"A" students work
(without solutions manual)
~ 10 problems/night.

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Module #15:
Introduction to Equilibrium

1. Define Equilibrium,
And equilibrium
constant

Gaseous Chemical Equilibrium

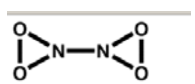
1. Can balance equations
2. Can predict direction of reaction (ΔH)
3. Can compute rates

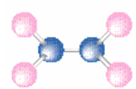
$$rate = -\frac{d[A]}{adt} = k[A]^m$$

4. Can we predict what happens at end?

Our Friend for this Chapter

Dinitrogen tetroxide





A. Intermediate in:
- nitric acid & sulfuric acid production
- nitration of organic compound & explosives
- manufacture of oxidized cellulose compound (hemostatic cotton)

B. Used to bleach flour

C. Proposed as oxidizing agent in rocket propulsion nitrogen dioxide.

We studied it's decomposition kinetics in
The preceding chapter

$$N_2O_{4,g} \rightarrow 2NO_{2,g}$$

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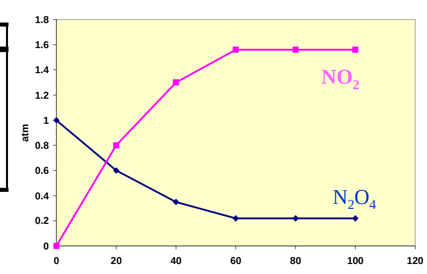
review

Consider the reaction at 100 ^oC, where the initial
Pressure of dinitrogen tetroxide is 1 atm:

$$N_2O_{4,g} \rightarrow 2NO_{2,g}$$

The decomposition of dinitrogen tetroxide vs time
Is shown in the table below

s	N2O4, atm	NO2, atm
0	1	0
20	0.6	0.8
40	0.35	1.3
60	0.22	1.56
80	0.22	1.56
100	0.22	1.56

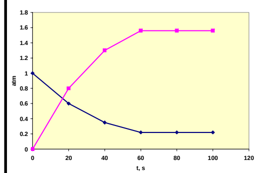


The reaction order and
Rate constant can be determined by various time/conc. plots

$$N_2O_{4,g} \rightarrow 2NO_{2,g}$$

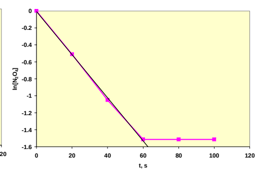
review

s	N2O4, atm	NO2, atm	1/N204	ln N204
0	1	0	1	0
20	0.6	0.8	1.67	-0.51
40	0.35	1.3	2.86	-1.05
60	0.22	1.56	4.55	-1.51
80	0.22	1.56	4.55	-1.51
100	0.22	1.56	4.55	-1.51



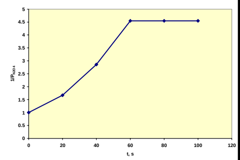
$rate = k[A]^0$

$[A_t] = [A_0] - kt$



$rate = k[A]^1$

$\ln[A_t] = \ln[A_o] - kt$



$rate = k[A]^2$

$\frac{1}{[A]} - \frac{1}{[A_0]} = kt$

1st order reaction

review

$rate = k[A]^1$

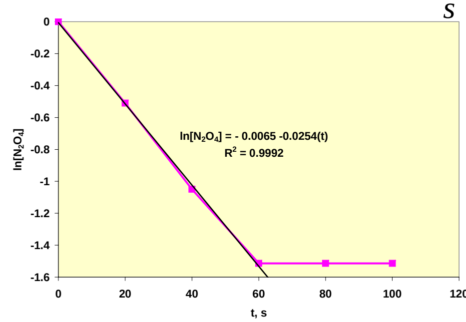
$\ln[A_t] = \ln[A_o] - kt$

$\ln P_{N_2O_4,t} = \ln P_{N_2O_4,t=0} - kt$

$\ln P_{N_2O_4,t} = \ln(1) - kt$

$\ln P_{N_2O_4,t} = 0 - kt$

$k = 0.0254\frac{1}{s}$



Using the rate Constants the Rate at each time Can be calculated

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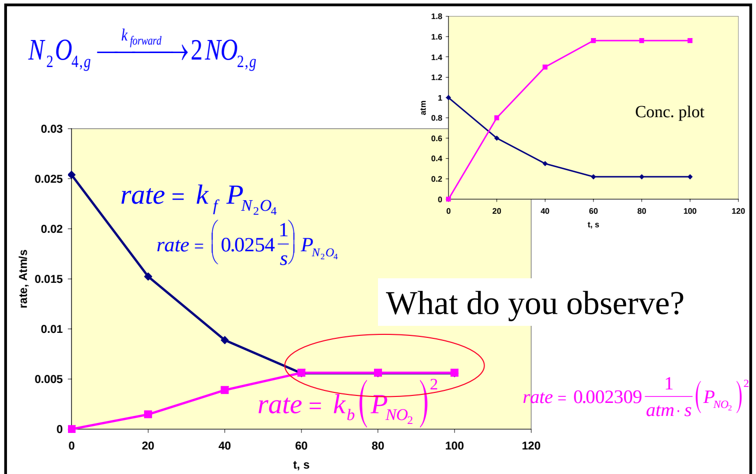
$N_2O_{4,g} \xrightarrow{k_{forward}} 2NO_{2,g}$



$rate = k_f\, P_{N_2O_4}$

$rate = \left(0.0254\frac{1}{s}\right) P_{N_2O_4}$

What do you observe?

$rate = k_b\left(P_{NO_2}\right)^2$

$rate = 0.002309\frac{1}{atm \cdot s}\left(P_{NO_2}\right)^2$

$2NO_{2,g} \xrightarrow{k_{backward}} N_2O_{4,g}$

1. Conc. Are "stable"
2. **Rate forward = rate backward**

"Equilibrium" = "steady state concentrations"

1. occurs when rate forward = rate backward

$Rate_{forward} = Rate_{backward}$

$k_f P_{N_2O_{4,g}} = k_b\left(P_{NO_{2,g}}\right)^2$

$\frac{k_f}{k_b} = \frac{\left(P_{NO_{2,g}}\right)^2}{P_{N_2O_{4,g}}}$

$N_2O_{4,g} \xrightarrow{k_{forward}=0.0254\frac{1}{s}} 2NO_{2,g}$

$2NO_{2,g} \xrightarrow{k_{backward}=0.002309\frac{1}{atm \cdot s}} N_2O_{4,g}$

2. concentrations are also constant (steady state)

$\frac{k_f}{k_b} = \frac{\left(P_{NO_{2,g}}\right)^2}{P_{N_2O_{4,g}}} = K_{equilibrium}$

$K_{equilibrium} = \frac{0.0254\frac{1}{s}}{0.002309\frac{1}{atm \cdot s}} = 11 atm$

3. BOTH reactions are occurring competitively

$N_2O_{4,g} \rightleftarrows 2NO_{2,g}$ ojo

4. An equilibrium constant describes the steady state concs at 100 °C for any starting set of concentrations

$$K_{equilibrium} = 11atm = \frac{\left(P_{NO_2}\right)^2}{P_{N_2O_4}}$$

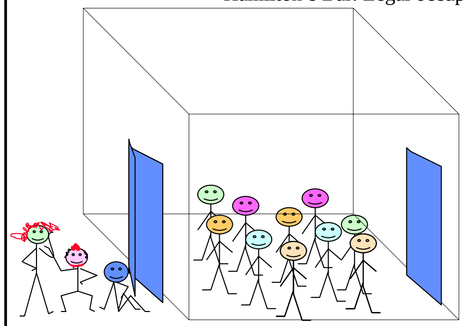
Experiment	1		2		3	
time	N2O4	NO2	N2O4	NO2	N2O4	NO2
t=0	1.00	0.00	0.00	1.00	1.00	1.00
t=equilibrium	0.22	1.56	0.07	0.86	0.42	2.16

$$K_{equilibrium} = 11atm = \frac{\left(P_{NO_{2,g}}\right)^2}{P_{N_2O_{4,g}}}$$

$$K_{equilibrium} = 11atm \stackrel{?}{=} \frac{(1.56atm)^2}{0.22atm} \qquad K_{equilibrium} = 11atm \stackrel{?}{=} \frac{(0.86atm)^2}{0.07atm} \qquad K_{equilibrium} = 11atm \stackrel{?}{=} \frac{(2.16atm)^2}{0.42atm}$$

$$11atm \stackrel{?}{=} 11.06atm \qquad 11atm \stackrel{?}{=} 10.56atm \qquad 11atm \stackrel{?}{=} 11.11atm$$

Hamilton's Bar: Legal occupancy: 10



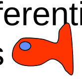
The stupid analogy

3 out   10 in

Hamilton's appears to have an unchanged population, but constant exchange of drinkers is occurring. The equilibrium is 10/3.

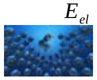
FITCH Rules

General

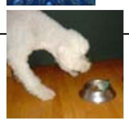
G1: Suzuki is Success
G2. Slow me down
G3. Scientific Knowledge is Referential
G4. Watch out for Red Herrings 
G5. Chemists are Lazy

Chemistry

C1. It's all about charge $E_{el} = k\left(\frac{q_1 q_2}{r_1 + r_2}\right)$
C2. Everybody wants to "be like Mike"
C3. Size Matters $E_{el} = k\left(\frac{q_1 q_2}{r_1 + r_2}\right)$
C4. Still Waters Run Deep
C5. Alpha Dogs eat first



Piranhas lurk



Apparent Lack of change, Constant microscopic change

The "Generic" Rule

Stoichiometry shows up as power

$$aA + bB \rightleftarrows cC + dD$$

$$K_{Pressure} = \frac{\left(P_C\right)^c \left(P_D\right)^d}{\left(P_A\right)^a \left(P_B\right)^b}$$

Pressure Of Products On top

Pressure Of reactants On bottom

An equilibrium constant can be written in terms of Molarity also

$$PV = nRT \qquad aA + bB \rightleftarrows cC + dD$$

$$\frac{P}{RT} = \frac{n}{V} = [molarity]$$

$$P = RT[molarity]$$

$$K_{Pressue} = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

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

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

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

$$K_{Pressue} = \left\{\frac{(RT)^c (RT)^d}{(RT)^a (RT)^b}\right\} K_{concentration}$$

$$K_{Pressue} = (RT)^{(c+d)-(a+b)} K_{concentration}$$

$$K_{Pressue} = (RT)^{\Delta n_{f-i}} K_{concentration}$$

When doing problems watch out that they are not switching units on you!!!!!

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Module #15: Introduction to Equilibrium

Sample calculation Of K

Calculate the K_c for the reaction at 25°C:

$$2NO_g + Cl_{2,g} \rightleftarrows 2NOCl_g$$

if the equilibrium pressures are P_{NOCl} = 1.2 atm; P_{NO} = 5.0x10^{-2} atm; and P_{Cl2} = 3.0x10^{-1} atm.

KNOW	DON'T	Red Herring?
P_{NOCl} = 1.2 atm; P_{NO} = 5.0x10^{-2} atm; P_{Cl2} = 3.0x10^{-1} atm (eq)	K_{conc}	none

$$K_P = \frac{(P_{NOCl})^2}{(P_{NO})^2 (P_{Cl_2})}$$

$$K_P = \frac{(1.2atm)^2}{(0.050atm)^2 (0.30atm)}$$

$$K_P = \frac{1.9x10^3 atm^2}{atm^3} = 1.9x10^3 atm^{-1}$$

$$K_{Pressue} = (RT)^{(c+d)-(a+b)} K_{concentration}$$

$$1.9x10^3 \frac{1}{atm} = (RT)^{(2)-(3)} K_{concentration}$$

$$1.9x10^3 \frac{1}{atm} = \left(0.0826 \frac{L \cdot atm}{mol \cdot K} \cdot 298K\right)^{-1} K_{concentration}$$

$$1.9x10^3 \frac{1}{atm} = \frac{1}{\left(0.0826 \frac{L \cdot atm}{mol \cdot K} \cdot 298K\right)} K_{concentration}$$

$$1.9x10^3 \frac{1}{atm}\left(0.0826 \frac{L \cdot atm}{mol \cdot K} \cdot 298K\right) = K_{concentration}$$

$$K_{concentration} = 4.6x10^4 \frac{1}{M}$$

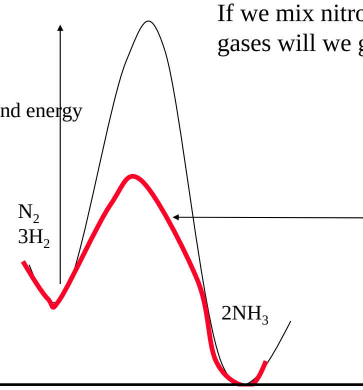
Consider the Haber Reaction which "fixes" nitrogen and is immensely

$$N_{2,g} + 3H_{2,g} \rightleftarrows 2NH_{3,g}$$

important for the large scale production of ammonia used in
- explosives
- fertilizers

If we mix nitrogen and hydrogen gases will we get ammonia?

N_2 941 kJ/mole bond energy
$3H_2$ 432 kJ/mole

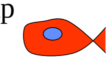


Haber found a Catalyst to make reaction go

Fitch Rule G3: Science is Referential

Example What is K_C for the Haber Process at 127°C if the equilibrium concentrations of gases are NH_3 = $3.1x10^{-2}$ mol/L; N_2 = $8.5x10^{-1}$ mol/L; and H_2 = $3.1x10^{-3}$ mol/L?

KNOW	DON'T KNOW	RED HERRING
$[NH_3]= 3.1x10^{-2}$, $[N_2] = 8.5x10^{-1}$, $[H_2] = 3.1x10^{-3}$ (eq)	K_C	Temp



Prison escapees were thought to drag red herrings across their trail to fool the tracking dogs.

Haber Process

$[NH_3]= 3.1x10^{-2}$
$[N_2] = 8.5x10^{-1}$
$[H_2] = 3.1x10^{-3}$

K=?

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$K = \frac{\left[3.1x10^{-2}\frac{mol}{L}\right]^2}{\left[8.5x10^{-1}\frac{mol}{L}\right]\left[3.1x10^{-3}\frac{mol}{L}\right]^3}$$

$$K = 3.8x10^4 \frac{1}{\left(\frac{mol}{L}\right)^2}$$

$$K = 3.8x10^4 \frac{1}{M^2}$$

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Let's reverse the reaction

$$2NH_3 \rightleftarrows N_2 + 3H_2$$

$$K_{reverse} = K' = \frac{[N_2][H_2]^3}{[NH_3]^2}$$

$$K' = \frac{1}{K}$$

$$K' = \frac{1}{3.8x10^4 \frac{1}{M^2}}$$

$$K' = 2.6x10^{-6}\ M^2$$

We will compile our rules
After a few examples.
What is the first rule we have shown here?

An example of adding chemical reactions

$$SO_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightleftarrows SO_{3(g)} \qquad K_{SO2} = 2.3$$

$$NO_{2(g)} \rightleftarrows NO_{(g)} + \tfrac{1}{2}O_{2(g)} \qquad K_{NO2} = 4.0$$

$$SO_{2(g)} + NO_{2(g)} \rightleftarrows NO_{(g)} + SO_{3(g)} \qquad K_{rx} = K_{SO2}K_{NO2}$$

$$K_{SO2} = \frac{[SO_{3(g)}]}{[SO_{2(g)}][O_{2(g)}]^{\frac{1}{2}}} \qquad K_{NO2} = \frac{[NO_{(g)}][O_{2(g)}]^{\frac{1}{2}}}{[NO_{2(g)}]}$$

$$(K_{SO2})(K_{NO2}) = \left(\frac{[SO_{3(g)}]}{[SO_{2(g)}][O_{2(g)}]^{\frac{1}{2}}}\right)\left(\frac{[NO_{(g)}][O_{2(g)}]^{\frac{1}{2}}}{[NO_{2(g)}]}\right) = \frac{[SO_{3(g)}][NO_{(g)}]}{[SO_{2(g)}][NO_{2(g)}]} = K_{rx}$$

$$K_{rx} = K_{SO2}K_{NO2} = 2.3x4.0 = 9.2$$

Reversing Reactions

$$aA + bB \rightleftarrows cC + dD \qquad K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$cC + dD \rightleftarrows aA + bB \qquad K'_C = \frac{1}{K_c} = \frac{[A]^a[B]^b}{[C]^c[D]^d}$$

Same patterns For K_p

Summing reactions

$$aA + bB \rightleftarrows cC + dD \qquad K_{AB}$$

$$cC + dD \rightleftarrows eE + fF \qquad K_{CD}$$

$$aA + bB \rightleftarrows eE + fF \qquad (K_{AB})(K_{CD})$$

Multiplying reactions

$$aA + bB \rightleftarrows cC + dD \qquad K$$

$$aA + bB \rightleftarrows cC + dD \qquad K$$

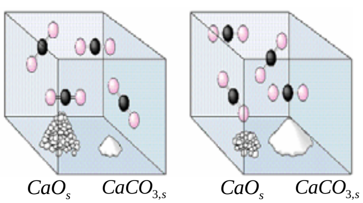
$$aA + bB \rightleftarrows cC + dD \qquad K$$

$$3aA + 3bB \rightleftarrows 3cC + 3dD \qquad KKK = K^3$$

$$n(aA + bB \rightleftarrows cC + dD) \qquad K_{rx} = K^n$$

Heterogeneous Equilibria

Are equilibria that involve more than one phase



$$CaCO_{3,s} \rightleftarrows CaO_s + CO_{2,g}$$

$$K_P = P_{CO_{2,g}}$$

The position of a heterogeneous equilibrium does not
Depend on the amounts of the pure solids or liquids present

Example Problem: Bone is called apatite and can dissolve:

$$Ca_{10}(PO_4)_6(OH)_{2,s} \rightleftarrows 10Ca^{2+}_{aq} + 6PO^{3-}_{4,aq} + 2OH^-_{aq}$$

What is the proper grammar for K?

$$K \stackrel{?}{=} \frac{[Ca^{2+}_{aq}]^{10}[PO^{3-}_{4,aq}]^6[OH^-_{aq}]^2}{[Ca_{10}(PO_4)_6(OH)_{2,s}]}$$

$$K = [Ca^{2+}_{aq}]^{10}[PO^{3-}_{4,aq}]^6[OH^-_{aq}]^2$$

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Module #15:
Introduction to Equilibrium

Calculating Equilibrium Concentrations; 4 examples

K_{conc}

1. We can express it.
2. We can compute it's numerical value
3. We can use it to:
   a: Tell if a rx will go
   b. Compute [eq]
   c. Compute [eq] after some change, Δ

---

3. Use K_{conc} to determine if a Rx will go:

a. Compute Q, the "reaction quotient"
b. if $Q < K_{conc}$, rx goes to right
   if $Q = K_{conc}$, rx is at equilibrium
   if $Q > K_{conc}$, rx goes to left

What is Q?

$$Q = \frac{[C_i]^c[D_i]^d}{[A_i]^a[B_i]^b}$$ i=initial

$$K_C = \frac{[C_{eq}]^c[D_{eq}]^d}{[A_{eq}]^a[B_{eq}]^b}$$

$$aA + bB \rightleftarrows cC + dD$$

Example 1: Use old friend N_2O_4

What happens when 0.2mole of N_2O_4 and 0.2 mole of NO_2 are added together in a 4 L vol? Recall K_{conc} = 0.36M

KNOW	Don't KNOW
mole = 0.2 mol	initial conc.
vol = 4 L	rx?
K = 0.36M	

$$N_2O_4 \rightleftarrows 2NO_{2(g)}$$

$$K = 0.36M = \frac{[NO_2]^2}{[N_2O_4]}$$

$$[N_2O_4]_{init} = \frac{0.2mol}{4L} = 0.05M$$

$$[NO_2]_{init} = \frac{0.2mol}{4L} = 0.05M$$

Q<,=,>K?
Which way will reaction go?

$$Q = \frac{[NO_2]_{init}^2}{[N_2O_4]_{init}} = \frac{(0.05M)^2}{0.05M} = 0.05M$$

$$Q = 0.05M < K = 0.36M; rx \xrightarrow{right}$$

K_{conc}

1. We can express it.

2. We can compute it's numerical value

3. We can use it to:
   a: Tell if a rx will go
   b. Compute [eq]
   c. Compute [eq] after some change, Δ

Rules for Equilibrium Calculations

1. Write balanced reaction
2. Write the equilibrium expression
3. Calculate the initial conc., C_i
4. Calculate Q and determine if rx goes to left or to right.
5. Express "equil. C" (C_{eq}) in terms of init C and change, x, ($C_{eq} = C_i$ "x)
6. Write K and put in C_{eq}, solve for x
7. Calculate equilibrium molarities

8**** Check your answer!!!!!

EXAMPLE 2: A BIT SIMPLE

For the system (all are gases) K_c is 0.64 at 900 K. :

$$CO_{2,g} + H_{2,g} \rightleftarrows CO_g + H_2O_g$$

Suppose we start with CO_2 and H_2, both at a concentration of 0.100 mol/L.
When the system reaches equilibrium, what are the concentrations of products and reactants at 900K?

Red herrings?

1. Balance Equation
   already done

$$CO_{2,g} + H_{2,g} \rightleftarrows CO_g + H_2O_g$$

K_c is 0.64 at 900 K. Suppose we start with CO_2 and H_2, both at a concentration of 0.100 mol/L.

2. Write K_c

$$K_C = \frac{[C_{eq}]^c[D_{eq}]^d}{[A_{eq}]^a[B_{eq}]^b}$$

$$K_C = \frac{[CO_g]^1[H_2O_g]^1}{[CO_{2,g}]^1[H_{2,g}]^1} = 0.64$$

3. Calculate Original or Initial Concentrations

$[CO_2]_{init}$ = 0.100 mol/L
$[H_2]_{init}$ = 0.100 mol/L

4. Calculate Q and determine if rx goes l or r.

$$Q = \frac{[CO]_{init}[H_2O]_{init}}{[CO_2]_{init}[H_2]_{init}} = \frac{0}{[0.100][0.100]}$$

$$Q = 0 < K_c = 0.64;\ rx \xrightarrow{right}$$

5. Express "equil. C" in terms of init C+ or - x

$CO_{2,g} + H_{2,g} \rightleftarrows CO_g + H_2O_g$ $Q = 0 < K_c = 0.64;\ rx \xrightarrow{right}$

Mass balance Limiting reaction

$[CO_2]_{eq} = [CO_2]_{init} - x$ $[CO]_{eq} = [CO]_{init} + x$

$[H_2]_{eq} = [H_2]_{init} - x$ $[H_2O]_{eq} = [H_2O]_{init} + x$

OR: Construct an **ICE** chart

Reaction:	$CO_{2,g}$ +	$H_{2,g} \rightleftarrows$	CO_g +	H_2O_g
stoichiometry	1	1	1	1
Initial conc	0.100	0.100	0	0
Change (to right)	- x	-x	+x	+x
Equil. conc	0.100-x	0.100-x	0+x	0+x

6. Write K and put in equil Conc.

$$K = \frac{[CO]_{eq}[H_2O]_{eq}}{[CO_2]_{eq}[H_2]_{eq}} = \frac{(x)(x)}{[0.100 - x][0.100 - x]} = \left(\frac{x}{0.100 - x}\right)^2$$

$$K = 0.64 = \left(\frac{x}{0.100 - x}\right)^2$$

$CO_{2,g} + H_{2,g} \rightleftarrows CO_g + H_2O_g$

K_c is 0.64 at 900 K. Suppose we start with CO_2 and H_2, both at a concentration of 0.100 mol/L.

$$0.8 = \frac{x}{0.100 - x}$$

$$0.8(0.100 - x) = x$$

$$0.0800 - 0.8x = x$$

$$0.0800 = x + 0.8x$$

$$0.0800 = 1.8x$$

$$\frac{0.0800}{1.8} = x = 0.0444$$

$x = 0.044$

Reminder – x is change
In concentration

x = 0.044

7. Calculate equilibrium molarities

	CO_2	H_2	CO	H_2O
stoichiometry	1	1	1	1
initial conc	0.100	0.100	0	0
change (to right)	- x	-x	+x	+x
Equil. conc	0.100-x	0.100-x	0+x	0+x

$[CO_2]_{eq} = [H_2]_{eq} = 0.100\text{-}x = 0.05556$ M

$[CO]_{eq} = [H_2O]_{eq} = 0.0444$ M

8**** Check your answer!!!!!

Suggestions for ways?

$$K = \frac{[CO]_{eq}[H_2O]_{eq}}{[CO_2]_{eq}[H_2]_{eq}} = 0.64 \stackrel{?}{=} \frac{(0.0444\,M)(0.0444\,M)}{(0.05556\,M)(0.05556\,M)} = 0.638$$

OJO: When I round first and then check I get:

$K_c = 0.60$.

EXAMPLE PROBLEM 3: More difficult

If we add 0.1 mol of N_2O_4 in 1 L, what are the equilibrium concentrations? Recall that K_c = 0.36M.

Red herrings?

1. Balance Equation

$$N_2O_4 \rightleftarrows 2NO_{2(g)}$$

2. Write K_c

$$K_C = \frac{[C_{eq}]^c[D_{eq}]^d}{[A_{eq}]^a[B_{eq}]^b} = \frac{[NO_{2,g,eq}]^2}{[N_2O_{4,g,eq}]} = 0.36M$$

3. Calculate Original or Initial Concentrations

0.1 mol of N_2O_4 in 1 L $[N_2O_4]_o = \frac{0.1mol}{1L} = 0.1M$

$$[NO_2]_o = \frac{0.0mol}{1L} = 0.00M$$

$N_2O_4 \rightleftarrows 2NO_{2(g)}$ $K = 0.36M$

Old Friend: N_2O_4

If we add 0.1 mol of N_2O_4 in 1 L, what are the equilibrium concentrations? Recall that K_c = 0.36 M.

$$K = 0.36M = \frac{[NO_2]^2}{[N_2O_4]}$$

$$[N_2O_4]_o = \frac{0.1mol}{1L} = 0.1M$$

$$[NO_2]_o = \frac{0.0mol}{1L} = 0.00M$$

4. Calculate Q and determine if rx goes l or r

$$Q = \frac{[NO_2]_{init}^2}{[N_2O_4]_{init}} = \frac{(0.0M)^2}{0.1M} = 0.0M < \boldsymbol{K_c}; rx \xrightarrow{right}$$

If we add 0.1 mol of N_2O_4 in 1 L, what are the equilibrium concentrations? Recall that K_c = 0.36 M.

5. Express "equil. C" in terms of orig C+ or - x

$$1\ N_2O_4 \rightleftarrows 2NO_{2(g)}\ 2$$ stoichiometry

	N2O4	NO2
Initial conc	0.1	0
Change (to right)	- x	+ 2x
Equil. conc	0.1-x	0+2x

OJO!!

6. Write K and put in equil Conc.

$N_2O_4 \rightleftarrows 2NO_{2(g)}$ $K = 0.36M$

$$K = 0.36M = \frac{[NO_2]_{eq}^2}{[N_2O_4]_{eq}} = \frac{([NO_2]_{init} + 2x)^2}{([N_2O_4]_{init} - x)} = \frac{(0+2x)^2}{(0.1-x)}$$

and solve for x

Old Friend: N_2O_4

If we add 0.1 mol of N_2O_4 in 1 L, what are the equilibrium concentrations? Recall that K_c = 0.36 M.

$$K = 0.36M = \frac{[NO_2]_{eq}^2}{[N_2O_4]_{eq}} = \frac{([NO_2]_{init} + 2x)^2}{([N_2O_4]_{init} - x)} = \frac{(0+2x)^2}{(0.1-x)}$$

$$K = \frac{(0+2x)^2}{(0.1-x)}$$

$$K(0.1-x) = (0+2x)^2$$

$$K0.1 - xK = (2x)^2 = 4x^2$$

$$4x^2 + xK - 0.1K = 0$$

$$ax^2 + bx + c = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$4x^2 + K_c x - 0.1K_c = 0$ $K_c = 0.36M$

$ax^2 + bx + c = 0$

$a = 4 \quad b = K_c \quad c = -0.1K_c$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-0.36 \pm \sqrt{(0.36)^2 - 4(4)(-0.036)}}{2(4)}$$

OJO!!!

$$x = \frac{-0.36 \pm \sqrt{(0.36)^2 + 0.5764(4)(0.036)}}{8}$$

$$x = \frac{-0.36 \pm \sqrt{0.7056}}{8} = \frac{-0.36 \pm 0.84}{8} = 0.06 \quad and \quad -0.15$$

Which is plausible?

If we add 0.1 mol of N_2O_4 in 1 L, what are the equilibrium concentrations? Recall that $K_c = 0.36$ M.

$$x = \frac{-0.36 \pm \sqrt{0.7056}}{8} = \frac{-0.36 \pm 0.84}{8} = 0.06 \quad and \quad -0.15$$

Plausible?

	N_2O_4	NO_2
Initial conc	0.1	0
Change (to right)	- x	+ 2x
Equil. conc	0.1-x	0+2x

No, not plausible. We would be forced to conclude:
x = -0.15
2x = $[NO_2]$ = -0.3 M

7. Calculate equilibrium molarities

x = 0.060

	N_2O_4	NO
Initial conc	0.1	0
Change (to right)	- x	+ 2x
Equil. conc	0.1-x $0.1 - 0.06 = 0.4$	0+2x $0 + 2(0.06) = 0.12$

Equilibrium $[N_2O_4]$ = 0.04 M

Equilibrium $[NO_2]$ = 0.12 M

8**** Check your answer!!!!!

$N_2O_4 \rightleftarrows 2NO_{2(g)}$

1. Plausible: $[N_2O_4]$ decreased? $0.1 \rightarrow .04$?
   Plausible: [NO] increased? $0 \rightarrow 0.12$?

2. Fits the equilibrium constant?

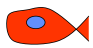
$$K = 0.36M = \frac{[NO_2]^2}{[N_2O_4]} = \frac{[0.12]^2}{[0.04]} = 0.36M$$

If we add 0.1 mol of N_2O_4 in 1 L, what are the equilibrium concentrations? Recall that $K_c = 0.36$ M.

Example 4: Do Units Matter in how we approach the problem?:

For the reaction of hydrogen gas with iodine gas at room temperature the K_p is $1x10^{-2}$. Suppose that you mix HI at 0.5, H_2 at 0.01 and I_2 at 0.005 atm in 5 liter volume. Calculate the equilibrium Pressures.

Beforehand: red herrings?



5L volume

1. Balance Equation

$$H_{2,g} + I_{2,g} \rightleftarrows 2HI_{(g)}$$

2. Write K

$$aA + bB \rightleftarrows cC + dD$$

$$K_{\text{Pressue}} = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

$$K_P = \frac{(P_{HI,eq})^2}{(P_{H_2,eq})(P_{I_2,eq})} = 1x10^{-2}$$

For the reaction of hydrogen gas with iodine gas at room temperature the K_p is $1x10^{-2}$. Suppose that you mix HI at 0.5, H_2 at 0.01 and I_2 at 0.005 atm in 5 liter volume. Calculate the equilibrium Pressures.

3. Calculate Original or Initial Conc or Pressure

A bit of red herring = already know them.

P_{HI} = 0.5 atm_{init}

P_{H2} = 0.01 atm_{init}

P_{I2} = 0.005 atm_{init}

4. Calculate Q and determine if rx goes l or r

$$Q = \frac{(P_{HI,init})^2}{(P_{H_2,init})(P_{I_2,init})} = \frac{(0.5atm)^2}{(0.1atm)\ (0.005atm)} = 5000 > K_p = 0.01; rx \xleftarrow{left}$$

For the reaction of hydrogen gas with iodine gas at room temperature the K_p is $1x10^{-2}$. Suppose that you mix HI at 0.5, H_2 at 0.01 and I_2 at 0.005 atm in 5 liter volume. Calculate the equilibrium Pressures.

OJO

5. Express "equil. C" in terms of orig C+ or - x

	H_2	I_2	HI
stoichiometry	1	1	2
Initial conc	.01	.005	0.5
Change (to **left**)	+ x	+x	-2x
Equil. conc	.01+x	.005+x	0.5-2x

6. Write K and put in equil Pressures

$$K_p = \frac{(0.5 - 2x)^2}{(0.01 + x)(0.005 + x)}$$

$$K_p = \frac{(0.5 - 2x)^2}{(0.01 + x)(0.005 + x)} \qquad K_p = 0.01$$

$$K_p(0.01 + x)(0.005 + x) = (0.5 - 2x)^2$$

$$K_p(5x10^{-5} + 0.015x + x^2) = 0.25 - 2x + 4x^2$$

$$5x10^{-5}K_p + 0.015xK_p + x^2K_p = 0.25 - 2x + 4x^2$$

$$0.25 - 2x + 4x^2 - (5x10^{-5}K_p + 0.015xK_p + x^2K_p) = 0$$

$$(4x^2 - 2x + 0.25) - 5x10^{-5}K_p - 0.015xK_p - x^2K_p =$$

$$(4x^2 - x^2K_p) + (-2x - 0.015xK_p) + (0.25 - 5x10^{-5}K_p) = 0$$

$$(4 - K_p)x^2 - x(2 + 0.015K_p) + (0.25 - 5x10^{-5}K_p) = 0$$

$$(4 - .01)x^2 - x(2 + 0.00015) + (0.25 - 5x10^{-7}) = 0$$

$$(3.99)x^2 - x(2.00015) + (0.2499995) = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \qquad (3.99)x^2 - x(2.00015) + (0.2499995) = 0$$

$$x = \frac{-(-2.00015) \pm \sqrt{(-2.00015)^2 - 4(3.99)(0.2499995)}}{2(3.99)}$$

$$x = \frac{2.00015 \pm \sqrt{4.0006 - 3.98992}}{7.98}$$

$$x = \frac{2.00015 \pm 0.102995}{7.98}$$

$x = 0.237739$

$x = 0.263552$

Which do we use + or -?

$x = 0.237739$

$x = 0.263552$

	H_2	I_2	HI
stoichiometry	1	1	2
Initial conc	.01	.005	0.5
Change (to **left**)	+ x	+x	-2x
Equil. conc	.01+x	.005+x	0.5-2x

If we use the second answer then we will get

$$P_{HI,eq} = 0.5 - 2x = 0.5 - 2(0.263552) = -0.0271$$

Not plausible

$x = 0.237739$

	H_2	I_2	HI
stoichiometry	1	1	2
Initial conc	.01	.005	0.5
Change (to **left**)	+ x	+x	-2x
Equil. conc	.01+x	.005+x	0.5-2x

$$P_{HI,eq} = 0.5 - 2x = 0.5 - 2(0.237739) = 0.024523$$

$$P_{I_2,eq} = 0.005 + x = 0.005 + 0.237739 = 0.242739$$

$$P_{H_2,eq} = 0.01 + x = 0.01 + 0.237739 = 0.247739$$

$$K = \frac{(P_{HI,eq})^2}{(P_{H_2,eq})(P_{I_2,eq})} = \frac{(0.024523)^2}{(0.242739)(0.247739)} = 0.01$$

Checks!!!

"A" students work
(without solutions manual)
~ 10 problems/night.

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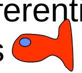
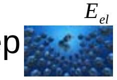
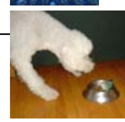
Module #15: Introduction to Equilibrium

Making Assumptions

FITCH Rules

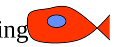
General
- G1: Suzuki is Success
- G2. Slow me down
- G3. Scientific Knowledge is Referential
- G4. Watch out for Red Herrings 
- G5. Chemists are Lazy

Chemistry
- C1. It's all about charge $E_{el} = k\left(\frac{q_1 q_2}{r_1 + r_2}\right)$
- C2. Everybody wants to "be like Mike"
- C3. Size Matters $E_{el} = k\left(\frac{q_1 q_2}{r_1 + r_2}\right)$
- C4. Still Waters Run Deep 
- C5. Alpha Dogs eat first 

For systems with multiple reactions
Need to simply = ASSUMPTIONS

Example on Using Simplifications

If 1.0 mol NOCl is placed in a 2.0 L flask what are the equilibrium concentrations of NO and Cl_2 given that at 35 °C the equilibrium constant, K_c, is 1.6×10^{-5} mol/L?

Red herrings: 35 °C is a red herring 

Clues?

K is "small" compared to others (<<< 1) we have worked with !!!!!

Example 2 $CO_{2,g} + H_{2,g} \rightleftarrows CO_g + H_2O_g$ K_c is 0.64.

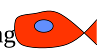
EXAMPLE 3: $N_2O_4 \rightleftarrows 2NO_{2(g)}$ $K_c = 0.36M$

Example 4: $H_{2,g} + I_{2,g} \rightleftarrows 2HI_{(g)}$ K_p is 1×10^{-2}.

We will define Small in the Next chapter!

Example on Using Simplifications

If 1.0 mol NOCl is placed in a 2.0 L flask what are the equilibrium concentrations of NO and Cl_2 given that at 35 °C the equilibrium constant, K_c, is 1.6×10^{-5} mol/L?

Red herrings: 35 °C is a red herring 

Clues?

K is "small" compared to others (<<< 1) we have worked with !!!!!

We are starting with reactants

1. Balance Equation

$$2NOCl \rightleftarrows 2NO + Cl_2$$

2. Write K

$$K_c = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

$$2NOCl \rightleftarrows 2NO + Cl_2$$

If 1.0 mol NOCl is placed in a 2.0 L flask what are the equilibrium concentrations of NO and Cl_2 given that at 35C the equilibrium constant is 1.6×10^{-5} mol/L?

3. Calculate or Initial Concentrations

$[NOCl_{init}] = 1.0$ mol/2L $= 0.5$ M
$[NO_{init}] = 0$ M
$[Cl_{2init}] = 0$ M

4. Calculate Q and determine if rx goes l or

$$Q = \frac{\left[NO_{g,init}\right]^2\left[Cl_{2,g,init}\right]}{\left[NOCl_{g,init}\right]^2} = \frac{(0)(0)}{0.5} = 0;\ rx \xrightarrow{right}$$

5. Express "equil. C" in terms of orig C+ or - x

$2NOCl \rightleftarrows 2NO + Cl_2$	NOCl	NO	Cl_2
stoichiometry	2	2	1
Initial conc	0.5	0	0
Change (to right)	-2x	+2x	x
Equil. conc	0.5-2x	0+2x	0 +x
Assumptions	~0.5	2x	x

Assumptions are based on
a) K is small so x is small
b) If x is small then sig fig rules eliminate x

$$\begin{array}{r} 0.5 \\ -\ 0.000x \\ \hline 0.4999z \xrightarrow{sig\,fig} 0.5 \end{array}$$

$$K = \frac{(2x)^2 x}{([NOCl_{init}] - 2x)^2} \approx \frac{(2x)^2 x}{[NOCl_{init}]^2}$$

6. Write K and put in equil Conc

$$K = \frac{(2x)^2 x}{(0.5)^2} = \frac{4x^3}{0.25} = 16x^3$$

$$K = 16x^3$$

$$1.6x10^{-5} = 16x^3$$

$$\frac{1.6x10^{-5}}{16} = x^3$$

$$10^{-6} = x^3$$

$$\sqrt[3]{10^{-6}} = x$$

$$x = 10^{-2}$$

7. Calculate equilibrium molarities

$$x = 10^{-2}$$

	NOCl	NO	Cl_2
stoichiometry	2	2	1
Initial conc	0.5	0	0
Change (to right)	-2x	+2x	x
Equil. conc	0.5-2x	0+2x	0 +x
Assumptions	~0.5	2x	x

$[NOCl_{g,eq}] = 0.5$

$[NO_{g,eq}] = 2x = 2x10^{-2}$

$[Cl_{2,g,eq}] = x = 10^{-2}$

ARE WE DONE?

CHECK ASSUMPTIONS

$[NOCl_{g,eq}] = 0.5 - 2x$

$[NOCl_{g,eq}] = 0.5 - 2(10^{-2})$

$[NOCl_{g,eq}] = 0.5 - 0.02$

$$\begin{array}{r} 0.5 \\ -\ 0.02 \\ \hline 0.48 \end{array}$$

Where are
The Sig Fig?

Answer 0.5

Accept error less than 5%

$$error = \left[\frac{real - estimated}{real}\right]100$$

$$error = \left[\frac{0.48 - .5}{0..48}\right]100 = 4\%$$

Are we done yet?

8**** Check your answer!!!!!

$\left[NOCl_{g,eq}\right] = 0.5$

$\left[NO_{g,eq}\right] = 2x = 2x10^{-2}$

$\left[Cl_{2,g,eq}\right] = x = 10^{-2}$

$$K_c = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = 1.6x10^{-5}\ M$$

$$K_c = \frac{[2x10^{-2}]^2[10^{-2}]}{[0.5]^2} \overset{?}{=} 1.6x10^{-5}\ M$$

$$K_c = 1.6x10^{-5} = 1.6x10^{-5}\ M$$

POINT of ASSUMPTIONS

1. Avoid using polynomial equations
2. Can do it with small K values
3. Assume little change (get rid of an x)
4. Must check the assumptions

Multiple Equilibria are not solvable
With simple cubic, quadratic equations

Chemists are Lazy!

"A" students work
(without solutions manual)
~ 10 problems/night.

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Module #15:
Introduction to Equilibrium

Qualitative Predictions
For direction of Equilibrium

Chemists are ________

If we don't have to calculate can we make **qualitative** descriptions of equilibrium?

Le Châtelier's Principle

if a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change

Fitch Rule G3: Science is Referential

Effects of Changes on the System

1. Addition of inert gas does not affect the equilibrium position.
2. Concentration: The system will shift away from the added component.
3. Decreasing the volume shifts the equilibrium toward the side with fewer moles.
4. Temperature: K will change depending upon the temperature (treat the energy change as a reactant).

LeChatlier Examples

Example: (Inert gas) Suppose we have the reaction initially at equilibrium

$$2SO_{2,g} + O_{2,g} \rightleftarrows 2SO_{3,g} \qquad K_{c,1000K} = 2.8x10^2$$

What happens when we add some $N_{2,g}$, does Q change?

$$K_C = \frac{[SO_{3,g,eq}]^2}{[O_{2,g,eq}][SO_{2,g,eq}]^2}$$

Addition of inert gas does not affect the equilibrium position. Similarly……

Example: (Effect of Solid)
What is the effect on equilibrium in the calcination (decomposition)

$$CaCO_{3,s} \rightleftarrows CaO_s + CO_{2,g}$$

of limestone produced by adding a small quantity of $CaCO_3$(s)?

$$K_c = \frac{[CO_{2,g}][CaO_s]}{[CaCO_{3,s}]} = [CO_{2,g}]$$

Change in quantity of solids do not affect direction of equilibria. So addition of more limestone is irrelevant.

Example What is the effect on equilibrium in the (decomposition)

$$CaCO_{3,s} \rightleftarrows CaO_s + CO_{2,g}$$

of removing some $CO_{2,g}$, does Q change?

Concentration: The system will shift toward from the removed component.

$$[CO_{2,g,new}] < [CO_{2,g,eq}] \qquad [CO_{2,g,new}] = \frac{[CO_{2,g,eq}]}{x} \qquad Q = \frac{[CO_{2,g,eq}]}{x} < K_c = [CO_{2,g,eq}];\ rx \xrightarrow{right}$$

Example Suppose we have the reaction initially at equilibrium:

$$2SO_{2,g} + O_{2,g} \rightleftarrows 2SO_{3,g} \qquad K_{c,1000K} = 2.8x10^2$$

What happens when we add some $SO_{3,g}$, does Q change?

$$[SO_{3,new}] > [SO_{3,eq}]$$
$$[SO_{3,new}] = x[SO_{3,eq}]$$

$$Q = \frac{(x[SO_{3,g,eq}])^2}{[O_{2,g,eq}][SO_{2,g,eq}]^2} > K_C = \frac{[SO_{3,g,eq}]^2}{[O_{2,g,eq}][SO_{2,g,eq}]^2};\ rx \xleftarrow{left}$$

Concentration: The system will shift away from the added component.

Example What happens if we decrease the volume of the container?

$2SO_{2,g} + O_{2,g} \rightleftarrows 2SO_{3,g}$

$$K_c = \frac{[SO_{3,g,eq}]^2}{[O_{2,eq,g}][SO_{2,g,eq}]^2} = \frac{\left[\frac{n_{SO_{3,g,eq}}}{V_{eq}}\right]^2}{\left[\frac{n_{O_{2,g,eq}}}{V_{eq}}\right]\left[\frac{n_{SO_{2,g,eq}}}{V_{eq}}\right]^2} = \frac{[n_{SO_{3,g,eq}}]^2}{[n_{O_{2,g,eq}}][n_{SO_{2,g,eq}}]^2}\frac{\left[\frac{1}{V_{eq}}\right]^2}{\left[\frac{1}{V_{eq}}\right]\left[\frac{1}{V_{eq}}\right]^2}$$

$$K_c = \frac{[n_{SO_{3,g,eq}}]^2}{[n_{O_{2,g,eq}}][n_{SO_{2,g,eq}}]^2}\frac{\left[\frac{1}{V_{eq}}\right]^2}{\left[\frac{1}{V_{eq}}\right]^3} = \frac{[n_{SO_{3,g,eq}}]^2}{[n_{O_{2,g,eq}}][n_{SO_{2,g,eq}}]^2}\frac{1}{\left[\frac{1}{V_{eq}}\right]} = \left(\frac{[n_{SO_{3,g,eq}}]^2}{[n_{O_{2,g,eq}}][n_{SO_{2,g,eq}}]^2}\right)V_{eq}$$

$V_{new} < V_{eq}$ $\quad V_{new} = \frac{V_{eq}}{x}$

$$Q = \left(\frac{[n_{SO_{3,g,eq}}]^2}{[n_{O_{2,g,eq}}][n_{SO_{2,g,eq}}]^2}\right)\frac{V_{eq}}{x} < K_c = \left(\frac{[n_{SO_{3,g,eq}}]^2}{[n_{O_{2,g,eq}}][n_{SO_{2,g,eq}}]^2}\right)V_{eq};\ rx \xrightarrow{right}$$

Q changes when we change volume because of differences in stoichiometry

Decreasing the volume (increasing P) shifts the equilibrium toward the side with fewer moles

---

$2SO_{2(g)} + O_{2(g)} \rightleftarrows 2SO_{3(g)}$ $\qquad K_c = 280_{1000K}$

Decrease volume, what happens?

Number of moles of reactants?
Number of moles of products?

If we form reactants we get 3 moles

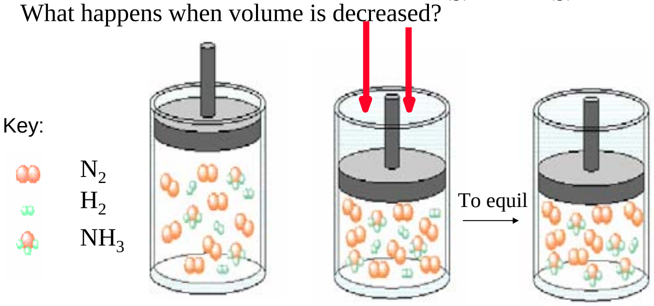
If we form products we get 2 moles.

reaction moves to decrease moles

moves to the right.

LeChatlier Example: Haber Process $\quad N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3(g)}$

What happens when volume is decreased?



7 N_2 4 H_2 3NH_3	7 N_2 4 H_2 3NH_3	To equil →	6 N_2 1H_2 5NH_3
14	14		12

Effect of Temperature????

Consider effect of raising temperature on two reactions:

$2SO_{2(g)} + O_{2(g)} \rightleftarrows 2SO_{3(g)} \qquad \Delta H^o = -180kJ$

$N_{2(g)} + O_{2(g)} \rightleftarrows 2NO_{2(g)} \qquad \Delta H^o = +181kJ$

What will happen?

Another way to see this is to write the rxs by considering heat As a product or reactant. Reaction shifts away from heat:

$2SO_{2(g)} + O_{2(g)} \rightleftarrows 2SO_{3(g)} + heat;\ rx \xleftarrow{left}$

$N_{2(g)} + O_{2(g)} + heat \rightleftarrows 2NO_{2(g)};\ rx \xrightarrow{right}$

Temperature: K will change depending upon the temperature (treat the energy change as a reactant).

Do you see a pattern?

$$\ln\left[\frac{K_1}{K_2}\right] = \frac{-\Delta H^{o}_{forward\,rx}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$ Van't Hoff equation (1852-1911)

$$\ln\left[\frac{k_1}{k_2}\right] = \left[\frac{-E_a}{R}\right]\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$ Arrhenius Equation

$$\ln\left[\frac{P_1}{P_2}\right] = \left[\frac{-\Delta H_{vaporization}}{R}\right]\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$ Clausius-Clapeyron equation

Fitch Rule G3: Science is Referential

$N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3(g)}$

$\Delta H^0 = -92.2kJ$

$K = 6x10^5|_{25C}$

What is K at 100 °C?

Predict first using LeChatelier's principle: will it get larger or smaller? You try it!, we will compare to calc.

$N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3(g)} + heat$

$$\ln\left[\frac{K_1}{K_2}\right] = \frac{-\Delta H^o}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$e^{\ln\left[\frac{6x10^5}{K_2}\right]} = \left[\frac{6x10^5}{K_2}\right] = e^{7.48628} = 1783.405$$

$$\ln\left[\frac{6x10^5}{K_2}\right] = \frac{-\left(-92.2x10^3\frac{J}{mol}\right)}{8.31\frac{J}{mol-K}}\left[\frac{1}{273+25K} - \frac{1}{273+100K}\right]$$

$$\ln\left[\frac{6x10^5}{K_2}\right] = \frac{11095.07}{\left(\frac{1}{Kelvin}\right)}\left[\frac{.000675}{Kelvin}\right] = 7.48628$$

$$\frac{6x10^5}{1783.405} = K_2 = 336.435$$

What have we learned?

1. Expression for K
2. Expression for Q
3. Distinguish between initial and final or equilibrium concentrations.
4. How to predict direction of a reaction
5. How to calculate the equilibrium conc.
6. How to make assumptions to ease the calculations.
7. How to check the calculations
8. How to use Le Chat.... principle to effect of conc., pressure, volume, and temp. on a reaction.

"A" students work
(without solutions manual)
~7 problems/night.