}{[A]^2} \Delta[A] = k \Delta t \quad (\text{Rearrange Equation for Integration})$$

$$-\int_{[A]_0}^{[A]} \frac{1}{[A]^2} d[A] = k \int_0^t dt \quad (\Delta t = dt \text{ and } \Delta[A] = d[A]; \text{ Integrate Both Sides: } -\int \frac{1}{x^2} dx = \frac{1}{x})$$

$$\left(\frac{1}{[A]} \right) - \left(\frac{1}{[A]_0} \right) = kt \quad (\text{Integrated Second Order Rate Law})$$

Graphing Integrated Second-Order Rate Law for Single Reactant

If $\left(\frac{1}{[A]} \right)$ versus t graph is a linear relation, then it is a Second Order Reaction

with $k = \text{slope}$ and $\left(\frac{1}{[A]_0} \right) = \text{y-intercept}$.

Half-Life for Second-Order Reaction with a Single Reactant

- at half-life, $t_{1/2}$, the reactant's concentration is $\frac{1}{2}[A]_0 = [A]$:

$$\left(\frac{1}{[A]} \right) - \left(\frac{1}{[A]_0} \right) = kt \Rightarrow \left(\frac{1}{\frac{1}{2}[A]_0} \right) - \left(\frac{1}{[A]_0} \right) = kt_{1/2} \Rightarrow \frac{2}{[A]_0} - \frac{1}{[A]_0} = kt_{1/2} \Rightarrow \frac{1}{[A]_0} = kt_{1/2}$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

Integrated Second Order Rate Laws for Single Reactant

$$\left(\frac{1}{[A]} \right) = kt + \left(\frac{1}{[A]_0} \right)$$

$[A]$ = Concentration of Reactant at time t
 $[A]_0$ = Concentration of Reactant at time 0

$$t_{1/2} = \frac{1}{k[A]_0}$$

k = Rate Constant
 t = time $t_{1/2}$ = half-life

3. Integrated Zero-Order Rate Law for Single Reactant

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k \quad (\text{Starting from Zero-Order Rate Law})$$

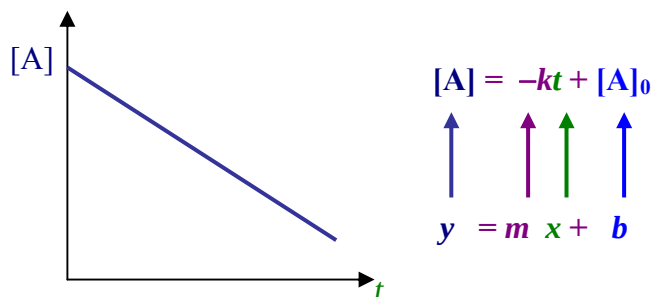
$$\Delta[A] = -k\Delta t \quad (\text{Rearrange Equation for Integration})$$

$$\int_{[A]_0}^{[A]} d[A] = -k \int_0^t dt \quad (\Delta t = dt \text{ and } \Delta[A] = d[A]; \text{ Integrate Both Sides: } \int dx = x)$$

$$[A] - [A]_0 = -kt \quad (\text{Integrated Zero Order Rate Law})$$

Graphing Integrated Zero-Order Rate Law for Single Reactant

Initial Graph of [A] versus t (No Need to Re-Graph)



If the initial graph of [A] versus t graph is a linear relation, then it is a Zero Order Reaction with k = -slope and [A]₀ = y-intercept.

Half-Life for Zero-Order Reaction with a Single Reactant

- at half-life, $t_{1/2}$, the reactant's concentration is $\frac{1}{2}[A]_0 = [A]$:

$$[A] - [A]_0 = -kt \Rightarrow \frac{1}{2}[A]_0 - [A]_0 = -kt_{1/2} \Rightarrow -\frac{[A]_0}{2} = -kt_{1/2}$$

$$t_{1/2} = \frac{[A]_0}{2k}$$

Integrated Zero Order Rate Laws for Single Reactant

$$[A] = -kt + [A]_0$$

$$t_{1/2} = \frac{[A]_0}{2k}$$

[A] = Concentration of Reactant at time t

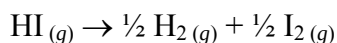
k = Rate Constant

[A]₀ = Concentration of Reactant at time 0

t = time

$t_{1/2}$ = half-life

Example 1: The decomposition of HI (g) at 716 K yields the following data.



Time (minutes)	[HI] mol/L
0.00	0.02000
1.00	0.01248
2.00	0.00911
3.00	0.00716
4.00	0.00587
5.00	0.00501
6.00	0.00433

- Complete the table below.
- Graph [HI] versus t , $\ln[\text{HI}]$ versus t , and $1/[\text{HI}]$ versus t . Assess the linearity to determine the overall rate order.
- State the integrated rate law for the decomposition of HI and find the rate constant.
- What is the half-life of this reaction?
- Calculate the time needed for the reactant to reach 10.0% of its original concentration.

Time (minutes)	[HI] mol/L	$\ln[\text{HI}]$	$1/[\text{HI}]$
0.00	0.02000		
1.00	0.01248		
2.00	0.00911		
3.00	0.00716		
4.00	0.00587		
5.00	0.00501		
6.00	0.00433		

- a. Using the TI-83 Plus Calculator, we can enter the experimental results in the STATS Editor and quickly manipulate the data.

1. Enter Values in the L₁ and L₂ Columns of Stats Editor

2. Enter " $\ln(L_2)$ " in the heading of L₃.
Enter " $1/L_2$ " in the heading of L₄.

STAT

ENTER

L1	L2	L3	2
0	.02	-----	
1	.01248		
2	.00911		
3	.00716		
4	.00587		
5	.00501		
6	.00433		

L2(7) = .00433

L1	L2	L3	# 3
0	.02	-3.912	
1	.01248	-4.384	
2	.00911	-4.698	
3	.00716	-4.939	
4	.00587	-5.138	
5	.00501	-5.296	
6	.00433	-5.442	

L3 = "ln(L2)"

Cursor must be on the column heading before entering formula

L2	L3	# 4	# 4
.02	-3.912	50	
.01248	-4.384	80.128	
.00911	-4.698	109.77	
.00716	-4.939	139.66	
.00587	-5.138	170.36	
.00501	-5.296	199.6	
.00433	-5.442	230.95	

L4 = "1/L2"

"must be used to enter formula

To access L₂, press

ALPHA

2nd

L2
2

MEM "**+**

3. Fill in the Table

Time (minutes)	[HI] mol/L	ln[HI]	1/[HI]
0.00	0.02000	-3.912	50
1.00	0.01248	-4.384	80.128
2.00	0.00911	-4.698	109.77
3.00	0.00716	-4.939	139.66
4.00	0.00587	-5.138	170.36
5.00	0.00501	-5.296	199.60
6.00	0.00433	-5.442	230.95

b. First, we Graph [HI] vs. t

1. Turn On STATS PLOT

2nd STAT PLOT ENTER

Y=

To access L₂, press

2nd L2 2

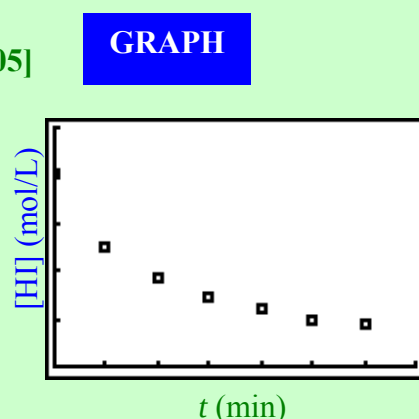
2. Set WINDOW

WINDOW

x: [0, 7, 1]
y: [0, 0.25, 0.005]

WINDOW
Xmin=0
Xmax=7
Xscl=1
Ymin=0
Ymax=.025
Yscl=.005
Xres=1

3. Graph



[HI] vs. t Graph is a Curve.
Hence, it is NOT a Zero-Order Reaction.

Next, we graph ln[HI] vs. t

1. Turn On STATS PLOT

2nd STAT PLOT ENTER

Y=

To access L₃, press

2nd L3 3

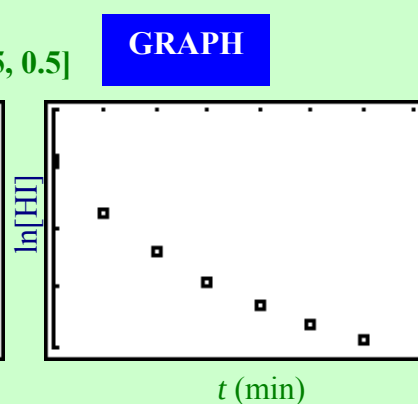
2. Set WINDOW

WINDOW

x: [0, 7, 1]
y: [-5.5, -3.5, 0.5]

WINDOW
Xmin=0
Xmax=7
Xscl=1
Ymin=-5.5
Ymax=-3.5
Yscl=.5
Xres=1

3. Graph



ln[HI] vs. t Graph is a Curve.
Hence, it is NOT a First-Order Reaction.

Lastly, we graph $1/[HI]$ vs. t

1. Turn On STATS PLOT

2nd STAT PLOT ENTER

Y=

To access L4, press

2nd L4 4

Plot1 Plot2 Plot3
Off Off Off
Type: [scatter] [line] [line with markers]
Xlist: L1
Ylist: L4
Mark: [square] +

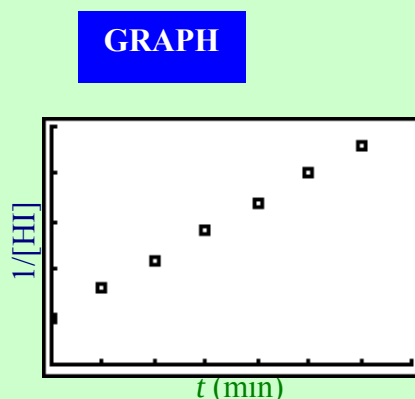
2. Set WINDOW

WINDOW

Xmin=0
Xmax=7
Xscl=1
Ymin=0
Ymax=250
Yscl=50
Xres=1

x: [0, 7, 1]
y: [0, 250, 50]

3. Graph



$1/[HI]$ vs. t Graph is a Straight Line.
Hence, it is a Second-Order Reaction.

- c. Since the reaction is second order, the integrated rate law has a form of $\left(\frac{1}{[HI]}\right) = kt + \left(\frac{1}{[HI]_0}\right)$. We can use the linear regression function of the calculator to find the value of the slope.

1. Turn Diagnostic On

2nd CATALOG 0

ENTER

DiagnosticOn Done

Again

ENTER

Select DiagnosticOn

Note: After **DiagnosticOn** is selected; it will remain ON even when the calculator is turned Off. However, resetting the calculator will turn the Diagnostic Off (factory setting).

2. Obtain LinReg ($ax + b$) L1, L4, Y1. Copy Equation to Y= Screen, and Graph Least Square Line on Scatter Plot.

STAT Select CALC, use

ENTER 2nd L1 1

VAR

2nd L4 4

To access Y1, press

Select Option 1 for Y1

ENTER

Choose Option 4 Linear Regression ($ax + b$)

DiagnosticOn Done
LinReg(ax+b) L1, L4,

VAR

Function...
2: Parametric...
3: Polar...
4: On/Off...

Select Option 1

Y1
2: Y2
3: Y3
4: Y4
5: Y5
6: Y6
7: Y7

ENTER

```
DiagnosticOn Done
LinReg(ax+b) L1,
L4,Y1
```

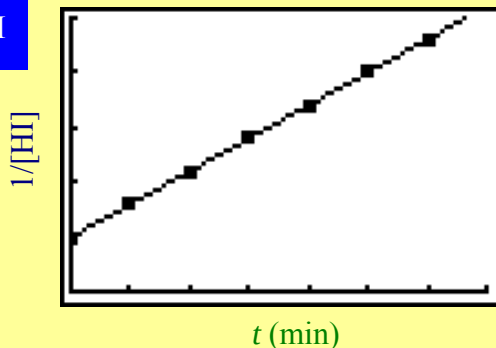
```
LinReg
y=ax+b
a=30.0847893
b=49.81247861
r^2=.9999552834
r=.9999776415
```

When r is extremely close to ± 1 , it indicates the line has a linear relationship.

Y=

Be Sure Plot1 is On

```
Y1=30.084789299
839X+49.81247861
1753
Y2=
Y3=
Y4=
Y5=
```

GRAPH
 $y = 30.0848x + 49.8125$ compares to

$$\left(\frac{1}{[\text{HI}]}\right) = kt + \left(\frac{1}{[\text{HI}]_0}\right)$$

$$k = 30.0848 \text{ L}/(\text{mol} \cdot \text{min})$$

$$\left(\frac{1}{[\text{HI}]_0}\right) = 49.8125 \text{ L/mol or } [\text{HI}]_0 = 0.0201 \text{ mol/L}$$

d. Half-Life

$$t_{1/2} = \frac{1}{k[\text{HI}]_0} = \left(\frac{1}{k}\right)\left(\frac{1}{[\text{HI}]_0}\right) = \left(\frac{1}{30.0848 \text{ L}/(\text{mol} \cdot \text{min})}\right)(49.8125 \text{ L/mol})$$

$$t_{1/2} = 1.656 \text{ min}$$

e. Time needed to reach 10.0% of $[\text{HI}]_0$

$$\left(\frac{1}{[\text{HI}]}\right) = kt + \left(\frac{1}{[\text{HI}]_0}\right)$$

$$[\text{HI}]_0 = 0.0201 \text{ mol/L}$$

$$[\text{HI}] = 0.100 \times 0.0201 \text{ mol/L}$$

$$[\text{HI}] = 0.00201 \text{ mol/L}$$

$$k = 30.0848 \text{ L}/(\text{mol} \cdot \text{min})$$

 $t = ?$

$$\left(\frac{1}{[\text{HI}]}\right) - \left(\frac{1}{[\text{HI}]_0}\right) = kt$$

$$t = \frac{\left(\frac{1}{[\text{HI}]}\right) - \left(\frac{1}{[\text{HI}]_0}\right)}{k} = \frac{\left(\frac{1}{0.00201 \text{ mol/L}}\right) - \left(\frac{1}{0.0201 \text{ mol/L}}\right)}{(30.0848 \text{ L}/(\text{mol} \cdot \text{min}))}$$

$$t = 14.88 \text{ min}$$

4. Integrated Rate Law for Multiple Reactants

Pseudo-First-Order Rate Law: - when there are multiple reactants, if we can have excess amount for all reactants except one, we can simplify the rate law so it behaves like a first-order reaction.

Pseudo-First-Order Rate Law

For reaction with Multiple Reactants, $aA + bB \rightarrow \text{Products}$ and $\text{Rate} = k[A][B]^n$,
if $[B]_0 \gg [A]_0$, then we can assume $[B] \approx [B]_0$.

We can simplify $\text{Rate} = k[A][B]^n$ to $\text{Rate} = k'[A]$ where $k' = k[B]^n$

Example 2: A reaction, $A + 3B + 2C \rightarrow 3D + E$, has a rate law of $Rate = k[A][B]^2[C]$. The concentrations at the beginning of the experiment are $[A]_0 = 0.0500 \text{ mol/L}$, $[B]_0 = 2.00 \text{ mol/L}$ and $[C]_0 = 3.00 \text{ mol/L}$. After 15.0 seconds, the concentration of A is 0.0342 mol/L.

- Calculate k for this reaction.
- Determine the half-life for this reaction.
- Find the concentrations of A and C after 50.0 seconds.

- a. Since $[B]_0$ and $[C]_0 \gg [A]_0$, we can assume that $[B] \approx [B]_0$ and $[C] \approx [C]_0$.
Therefore, $Rate = k[A][B]^2[C]$ can be simplified to $Rate = k'[A]$ where $k' = k[B]^2[C]$.

$$Rate = -k'[A] \quad (\text{Pseudo-First-Order Rate Law})$$

$$\ln[A] = -k't + \ln[A]_0 \quad (\text{Pseudo-Integrated-First-Order Rate Law})$$

$$[A]_0 = 0.0500 \text{ mol/L} \quad t = 15.0 \text{ s} \quad [A] = 0.0342 \text{ mol/L}$$

$$\ln[A] - \ln[A]_0 = -k't$$

$$k' = \frac{\ln[A] - \ln[A]_0}{-t} = \frac{\ln(0.0342) - \ln(0.0500)}{-15.0 \text{ s}} \quad k' = 0.0253 \text{ s}^{-1}$$

Finally, we have to convert k' back to k .

$$k' = k[B]^2[C]$$

$$k = \frac{k'}{[B]^2[C]} = \frac{(0.0253 \text{ s}^{-1})}{(2.00 \text{ mol/L})^2(3.00 \text{ mol/L})}$$

$$k = 0.00211 \text{ L}^3/(\text{mol}^3 \cdot \text{s})$$

- b. Because we used the **Pseudo-Integrated-First-Order Rate Law**, the corresponding half-life is:
(Note: we are using k')

$$t_{1/2} = \frac{\ln(2)}{k'} = \frac{\ln(2)}{0.0253 \text{ s}^{-1}} \quad t_{1/2} = 27.4 \text{ s}$$

- c. At $t = 50.0 \text{ s}$, $[A] = ?$

Because $[C] \approx [C]_0 = 3.00 \text{ mol/L}$, at 50.0 s,

$$\ln[A] = -k't + \ln[A]_0$$

$$\ln[A] = -(0.0253 \text{ s}^{-1})(50.0 \text{ s}) + \ln(0.0500)$$

$$\ln[A] = -4.260732274$$

$$[A] = e^{-4.260732274}$$

$$[A] = 0.0141 \text{ mol/L}$$

$$[C] \approx 3.00 \text{ mol/L}$$

In reality, $[A]_{\text{reacted}} = [A]_0 - [A]$

$$[A]_{\text{reacted}} = 0.0500 \text{ mol/L} - 0.0141 \text{ mol/L}$$

$$[A]_{\text{reacted}} = 0.0359 \text{ mol/L}$$

$$[C]_{\text{reacted}} = \frac{2 \text{ mol C}}{1 \text{ mol A}} \times 0.0359 \text{ mol/L of A} = 0.0718 \text{ mol/L}$$

$$[C] = [C]_0 - [C]_{\text{reacted}} = 3.00 \text{ mol/L} - 0.0718 \text{ mol/L}$$

$$[C] = 2.93 \text{ mol/L}$$

Summary of Rate Laws for Reactions with Single Reactant $aA \rightarrow \text{Products}$

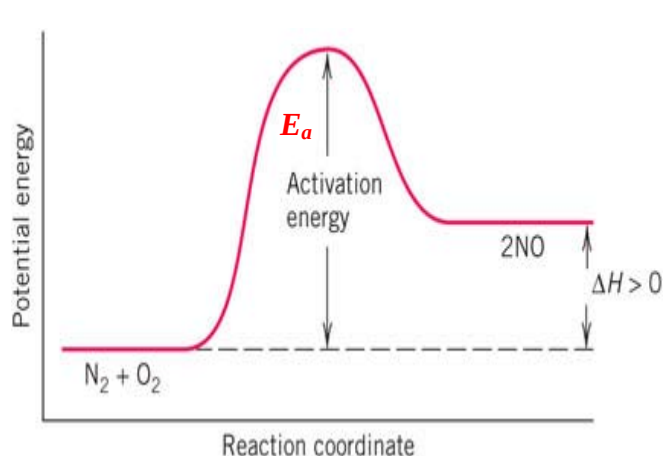
Order	First	Second	Zero
Rate Law	$\text{Rate} = k[A]$	$\text{Rate} = k[A]^2$	$\text{Rate} = k$
Unit of k	s^{-1} or min^{-1}	$L/(\text{mol} \cdot s)$ or $L/(\text{mol} \cdot \text{min})$	$\text{mol}/(L \cdot s)$ or $\text{mol}/(L \cdot s)$
Integrated Rate Law	$\ln[A] = -kt + \ln[A]_0$	$\left(\frac{1}{[A]}\right) = kt + \left(\frac{1}{[A]_0}\right)$	$[A] = -kt + [A]_0$
Relationship with k and Linear Slope	Slope = $-k$	Slope = k	Slope = $-k$
Half-Life	$t_{1/2} = \frac{\ln 2}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$	$t_{1/2} = \frac{[A]_0}{2k}$

Assignment

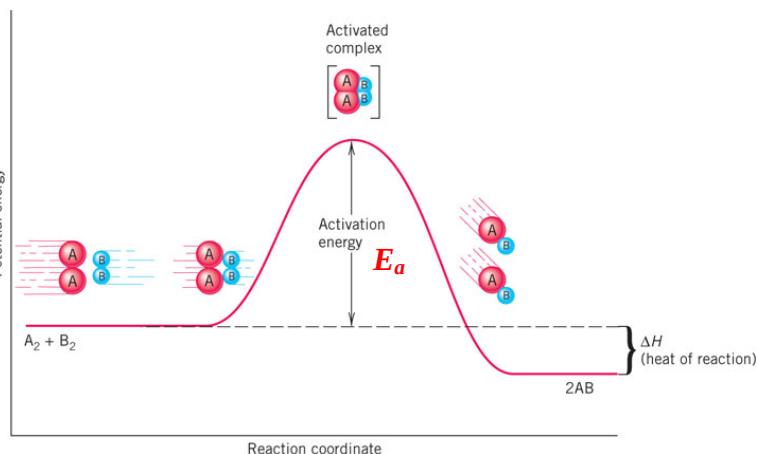
13.3 pg. 590–591 #23 to 30; pg. 594–595 #88 and 94

13.4: A Model for Chemical KineticsCollision Model: - a model that state for a reaction to occur, molecules must collide with each other.Factors Affecting the Collision Model:

- Activation Energy (E_a): - the threshold energy molecules needed to overcome to cause a chemical reaction that was first proposed by Svante Arrhenius.
 - E_a is the highest energy (top of the hill - E_{max}) minus the sum of energy of the reactants ($\Sigma H_{\text{reactants}}$) on the potential energy diagram.

Activated Complex: - sometimes refer to as transition state. It is the transitional molecule found at the top “hill” of the activation energy.

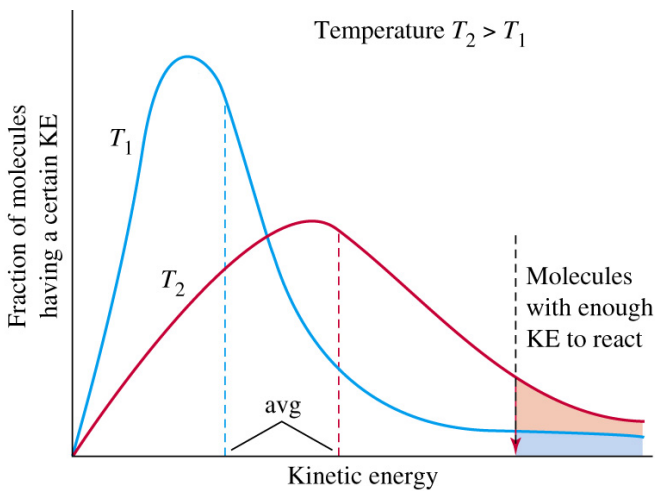
Activation Energy of an Endothermic Reaction



Activation Energy of an Exothermic Reaction

2. **Temperature (T)**: - the effective number of collisions increases exponentially with temperature.

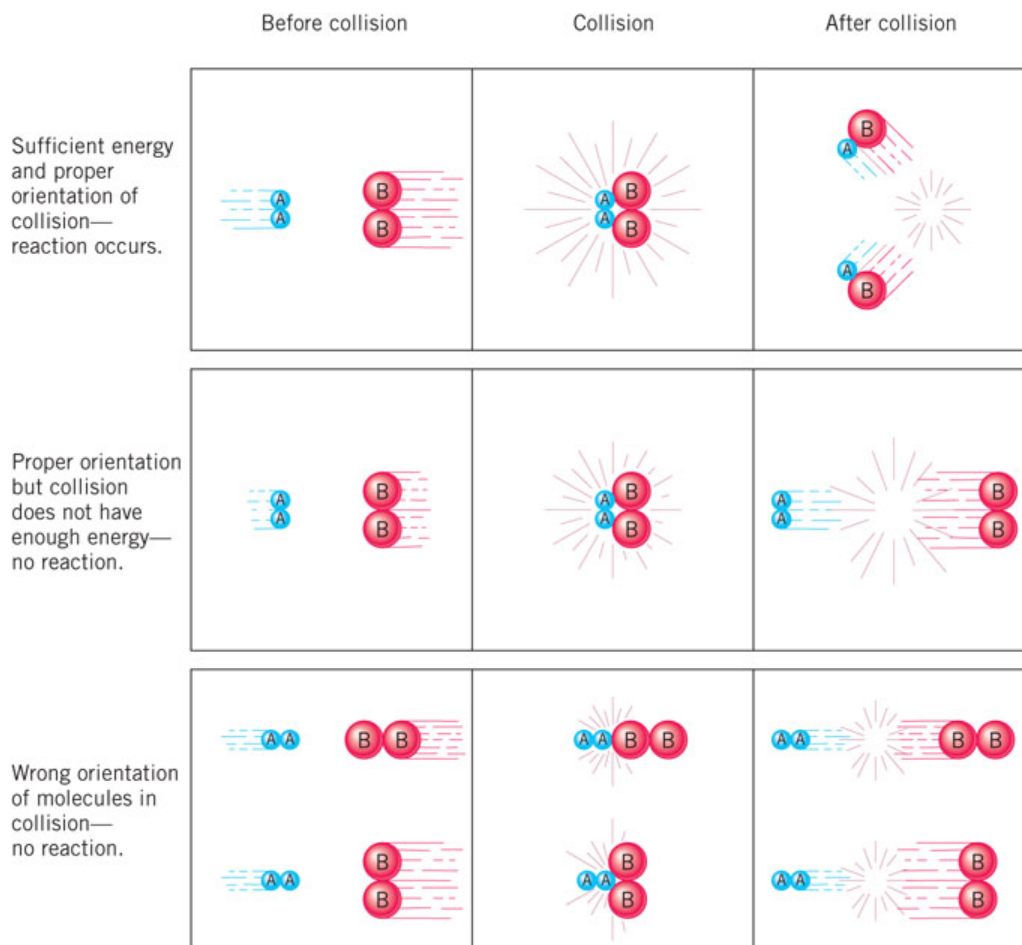
Collision Frequency (z): - measures how often effective collision occurs.



Because $T_2 > T_1$, there are more molecules colliding with enough Kinetic Energy causing a reaction to occur.

3. **Molecular Orientation**: - the number of ways molecules collide that will lead to a reaction.

Steric Factor (p): - a measure that reflects the fraction of collisions with the effective orientations ($p < 1$).



Arrhenius Equation: - developed by Arrhenius to relate **rate constant (k)** using the three factors that affect the collision model (**Activation Energy**, **Temperature** with **Collision Frequency**, and **Steric Factor**)

<u>Arrhenius Equation</u>		
$k = zp e^{\frac{-E_a}{RT}}$	$k = A e^{\frac{-E_a}{RT}}$	
k = Rate Constant	E_a = Activation Energy (J)	T = Temperature (K)
z = Collision Frequency	p = Steric Factor	$A = zp$ = Frequency Factor
R = Gas Constant (8.314 J/(K • mol))		

Linear Form of Arrhenius Equation

$$k = A e^{\frac{-E_a}{RT}} \quad (\text{Arrhenius Equation})$$

$$\ln(k) = \ln\left(A e^{\frac{-E_a}{RT}}\right) \quad (\text{Natural-log both sides})$$

$$\ln(k) = \ln\left(e^{\frac{-E_a}{RT}}\right) + \ln(A) \quad (\text{Applying Law of Logarithm: } \log(MN) = \log M + \log N)$$

$$\ln(k) = -\frac{E_a}{RT} + \ln(A) \quad (\text{Applying Law of Logarithm: } \ln e^x = x)$$

$$\ln(k) = -\frac{E_a}{R} \left(\frac{1}{T}\right) + \ln(A) \quad (\text{We can graph } \ln(k) \text{ versus } (1/T) \text{ from an experiment to determine } E_a)$$

$\uparrow$
 y

$\uparrow$
 m

$\uparrow$
 x

$\uparrow$
 b

We can also compare the rate constants and temperature from two different points on the graph.

$$\ln(k_2) - \ln(k_1) = \left[-\frac{E_a}{RT_2} + \ln(A) \right] - \left[-\frac{E_a}{RT_1} + \ln(A) \right]$$

$$\ln(k_2) - \ln(k_1) = -\frac{E_a}{RT_2} + \ln(A) + \frac{E_a}{RT_1} - \ln(A) \quad \ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

<u>Alternate Arrhenius Equation</u>		
$\ln(k) = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \ln(A)$	$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$	
k = Rate Constant	E_a = Activation Energy (J)	T = Temperature (K)
A = Frequency Factor R = Gas Constant (8.314 J/(K • mol))		

Example 1: The decomposition of $\text{N}_2\text{O}_4(g) \rightarrow 2 \text{NO}_2(g)$ is a first order reaction. One experiment at 274 K, its rate constant is calculated to be $4.50 \times 10^3 \text{ s}^{-1}$. At another experiment at 283 K, its rate constant was determined to be $1.00 \times 10^4 \text{ s}^{-1}$. Find the activation energy of the decomposition of $\text{N}_2\text{O}_4(g)$.

$T_1 = 274 \text{ K}$ $k_1 = 4.50 \times 10^3 \text{ s}^{-1}$ $T_2 = 283 \text{ K}$ $k_2 = 1.00 \times 10^4 \text{ s}^{-1}$ $R = 8.314 \text{ J/(K • mol)}$ $E_a = ?$	$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$ $E_a = \frac{R \left[\ln\left(\frac{k_2}{k_1}\right) \right]}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} = \frac{(8.314 \text{ J/(K • mol)}) \left[\ln\left(\frac{4.50 \times 10^3 \text{ s}^{-1}}{1.00 \times 10^4 \text{ s}^{-1}}\right) \right]}{\left(\frac{1}{274 \text{ K}} - \frac{1}{283 \text{ K}} \right)} = 57201 \text{ J/mol}$ $E_a = 57.2 \text{ kJ/mol}$
--	--

Example 2: The decomposition of $2 \text{N}_2\text{O}_{(g)} \rightarrow 2 \text{N}_{2(g)} + \text{O}_{2(g)}$ yields the following data.

Temperature (K)	k (L/(mol • s))
1125	11.59
1053	1.67
1001	0.38
838	0.0011

- Complete the table below.
- Graph $\ln(k)$ versus $(1/T)$. Assess the linearity to determine the activation energy.
- Draw the potential energy diagram for the decomposition of $\text{N}_2\text{O}_{(g)}$ at 298 K. ($\Delta H^\circ_f = 82 \text{ kJ/mol}$)

Temperature (K)	k (L/(mol • s))	$1/T$ (K^{-1})	$\ln(k)$
1125	11.5900		
1053	1.6700		
1001	0.3800		
838.0	0.0011		

- a. Using the TI-83 Plus Calculator, we can enter the experimental results in the STATS Editor and quickly manipulate the data.

1. Enter Values in the L_1 and L_2 Columns of Stats Editor

STAT	L1	L2	L3	2
ENTER	1125	11.59	-----	
	1053	1.67	-----	
	1001	.38	-----	
	838	.0011	-----	
	-----	-----	-----	
	L2(S) =			

2. Enter " $1/L_1$ " in the heading of L_3 .
Enter " $\ln(L_2)$ " in the heading of L_4 .

L1	L2	L3	# 3
1125	11.59	8.89E-4	
1053	1.67	9.5E-4	
1001	.38	1E-3	
838	.0011	.00119	
-----	-----	-----	
L3 = "1/L1"			

Cursor must be on the column heading before entering formula

L2	L3	# 4	# 4
11.59	8.89E-4	2.4501	
1.67	9.5E-4	.51282	
.38	1E-3	-.9676	
.0011	.00119	-6.812	
-----	-----	-----	
L4 = "ln(L2)"			

"must be used to enter formula

To access L_2 , press

ALPHA

2nd

L2
2

MEM "
+

4. Fill in the Table

Temperature (K)	k (L/(mol • s))	$1/T$ (K^{-1})	$\ln(k)$
1125	11.5900	8.889×10^{-4}	2.4501
1053	1.6700	9.497×10^{-4}	0.5128
1001	0.3800	9.990×10^{-4}	-0.9676
838.0	0.0011	0.001193	-6.8124

b. Graph $\ln(k)$ versus $(1/T)$. Assess the linearity to determine the activation energy.

1. Turn On STATS PLOT

2nd STAT PLOT ENTER

Y=

To access L3, press

2nd L3 3

To access L4, press

2nd L4 4

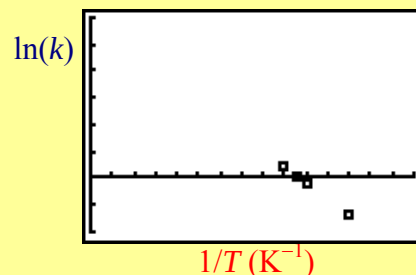
2. Set WINDOW

WINDOW x: [0, 0.0015, 0.0001]
y: [-10, 30, 5]

WINDOW
Xmin=0
Xmax=.0015
Xscl=1E-4
Ymin=-10
Ymax=30
Yscl=5
Xres=1

3. Graph

GRAPH



$\ln(k)$ versus $(1/T)$ Graph forms Straight Line.

We can use the linear regression function of the calculator to find the value of the **slope** and **y-intercept** for calculating ΔE_a and A respectively.

1. Turn Diagnostic On

2nd CATALOG

ENTER

Again

ENTER

Select DiagnosticOn

DiagnosticOn Done

Note: After DiagnosticOn is selected; it will remain ON even when the calculator is turned Off. However, resetting the calculator will turn the Diagnostic Off (factory setting).

2. Obtain LinReg ($ax + b$) L3, L4, Y1. Copy Equation to Screen, and Graph Least Square Line on Scatter Plot.

STAT Select CALC, use

ENTER 2nd L3 3

To access Y1, press

Vars

Select Option 1 for Y1

ENTER

Choose Option 4 Linear Regression ($ax + b$)

DiagnosticOn Done

LinReg($ax+b$) L3, L4,

Vars Y-VARS

Select Option 1

FUNCTION

1:Y1

2:Y2

3:Y3

4:Y4

5:Y5

6:Y6

7:Y7

ENTER

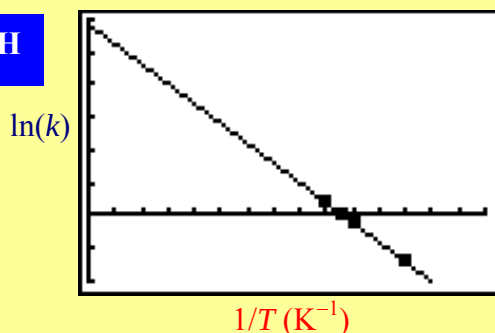
```
DiagnosticOn Done
LinReg(ax+b) L3,
L4,Y1
```

```
LinReg
y=ax+b
a=-30316.56709
b=29.34630683
r^2=.999882188
r=-.9999410923
```

When r is extremely close to ± 1 , it indicates the line has a linear relationship.

Y=**Be Sure Plot1 is On**

```
Plot1 Plot2 Plot3
Y1=-30316.56709
117X+29.34630682
7127
Y2=
Y3=
Y4=
Y5=
```

GRAPH

$$y = -30316.56709117x + 29.346306827127$$

compares to

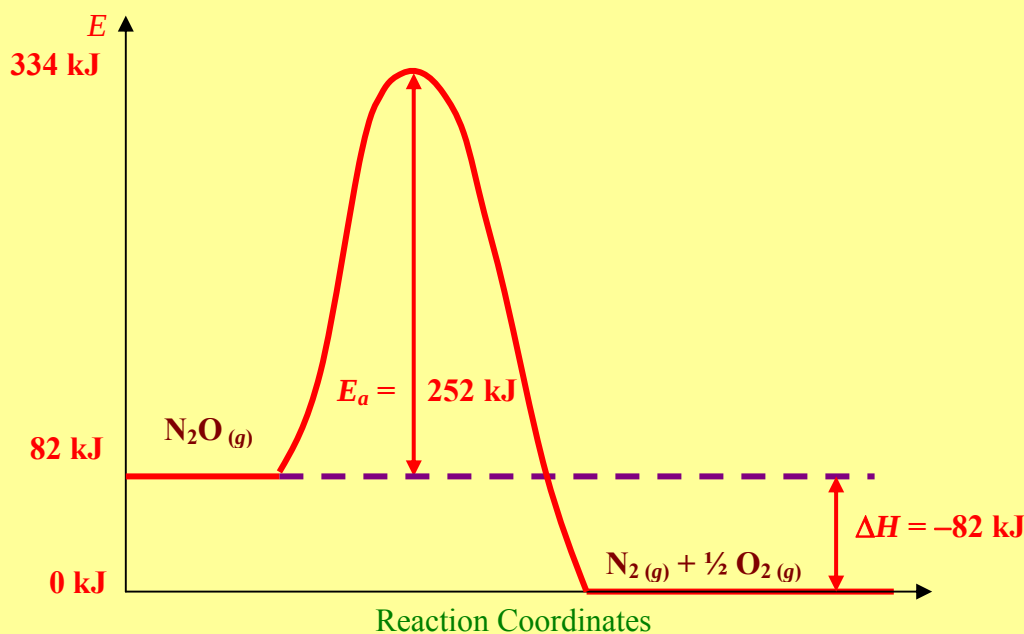
$$\ln(k) = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \ln(A)$$

$$\text{slope} = -30316.56709117 \text{ K}$$

$$-\frac{E_a}{R} = \text{slope} \quad E_a = -(\text{slope})R = -(-30316.56709117 \text{ K})(8.314 \text{ J/(mol} \cdot \text{K)}) = 251930.6725 \text{ J/mol}$$

$$E_a = 252 \text{ kJ/mol}$$

c. Draw the potential energy diagram for the decomposition of $\text{N}_2\text{O}_{(g)}$ at 298 K. ($\Delta H^\circ_f = 82 \text{ kJ/mol}$)



Assignment

13.4 pg. 590–591 #31 to 42; pg. 596 #109, 110, 112

13.5: Reaction Mechanisms

Reaction Mechanisms: - the series of steps involve in most chemical reactions.

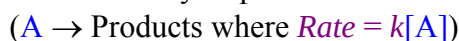
Intermediates: - a chemical species that is produced in the initial reaction but is consumed by the final reaction step.

- an intermediate does NOT appear in the overall reaction.

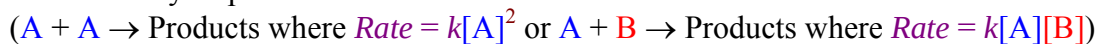
Molecularity: - the number of chemical species that must **COLLIDE** in a reaction step.

Elementary Step: - a reaction step for which its rate can be written based on its molecularity.

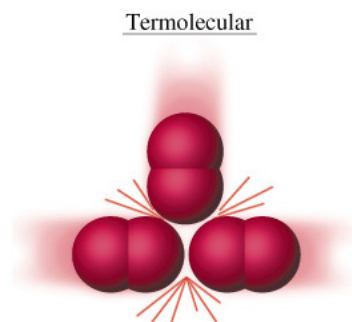
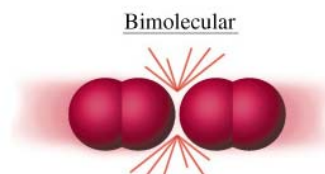
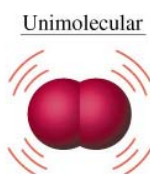
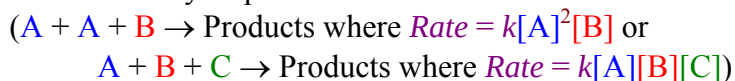
1. **Unimolecular:** - an elementary step where *one* molecule dissociates.



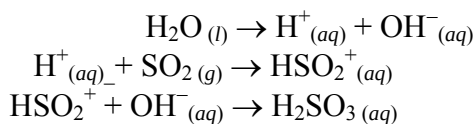
2. **Bimolecular:** - an elementary step where *two* molecules collide.



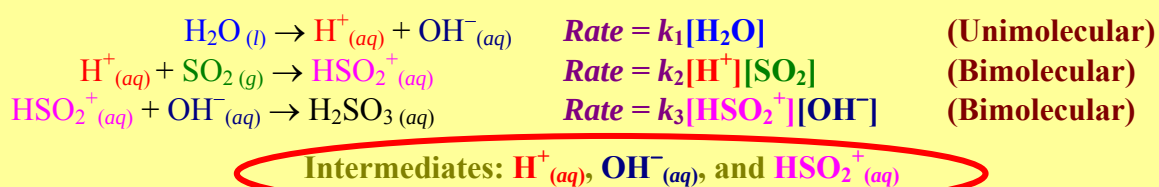
3. **Termolecular:** - an elementary step where *three* molecules collide.



Example 1: The reaction, $\text{SO}_2(g) + \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{SO}_3(aq)$, has the following reaction mechanism.



Determine the rate law for each of the elementary step above and state their molecularity. Identify all intermediates.



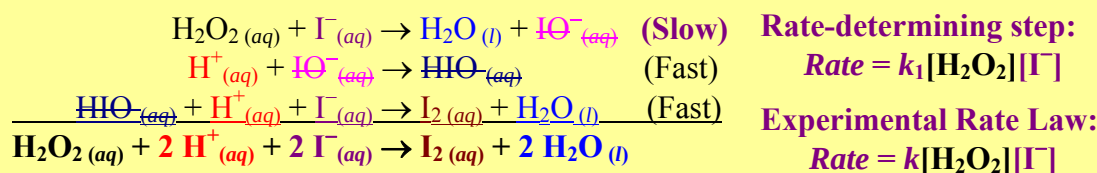
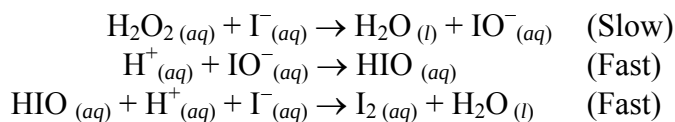
Rate-Determining Step: - the slowest step of the reaction mechanism for which the overall reaction rate is based on.

Deduction of Reaction Mechanism: - possible reaction mechanisms are deduced by the overall reaction rate from experimentation and chemical experience.
 - a given rate law can give rise to many possible reaction mechanism.
 That is, a reaction mechanism can never be proven absolutely

Two Conditions for a Possible Reaction Mechanism

1. All reaction steps should add up to the final balanced reaction.
2. The rate law as determined by experimentation must agree with the rate law of the rate-determining step.

Example 2: The reaction, $\text{H}_2\text{O}_2(aq) + 2 \text{H}^+(aq) + 2 \text{I}^-(aq) \rightarrow \text{I}_2(aq) + 2 \text{H}_2\text{O}(l)$, has a experimental rate law of $\text{Rate} = k[\text{H}_2\text{O}_2][\text{I}^-]$. Are the following steps a possible reaction mechanism?



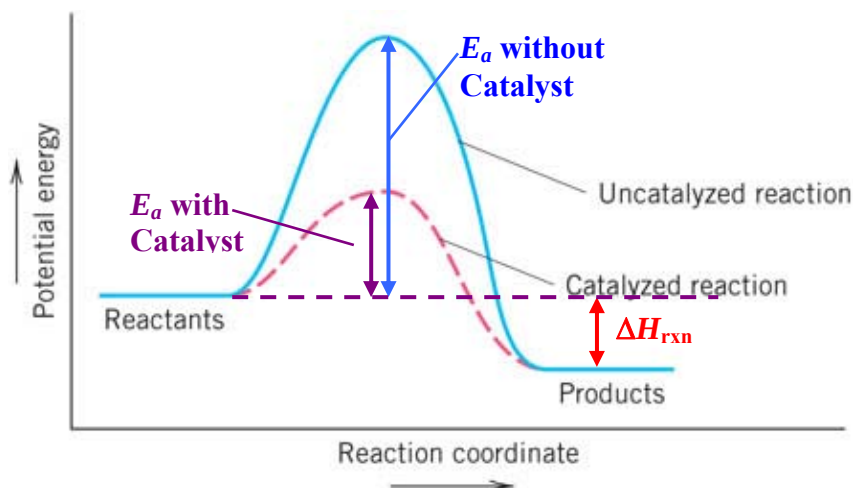
Steps of the Reaction Mechanism added up to the final reaction (1st condition met).
Rate-determining elementary step gives the same rate law compared to that from experiments (2nd condition met). **Therefore, the proposed mechanism is a possible pathway for the overall final reaction.**

Assignment

13.5 pg. 591–595 #43 to 49, 51 to 54, 68, 70, 73, 99

13.6: Catalysis

Catalyst: - a substance that speeds up the reaction **without** being consumed in the reaction.
 - unlike intermediates, catalyst is used and recycled in the reaction.
 - lowers activation energy by providing an alternate reaction pathway.
(ΔE_a is lowered but ΔH_{rxn} remains the same.)



Three Types of Catalyst

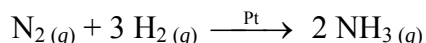
1. **Heterogeneous Catalyst:** - a catalyst that exists in a different phase compared to the reactants.
 - utilizes the concept of **adsorption** to “hold down” the reactants for faster reaction rate.

Adsorption: - collection of a substance on the surface of another substance.
 - the opposite of *absorption* (passing a substance through another).

In general, heterogeneous catalytic reaction involves four steps.

1. *Adsorption* of the reactants and activation of the heterogeneous catalyst on the surface.
2. *Migration* of the adsorbed reactants on the catalytic surface.
3. *Reaction* of the adsorbed substances.
4. *Desorption* or release of the products.

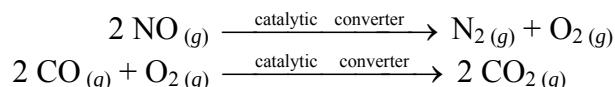
Examples: a. Ammonia is formed from its elements using heterogeneous catalyst such as Pt_(s):



(Check out Video at <http://www.dac.neu.edu/physics/b.maheswaran/phy1121/data/ch11/anim/anim11-5b.mov>)



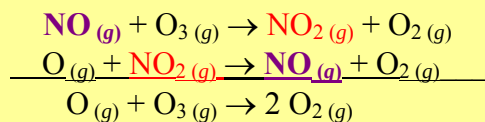
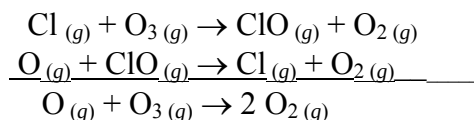
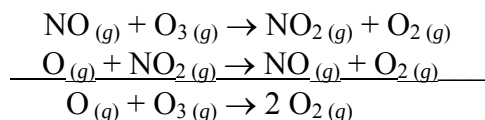
- b. The catalytic converter converts NO_(g) (result of burning nitrogen at high temperature) to N_{2(g)} and O_{2(g)}. The O_{2(g)} along with the catalytic converter is used to produce CO_{2(g)} from CO_(g).



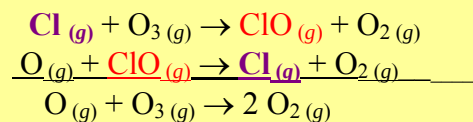
A catalytic converter for most modern vehicle. Leaded gasoline deactivates catalytic converter. Therefore, they are not legally used in vehicles

2. **Homogeneous Catalyst:** - a catalyst that exists in the same phase as the reactants.

Example 1: The destruction of ozone in upper atmosphere can be attributed to NO_(g) and CFCs acting as catalysts. NO_(g) is produced from the combustion of N_{2(g)} at high temperature commonly found in internal combustion engine (high-altitude aircraft produces lots of NO_(g)). CFCs (chloro-fluoro-carbon compounds) are found in aerosol can propellants, refrigerators, and air conditioners. They break down to form Cl_(g) with the presence of light. Use the following two reaction mechanisms; identify the intermediates and catalysts for the decomposition processes of ozone in the upper atmosphere.

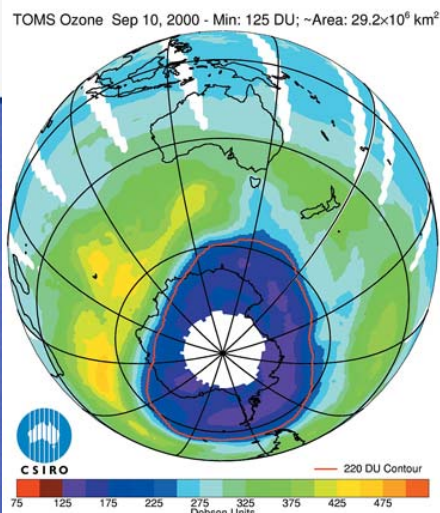
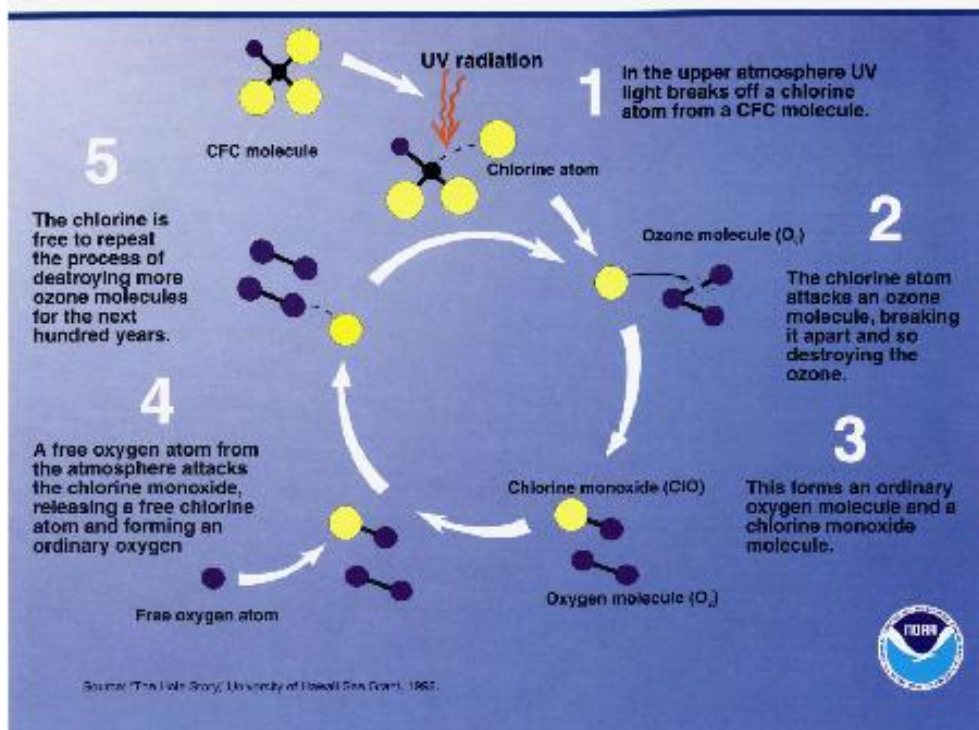


Intermediate: NO_{2(g)}
 Catalyst: NO_(g)



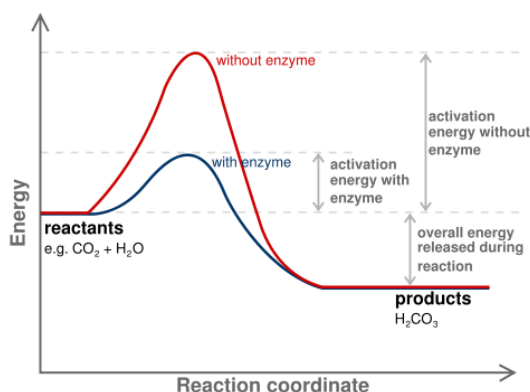
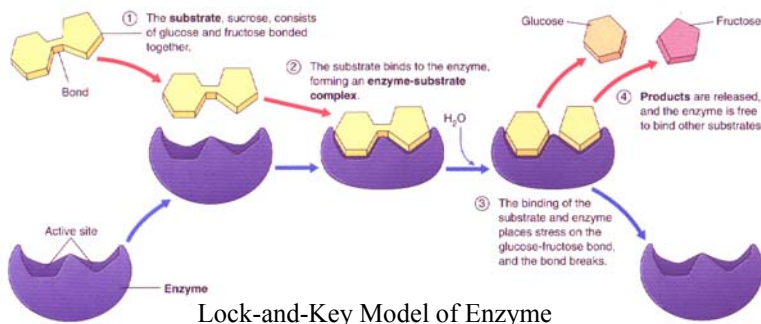
Intermediate: ClO_(g)
 Catalyst: Cl_(g)

How OZONE IS DESTROYED



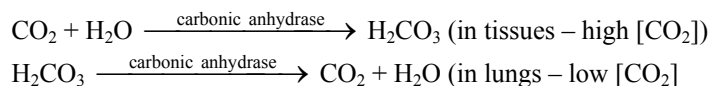
(Above) The Ozone Hole over the South Pole (Sept 2000). A similar hole is present over the Arctic. (Left) Process of Ozone Depletion. Ozone blocks harmful UV rays that can otherwise cause skin cancer.

3. **Enzyme Catalyst:** - a biological catalysts that speeds up certain types of chemical reaction in living beings.
- an enzyme is typically a large protein molecule.
 - an average cell can consist of over 3000 different enzymes.
 - a specific enzyme only acts on specific molecule called substrate (or reactant). It can be viewed as the "lock-and-key" model as first developed by Emil Fischer in 1894 (see diagram below).
 - many enzymes have multiple active sites for the interactions of substrates.
 - thermodynamically, the main goal of enzymes is to lower ΔG , thereby increasing thermodynamic spontaneity. ΔS is reduced by bringing the substrates in the correct orientation to react.
 - kinetically, the speed of the reaction is increased due to lowering of the energy of the activation complex (transition state). Some enzymes can catalyze the forward and reverse reaction equally, such as carbonic anhydrase. In either case, the activation energy is lowered.



Assignment

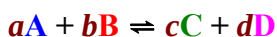
13.6 pg. 592–595 #55 to 58, 62, 64, 65, 80, 84, 96



Chapter 14: Chemical Equilibrium

14.1: The Concept of Equilibrium and the Equilibrium Constant

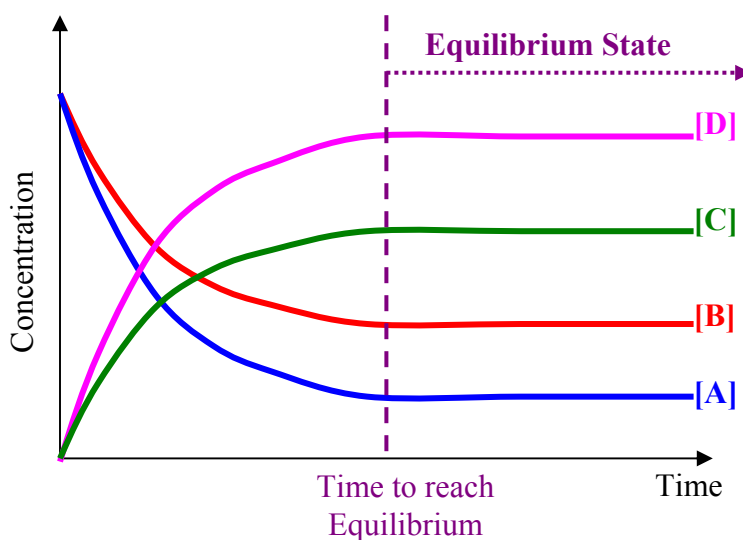
- Chemical Equilibrium:** - the state at which the concentrations of all reactants and products remain constant with time (**the Forward Reaction Rate = Reverse Reaction Rate**).
- **the equilibrium state is dynamic (not static).** Chemical species are continuously converting from reactants to products and vice versa. It appears that the reaction has stopped only because the rate of consumption = rate of production.
 - **if an equilibrium state is disturbed** (changing concentrations of species, pressure, volume and temperature change), **the reaction will shift towards one side in order to re-establish the new equilibrium state.**
 - like reaction rate, **Equilibrium is affected by Temperature.**



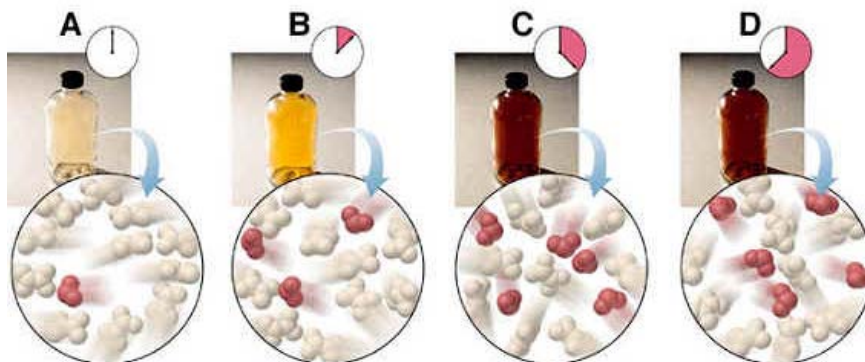
a and b: Coefficients of reactant species **A** and **B**

c and d: Coefficients of product species **C** and **D**

$\rightleftharpoons$ equilibrium symbol (indicating forward and reverse reactions)



(Check out Video at http://www.mhhe.com/physsci/chemistry/animations/chang_7e_esp/kim2s2_5.swf)



The $N_2O_4(g) \rightleftharpoons 2 NO_2(g)$ equilibrium.

Initially (Picture A), there were very little $NO_2(g)$. As time proceeded forward, more $NO_2(g)$ (brown color) is produced (Pictures B & C). However, there are still $N_2O_4(g)$ present at the equilibrium state (Picture D).

Law of Mass Action: - a reversible reaction at equilibrium and a constant temperature, a certain ratio of reactant and product concentrations (**Equilibrium Expression**) has a constant value, **K – equilibrium constant**.

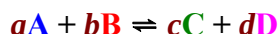
Equilibrium Expression: - an expression **relating the concentrations or pressures of the reactants and products when they are at the state of equilibrium**.

- it takes the form of the individual products raised to the power of their respective coefficients divided by the individual reactants raised to the power of their respective coefficients.
- **the equilibrium expression is unique for each reaction, but it is the same for that particular reaction regardless of temperature.**

Equilibrium Constant (K): - the **unitless numerical value of the equilibrium expression**.

- **the equilibrium constant is the same for a particular reaction if it remains at the same temperature.**

Equilibrium Expression and Constant of a Reaction



$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b} \leftarrow \text{Equilibrium Expressions}$$

a and b : Coefficients of reactant species **A** and **B**

c and d : Coefficients of product species **C** and **D**

$[A]$, $[B]$, $[C]$ & $[D]$ = Equilibrium Concentrations of Chemicals

K = Equilibrium Constant (Concentrations)

Assignment

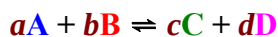
14.1 pg. 633 #1 to 4

14.2: Writing Equilibrium Constant Expressions

Homogeneous Equilibria: - an equilibrium system where all chemical species are in the same phase.

Equilibrium Constant (K): - the symbol for equilibrium constant when the expression deals with **concentrations** is simply **K** or **K_c** . When the expression deals with **pressures**, it is symbolized as **K_p** .

- for equilibrium of an ideal system, the activity of a substance is the ratio of its concentration or partial pressure to a standard value of 1 M or 1 atm. The procedure eliminates all units but does not alter the numerical value of the concentrations and pressures. Therefore, **K has no units**.

Equilibrium Expression and Constant of a Reaction

$$K = K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

a and b: Coefficients of reactant species **A** and **B** **c and d:** Coefficients of product species **C** and **D**

[A], [B], [C] & [D] = [A]_{eq}, [B]_{eq}, [C]_{eq} & [D]_{eq} = Equilibrium Concentrations of Chemicals (mol/L)

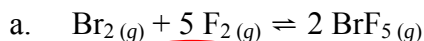
P_A, P_B, P_C & P_D = P_{A,eq}, P_{B,eq}, P_{C,eq} & P_{D,eq} = Equilibrium Pressures of Chemicals (atm)

K or K_c = Equilibrium Constant (Concentrations)

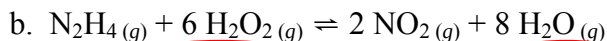
K_p = Equilibrium Constant (Pressures)

Both K_c and K_p are Unitless

Example 1: Write the equilibrium expression of the following reactions.



$$K = \frac{[\text{BrF}_5]^2}{[\text{Br}_2][\text{F}_2]^5} \quad K_p = \frac{P_{\text{BrF}_5}^2}{P_{\text{Br}_2} P_{\text{F}_2}^5}$$



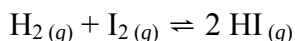
$$K = \frac{[\text{NO}_2]^2 [\text{H}_2\text{O}]^8}{[\text{N}_2\text{H}_4] [\text{H}_2\text{O}_2]^6} \quad K_p = \frac{P_{\text{NO}_2}^2 P_{\text{H}_2\text{O}}^8}{P_{\text{N}_2\text{H}_4} P_{\text{H}_2\text{O}_2}^6}$$

Equilibrium Position: - the **concentrations or pressures of all chemical species at equilibrium state**.

- **depends strongly on the Initial Concentrations of the chemical species.** (In contrast, **K** does **NOT** depend on initial concentrations, only on temperature and the specific reaction.)
- since there are many possible initial concentrations for any one reaction, **there are infinite number of equilibrium position for a particular reaction.**

Note: **Do NOT confuse initial concentrations [A]₀ with equilibrium concentration [A]_{eq}!!** We **only use Equilibrium Concentrations to calculate K** by substituting them into the equilibrium expression.

Example 2: The formation of HI_(g) is an equilibrium reaction. Several experiments are performed at 710 K using different initial concentrations.



Experiment 1		Experiment 2	
Initial	Equilibrium	Initial	Equilibrium
[H ₂] ₀ = 0.100 M	[H ₂] _{eq} = 0.0222 M	[H ₂] ₀ = 0 M	[H ₂] _{eq} = 0.0350 M
[I ₂] ₀ = 0.100 M	[I ₂] _{eq} = 0.0222 M	[I ₂] ₀ = 0.0100 M	[I ₂] _{eq} = 0.0450 M
[HI] ₀ = 0 M	[HI] _{eq} = 0.156 M	[HI] ₀ = 0.350 M	[HI] _{eq} = 0.280 M

Experiment 3		Experiment 4	
Initial	Equilibrium	Initial	Equilibrium
[H ₂] ₀ = 0.00150 M	[H ₂] _{eq} = 0.0150 M	[H ₂] ₀ = 0 M	[H ₂] _{eq} = 0.0442 M
[I ₂] ₀ = 0 M	[I ₂] _{eq} = 0.0135 M	[I ₂] ₀ = 0 M	[I ₂] _{eq} = 0.0442 M
[HI] ₀ = 0.127 M	[HI] _{eq} = 0.100 M	[HI] ₀ = 0.400 M	[HI] _{eq} = 0.311 M

- Write the equilibrium expression for the formation of HI_(g).
- Calculate the equilibrium constant for each experiment, and average them for an overall value.

a. **Equilibrium Expression:** $K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$

b. **Equilibrium Constant:**

Experiment 1: $K_1 = \frac{[\text{HI}]_{\text{eq}}^2}{[\text{H}_2]_{\text{eq}}[\text{I}_2]_{\text{eq}}} = \frac{(0.156)^2}{(0.0222)(0.0222)}$ Experiment 2: $K_2 = \frac{[\text{HI}]_{\text{eq}}^2}{[\text{H}_2]_{\text{eq}}[\text{I}_2]_{\text{eq}}} = \frac{(0.280)^2}{(0.0350)(0.0450)}$

$K_1 = 49.4$

$K_2 = 49.8$

Experiment 3: $K_3 = \frac{[\text{HI}]_{\text{eq}}^2}{[\text{H}_2]_{\text{eq}}[\text{I}_2]_{\text{eq}}} = \frac{(0.100)^2}{(0.0150)(0.0135)}$ Experiment 4: $K_4 = \frac{[\text{HI}]_{\text{eq}}^2}{[\text{H}_2]_{\text{eq}}[\text{I}_2]_{\text{eq}}} = \frac{(0.311)^2}{(0.0442)(0.0442)}$

$K_3 = 49.3$

$K_4 = 49.5$

Average $K = \frac{49.4 + 49.8 + 49.3 + 49.5}{4}$

$K_{\text{avg}} = 49.5$

Converting K_c to K_p :

$PV = nRT$

(Ideal Gas Law)

$P = \left(\frac{n}{V}\right)RT = CRT$

(Solving for P and let $\frac{n}{V} = \text{Concentration}$)

$K_p = \frac{P_c^c P_d^d}{P_a^a P_b^b}$

(Equilibrium Expression and Constant for $aA + bB \rightleftharpoons cC + dD$)

Substituting pressures for each chemical species into the equilibrium expression:

$(P_A = [A]RT ; P_B = [B]RT ; P_C = [C]RT ; \text{ and } P_D = [D]RT)$

$K_p = \frac{([C]RT)^c ([D]RT)^d}{([A]RT)^a ([B]RT)^b} = \frac{[C]^c (RT)^c [D]^d (RT)^d}{[A]^a (RT)^a [B]^b (RT)^b}$

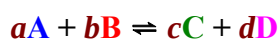
(Combine exponents on common base RT using Laws of Exponents)

$K_p = \frac{[C]^c [D]^d (RT)^{c+d}}{[A]^a [B]^b (RT)^{a+b}} = \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{(c+d)-(a+b)}$

(Replace $\frac{[C]^c [D]^d}{[A]^a [B]^b}$ with K_c)

$K_p = K_c (RT)^{(c+d)-(a+b)}$

Conversion between Concentration and Pressure Equilibrium Constants



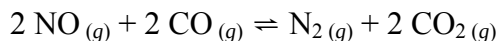
$K_p = K_c (RT)^{\Delta n}$

where $\Delta n = \Sigma \text{ Coefficients of Products} - \Sigma \text{ Coefficients of Reactants} = (c + d) - (a + b)$

$R = 0.08206 \text{ K}^{-1} \quad T = \text{Temperature in K}$

R has a unit of K^{-1} to cancel out with the Kelvin from Temperature only, therefore K calculated will remain unitless

Example 3: One possible way of removing $\text{NO}_{(g)}$ from the exhaust of an internal combustion engine is to cause it to react with $\text{CO}_{(g)}$ in the presence of suitable catalyst.



At 575 K, the reaction has $K = 2.2 \times 10^{59}$. What is K_p of the same reaction at 575 K?

$$K = K_c = 2.2 \times 10^{59}$$

$$R = 0.08206 \text{ K}^{-1}$$

$$T = 575 \text{ K}$$

$$\Delta n = \sum n_{\text{products}} - \sum n_{\text{reactants}}$$

$$\Delta n = (1 + 2) - (2 + 2) = 3 - 4$$

$$\Delta n = -1$$

$$K_p = ?$$

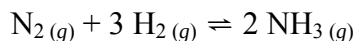
$$K_p = K_c(RT)^{\Delta n}$$

$$K_p = (2.2 \times 10^{59})[(0.08206 \text{ K}^{-1})(575 \text{ K})]^{-1}$$

$$K_p = (2.2 \times 10^{59})[47.1845]^{-1}$$

$$K_p = 4.7 \times 10^{57}$$

Example 4: The German's Haber-Bosch process developed in 1913 utilizes an iron surface that contains traces of aluminium and potassium oxide as a catalyst to manufacture ammonia from nitrogen and hydrogen. It is an important process as ammonia is commonly used in fertilizer and ammunition. In 1918, the scientist Fritz Haber won the Nobel Prize in chemistry for his contribution.



- At 400 K, $P_{\text{NH}_3} = 0.1024 \text{ atm}$, $P_{\text{N}_2} = 2.8084 \text{ atm}$ and $P_{\text{H}_2} = 0.0102 \text{ atm}$. Write the equilibrium expression in terms of pressure and calculate K_p .
- Convert the calculated K_p above to K .

a. **Equilibrium Expression:** $K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3}$

Equilibrium Constant: $K_p = \frac{(0.1024)^2}{(2.8084)(0.0102)^3}$

$$K_p = 3.52 \times 10^3$$

b. $K_p = 3.52 \times 10^3$

$$R = 0.08206 \text{ K}^{-1} \quad T = 400 \text{ K}$$

$$K_p = K_c(RT)^{\Delta n}$$

$$\Delta n = \sum n_{\text{products}} - \sum n_{\text{reactants}}$$

$$\Delta n = (2) - (1 + 3) = 2 - 4$$

$$\Delta n = -2$$

$$K_p = ?$$

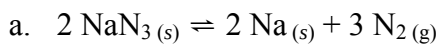
$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{(3.52 \times 10^3)}{[(0.08206 \text{ K}^{-1})(400 \text{ K})]^{-2}}$$

$$K_c = 3.79 \times 10^7$$

Heterogeneous Equilibria: - an equilibrium system where some chemical species are in different phase compare to the others.

- **chemical species that are Pure Solid or Pure Liquid are NOT Included in the Equilibrium Expression.** This is due to the fact that pure solids and liquids do not have concentrations.

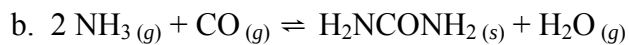
Example 5: Write the equilibrium expression for the following systems.



$$K = [\text{N}_2]^3$$

$$K_P = P_{\text{N}_2}^3$$

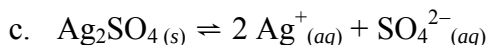
(NaN_3 and Na are Pure Solids)



$$K = \frac{[\text{H}_2\text{O}]}{[\text{NH}_3]^2 [\text{CO}]}$$

$$K_P = \frac{P_{\text{H}_2\text{O}}}{P_{\text{NH}_3}^2 P_{\text{CO}}}$$

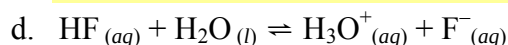
(H_2NCONH_2 is a Pure Solid)



$$K = [\text{Ag}^+]^2 [\text{SO}_4^{2-}]$$

(Ag_2SO_4 is a Pure Solid)

(No K_P because there are no gases.)



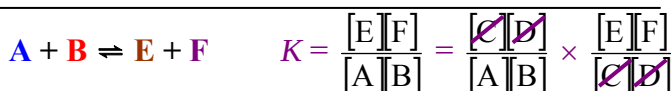
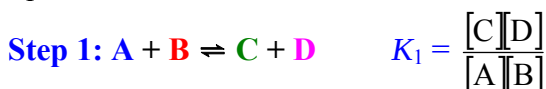
$$K = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]}$$

(H_2O is a Pure Liquid)

(No K_P because there are no gases.)

Multiple Equilibria: - the overall equilibrium constant of a multi-steps systems is the product of all the equilibrium constants of the individual steps involved.

Consider the following multiple equilibria:



$$K = K_1 \times K_2$$

Multiple Equilibria

$$K = K_1 \times K_2 \times K_3 \times \dots$$

Working with Equilibrium Constant and Equations:

- reversing equilibrium reaction will cause the reciprocate the equilibrium constant ($1/K$)
- multiplying the equation by a multiple n will result in raising the K by the power of n .

Reversing Equilibrium Reaction



$$K' = \frac{[\text{A}]^a [\text{B}]^b}{[\text{C}]^c [\text{D}]^d} = \left(\frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \right)^{-1} = K^{-1} = \frac{1}{K}$$

K' = Reverse Equilibrium Constant

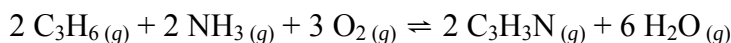
Multiplying Equilibrium Reaction by a Factor of n



$$K'' = \frac{[\text{C}]^{nc} [\text{D}]^{nd}}{[\text{A}]^{na} [\text{B}]^{nb}} = \left(\frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} \right)^n = K^n$$

K'' = New Equilibrium Constant

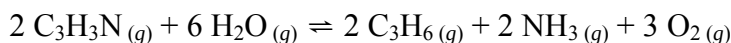
Example 6: For the following reaction and the equilibrium concentrations at 300 K.



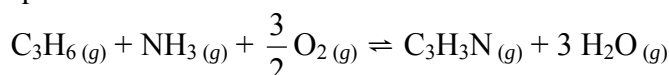
$$[\text{C}_3\text{H}_6]_{eq} = 0.500 \text{ M} \quad [\text{NH}_3]_{eq} = 0.250 \text{ M} \quad [\text{O}_2]_{eq} = 0.350 \text{ M}$$

$$[\text{C}_3\text{H}_3\text{N}]_{eq} = 2.50 \text{ M} \quad [\text{H}_2\text{O}]_{eq} = 3.00 \text{ M}$$

- Write the equilibrium expression and determine the equilibrium constant.
- Write the equilibrium expression and calculate the equilibrium constant for the following reaction with the same equilibrium concentrations.



- Write the equilibrium expression and find the equilibrium constant for the following reaction with the same equilibrium concentrations.



a. **Equilibrium Expression:** $K = \frac{[\text{C}_3\text{H}_3\text{N}]^2 [\text{H}_2\text{O}]^6}{[\text{C}_3\text{H}_6]^2 [\text{NH}_3]^2 [\text{O}_2]^3}$

Equilibrium Constant: $K = \frac{[\text{C}_3\text{H}_3\text{N}]^2 [\text{H}_2\text{O}]^6}{[\text{C}_3\text{H}_6]^2 [\text{NH}_3]^2 [\text{O}_2]^3} = \frac{(2.50)^2 (3.00)^6}{(0.500)^2 (0.250)^2 (0.350)^3} = 6.80 \times 10^6$

b. **Equilibrium Expression:** $K' = \frac{[\text{C}_3\text{H}_6]^2 [\text{NH}_3]^2 [\text{O}_2]^3}{[\text{C}_3\text{H}_3\text{N}]^2 [\text{H}_2\text{O}]^6}$ (Reverse Equilibrium)

Equilibrium Constant: $K' = \frac{[\text{C}_3\text{H}_6]^2 [\text{NH}_3]^2 [\text{O}_2]^3}{[\text{C}_3\text{H}_3\text{N}]^2 [\text{H}_2\text{O}]^6} = \left(\frac{[\text{C}_3\text{H}_3\text{N}]^2 [\text{H}_2\text{O}]^6}{[\text{C}_3\text{H}_6]^2 [\text{NH}_3]^2 [\text{O}_2]^3} \right)^{-1} = K^{-1}$

$K' = (6.80 \times 10^6)^{-1} = 1.47 \times 10^{-7}$

c. **Equilibrium Expression:** $K'' = \frac{[\text{C}_3\text{H}_3\text{N}] [\text{H}_2\text{O}]^3}{[\text{C}_3\text{H}_6] [\text{NH}_3] [\text{O}_2]^{\frac{3}{2}}}$ (All Coefficients Multiplied by $\frac{1}{2}$)

Equilibrium Constant: $K'' = \frac{[\text{C}_3\text{H}_3\text{N}] [\text{H}_2\text{O}]^3}{[\text{C}_3\text{H}_6] [\text{NH}_3] [\text{O}_2]^{\frac{3}{2}}} = \left(\frac{[\text{C}_3\text{H}_3\text{N}]^2 [\text{H}_2\text{O}]^6}{[\text{C}_3\text{H}_6]^2 [\text{NH}_3]^2 [\text{O}_2]^3} \right)^{\frac{1}{2}} = K^{\frac{1}{2}}$

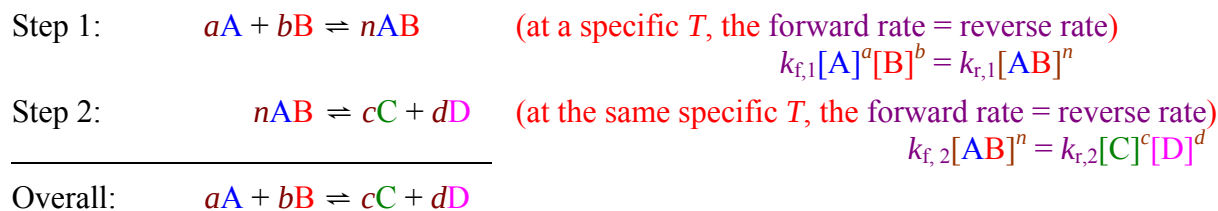
$K'' = (6.80 \times 10^6)^{\frac{1}{2}} = 2.61 \times 10^3$

Assignment

14.2 pg. 633–635 #5 to 11, 13, 14, 16, 18, 20, 22 to 24, 26 to 28, 30 to 32; pg. 639 #92

14.3: The Relationship Between Chemical Kinetics and Chemical Equilibrium

Suppose we have the following elementary steps of an overall system, $aA + bB \rightleftharpoons cC + dD$



Equilibrium Constant (K) can be written as the ratio of rate constants of the forward and reverse reactions.

For Step 1, we have $K_1 = \frac{k_{f,1}}{k_{r,1}} = \frac{[AB]^n}{[A]^a[B]^b}$. Similarly, for Step 2, we have $K_2 = \frac{k_{f,2}}{k_{r,2}} = \frac{[C]^c[D]^d}{[AB]^n}$.

From what we have learned about multiple equilibria (section 14.2), $K = K_1 \times K_2$. Therefore,

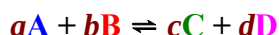
$$K = \frac{k_{f,1}}{k_{r,1}} \times \frac{k_{f,2}}{k_{r,2}} \longrightarrow K = \frac{\cancel{[AB]}^n}{[A]^a[B]^b} \times \frac{[C]^c[D]^d}{\cancel{[AB]}^n}$$

Now, the overall reaction of, $aA + bB \rightleftharpoons cC + dD$, would have an equilibrium expression of $K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$.

Since the rate constant is dependent on temperature, and equilibrium constant is a ratio of rate constants,

Equilibrium Constant (K) is highly dependent on temperature (T).

Assignment
14.3 pg. 635 #33 and 34

14.4: What Does the Equilibrium Constant Tell Us?**Important Notes Regarding the Size of the Equilibrium Constant (K):**

$$K = K_c = \frac{[C]_{eq}^c [D]_{eq}^d}{[A]_{eq}^a [B]_{eq}^b} \quad K_p = \frac{P_{C,eq}^c P_{D,eq}^d}{P_{A,eq}^a P_{B,eq}^b}$$

- When $K \gg 1$, the equilibrium **system favours the products**. There are more products than reactants at the state of equilibrium. ($[C]_{eq}$ and $[D]_{eq}$ or $P_{C,eq}$ and $P_{D,eq} \gg [A]_{eq}$ and $[B]_{eq}$ or $P_{A,eq}$ and $P_{B,eq}$)
- When $K \ll 1$, the equilibrium **system favours the reactants**. There are less products than reactants at the state of equilibrium. ($[A]_{eq}$ and $[B]_{eq}$ or $P_{A,eq}$ and $P_{B,eq} \gg [C]_{eq}$ and $[D]_{eq}$ or $P_{C,eq}$ and $P_{D,eq}$)
- When $K \approx 1$, the equilibrium system **favours neither the products nor the reactants**. There are roughly the same amount of products and reactants at the state of equilibrium. ($[C]_{eq}$ and $[D]_{eq}$ or $P_{C,eq}$ and $P_{D,eq} \approx [A]_{eq}$ and $[B]_{eq}$ or $P_{A,eq}$ and $P_{B,eq}$)
- The **Size of K has NO Relationship with the Rate of Reaction** to reach the state of equilibrium. Reaction Rate is dependent on Activation Energy and Temperature (T) (NOT K).
- The **Size of K depends on Free Energy (G) and Temperature (T).**

Reaction Quotient (Q): - the mass action expression under any set of conditions (not necessarily equilibrium).
 - its magnitude relative to K determines the direction in which the reaction must occur to establish equilibrium.

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- When $Q > K$, the system shifts to the reactants. At a specific condition, Q indicates that there are too much products. Therefore, the system has to shift back to the left.
- When $Q < K$, the system shifts to the products. At a specific condition, Q indicates that there are not enough products. Therefore, the system has to shift forward to the right.
- When $Q = K$, the system is at equilibrium. At a specific condition, Q indicates that all concentrations are that of the equilibrium state. Therefore, there will be no shifting.

Example 1: The reaction, $2 \text{NO}_{(g)} + \text{O}_{2(g)} \rightleftharpoons 2 \text{NO}_{2(g)}$ has an equilibrium constant of $K = 29.54$ at 600 K. Indicate the direction in which the system will shift to reach equilibrium when the $[\text{NO}]_0 = 0.300 \text{ M}$, $[\text{O}_2]_0 = 0.250 \text{ M}$, and $[\text{NO}_2]_0 = 0.500 \text{ M}$.

$[\text{NO}]_0 = 0.300 \text{ M}$
 $[\text{O}_2]_0 = 0.250 \text{ M}$
 $[\text{NO}_2]_0 = 0.500 \text{ M}$

$$Q = \frac{[\text{NO}_2]_0^2}{[\text{NO}]_0^2 [\text{O}_2]_0} = \frac{(0.500)^2}{(0.300)^2 (0.250)}$$

$$Q = 11.1$$

$Q = ?$

Since $Q < K$ ($11.1 < 29.54$), the system will shift to the product (NO_2). There are not enough NO_2 at the initial conditions.

Example 2: The reaction, $\text{Cl}_2(\text{g}) + 3 \text{F}_2(\text{g}) \rightleftharpoons 2 \text{ClF}_3(\text{g})$ at 350 K has $K = 50.2$. If the equilibrium concentrations of $\text{Cl}_2(\text{g})$ and $\text{ClF}_3(\text{g})$ are 0.149 M and 0.205 M respectively, what is the equilibrium concentration of $\text{F}_2(\text{g})$?

$$\begin{aligned} [\text{Cl}_2]_{\text{eq}} &= 0.149 \text{ M} \\ [\text{ClF}_3]_{\text{eq}} &= 0.205 \text{ M} \\ K &= 50.2 \end{aligned}$$

$$K = \frac{[\text{ClF}_3]_{\text{eq}}^2}{[\text{Cl}_2]_{\text{eq}} [\text{F}_2]_{\text{eq}}^3} \quad 50.2 = \frac{(0.205)^2}{(0.149)[\text{F}_2]_{\text{eq}}^3}$$

$$[\text{F}_2]_{\text{eq}} = ?$$

$$[\text{F}_2]_{\text{eq}}^3 = \frac{(0.205)^2}{(50.2)(0.149)}$$

$$[\text{F}_2]_{\text{eq}} = \sqrt[3]{\frac{(0.205)^2}{(50.2)(0.149)}}$$

$$[\text{F}_2]_{\text{eq}} = 0.178 \text{ M}$$

ICE Box: - stands for **Initial, Change, and Equilibrium**. It is a table that organizes information to calculate final equilibrium concentrations given the equilibrium constant and initial concentration.

Example 3: The formation of $\text{HCl}(\text{g})$ from its elements, $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2 \text{HCl}(\text{g})$ has $K = 0.404$ at 250 K. A 5.00 L flask at 250 K contained an initial concentration of 3.00 mol of $\text{HCl}(\text{g})$ and 3.85 mol of $\text{H}_2(\text{g})$. When the system reached equilibrium, it was found that there were 0.860 mol of $\text{Cl}_2(\text{g})$. Determine the concentrations of $\text{H}_2(\text{g})$ and $\text{HCl}(\text{g})$ at equilibrium.

$$K = 0.404$$

$$[\text{H}_2]_0 = \frac{3.85 \text{ mol}}{5.00 \text{ L}} = 0.770 \text{ M}$$

$$[\text{HCl}]_0 = \frac{3.00 \text{ mol}}{5.00 \text{ L}} = 0.600 \text{ M}$$

$$[\text{Cl}_2]_0 = 0 \text{ M}$$

$$[\text{Cl}_2]_{\text{eq}} = \frac{0.860 \text{ mol}}{5.00 \text{ L}} = 0.172 \text{ M}$$

$$[\text{H}_2]_{\text{eq}} = ?$$

$$[\text{HCl}]_{\text{eq}} = ?$$

The system must **shift to the left** because initially, we are missing **one reactant** ($[\text{Cl}_2]_0 = 0 \text{ M}$). Hence, the change to the H_2 is positive, and the change to the HCl would be negative.

Since there is **0.172 M of Cl_2 at equilibrium**, it means **0.172 M of H_2 is added** (1:1 mol ratio between Cl_2 and H_2). It also means that there is **2(0.172 M) less HCl** (2:1 mol ratio between Cl_2 and HCl).

	$\text{H}_2(\text{g})$	+	$\text{Cl}_2(\text{g})$	$\rightleftharpoons$	$2 \text{HCl}(\text{g})$
Initial	0.770 M		0 M		0.600 M
Change	+ 0.172 M		+ 0.172 M		-2(0.172 M)
Equilibrium	0.942 M		0.172 M		0.256 M

Verify with K :

$$K = \frac{[\text{HCl}]_{\text{eq}}^2}{[\text{H}_2]_{\text{eq}} [\text{Cl}_2]_{\text{eq}}} = \frac{(0.256)^2}{(0.942)(0.172)}$$

$$K = 0.404$$

This matches with K given in the question.

Therefore, the equilibrium concentrations are:

$$[\text{H}_2]_{\text{eq}} = 0.942 \text{ M}, [\text{Cl}_2]_{\text{eq}} = 0.172 \text{ M} \text{ and } [\text{HCl}]_{\text{eq}} = 0.256 \text{ M}$$

Example 4: The reaction, $2 \text{NO}_2(\text{g}) \rightleftharpoons \text{NO}_3(\text{g}) + \text{NO}(\text{g})$ has $K = 31.7$ at 700 K. A 2.50 L flask at 700 K has 1.00 mol of each species initially. Calculate the concentrations of all species at equilibrium.

$$K = 31.7$$

$$[\text{NO}_2]_0 = \frac{1.00 \text{ mol}}{2.50 \text{ L}} = 0.400 \text{ M}$$

$$[\text{NO}_3]_0 = \frac{1.00 \text{ mol}}{2.50 \text{ L}} = 0.400 \text{ M}$$

$$[\text{NO}]_0 = \frac{1.00 \text{ mol}}{2.50 \text{ L}} = 0.400 \text{ M}$$

$$[\text{NO}_2]_{\text{eq}} = ?$$

$$[\text{NO}_3]_{\text{eq}} = ?$$

$$[\text{NO}]_{\text{eq}} = ?$$

First, we must determine Q and the direction of the shift.

$$Q = \frac{[\text{NO}_3]_0 [\text{NO}]_0}{[\text{NO}_2]_0^2} = \frac{(0.400)(0.400)}{(0.400)^2} \quad Q = 1.00$$

Since $Q < K$ ($1.00 < 31.7$), the system will shift to the products (NO_3 and NO). There are not enough products at the initial conditions. Hence, the change to the NO_2 is negative, and the changes to the NO_3 and NO would be positive.

Let x = amount of change per mole, since there are 2 moles of NO_2 reacted; NO_2 will be lowered by $2x$. Similarly, NO_3 and NO will be increased by $1x$ each.

	$2 \text{NO}_2(\text{g})$	$\rightleftharpoons$	$\text{NO}_3(\text{g})$	+	$\text{NO}(\text{g})$
Initial	0.400 M		0.400 M		0.400 M
Change	$-2x$		$+x$		$+x$
Equilibrium	$(0.400 - 2x) \text{ M}$		$(0.400 + x) \text{ M}$		$(0.400 + x) \text{ M}$

Next, we set up the equilibrium expression, substitute the above mathematical expressions and solve for x .

(Since we have a set of common exponents we can group it and square root both sides.)

$$K = \frac{[\text{NO}_3]_{\text{eq}} [\text{NO}]_{\text{eq}}}{[\text{NO}_2]_{\text{eq}}^2} \quad 31.7 = \frac{(0.4 + x)(0.4 + x)}{(0.4 - 2x)^2} = \frac{(0.4 + x)^2}{(0.4 - 2x)^2} = \left[\frac{(0.4 + x)}{(0.4 - 2x)} \right]^2$$

$$\sqrt{31.7} = \sqrt{\left[\frac{(0.4 + x)}{(0.4 - 2x)} \right]^2}$$

$$5.630275304 = \frac{(0.4 + x)}{(0.4 - 2x)}$$

$$5.630275304 (0.4 - 2x) = 0.4 + x$$

$$2.252110122 - 11.26055061x = 0.4 + x$$

$$-12.26055061x = -1.852110122$$

$$x = \frac{-1.852110122}{-12.26055061}$$

$$x = 0.15106$$

Verify with K :

$$K = \frac{[\text{NO}_3]_{\text{eq}} [\text{NO}]_{\text{eq}}}{[\text{NO}_2]_{\text{eq}}^2} = \frac{(0.551)(0.551)}{(0.0979)^2} \quad K = 31.7$$

This matches with the K given in the question.

Finally, substitute x back into the mathematical expressions.

$$[\text{NO}_2]_{\text{eq}} = 0.400 - 2x = 0.400 - 2(0.15106)$$

$$[\text{NO}_2]_{\text{eq}} = 0.0979 \text{ M}$$

$$[\text{NO}_3]_{\text{eq}} = 0.400 + x = 0.400 + (0.15106)$$

$$[\text{NO}_3]_{\text{eq}} = 0.551 \text{ M}$$

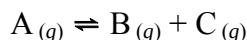
$$[\text{NO}]_{\text{eq}} = 0.400 + x = 0.400 + (0.15106)$$

$$[\text{NO}]_{\text{eq}} = 0.551 \text{ M}$$

Using the TI-Graphing Calculator to Solve Higher Degree Equations:

Sometimes we may encounter equations with higher degrees when solving for equilibrium pressures or concentrations. In some cases, we may be able to use the quadratic formula, but for cubic and higher degrees equations, they can become quite difficult. The TI-Graphing Calculator has a SOLVE function to aid the determination of the roots.

Example: Solve for the final concentrations of both products in the following equilibrium system when the initial concentration of the reactant is 0.400 mol/L, and $K = 2.4 \times 10^{-2}$.



	$A_{(g)}$	$\rightleftharpoons$	$B_{(g)}$	+	$C_{(g)}$
Initial	0.400 M		0 M		0 M
Change	$-x$		$+x$		$+x$
Equilibrium	$(0.400 - x) \text{ M}$		$x \text{ M}$		$x \text{ M}$

1. Manipulate the Equation so one-side is equal to 0.

Example: $2.4 \times 10^{-2} = \frac{x^2}{(0.4 - x)}$ becomes $0 = \frac{x^2}{(0.4 - x)} - 2.4 \times 10^{-2}$

2. Callout the **solve** function.

solve (Equation Expression, X, guess, {lower boundary, upper boundary})

Enter 0 Enter 0 Enter Highest Initial Concentration / Pressure Given

2nd CATALOG 0 , X,T,θ,n 2nd {

Scroll Down from S

ENTER

ENTER

ENTER

Value of x

0.0867117014

Therefore, the concentrations of the products are:

$$x = [B]_{eq} = [C]_{eq} = 0.0867 \text{ mol/L}$$

Example 5: The reaction, $\text{SO}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2\text{Cl}_2(\text{g})$, has an equilibrium constant of 0.486 at 500 K. Determine the equilibrium concentrations of all species if there are 2.00 mol of each species in 10.0 L container at 500 K.

$$K = 0.486$$

$$[\text{SO}_2]_0 = \frac{2.00 \text{ mol}}{10.0 \text{ L}} = 0.200 \text{ M}$$

$$[\text{Cl}_2]_0 = \frac{2.00 \text{ mol}}{10.0 \text{ L}} = 0.200 \text{ M}$$

$$[\text{SO}_2\text{Cl}_2]_0 = \frac{2.00 \text{ mol}}{10.0 \text{ L}} = 0.200 \text{ M}$$

$$[\text{SO}_2]_{\text{eq}} = ?$$

$$[\text{Cl}_2]_{\text{eq}} = ?$$

$$[\text{SO}_2\text{Cl}_2]_{\text{eq}} = ?$$

First, we must determine Q and the direction of the shift.

$$Q = \frac{[\text{SO}_2\text{Cl}_2]_0}{[\text{SO}_2]_0[\text{Cl}_2]_0} = \frac{(0.200)}{(0.200)(0.200)} \quad Q = 5.00$$

Since $Q > K$ ($5.00 > 0.486$), the system will shift to the reactants (SO_2 and Cl_2). There is too much product at the initial conditions. Hence, the changes to the SO_2 and Cl_2 are positive, and the change to the SO_2Cl_2 would be negative.

Let x = amount of change per mole, since there is 1 mole of SO_2 reacted; SO_2 will increase by $1x$. Similarly, Cl_2 will increase by $1x$. SO_2Cl_2 , on the other hand, will decrease by $1x$.

	$\text{SO}_2(\text{g})$	+	$\text{Cl}_2(\text{g})$	$\rightleftharpoons$	$\text{SO}_2\text{Cl}_2(\text{g})$
Initial	0.200 M		0.200 M		0.200 M
Change	$+x$		$+x$		$-x$
Equilibrium	$(0.200 + x) \text{ M}$		$(0.200 + x) \text{ M}$		$(0.200 - x) \text{ M}$

Next, we set up the equilibrium expression, substitute the above mathematical expressions and solve for x .

(Since we don't have any common exponent, we have to expand the denominator.)

$$K = \frac{[\text{SO}_2\text{Cl}_2]_{\text{eq}}}{[\text{SO}_2]_{\text{eq}}[\text{Cl}_2]_{\text{eq}}} \quad 0.486 = \frac{(0.2 - x)}{(0.2 + x)(0.2 + x)} = \frac{(0.2 - x)}{(0.04 + 0.4x + x^2)}$$

$$0.486(0.04 + 0.4x + x^2) = (0.2 - x)$$

$$0.01944 + 0.1944x + 0.486x^2 = 0.2 - x$$

$$0.486x^2 + 1.1944x - 0.18056 = 0 \quad (\text{Quadratic Equation: Apply the Quadratic Formula!})$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad a = 0.486 \quad b = 1.1944 \quad c = -0.18056$$

$$x = \frac{-(1.1944) \pm \sqrt{(1.1944)^2 - 4(0.486)(-0.18056)}}{2(0.486)}$$

$$x = 0.14287 \quad x = -2.6005 \text{ (omit negative } x)$$

Verify with K :

$$K = \frac{[\text{SO}_2\text{Cl}_2]_{\text{eq}}}{[\text{SO}_2]_{\text{eq}}[\text{Cl}_2]_{\text{eq}}} = \frac{(0.0571)}{(0.343)(0.343)} \quad K = 0.485$$

This matches closely with the K given in the question.

Finally, substitute x back into the mathematical expressions.

$$[\text{SO}_2]_{\text{eq}} = 0.200 + x = 0.200 + (0.14287)$$

$$[\text{SO}_2]_{\text{eq}} = 0.343 \text{ M}$$

$$[\text{Cl}_2]_{\text{eq}} = 0.200 + x = 0.200 + (0.14287)$$

$$[\text{Cl}_2]_{\text{eq}} = 0.343 \text{ M}$$

$$[\text{SO}_2\text{Cl}_2]_{\text{eq}} = 0.200 - x = 0.200 - (0.14287)$$

$$[\text{SO}_2\text{Cl}_2]_{\text{eq}} = 0.0571 \text{ M}$$

Steps to Solve Equilibrium Problems:

1. **Write the Balanced Chemical Equation for the system.** This **includes all the correct states** for all species.
2. **Write the Equilibrium Expression** and equate it to K value given.
3. **List the Initial Concentrations.**
4. **Determine Q and compare it to K to determine the direction of the shift** to equilibrium.
5. **Construct the ICE Box and define the change amount of change per mole as x .** Using the coefficients and the direction of the shifts, state the mathematical expressions of each species at equilibrium.
6. **Solve for x after substituting the mathematical expressions into the equilibrium expression.** (Look for methods of simplifying like common exponents if they exist. Otherwise, the quadratic equation will be needed to solve for x .)
7. **Calculate the equilibrium concentrations** of each species and **verify that they indeed give the value of K .**
8. **For equilibrium involving pressures, the procedure is the same as above.**

Example 6: The equilibrium constant for the system, $\text{C}_2\text{H}_6(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{C}_2\text{H}_5\text{Cl}(\text{s}) + \text{HCl}(\text{g})$, at 283 K is 0.100. If we had 6.00 mol of $\text{C}_2\text{H}_6(\text{g})$, 6.00 mol of $\text{Cl}_2(\text{g})$ and 6.00 mol $\text{HCl}(\text{g})$ originally in a 3.00 L container at 283 K, determine the equilibrium concentrations for all species.

$$K = 0.100$$

$$[\text{C}_2\text{H}_6]_0 = \frac{6.00 \text{ mol}}{3.00 \text{ L}} = 2.00 \text{ M}$$

$$[\text{Cl}_2]_0 = \frac{6.00 \text{ mol}}{3.00 \text{ L}} = 2.00 \text{ M}$$

$$[\text{HCl}]_0 = \frac{6.00 \text{ mol}}{3.00 \text{ L}} = 2.00 \text{ M}$$

$$[\text{C}_2\text{H}_6]_{\text{eq}} = ?$$

$$[\text{Cl}_2]_{\text{eq}} = ?$$

$$[\text{HCl}]_{\text{eq}} = ?$$

First, we must determine Q and the direction of the shift. (Be careful! This is a heterogeneous system. $\text{C}_2\text{H}_5\text{Cl}$ is a pure solid and it is not involved in the equilibrium expression.)

$$Q = \frac{[\text{HCl}]_0}{[\text{C}_2\text{H}_6]_0[\text{Cl}_2]_0} = \frac{(2.00)}{(2.00)(2.00)} \quad Q = 0.500$$

Since $Q > K$ ($0.500 > 0.100$), the system will shift to the reactants (C_2H_6 and Cl_2). There are too much products at the initial conditions. Hence, the changes to the C_2H_6 and Cl_2 are positive, and the change to the HCl would be negative.

Let x = amount of change per mole, since there is 1 mole of C_2H_6 reacted; C_2H_6 will increase by $1x$. Similarly, Cl_2 will increase by $1x$. HCl , on the other hand, will decrease by $1x$.

	$\text{C}_2\text{H}_6(\text{g})$	+	$\text{Cl}_2(\text{g})$	$\rightleftharpoons$	$\text{C}_2\text{H}_5\text{Cl}(\text{s})$	+	$\text{HCl}(\text{g})$
Initial	2.00 M		2.00 M		-----		2.00 M
Change	$+x$		$+x$		-----		$-x$
Equilibrium	$(2.00 + x) \text{ M}$		$(2.00 + x) \text{ M}$		-----		$(2.00 - x) \text{ M}$

Next, we set up the equilibrium expression, substitute the above mathematical expressions and solve for x .

(Since we have a set of common exponents we can group it and square root both sides.)

$$K = \frac{[\text{HCl}]_0}{[\text{C}_2\text{H}_6]_0[\text{Cl}_2]_0} \quad 0.100 = \frac{(2-x)}{(2+x)(2+x)} = \frac{(2-x)}{(4+4x+x^2)}$$

$$0.100(4+4x+x^2) = (2-x)$$

$$0.4 + 0.4x + 0.1x^2 = 2 - x$$

$$0.1x^2 + 1.4x - 1.6 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad a = 0.1 \quad b = 1.4 \quad c = -1.6$$

$$x = \frac{-(1.4) \pm \sqrt{(1.4)^2 - 4(0.1)(-1.6)}}{2(0.1)}$$

$$x = 1.062258 \quad x = -15.06226 \text{ (omit negative } x)$$

Finally, substitute x back into the mathematical expressions.

$$[\text{C}_2\text{H}_6]_{eq} = 2.00 + x = 2.00 + (1.062257748)$$

$$[\text{C}_2\text{H}_6]_{eq} = 3.06 \text{ M}$$

$$[\text{Cl}_2]_{eq} = 2.00 + x = 2.00 + (1.062257748)$$

$$[\text{Cl}_2]_{eq} = 3.06 \text{ M}$$

$$[\text{HCl}]_{eq} = 2.00 - x = 2.00 - (1.062257748)$$

$$[\text{HCl}]_{eq} = 0.938 \text{ M}$$

Verify with K :

$$K = \frac{[\text{HCl}]_0}{[\text{C}_2\text{H}_6]_0[\text{Cl}_2]_0} = \frac{(0.938)}{(3.06)(3.06)} \quad K = 0.100$$

This matches closely with the K given in the question.

Example 7: The reaction of $\text{CO}_{(g)} + \text{Cl}_{2(g)} \rightleftharpoons \text{COCl}_{2(g)}$ has an equilibrium constant of $K_p = 0.289$ at 450 K. The initial pressures of $\text{CO}_{(g)}$, $\text{Cl}_{2(g)}$ and $\text{COCl}_{2(g)}$ are 0.800 atm, 0.900 atm and 0.150 atm respectively. They are all mixed in a 7.50 L flask at 450 K. Find the equilibrium pressures.

$$K_p = 0.289$$

$$P_{\text{CO},0} = 0.800 \text{ atm}$$

$$P_{\text{Cl}_2,0} = 0.900 \text{ atm}$$

$$P_{\text{COCl}_2,0} = 0.150 \text{ atm}$$

First, we must determine Q and the direction of the shift.

$$Q_p = \frac{P_{\text{COCl}_2,0}}{P_{\text{CO},0}P_{\text{Cl}_2,0}} = \frac{(0.150)}{(0.800)(0.900)} \quad Q_p = 0.208$$

Since $Q < K$ ($0.208 < 0.289$), the system will shift to the product (COCl_2).

There is too little product at the initial conditions. Hence, the changes to the CO and Cl_2 are negative, and the change to the COCl_2 would be positive.

$$P_{\text{CO},eq} = ?$$

$$P_{\text{Cl}_2,eq} = ?$$

$$P_{\text{COCl}_2,eq} = ?$$

Let x = amount of change per mole, since there is 1 mole of CO reacted; CO will decrease by $1x$. Similarly, Cl_2 will decrease by $1x$. COCl_2 , on the other hand, will increase by $1x$.

	$\text{CO}_{(g)}$	+	$\text{Cl}_{2(g)}$	$\rightleftharpoons$	$\text{COCl}_{2(g)}$
Initial	0.800 atm		0.900 atm		0.150 atm
Change	$-x$		$-x$		$+x$
Equilibrium	$(0.800 - x) \text{ atm}$		$(0.900 - x) \text{ atm}$		$(0.150 + x) \text{ M}$

Next, we set up the equilibrium expression, substitute the above mathematical expressions and solve for x .

(Since we don't have any common exponent, we have to expand the denominator.)

$$K_P = \frac{P_{\text{COCl}_2, \text{eq}}}{P_{\text{CO}, \text{eq}} P_{\text{Cl}_2, \text{eq}}} \quad 0.289 = \frac{(0.15 + x)}{(0.8 - x)(0.9 - x)} = \frac{(0.15 + x)}{(0.72 - 1.7x + x^2)}$$

$$0.289(0.72 - 1.7x + x^2) = (0.15 + x)$$

$$0.20808 - 0.4913x + 0.289x^2 = 0.15 + x$$

$$0.289x^2 - 1.4913x + 0.05808 = 0 \quad (\text{Quadratic Equation: Apply the Quadratic Formula!})$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad a = 0.289 \quad b = -1.4913 \quad c = 0.05808$$

$$x = \frac{-(-1.4913) \pm \sqrt{(-1.4913)^2 - 4(0.289)(0.05808)}}{2(0.289)}$$

$$x = 5.120963266 \text{ (omit larger value - bigger than 0.800 atm and 0.900 atm)}$$

$$x = 0.0392443468$$

Verify with K :

$$K_P = \frac{P_{\text{COCl}_2, \text{eq}}}{P_{\text{CO}, \text{eq}} P_{\text{Cl}_2, \text{eq}}} = \frac{(0.189)}{(0.761)(0.861)}$$

$$K_P = 0.288 \quad (\text{This matches closely with the } K_P \text{ given in the question.})$$

Finally, substitute x back into the mathematical expressions.

$$P_{\text{CO}, \text{eq}} = 0.800 - x = 0.800 - (0.0392443468)$$

$$P_{\text{CO}, \text{eq}} = 0.761 \text{ atm}$$

$$P_{\text{Cl}_2, \text{eq}} = 0.900 - x = 0.900 - (0.0392443468)$$

$$P_{\text{Cl}_2, \text{eq}} = 0.861 \text{ atm}$$

$$P_{\text{COCl}_2, \text{eq}} = 0.150 + x = 0.150 + (0.0392443468)$$

$$P_{\text{COCl}_2, \text{eq}} = 0.189 \text{ M}$$

Assignment

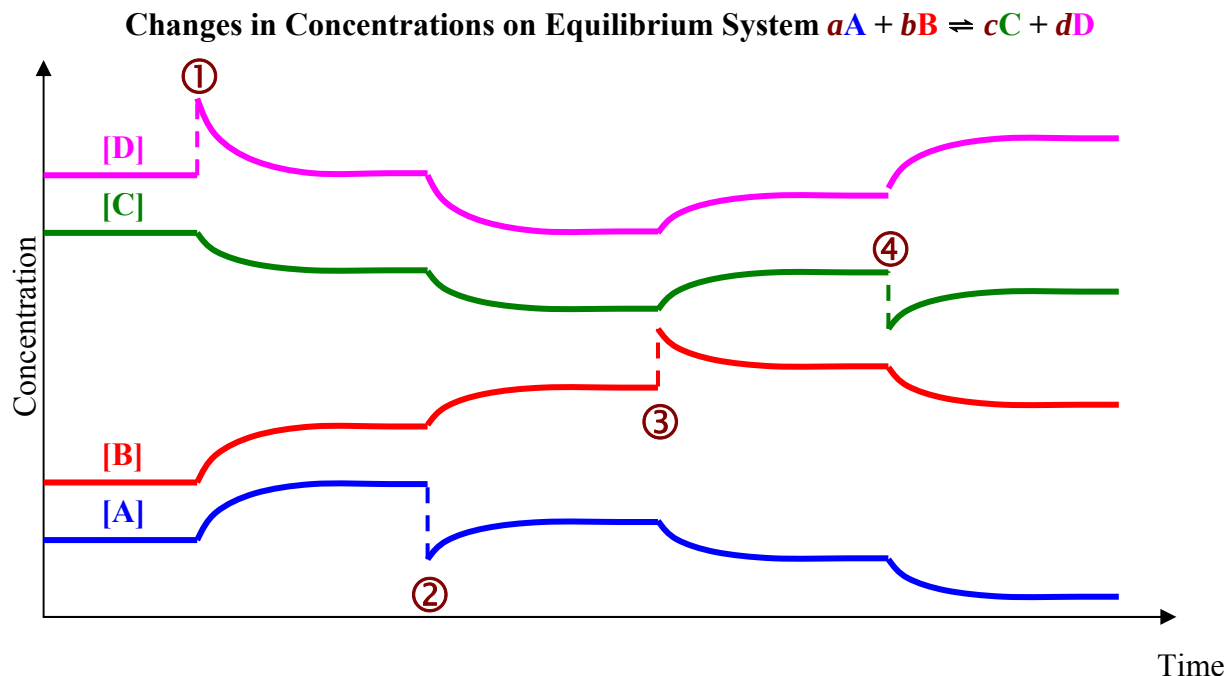
14.4 pg. 635–636 #37 to 48; pg. 637–641 #64, 70 to 78 (even), 82, 84, 108

14.5: Factors That Affect Chemical Equilibrium

Le Châtelier's Principle: - a qualitative method to **predict the shift on an equilibrium system** if it is disturbed by means of **changing concentration, pressure and temperature**.
- **the equilibrium will shift in the direction that minimizes the change imposed on the system.**

1. Effects of a Change in Concentration:

- An ADDITION of a species on one side of the equilibrium will Drive the System TOWARDS the Opposite Side.** (There is more concentration of the species being added. Hence, the system will shift towards the opposite side to reduce the increased amount of that particular species.)
- A REMOVAL of a species on one side of the equilibrium will Drive the system TOWARDS the Same Side.** (There is less concentration of the species being removed. Hence, the system will shift towards the removal side to compensate.)

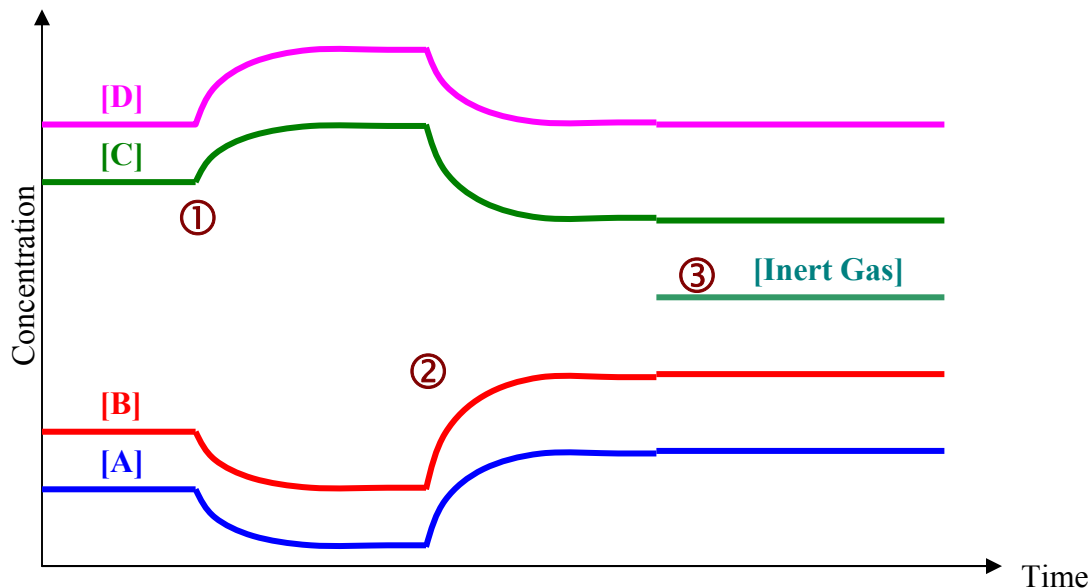


- ① **indicates an Increase in [D].** As $[D] \uparrow$, equilibrium shifts to the left ($aA + bB \rightleftharpoons cC + dD$). Hence, $[A] \uparrow$, $[B] \uparrow$, and $[C] \downarrow$.
- ② **indicates a Decrease in [A].** As $[A] \downarrow$, equilibrium shifts to the left ($aA + bB \rightleftharpoons cC + dD$). Hence, $[B] \uparrow$, $[C] \downarrow$, and $[D] \downarrow$.
- ③ **indicates an Increase in [B].** As $[B] \uparrow$, equilibrium shifts to the right ($aA + bB \rightleftharpoons cC + dD$). Hence, $[A] \downarrow$, $[C] \uparrow$, and $[D] \uparrow$.
- ④ **indicates a Decrease in [C].** As $[C] \downarrow$, equilibrium shifts to the right ($aA + bB \rightleftharpoons cC + dD$). Hence, $[A] \downarrow$, $[B] \downarrow$, and $[D] \uparrow$.

2. Effects of a Change in Pressure:

- a. Adding an Inert Gas has NO CHANGE on the equilibrium system. This is because an inert gas does not participate in the forward or reverse reaction.
- b. Reducing the Volume will Drive the System TOWARDS the Side With LESS Gaseous Molecules. Since there are less space for the number of molecules, the system will have to shift to the side with lesser gaseous molecules to compensate.
- c. Conversely, Expanding the Volume will Drive the System TOWARDS the Side With MORE Gaseous Molecules. Now that there is more room for the molecules to move about, the system will shift to the side that has more gaseous molecules to adjust to the new condition.
- d. When there are Equal Number of Gaseous Molecules on Both Side of the Equilibrium, any Change in Volume will NOT Affect System.

Changes in Pressures on a Gaseous Equilibrium System $aA + bB \rightleftharpoons cC + dD$ when $(c + d) > (a + b)$



- ① indicates an Increase in Volume. As $V \uparrow$, equilibrium shifts to the right ($aA + bB \rightleftharpoons cC + dD$) since there are more gaseous molecules on the product side $[(c + d) > (a + b)]$. Hence, $[A] \downarrow$, $[B] \downarrow$, $[C] \uparrow$, and $[D] \uparrow$.
- ② indicates a Decrease in Volume. As $V \downarrow$, equilibrium shifts to the left ($aA + bB \rightleftharpoons cC + dD$) since there are LESS gaseous molecules on the reactant side $[(c + d) > (a + b)]$. Hence, $[A] \uparrow$, $[B] \uparrow$, $[C] \downarrow$, and $[D] \downarrow$.
- ③ indicates an Addition of an Inert Gas. There is no shifting of the equilibrium. ($aA + bB \rightleftharpoons cC + dD$) as inert gas does not affect the system. Hence, $[A]$, $[B]$, $[C]$, and $[D]$ remain unchanged.

(See the Video at <http://www.sasked.gov.sk.ca/docs/chemistry/mission2mars/contents/chapter3/images/pn2o4.mpg>)

3. Effects of a Change in Temperature: - look at the energy (written in the reactant or product side) as a chemical species. Then, the predictions will be the same as those found with changing the concentrations.

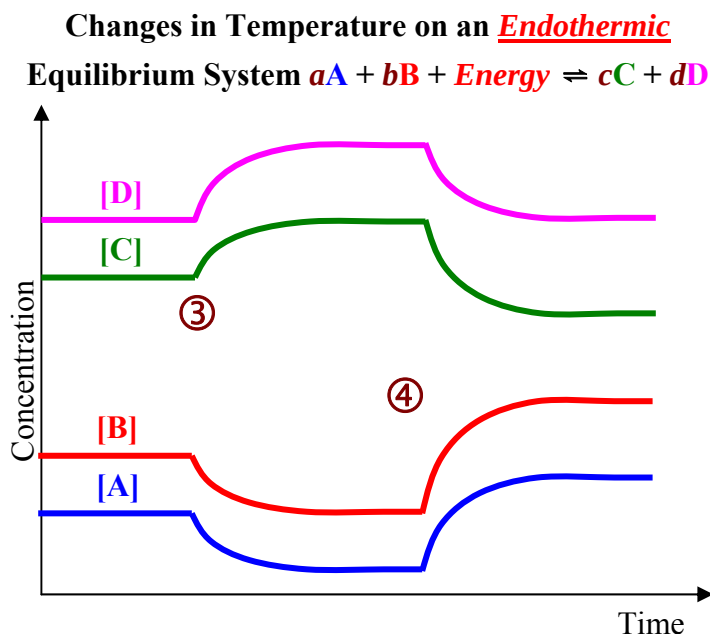
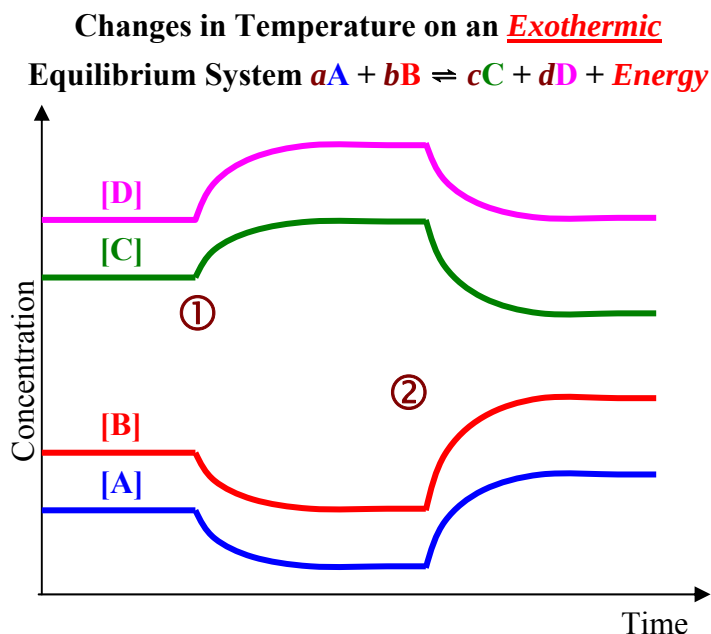
a. For an Exothermic Equilibrium System:



- an Increase in Temperature will drive the system to the left ($aA + bB \rightleftharpoons cC + dD + \text{Energy}$). There is more heat added and because energy is written on the product side, the system will shift to the opposite side to re-establish equilibrium. Hence, $[A] \uparrow$, $[B] \uparrow$, $[C] \downarrow$, and $[D] \downarrow$.
- a Decrease in Temperature will drive the system to the right ($aA + bB \rightleftharpoons cC + dD + \text{Energy}$). There is less heat overall and because energy is written on the product side, the system will shift to the products to compensate. Hence, $[A] \downarrow$, $[B] \downarrow$, $[C] \uparrow$, and $[D] \uparrow$.

b. For Endothermic Equilibrium System: $aA + bB + \text{Energy} \rightleftharpoons cC + dD$

- a Decrease in Temperature will drive the system to the left ($aA + bB + \text{Energy} \rightleftharpoons cC + dD$). There is less heat overall and because energy is written on the reactant side, the system will shift to the reactants to compensate. Hence, $[A]\uparrow$, $[B]\uparrow$, $[C]\downarrow$, and $[D]\downarrow$.
- an Increase in Temperature will drive the system to the right ($aA + bB + \text{Energy} \rightleftharpoons cC + dD$). There is more heat added and because energy is written on the reactant side, the system will shift to the opposite side to re-establish equilibrium. Hence, $[A]\downarrow$, $[B]\downarrow$, $[C]\uparrow$, and $[D]\uparrow$.



- ① indicates a Decrease in Temperature. As $T\downarrow$, equilibrium shifts to the right of an exothermic system ($aA + bB \rightleftharpoons cC + dD + \text{Energy}$). Hence, $[A]\downarrow$, $[B]\downarrow$, $[C]\uparrow$, and $[D]\uparrow$.
- ② indicates an Increase in Temperature. As $T\uparrow$, equilibrium shifts to the left of an exothermic system ($aA + bB \rightleftharpoons cC + dD + \text{Energy}$). Hence, $[A]\uparrow$, $[B]\uparrow$, $[C]\downarrow$, and $[D]\downarrow$.
- ③ indicates an Increase in Temperature. As $T\uparrow$, equilibrium shifts to the right of an endothermic reaction ($aA + bB + \text{Energy} \rightleftharpoons cC + dD$). Hence, $[A]\downarrow$, $[B]\downarrow$, $[C]\uparrow$, and $[D]\uparrow$.
- ④ indicates a Decrease in Temperature. As $T\downarrow$, equilibrium shifts to the left of an endothermic reaction ($aA + bB + \text{Energy} \rightleftharpoons cC + dD$). Hence, $[A]\uparrow$, $[B]\uparrow$, $[C]\downarrow$, and $[D]\downarrow$.

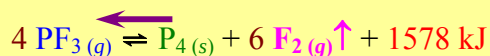
4. Effects of Adding a Catalyst: - has NO CHANGE on the equilibrium system.

(See Video at <http://www.sasked.gov.sk.ca/docs/chemistry/mission2mars/contents/chapter3/images/catalyst.avi>)

Example 1: The equilibrium system, $4 \text{PF}_3(\text{g}) \rightleftharpoons \text{P}_4(\text{s}) + 6 \text{F}_2(\text{g}) + 1578 \text{ kJ}$, is put under the following changes. Predict the shift of the system and the resulting concentrations of all species for each case.

a. an increase in the concentration of $\text{F}_2(\text{g})$.

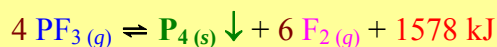
The system will shift to the LEFT.



Effect: $[\text{PF}_3] \uparrow$ (increase)

b. a decrease in the concentration of $\text{P}_4(\text{s})$

There will be NO SHIFT on the system.

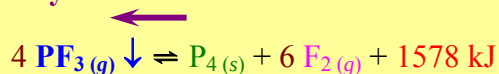


(P_4 is a pure solid and does not involve with the equilibrium system)

Effect: $[\text{PF}_3]$ and $[\text{F}_2]$ remain the same.

c. a decrease in the concentration of $\text{PF}_3(\text{g})$.

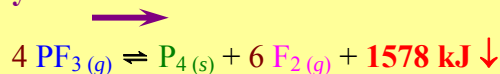
The system will shift to the LEFT.



Effect: $[\text{F}_2] \downarrow$ (decrease)

d. a decrease in Temperature.

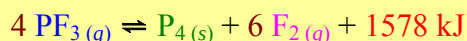
The system will shift to the RIGHT.



Effect: $[\text{PF}_3] \downarrow$ (decrease) and $[\text{F}_2] \uparrow$ (increase)

e. an addition of $\text{He}(\text{g})$.

There will be NO SHIFT on the system.

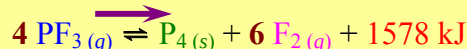


(He is an inert gas and does not involve with the equilibrium system)

Effect: $[\text{PF}_3]$ and $[\text{F}_2]$ remain the same.

f. an increase in volume.

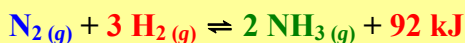
The system will shift to the RIGHT.



(There are more gaseous molecules on the product side – 6 moles of $\text{F}_2(\text{g})$ versus 4 moles of $\text{PF}_3(\text{g})$)

Effect: $[\text{PF}_3] \downarrow$ (decrease) and $[\text{F}_2] \uparrow$ (increase)

Example 2: The Haber-Bosch process, $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g}) + 92 \text{ kJ}$ is essentially an equilibrium system. A chemical engineer would like the highest yield of ammonia. List all the possible method of production that will ensure maximum amount of $\text{NH}_3(\text{g})$ produced.



(Desire Effect: $[\text{NH}_3] \uparrow$, which means driving the system forward.)

1. Increase the concentrations of $\text{N}_2(\text{g})$ or $\text{H}_2(\text{g})$ or both will drive the system forward.
2. Decrease the concentration of $\text{NH}_3(\text{g})$ as it is produced will shift the system forward.
3. Lower the Temperature will drive the system to the product side.
4. Decrease the Volume of the system will shift the system to the right due to smaller number of gaseous molecules on the product side.

Assignment

14.5 pg. 636–640 #49 to 52, 56 to 62 (even), 65 to 69, 90, 98, 106

18.6: Free Energy and Chemical Equilibrium

Relationship between Free Energy and Pressure: - the free energy of a gas at any pressure, G , can be calculated when comparing it to the free energy at standard pressures (1 atm), G° , along with the stated temperature in Kelvin and the gas constant.

Relationship between Free Energy and Pressure

$$G = G^\circ + RT \ln(P)$$

G = Free Energy (J) of the gas at Pressure of P atm

G° = Free Energy (J) of gas at Standard Pressure of 1 atm

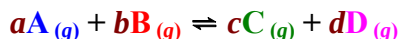
R = Gas Constant 8.314 J/K

T = Temperature in K

P = Pressure of Gas in atm

When $P = 1$ atm, then $G = G^\circ + RT \ln(1)$ and $G = G^\circ$ because $\ln(1) = 0$

Calculating the ΔG of a System with Gaseous Products and Reactants at any Pressure, P :



$$\Delta G = cG_C + dG_D - aG_A - bG_B \quad (\Delta G = \sum nG_{\text{products}} - \sum nG_{\text{reactants}})$$

$$\Delta G = c[G^\circ_C + RT \ln(P_C)] + d[G^\circ_D + RT \ln(P_D)] - a[G^\circ_A + RT \ln(P_A)] - b[G^\circ_B + RT \ln(P_B)]$$

(Expand each term using $G = G^\circ + RT \ln(P)$)

$$\Delta G = cG^\circ_C + cRT \ln(P_C) + dG^\circ_D + dRT \ln(P_D) - aG^\circ_A - aRT \ln(P_A) - bG^\circ_B - bRT \ln(P_B)$$

(Multiply moles into each brackets)

$$\Delta G = [cG^\circ_C + dG^\circ_D - aG^\circ_A - bG^\circ_B] + cRT \ln(P_C) + dRT \ln(P_D) - aRT \ln(P_A) - bRT \ln(P_B)$$

(Collect G° terms: $[cG^\circ_C + dG^\circ_D - aG^\circ_A - bG^\circ_B] = \Delta G^\circ$)

$$\Delta G = \Delta G^\circ + RT [c \ln(P_C) + d \ln(P_D) - a \ln(P_A) - b \ln(P_B)] \quad (\text{Take out common factor } RT \text{ from other terms})$$

$$\Delta G = \Delta G^\circ + RT [\ln(P_C^c) + \ln(P_D^d) - \ln(P_A^a) - \ln(P_B^b)] \quad (\text{Apply law of logarithm: } n \log x = \log x^n)$$

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{P_C^c P_D^d}{P_A^a P_B^b} \right) \quad [\text{Apply logarithm laws: } \log m + \log n = \log(mn) \text{ and } \log m - \log n = \log(m/n)]$$

$$\Delta G = \Delta G^\circ + RT \ln(Q) \quad [\text{Substitute Reaction } Q \text{ as } \left(\frac{P_C^c P_D^d}{P_A^a P_B^b} \right)]$$

Free Energy and Pressures of Gaseous System $aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

ΔG = Free Energy (J) of the gas at Pressure of P atm

ΔG° = Free Energy (J) of gas at Standard Pressure of 1 atm

R = Gas Constant 8.314 J/K

T = Temperature in K

$$Q = \text{Reaction Quotient of Gaseous Species} = \left(\frac{P_C^c P_D^d}{P_A^a P_B^b} \right)$$

When $Q = 1$, then $\Delta G = \Delta G^\circ + RT \ln(1)$ and $\Delta G = \Delta G^\circ$ because $\ln(1) = 0$

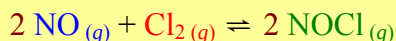
Example 1: At 25°C, the system, $2 \text{NO}_{(g)} + \text{Cl}_{2(g)} \rightleftharpoons 2 \text{NOCl}_{(g)}$ has the following partial pressures of $\text{NO}_{(g)}$, $\text{Cl}_{2(g)}$, and $\text{NOCl}_{(g)}$ are 2.40 atm, 5.30 atm and 3.25 atm respectively. Determine the change in free energy for the system at the partial pressures indicated. (G° of $\text{NO}_{(g)} = 87 \text{ kJ/mol}$, G° of $\text{Cl}_{2(g)} = 0 \text{ kJ/mol}$ and G° of $\text{NOCl}_{(g)} = 66 \text{ kJ/mol}$)

$$\begin{aligned} G^\circ_{\text{NO}} &= 87 \text{ kJ/mol} \\ G^\circ_{\text{Cl}_2} &= 0 \text{ kJ/mol} \\ G^\circ_{\text{NOCl}} &= 66 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} P_{\text{NO}} &= 2.40 \text{ atm} \\ P_{\text{Cl}_2} &= 5.30 \text{ atm} \\ P_{\text{NOCl}} &= 3.25 \text{ atm} \end{aligned}$$

$$T = 25^\circ\text{C} = 298.15 \text{ K}$$

$$\begin{aligned} \Delta G^\circ &= ? \quad Q = ? \\ \Delta G &= ? \end{aligned}$$



$$\Delta G^\circ = \Sigma G^\circ_{\text{products}} - \Sigma G^\circ_{\text{reactants}}$$

$$\Delta G^\circ = [(2 \text{ mol})(66 \text{ kJ/mol})] - [(2 \text{ mol})(87 \text{ kJ/mol}) + (1 \text{ mol})(0 \text{ kJ/mol})]$$

$$\Delta G^\circ = -42 \text{ kJ} = -4.2 \times 10^4 \text{ J} \quad (\Delta G^\circ < 0; \text{Forward Reaction is Spontaneous})$$

$$Q = \frac{P_{\text{NOCl}}^2}{P_{\text{NO}}^2 P_{\text{Cl}_2}} = \frac{(3.25)^2}{(2.40)^2 (5.30)} \quad Q = 0.3459938417$$

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

$$\Delta G = (-4.2 \times 10^4 \text{ J}) + (8.314 \text{ J/K})(298.15 \text{ K}) \ln(0.3459938417)$$

$$\Delta G = -44630.85574 \text{ J}$$

$$\Delta G = -45 \text{ kJ}$$

(It became more spontaneous towards the product side. This probably means that $Q < K$ or $K > 0.346$)

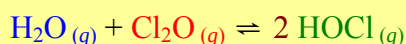
Example 2: At 25°C, the system, $\text{H}_2\text{O}_{(g)} + \text{Cl}_2\text{O}_{(g)} \rightleftharpoons 2 \text{HOCl}_{(g)}$ has the following partial pressures of $\text{H}_2\text{O}_{(g)}$, $\text{Cl}_2\text{O}_{(g)}$, and $\text{HOCl}_{(g)}$ are 0.350 atm, 0.220 atm and 0.860 atm respectively. Determine the change in free energy for the system at the partial pressures indicated. (G° of $\text{H}_2\text{O}_{(g)} = -229 \text{ kJ/mol}$, G° of $\text{Cl}_2\text{O}_{(g)} = 98 \text{ kJ/mol}$ and G° of $\text{HOCl}_{(g)} = 0 \text{ kJ/mol}$)

$$\begin{aligned} G^\circ_{\text{H}_2\text{O}} &= -229 \text{ kJ/mol} \\ G^\circ_{\text{Cl}_2\text{O}} &= 98 \text{ kJ/mol} \\ G^\circ_{\text{HOCl}} &= 0 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} P_{\text{H}_2\text{O}} &= 0.350 \text{ atm} \\ P_{\text{Cl}_2\text{O}} &= 0.220 \text{ atm} \\ P_{\text{HOCl}} &= 0.860 \text{ atm} \end{aligned}$$

$$T = 25^\circ\text{C} = 298.15 \text{ K}$$

$$\begin{aligned} \Delta G^\circ &= ? \quad Q = ? \\ \Delta G &= ? \end{aligned}$$



$$\Delta G^\circ = \Sigma G^\circ_{\text{products}} - \Sigma G^\circ_{\text{reactants}}$$

$$\Delta G^\circ = [(2 \text{ mol})(0 \text{ kJ/mol})] - [(1 \text{ mol})(-229 \text{ kJ/mol}) + (1 \text{ mol})(98 \text{ kJ/mol})]$$

$$\Delta G^\circ = 131 \text{ kJ} = 1.31 \times 10^5 \text{ J} \quad (\Delta G^\circ > 0; \text{Forward Reaction is Non-spontaneous})$$

$$Q = \frac{P_{\text{HOCl}}^2}{P_{\text{H}_2\text{O}} P_{\text{Cl}_2\text{O}}} = \frac{(0.860)^2}{(0.350)(0.220)} \quad Q = 9.605194805$$

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

$$\Delta G = (1.31 \times 10^5 \text{ J}) + (8.314 \text{ J/K})(298.15 \text{ K}) \ln(9.605194805) = 136608.1798 \text{ J}$$

$$\Delta G = 137 \text{ kJ}$$

(It became more spontaneous towards the reactants (even more non-spontaneous towards the product side). This probably means that $Q > K$ or $K < 9.605194805$)

- Equilibrium Point:** - the point where the system attains thermodynamic equilibrium – *the lowest value of free energy available to the equilibrium system.*
- this occurs when $Q = K_P$ and $\Delta G = 0$ at certain partial pressures.
 - we can use equilibrium point to calculate the value of the equilibrium constant K from ΔG°

Equilibrium Point ($Q = K_P$ and $\Delta G = 0$) of a Gaseous System $aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$

$$0 = \Delta G^\circ + RT \ln(K) \quad \text{or} \quad \Delta G^\circ = -RT \ln(K)$$

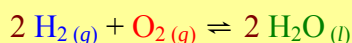
ΔG° = Free Energy (J) of gas at Standard Pressure of 1 atm R = Gas Constant 8.3145 J/K

K_P = Equilibrium Constant of Gaseous System = $\left(\frac{P_{C,eq}^c P_{D,eq}^d}{P_{A,eq}^a P_{B,eq}^b} \right)$ T = Temperature in K

Qualitative Relationship between ΔG and K_P : $\Delta G^\circ = -RT \ln(K_P)$

$K_P > 1$ $\ln(K_P) > 0$ (Positive) $\Delta G^\circ < 0$ (Negative)	<u>Products are favoured</u> over the Reactants (Forward Reaction is Spontaneous)
$K_P = 1$ $\ln(K_P) = 0$ $\Delta G^\circ = 0$	Products and Reactants are <u>Equally favoured</u>
$K_P < 1$ $\ln(K_P) < 0$ (Negative) $\Delta G^\circ > 0$ (Positive)	<u>Reactants are favoured</u> over the Products (Reverse Reaction is Spontaneous)

Example 3: Calculate the equilibrium constant of the formation of water at 25.0°C. (G° of $H_{2(g)}$ = 0 kJ/mol, G° of $O_{2(g)}$ = 0 kJ/mol and G° of $H_2O_{(l)}$ = -237 kJ/mol)



$$\Delta G^\circ = \Sigma G^\circ_{\text{products}} - \Sigma G^\circ_{\text{reactants}}$$

$$\Delta G^\circ = [(2 \text{ mol})(-237 \text{ kJ/mol})] - [(2 \text{ mol})(0 \text{ kJ/mol}) + (1 \text{ mol})(0 \text{ kJ/mol})]$$

$$\Delta G^\circ = -474 \text{ kJ} = -4.74 \times 10^5 \text{ J} \quad (\Delta G^\circ < 0; \text{Forward Reaction is Spontaneous})$$

$$\Delta G^\circ = -RT \ln(K_P) \text{ at thermodynamic equilibrium}$$

$$\ln(K_P) = -\frac{\Delta G^\circ}{RT} = \frac{-(-4.74 \times 10^5 \text{ J})}{(8.3145 \text{ J/K})(298.15 \text{ K})} = 191.2085862$$

$$K_P = e^{191.2085862}$$

$$K_P = 1.10 \times 10^{83}$$

Since $K_P \gg 1$, the equilibrium is extremely favourable towards the product at 25°C. This is in agreement with the conclusion made using the thermodynamic quantity of $\Delta G^\circ \ll 0$.

Example 4: Given that $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$ has the following thermodynamic values, calculate ΔG° and K_p of the given equilibrium at 25.0°C .

Chemicals	H° (kJ/mol)	S° [J/(K • mol)]
$\text{N}_2(\text{g})$	0	192
$\text{H}_2(\text{g})$	0	131
$\text{NH}_3(\text{g})$	-46	193

$$\Delta H^\circ = \sum H^\circ_{\text{products}} - \sum H^\circ_{\text{reactants}} = [(2 \text{ mol})(-46 \text{ kJ/mol})] = -92 \text{ kJ}$$

$$\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

$$\Delta S^\circ = [(2 \text{ mol})(193 \text{ J/(K • mol)})] - [(1 \text{ mol})(192 \text{ J/(K • mol)}) + (3 \text{ mol})(131 \text{ J/(K • mol)})] = -199 \text{ J/K}$$

$$\Delta H^\circ = -92 \text{ kJ} = -92000 \text{ J}$$

$$\Delta S^\circ = -199 \text{ J/K}$$

$$T = 25.0^\circ\text{C} = 298.15 \text{ K}$$

$$\Delta G^\circ = ?$$



$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = (-92000 \text{ J}) - (298.15 \text{ K})(-199 \text{ J/K}) = -32668.15 \text{ J}$$

$$\Delta G^\circ = -3.3 \times 10^4 \text{ J at } 25.0^\circ\text{C}$$

Since $\Delta G^\circ < 0$, the Forward Reaction is Spontaneous

$$R = 8.3145 \text{ J/K}$$

$$\Delta G^\circ = -32.66815 \text{ kJ} = -32668.15 \text{ J}$$

$$K_p = ?$$

$$\Delta G^\circ = -RT \ln(K_p) \text{ at thermodynamic equilibrium}$$

$$\ln(K_p) = -\frac{\Delta G^\circ}{RT} = \frac{-(-32668.15 \text{ J})}{(8.3145 \text{ J/K})(298.15 \text{ K})}$$

$$\ln(K_p) = 13.178124$$

$$K_p = e^{13.178124} = 528672.2741$$

$$K_p = 5.3 \times 10^5$$

As we can see $K_p \gg 1$, which indicates the equilibrium is favouring the product at 25°C . This is in agreement with the conclusion made using the thermodynamic quantity of $\Delta G^\circ < 0$.

Temperature Dependence on K_p :

$$-RT \ln(K_p) = \Delta G^\circ$$

$$-RT \ln(K_p) = \Delta H^\circ - T\Delta S^\circ$$

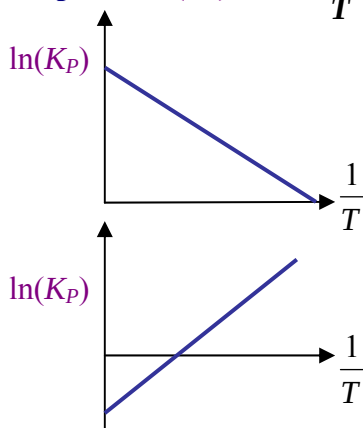
$$\ln(K_p) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

(Start with Free Energy Formula with Equilibrium Constant)

(Substitute ΔG° with $\Delta H^\circ - T\Delta S^\circ$)

(Divide both sides by $-RT$ and simplify)

Graphs of $\ln(K_p)$ versus $\frac{1}{T}$



$$\ln(K_p) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R}$$

$$\begin{matrix} \uparrow & & \uparrow & \uparrow & \uparrow \\ y & = & m & x & + & b \end{matrix}$$

When $\ln(K_p)$ is graphed against $(1/T)$:

$$\Delta H^\circ = -\text{slope} \times R$$

$$\Delta S^\circ = (\text{y-intercept}) \times R$$

$m < 0$ when $\Delta H^\circ > 0$ (negative slope if system is endothermic)

$m > 0$ when $\Delta H^\circ < 0$ (positive slope if system is exothermic)

$b < 0$ when $\Delta S^\circ < 0$ (negative y-int if system becomes less random)

$b > 0$ when $\Delta S^\circ > 0$ (positive y-int if system becomes more random)

Example 5: The equilibrium constant of the system, $2 \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$, is allowed to varied with the change in temperature. The experimental data are shown below.

Temperature	Equilibrium Constant (K_p)
373 K	0.067
273 K	58
195 K	1.4×10^6
77 K	3.8×10^{29}

- Complete the table below.
- Graph $\ln(K_p)$ versus $1/T$. Determine the slope and y-intercept of the graph using linear regression of your graphing calculator.
- Calculate the ΔH° and ΔS° of this equilibrium system.
- Comment on the thermodynamic spontaneity of the equilibrium system at various temperatures.

Temperature	Equilibrium Constant (K_p)	$1/T$ (K^{-1})	$\ln(K_p)$
373 K	0.067		
273 K	58		
195 K	1.4×10^6		
77 K	3.8×10^{29}		

- a. Using the TI-83 Plus Calculator, we can enter the experimental results in the STATS Editor and quickly manipulate the data.

1. Enter Values in the L_1 and L_2 Columns of Stats Editor

STAT	L1	L2	L3	2
	373	.067		
	273	58		
	195	1.4E6		
	77	3.8E29		
	---	---		
ENTER	L2(5) =			

2. Enter " $1/L_1$ " in the heading of L_3 .
Enter " $\ln(L_2)$ " in the heading of L_4 .

L1	L2	L3	3
373	.067	.00268	
273	58	.00366	
195	1.4E6	.00513	
77	3.8E29	.01299	
---	---	---	
	L3 = "1/L1"		

Cursor must be on the column heading before entering formula

L2	L3	L4	4
.067	.00268	-2.703	
58	.00366	4.0604	
1.4E6	.00513	14.152	
3.8E29	.01299	68.11	
---	---	---	
	L4 = "ln(L2)"		

" must be used to enter formula

ALPHA

MEM "+"

To access L_2 , press

2nd

L2
2

3. Fill in the Table

Temperature	Equilibrium Constant (K_p)	$1/T$ (K^{-1})	$\ln(K_p)$
373 K	0.067	0.00268	-2.703
273 K	58	0.00366	4.0604
195 K	1.4×10^6	0.00513	14.152
77 K	3.8×10^{29}	0.01299	68.110

b. Graph $\ln(K_p)$ versus $1/T$. Determine the **slope** and **y-intercept** of the graph using linear regression of your graphing calculator.

1. Turn On STATS PLOT

2nd **STAT PLOT** **ENTER** **Y=**

To access L_3 , press 2nd **L3** 3

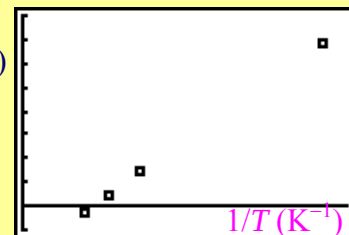
To access L_4 , press 2nd **L4** 4

2. Set WINDOW

WINDOW x: [0, 0.014, 0.002]
y: [-10, 80, 10]

WINDOW
Xmin=0
Xmax=.014
Xscl=.02
Ymin=-10
Ymax=80
Yscl=10
Xres=1

3. Graph

GRAPH

$\ln(K_p)$ versus $(1/T)$ Graph forms a Straight Line.

We can use the linear regression function of the calculator to find the value of the **slope** and **y-intercept** for calculating ΔH° and ΔS° respectively.

1. Turn Diagnostic On

2nd **CATALOG** 0

ENTER **Again** **ENTER**

Select DiagnosticOn

Note: After **DiagnosticOn** is selected; it will remain ON even when the calculator is turned Off. However, resetting the calculator will turn the Diagnostic Off (factory setting).

2. Obtain **LinReg** ($ax + b$) L_3 , L_4 , Y_1 . Copy Equation to **Y=** Screen, and Graph Least Square Line on Scatter Plot.

STAT Select CALC, use **ENTER** 2nd **L3** 3

ENTER 2nd **L4** 4

To access Y_1 , press **VARS** Select Option 1 for Y_1

ENTER

Choose Option 4 Linear Regression ($ax + b$)

ENTER **Function** 1: Y_1 2: Y_2 3: Y_3 4: Y_4 5: Y_5 6: Y_6 7: Y_7

Select Option 1

ENTER

```
DiagnosticOn
Done
LinReg(ax+b) L3,
L4,Y1
```

```
LinReg
y=ax+b
a=6869.828267
b=-21.10277046
r^2=.9999996856
r=.9999998428
```

Y=

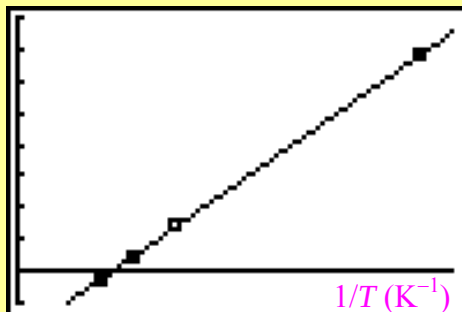
Be Sure Plot1 is On

```
Plot1 Plot2 Plot3
Y1=6869.8282669
823X+ -21.1027704
55077
Y2=
Y3=
Y4=
Y5=
```

When r is extremely close to ± 1 , it indicates the line has a linear relationship.

GRAPH

x: [0, 0.014, 0.002]
y: [-10, 80, 10]

 $\ln(K_p)$ 

$$y = 6869.8282669823x - 21.102770455077$$

compares to

$$\ln(K_p) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R}$$

$$\text{slope} = 6869.8282669823 \text{ K}$$

$$\text{y-intercept} = -21.102770455077$$

- c. Calculate the ΔH° and ΔS° of this equilibrium system.

$$-\frac{\Delta H^\circ}{R} = \text{slope}$$

$$\Delta H^\circ = -(\text{slope})R = -(6869.8282669823 \text{ K})(8.3145 \text{ J/K}) = -57119.18713 \text{ J}$$

$$\Delta H^\circ = -57 \text{ kJ}$$

$$\frac{\Delta S^\circ}{R} = \text{y-intercept}$$

$$\Delta S^\circ = (\text{y-int})R = (-21.102770455077)(8.3145 \text{ J/K}) = -175.4589849 \text{ J/K}$$

$$\Delta S^\circ = -0.18 \text{ kJ/K}$$

For the equilibrium system, $2 \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$, it makes sense that $\Delta S^\circ < 0$ because it is proceeding from two molecules of gas to one molecule of gas.

- d. Comment on the thermodynamic spontaneity of the equilibrium system at various temperatures.



At LOW Temperature, $\Delta G^\circ < 0$ (Spontaneous Forward Reaction) because $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$ ($- = (-) - \text{small } (-)$). This agrees with the fact that $K_p \gg 1$ at Low Temperature, which indicates that the system favors the product side. (Applying *Le Châtelier's Principle* will conclude that that at Low Temperature, $[\text{N}_2\text{O}_4] \uparrow$ and $[\text{NO}_2] \downarrow$)

At HIGH Temperature, $\Delta G^\circ > 0$ (Spontaneous Reverse Reaction) because $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$ ($- = (-) - \text{big } (-)$). This agrees with the fact that $K_p < 1$ at High Temperature, which indicates that the system favors the reactant side. (Applying *Le Châtelier's Principle* will conclude that at High Temperature, $[\text{N}_2\text{O}_4] \downarrow$ and $[\text{NO}_2] \uparrow$)

Assignment

18.6 pg. 811–814 #21, 22, 24, 26 to 32, 49, 64, 66, 76, 80