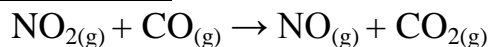


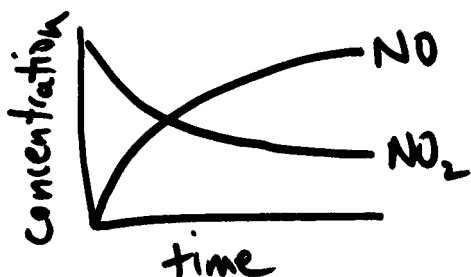
#73 Notes **Unit 9: Kinetics and Equilibrium**
Ch. Kinetics and Equilibriums

I. Reaction Rates



Rate is defined in terms of the rate of disappearance of one of the reactants, but it can also be defined by the rate of appearance of one of the products.

$$\text{Rate} = \frac{-\Delta[\text{NO}_2]}{\Delta t} = \frac{-\Delta[\text{CO}]}{\Delta t} = \frac{\Delta[\text{NO}]}{\Delta t} = \frac{\Delta[\text{CO}_2]}{\Delta t}$$



- rate can be measured for a specific time
 (instantaneous rate = slope)
 or over a time interval (average rate)

II. Integrated Rate Laws

$$\text{Rate} = k [\text{reactant 1}]^x [\text{reactant 2}]^y$$

-x,y are usually integers

↑ ↑
 ↑ concentrations (molarity)

rate constant, (k), depends on size, speed, kind of molecule, temperature, etc.

Ex. 1) $\text{A} + \text{B} \rightarrow \text{C}$

	initial [A]	initial [B]	initial rate	rate = $\frac{-\Delta[\text{B}]}{\Delta t}$
row 1	0.100 M	0.100 M	4.0×10^{-5}	
row 2	0.100 M	0.200 M	4.0×10^{-5}	
row 3	0.200 M	0.100 M	$1.6 \times 10^{-4} = 16 \times 10^{-5}$	

Compare two rows where only one concentration is changing (only "A" or only "B").

comparing row 1 & 2: A remains the same, B is doubling and the rate is the same.

(going down the rows) $\text{rate} = k [\text{A}]^1 [\text{B}]^2$
 $1X \quad \quad 2X \quad \quad 2^0 \text{ equals } 1, \text{ so } [\text{B}]^0$

comparing row 1 & 3: A is doubling, B is the same and the rate is four times bigger.

(going down the rows) rate = k [A] [B]
4X 2X

2^2 equals 4, so $[A]^2$

Rate = k[A]²[B]⁰ or Rate = k[A]²

(2nd order, since powers add up to "2")
(A is 2nd order, B is zero order)

Find rate constant:

$$\text{Rate} = k[A]^2$$
$$4.0 \times 10^{-5} = k (0.100 \text{ M})^2 \quad \text{plugging in values from row \#1.}$$
$$\mathbf{4.0 \times 10^{-3} = k} \leftarrow \text{Book does all 3 rows and averages (just do one row).}$$

Ex. 2) $(\text{CH}_3)_3\text{CBr} + \text{OH}^- \rightarrow (\text{CH}_3)_3\text{COH} + \text{Br}^-$

	$[(\text{CH}_3)_3\text{CBr}]_0$	$[\text{OH}^-]_0$	$\text{rate} = \frac{+\Delta[\text{Br}^-]}{\Delta t}$
row 1	0.10 M	0.18 M	1.0×10^{-3}
row 2	0.20 M	0.10 M	2.0×10^{-3}
row 3	0.10 M	0.10 M	1.0×10^{-3}

comparing row 1 & 3: $(\text{CH}_3)_3\text{CBr}$ is the same,

(going up the row)

OH^- is basically doubling and the rate is the same.

rate = k $[(\text{CH}_3)_3\text{CBr}] [\text{OH}^-]$

1X

2X

2^0 equals 1, so $[\text{OH}^-]^0$

comparing row 2 & 3: $(\text{CH}_3)_3\text{CBr}$ is doubling,

(going up the row)

OH^- is the same and the rate is doubling.

rate = k $[(\text{CH}_3)_3\text{CBr}] [\text{OH}^-]$

2X

2X

2^1 equals 2, so $[(\text{CH}_3)_3\text{CBr}]^1$

$$\mathbf{\text{rate} = k [(\text{CH}_3)_3\text{CBr}]^1 [\text{OH}^-]^0 = k [(\text{CH}_3)_3\text{CBr}]^1} \quad (1^{\text{st}} \text{ order overall})$$

Find the rate constant:

$$\text{rate} = k [(\text{CH}_3)_3\text{CBr}]^1$$

$$(1.0 \times 10^{-3}) = k (0.10 \text{ M}) \quad \text{using row \#1}$$

$$\mathbf{1.0 \times 10^{-2} = k}$$

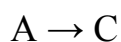
What would the rate be, if $[(\text{CH}_3)_3\text{CBr}] = 0.26 \text{ M}$ & $[\text{OH}^-] = 0.45 \text{ M}$?

$$\text{rate} = k [(\text{CH}_3)_3\text{CBr}]^1$$

$$\text{rate} = (1.0 \times 10^{-2}) (0.26 \text{ M})$$

$$\mathbf{\text{rate} = 2.6 \times 10^{-3}}$$

#74 Notes III. First Order Rate Law



$$\text{Rate} = \frac{-\Delta[A]}{\Delta t} = k [A]^1$$

$$\int \frac{\Delta[A]}{[A]} = \int -k dt$$

$$\ln [A] = -kt + C \quad \text{if } t = 0, \ln [A]_0 = C \quad \text{substitute this in}$$

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

$$y = mx + b \quad \text{slope} = -k$$



Half-life

$$\text{mult by } -1: -\ln [A] = kt - \ln [A]_0$$

$$\ln [A]_0 - \ln [A] = kt$$

$$\ln ([A]_0 / [A]) = kt$$

$$\text{For } 1/2 \text{ life} \quad \ln ([A]_0 / \{ [A]_0 / 2 \}) = k t_{1/2}$$

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

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

$$\mathbf{0.693 / k = t_{1/2}}$$

IV. Second Order Rate Law



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

$$\int \frac{-\Delta[A]}{[A]^2} = \int k \Delta t$$

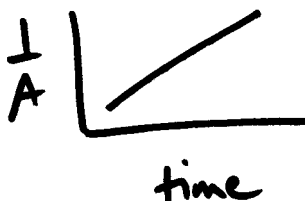
$$+[A]^{-1} = kt + C$$

integral of $x^{-2} dx = -x^{-1}$ (raise power and divide coefficient by it)

$$\frac{1}{[A]} = kt + C \quad \text{if } t = 0, \quad C = \frac{1}{[A]_0}$$

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \quad \text{slope} = k$$

$$y = mx + b$$



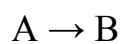
Half-life

$$\frac{1}{([A]_0/2)} = kt_{1/2} + \frac{1}{[A]_0}$$

$$\frac{2}{[A]_0} = kt_{1/2} + \frac{1}{[A]_0}$$

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

V. Zero Order



$$\text{Rate} = \frac{-\Delta[A]}{\Delta t} = k[A]^0 \quad \text{since } [A]^0 = 1$$

$$\int \Delta[A] = \int -k \Delta t$$

$$[A] = -kt + C \quad \text{at } t = 0 \quad C = [A]_0$$

$$[A] = -kt + [A]_0 \quad \text{slope} = -k$$

$$y = mx + b$$



Half-life

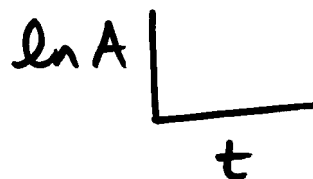
$$\frac{[A]_0}{2} = -kt_{1/2} + [A]_0$$

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

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

If given: $[\text{CH}_4]$ time
 # #
 # #
 # #

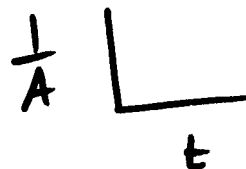
1) Graph



If the line is **straight**, it is 1st order, rate = $k [\text{A}]^1$

If the line is **not straight**, then

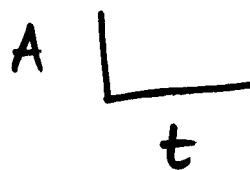
2) Graph



If the line is **straight**, it is 2nd order, rate = $k [\text{A}]^2$

If the line is **not straight**, then

3) Graph



If the line is **straight**, it is zero order, rate = $k [\text{A}]^0$

Ex.1) Find the half-life for an element with a 1st order Rate law (or $\ln A$ vs. time is a straight line), if the reaction is 35% complete in 5 minutes.

(35% has reacted, so 35% has decayed)

100g beginning

- 35g

65g remaining, so $[\text{A}]_0 = 100 \text{ g}$ & $[\text{A}] = 65 \text{ g}$

$$\ln [\text{A}] = -kt + \ln [\text{A}]_0$$

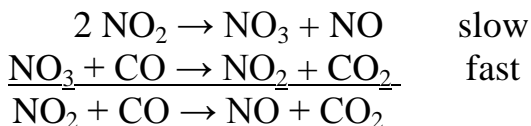
Solve for k , then find $t_{1/2}$

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

#75 Notes VI. Reaction Mechanisms

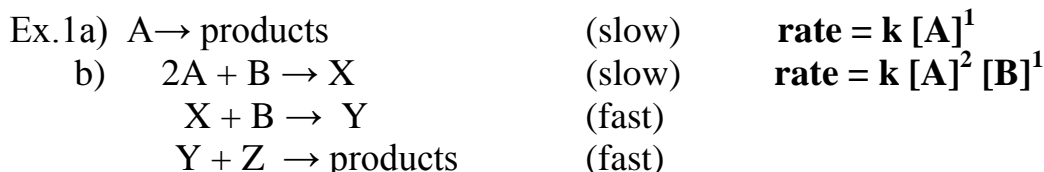
-are the series of steps or reactions necessary to achieve an overall process.

*The slowest step always determines the rate law.



*NO₃ is an intermediate. (It's first a product, then a reactant, which cancel.)

Rate = $k [\text{NO}_2]^2$ rate law from the slowest step!



*Find the slow reaction or if only one reaction, assume it is slow! Use the slow reaction.

VII. Chemical Kinetics/ Collision Model

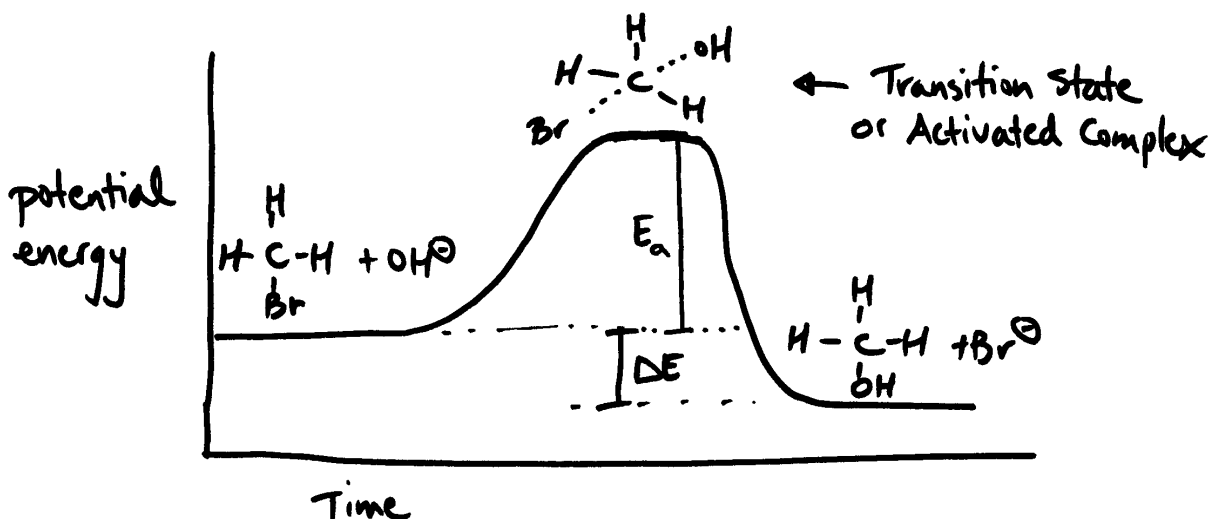


Ionic compounds in reactions do not need to rearrange their electrons, since the ions just change partners. These reactions occur quickly.

Covalent compounds in reactions must change their electron clouds. The energy to do this comes from collisions! *The rate can be increased by increasing the temperature, since this increases the velocity of the particles ($\text{KE} = \frac{1}{2} m v^2$). The number and power of collisions increase.

But the rate does not go up by as much as it should.

Arrhenius proposed the existence of a threshold or activation energy that must be overcome in order to produce a reaction.



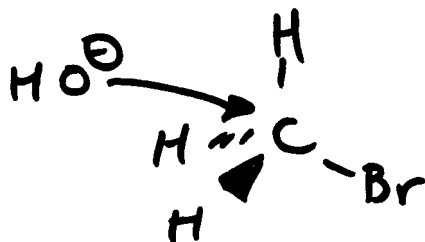
E_a = activation energy needed for reaction to occur.

ΔE = overall energy change for the reaction, above it is (-) so exothermic.

The kinetic energy of the moving molecules is changed into potential energy as the bonds are broken and formed.

**Only collisions with enough energy (activation energy) will be able to form the activated complex and then the products.

The reaction rate is still smaller, than the rate of collisions with enough energy to form the activated complex, because of molecular orientations.



The OH^- must hit from the opposite side to eject the Br^- .

*Catalysts: lower the E_a , allowing reactions to go faster.

*Inhibitors: slow the reaction.

$$k = z p e^{\frac{-E_a}{RT}}$$

k = rate constant

z = collision frequency

p = steric factor (structure of molecule, orientation etc.)

E_a = activation energy

R = 8.31 J/mol•K

T = Kelvin

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

To compare 2 rates:

$$\frac{k_1}{k_2} = \frac{A e^{-E_{a1}/(RT)}}{A e^{-E_{a2}/(RT)}}$$

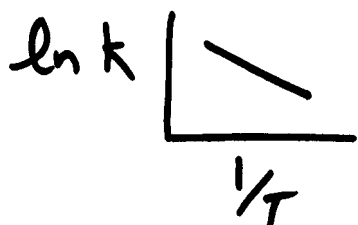
A's cancel, plug in E_a 's, R and T's to get ratio.

To graph: (1st order rates)

$$\ln k = \ln A - E_a / (RT)$$

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

$$y = m x + b$$



slope = $- E_a / R$

k	T	$\ln k$	$1/T$
#	#	#	#
#	#	#	#
#	#	#	#

For 2 values: $\ln(k_2/k_1) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$

E_a must be in J/mol, since R = 8.31 J/mol•K

IX. Catalysis

Catalysts speed up reactions by **lowering** E_a , but they are not consumed.

(If the hill is lower, more collisions will have enough energy to form product.)

These are **first** reactants, **then** products, which cancel.

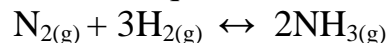
Homogeneous Catalysts: are present in the same phase as the reactants.

(Cl_(g) in O_{3(g)} destruction).

Heterogeneous Catalysts: are present in a different phase.
(catalytic converter_(s) for car exhaust_(g) systems.)

Ch. Chemical Equilibrium

I. Equilibrium Equations



at equilibrium:

Forward Rate = Reverse Rate

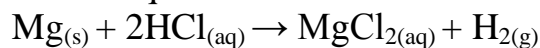
$$k_f[\text{N}_2]^1[\text{H}_2]^3 = k_r[\text{NH}_3]^2$$

$$\frac{k_f}{k_r} = \frac{[\text{NH}_3]^2}{[\text{N}_2]^1[\text{H}_2]^3}$$

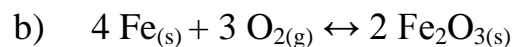
$$\mathbf{K} = \frac{[\text{NH}_3]^2}{[\text{N}_2]^1[\text{H}_2]^3} \quad \leftarrow \text{Molarity} \quad \begin{array}{l} \leftarrow \text{products} \\ \leftarrow \text{reactants} \end{array}$$

*Exception: Pure solids and pure liquids are not included (“aq” and “g” are included).
{H₂O_(l) not included, H₂O_(g) included}

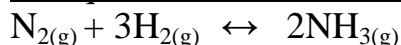
Ex. 1a) Write the K equation for:



$$\mathbf{K} = \frac{[\text{MgCl}_2]^1 [\text{H}_2]^1}{[\text{HCl}]^2}$$



$$\mathbf{K} = \frac{1}{[\text{O}_2]^3}$$

II. Equilibrium and Pressure

$$K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3}$$

Remember:

$$PV = nRT$$

$$P = \frac{n}{V} RT \text{ where } (n/V) = \text{Molarity}$$

$$\text{so, } P = M RT$$

$$K_p = \frac{(M_{\text{NH}_3} RT)^2}{(M_{\text{N}_2} RT)^1 (M_{\text{H}_2} RT)^3}$$

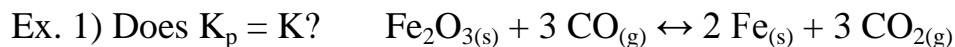
$$K_p = \frac{[M_{\text{NH}_3}]^2}{[M_{\text{N}_2}]^1 [M_{\text{H}_2}]^3} \cdot \frac{(RT)^2}{(RT)^1 (RT)^3}$$

$$\text{Since, } K = \frac{[\text{NH}_3]^2}{[\text{N}_2]^1 [\text{H}_2]^3} \quad (\text{These are molarities.})$$

$$K_p = K \cdot (RT)^{-2} \leftarrow (\text{mols products} - \text{mols reactants})$$

$$K_p = K(RT)^{\Delta n} \quad \mathbf{R = 0.08206 \frac{L \cdot atm}{mol \cdot K}}$$

$$\Delta n = \text{mols products} - \text{mols reactants}$$



**(Solids and liquids do not count in either equation.)

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

$$K_p = K (RT)^{3 \text{ mols product} - 3 \text{ mols reactant}}$$

$$K_p = K (RT)^0 \text{ so } \mathbf{K_p = K}$$

Ex.2) For $\text{N}_{2(g)} + 3 \text{H}_{2(g)} \leftrightarrow 2 \text{NH}_{3(g)}$: What is the concentration of NH_3 at equilibrium, if at equilibrium there is 0.0402 mol N_2 and 0.1207 mol H_2 in 2.00 L? $K = 0.105$

$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2] [\text{H}_2]^3} \quad M_{\text{N}_2} = \frac{0.0402 \text{ mol}}{2.00 \text{ L}} = 0.0201 \text{ M} \quad M_{\text{H}_2} = \frac{0.1207 \text{ mol}}{2.00 \text{ L}} = 0.06035 \text{ M}$$

$$0.105 = \frac{[\text{NH}_3]^2}{(0.0201\text{M})^1 (0.06035 \text{ M})^3}$$

$$4.64 \times 10^{-7} = [\text{NH}_3]^2$$

$$6.81 \times 10^{-4} \text{ M} = [\text{NH}_3]$$

III. Applications of K_{eq}

$K = \text{products} / \text{reactants}$

so if $K > 1$, more products are present

if $K < 1$, more reactants are present

Steps to solve K_{eq} with initial concentrations (NOT at equilibrium):

1) Find Q to determine the shift in equilibrium.

(Q is the K with the initial concentrations)

If $Q = K$, it is already at equilibrium.

If $Q > K$, too many products are present and they need shifted to the reactant side.

If $Q < K$, too many reactants are present and they need shifted to the product side.

2) Define the above change to the initial concentrations.

3) Substitute into equations and solve.

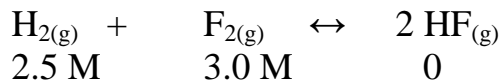
4) Check work.

#78 Notes



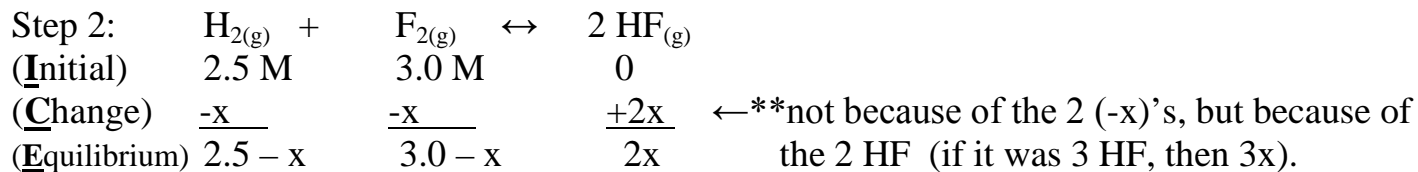
Calculate the equilibrium concentrations, if initially there is 5.00 mol H_2 and 6.00 mol F_2 in a 2.0 L flask. Assume $K = 115$.

$$5.00 \text{ mol} / 2.0 \text{ L} = 2.5 \text{ M } \text{H}_2 \quad 6.00 \text{ mol} / 2.0 \text{ L} = 3.0 \text{ M } \text{F}_2$$



$$K = \frac{[\text{HF}]^2}{[\text{H}_2]^1 [\text{F}_2]^1}$$

Step 1: $Q = \frac{(0)^2}{(2.5)^1 (3.0)^1} = 0$ Q of $0 < K$ of 115, so it needs more products (shift right)



Step 3: $115 = \frac{(2x)^2}{(2.5 - x)^1 (3.0 - x)^1}$

In this case x is large, we need to move a lot to the products to make the fraction increase from 0 to 115.

** If the K is smaller than the Concentrations by 10^3 or more, we can make an assumption that " x " is small. For example, if K was $1 \times 10^{-4} = \frac{(2x)^2}{(2.5 - x)^1 (3.0 - x)^1}$

$$1 \times 10^{-4} \text{ vs. } 2.5 \times 10^0$$

If x is very small: $2.5 - x \approx$ just 2.5, $3.0 - x \approx$ just 3.0

so $1 \times 10^{-4} = \frac{(2x)^2}{(2.5)^1 (3.0)^1}$ no quadratic

In our case we need to solve it without assumptions, since x is not small.

$$115 = \frac{(2x)^2}{(2.5 - x)^1 (3.0 - x)^1}$$

$$115 = \frac{4x^2}{(7.5 - 5.5x + x^2)}$$

$$862.5 - 632.5x + 115x^2 = 4x^2$$

$$111x^2 - 632.5x + 862.5 = 0$$

a b c

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{632.5 \pm \sqrt{(-632.5)^2 - (4)(111)(862.5)}}{2(111)}$$

$$= \frac{632.5 \pm 131}{222} = 3.44 \text{ or } \mathbf{2.25} \quad (3.44 \text{ is impossible, since (-) concentrations are impossible.})$$

$$[\text{H}_2] = 2.5 - x = 2.5 - 2.25 = \mathbf{0.25 \text{ M H}_2}$$

$$[\text{F}_2] = 3.0 - x = 3.0 - 2.25 = \mathbf{0.75 \text{ M F}_2}$$

$$[\text{HF}] = 2x = 2(2.25) = \mathbf{4.5 \text{ M HF}}$$

Step 4: Check $115 = ? \frac{(4.5)^2}{(0.25)^1 (0.75)^1}$

$$115 = ? 108$$

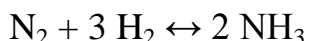
$$\frac{108 - 115}{115} \times 100\% = -6\% < 10\% \text{ is OK}$$

look for perfect squares: $115 = \frac{(2x)^2}{(2.5-x)^1(2.5-x)^1} \rightarrow \sqrt{115} = \frac{(2x)}{(2.5-x)}$

#79 Notes IV. Le Chatelier's Principle

If a system is in equilibrium and a condition is changed, then the system will shift toward restoring the equilibrium.

A) Concentration



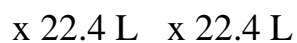
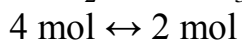
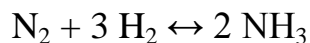
Ex. 1) increase N_2 : increases collisions, so it speeds the reaction going to the right
(products)
shifts right (*too much N_2 , so it will shift to the other side (products)*)

Ex. 2) increase NH_3 : **shifts left** (*too much NH_3 , shifts to the other side (reactants)*)

Ex. 3) decrease H_2 : **shifts left** (*too little H_2 , so it must shift toward H_2 to increase it (reactants)*)

B) Pressure (only affects gases)

Ex. 1) increase P, by decreasing volume (*if decreasing volume, the reaction will shift toward the side that is the most compact (smallest volume)*)



the right side is more compact **shifts right**

(if increase volume, shifts to the left, larger volume side)

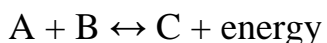
Ex. 2) increase P, by adding Ne, **no change** (Ne is not in the reaction, other gases will not change the volume, since gases are "point masses" (ideal))

C) Temperature

Ex. 1) $\text{Girls} + \text{Boys} \leftrightarrow \text{Dancing} + \text{heat}$ (exothermic, heat produced, $\Delta H = (-)$
energy on product side)

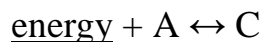
Increase Temperature, Add heat, less dancing, **shifts left**

Ex. 2) Decrease T, for exothermic reaction ($\Delta H = (-)$, energy on product side)



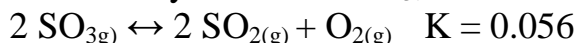
decrease T, too little energy, **shifts right**

Ex. 3) Increase T for endothermic reaction ($\Delta H = (+)$, energy on reactant side)



increase T, too much energy, **shifts right**

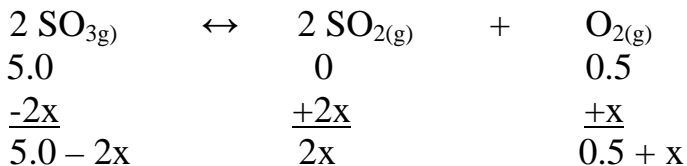
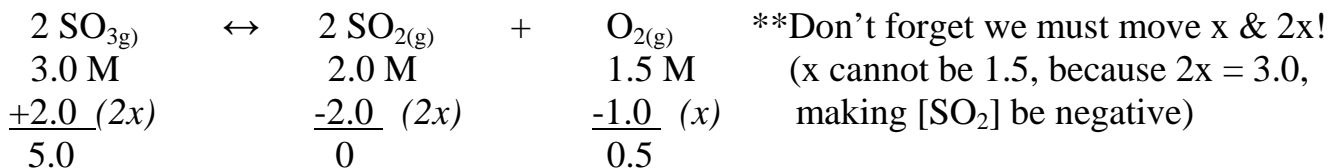
Ex. 1) Find the equilibrium concentrations,
if it initially has 3.0 M SO_3 , 2.0 M SO_2 , and 1.5 M O_2 .



$$3.0 \text{ M} \quad 2.0 \text{ M} \quad 1.5 \text{ M} \quad Q = \frac{(2.0 \text{ M})^2 (1.5 \text{ M})^1}{(3.0 \text{ M})^2} = 0.66$$

Q of 0.66 > K of 0.056, reaction needs less products, shifts left.

Since it will be cubed, x needs to be as small as possible, so that we can assume x is small. We need much less products, so **we will shift as much as possible to the reactant side and then move "x" back to the products. (Hopefully making "x" small.)



$$K = 0.056 = \frac{(2x)^2 (0.5 + x)^1}{(5.0 - 2x)^2}$$

Assume x is small, K is smaller than the concentrations by only 2 powers (5.6×10^{-2} vs. 5.0×10^0), but we have cubes (we can't do the quadratic).

$$0.5 + x \approx 0.5$$

$$5.0 - 2x \approx 5.0$$

$$0.056 = \frac{(2x)^2 (0.5)^1}{(5.0)^2}$$

$$1.4 = (4x^2) (0.5)$$

$$1.4 = 2x^2$$

$$0.84 = x$$

$$\text{SO}_3 = 5.0 - 2x = \mathbf{3.3 M SO}_3$$

$$\text{SO}_2 = 2x = \mathbf{1.7 M SO}_2$$

$$\text{O}_2 = 0.5 + x = \mathbf{1.3 M O}_2$$

**Checking this, K comes out to 0.34, which is off, because x is not that small. It is better than before (Q was 0.66), but now you would have to repeat the problem with these answers. And keep repeating over and over until the answers do check. (Method of Successive Approximations)

End of Notes (Assignments #80-81 are Review Assignments. There are no notes for these assignments.)