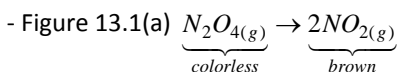
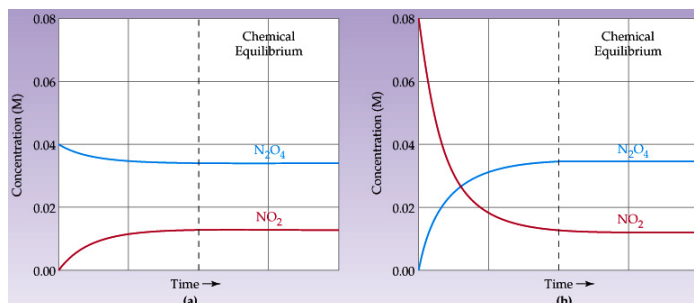


## Chapter 15 – Chemical Equilibrium

### • 15.1 The Concept of Equilibrium

Figure: 13.1 from *Chemistry* by McMurray & Fey



-- we start with reactant,  $N_2O_4$ , so the solution is colorless

-- as time progresses we generate product,  $NO_2$

-- after a certain length of time:

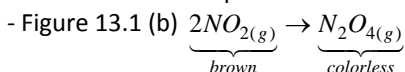
--- the concentration of  $N_2O_4$  stops decreasing

--- the concentration of  $NO_2$  stops increasing

--- the solution goes back and forth between clear and brown

--- at this point the forward rate = reverse rate

--- the production of  $NO_2$  and the consumption of  $N_2O_4$  is equal



-- this time we start with  $NO_2$

-- as time progresses we once again reach a point in which:

--- the concentration of  $NO_2$  stops decreasing

--- the concentration of  $N_2O_4$  stops increasing

--- the solution goes back and forth between brown and clear

--- at this point the forward rate = reverse rate

--- the production of  $N_2O_4$  and the consumption of  $NO_2$  is equal

- this is an example of chemical equilibrium or dynamic equilibrium: a phenomenon in which the concentrations of reactants and products remain constant over time

- NOTE: this does not mean that the concentrations go to zero

- we can rewrite the above eqn as  $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

### • 15.2 The Equilibrium Constant

- Evaluating  $K_c$

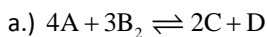
$$aA + bB \rightleftharpoons cC + dD \quad K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

-- this is called the equilibrium constant expression or mass action expression

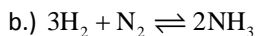
-- we call  $K_c$  the equilibrium constant since there is a certain set of concentrations for the species in our general equation which corresponds to equilibrium

-- law of mass action: the chemical equilibrium expression will give rise to a characteristic value for a given temperature

- Example: Write the equilibrium expression for the forward and the reverse reactions for the following:



$$K_c = \frac{[C]^2[D]}{[A]^4[B]^3} \quad K'_c = \frac{[A]^4[B]^3}{[C]^2[D]}$$



$$K_c = \frac{[NH_3]^2}{[H_2]^3[N_2]} \quad K'_c = \frac{[H_2]^3[N_2]}{[NH_3]^2}$$

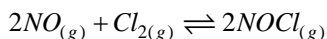
- In both examples the equilibrium constant in the forward direction is the inverse of the equilibrium constant in the reverse direction:  $K_c = \frac{1}{K'_c}$

-- this means that when we reverse an eq reaction we must take the inverse of it's eq constant to get the reverse eq constant

- Equilibrium Constants in Terms of  $K_p$

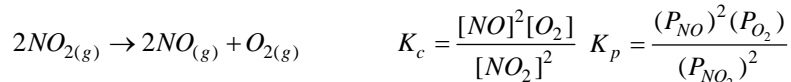
- if A, B, C, and D are gases then we would write:  $K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$

-- Example: What is  $K_c$  and  $K_p$  for the following reaction?



$$K_c = \frac{[NOCl]^2}{[NO]^2[Cl_2]} \quad K_p = \frac{(P_{NOCl})^2}{(P_{NO})^2(P_{Cl_2})}$$

- How are  $K_c$  and  $K_p$  related?



-- looking at the ideal gas law:  $P = \frac{n}{V} RT = \underline{M}RT \rightarrow \underline{M} = P \frac{1}{RT}$

-- plugging this expression into  $K_c$  gives:

$$K_c = \frac{[NO]^2[O_2]}{[NO_2]^2} = \frac{\left(\frac{P_{NO}}{RT}\right)^2 \left(\frac{P_{O_2}}{RT}\right)}{\left(\frac{P_{NO_2}}{RT}\right)^2} = \frac{(P_{NO})^2(P_{O_2})}{(P_{NO_2})^2} \frac{1}{RT}$$

-- therefore the relationship btwn  $K_c$  &  $K_p$  for this equation is:

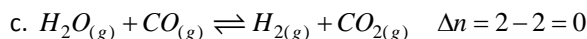
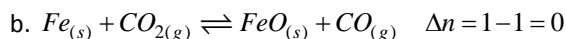
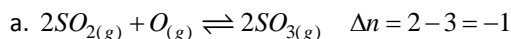
$$K_c = K_p \frac{1}{RT} \rightarrow K_p = K_c(RT)$$

-- In general,  $K_p = K_c(RT)^{\Delta n}$  where  $\Delta n = \text{moles}_{(g)\text{products}} - \text{moles}_{(g)\text{reactants}}$

--- in this example  $\Delta n = 1$

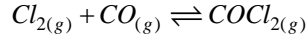
--- when  $\Delta n = 0$  then  $K_c = K_p$

-- Example: For which of the following reaction will  $K_c = K_p$ ?



therefore for b. & c.

-- Example: What is the  $K_p$  of the reaction below at 325°C given  $K_c = 5.0$ ?



$$K_p = K_c (RT)^{\Delta n} = 5.0 \frac{L}{mol} \left( 0.08206 \frac{L \cdot atm}{mol \cdot K} \times (325 + 273.15) K \right)^{(1-2)}$$

$$K_p = 0.10$$

<5>

### • 15.3 Understanding & Working with Equilibrium Constants

- The Magnitude of Equilibrium Constants

--  $K_c > 10^3$ , products predominate over reactants:

--- reaction proceeds to completion - generating product

--- very little reactant is left

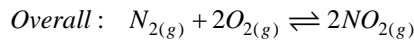
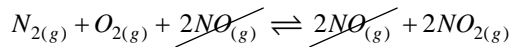
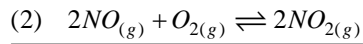
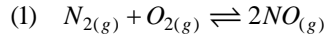
--  $K_c < 10^{-3}$ , reactants predominate over products:  $K_c = \frac{[\text{products}]}{[\text{reactants}]}$

--- reaction proceeds hardly at all

--- very little product is generated

--  $10^3 > K_c > 10^{-3}$ , both reactants and products are present at eq

- **Handling Combined Equations**



- the mass action exp'n for the overall reaction is:  $K_c = \frac{[NO_2]^2}{[N_2][O_2]}$

- the mass action exp'n for (1) is:  $K_1 = \frac{[NO]^2}{[N_2][O_2]}$

- the mass action exp'n for (2) is:  $K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]}$

- we derive the mass action exp'n from (1) & (2) for the overall reaction thru  $K_1 \times K_2$

$$K_1 \times K_2 = \frac{[NO]^2}{[N_2][O_2]} \times \frac{[NO_2]^2}{[NO]^2[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2}$$

- In general:  $K_{\text{overall}} = K_1 \times K_2 \times \dots$

- Example: Calculate the eq const for  $2D \rightleftharpoons A + 2B$  given the info below.



- we need to look from the reverse direction for both of these reactions

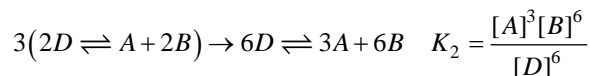
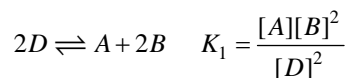
$$C \rightleftharpoons A + 2B \quad K_c = \frac{1}{3.3} = 0.303$$

$$2D \rightleftharpoons C \quad K_c = \frac{1}{0.041} = 24.4$$

$$2D \rightleftharpoons A + 2B \quad K_c = 0.303 \times 24.4 = 7.39$$

- **How does multiplying a reaction by a constant affect the eq. const?**

- the eq. constant is raised by the exponential value of the constant



$$\therefore K_2 = (K_1)^3$$

- Example: If the eq. constant at a given temperature is  $2.4 \times 10^{-3}$  for

$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$  what is the eq. constant for the reactions below?



- **Summary of manipulating the mass action expression**

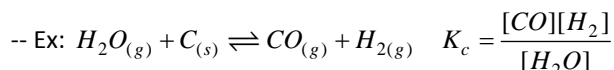
<u>Action</u>	<u>New Eq Constant</u>
Reversing an equilibrium reaction	$K'_c = 1/K_c$
Multiplying an equilibrium reaction by n	$K'_c = (K_c)^n$
Adding several eq reactions together	$K'_c = K_1 \times K_2 \dots$

## • 15.4 Heterogeneous Equilibria

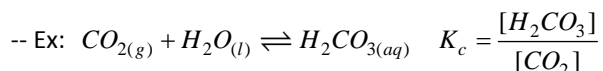
- so far we have dealing with reactions in which everything is either in solution or is a gas - homogeneous eq

- heterogeneous equilibrium: when the reactants/products are in more than one phase

- the eq constant is independent of solid species - solids have no pressure and the concentration is constant (they are not in solution)



- the eq constant is independent of  $H_2O_{(l)}$  since it is the solvent and therefore in excess



## • 15.5 Calculating Equilibrium Constants

- **When Eq concentrations are known:** it is a matter of plugging them into the equilibrium expression

-- Ex: What is the  $K_c$  for  $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$  if their equilibrium concentrations are  $[SO_2]=0.15$  M,  $[O_2]=0.68$ ,  $[SO_3]=1.5$

1. Write down the equilibrium expression symbolically:

$$K_c = \frac{[SO_3]^2}{[SO_2]^2 [O_2]}$$

2. Plug the give equilibrium values into the expression and solve:

$$K_c = \frac{[SO_3]^2}{[SO_2]^2 [O_2]} = \frac{[1.5]^2}{[0.15]^2 [0.68]} = 1.5 \times 10^2$$

- **When initial concentrations and some equilibrium concentrations are known:** we use an "ICE" table, "I"nitial, "C"hange, "E"q & stoichiometry

-- Ex: What is the  $K_c$  for  $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$  if the initial concentrations of reactants were  $[SO_2]=0.150M$  and  $[O_2]=0.680M$  and the equilibrium concentration of the product is  $[SO_3]=0.050M$ ?

1. Setup the ICE table

	SO <sub>2</sub>	O <sub>2</sub>	SO <sub>3</sub>
Initial	0.15	0.68	0.0
Change	-2x	-x	+2x
Eq	?	?	0.05

2. Use the given equilibrium concentration to identify x

$$2x = 0.050 \rightarrow x = 0.025$$

3. Plug x into the table to get the missing equilibrium concentrations

	SO <sub>2</sub>	O <sub>2</sub>	SO <sub>3</sub>
Initial	0.150	0.680	0.00
Change	-2(0.025)	-0.025	+2x
Eq	0.100	0.655	0.05

4. Write down the equilibrium expression symbolically and plug in values

$$K_c = \frac{[SO_3]^2}{[SO_2]^2 [O_2]} = \frac{[0.05]^2}{[0.10]^2 [0.655]} = 3.8 \times 10^{-1}$$

- When the initial concentrations and %dissociation is known:

-- Ex: What is the  $K_c$  for  $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$  if 0.500M of both reactants will be 0.5% dissociated in order to reach equilibrium?

1. Setup the ICE table

	SO <sub>2</sub>	O <sub>2</sub>	SO <sub>3</sub>
Initial	0.500	0.500	0.0
Change	-2x	-x	+2x
Eq	?	?	?

2. Use the given %dissociation to identify x

$$x = \frac{\% \text{ dissociation}}{100} \cdot [\text{initial concentration}] \rightarrow x = \frac{0.5}{100} \cdot 0.5 = 0.0025$$

3. Plug x into the table to get the missing equilibrium concentrations

	SO <sub>2</sub>	O <sub>2</sub>	SO <sub>3</sub>
Initial	0.500	0.500	0.00
Change	-2(0.0025)	-0.0025	+2x
Eq	0.4950	0.4975	0.0050

4. Write down the equilibrium expression symbolically and plug in values

$$K_c = \frac{[SO_3]^2}{[SO_2]^2 [O_2]} = \frac{[0.0050]^2}{[0.4950]^2 [0.4975]} = 2.05 \times 10^{-4}$$

## • 15.6 Application of Equilibrium Constants

- Predicting the Direction of Reaction

-- when a reaction is not in equilibrium, the mass action expression becomes:

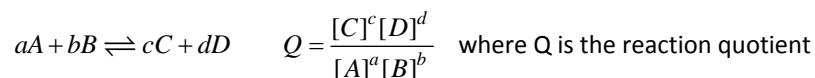
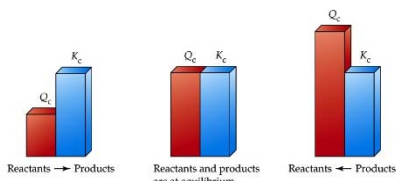
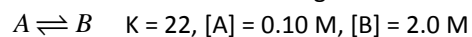


Figure: 13.5 from *Chemistry* by McMurray & Fey



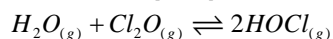
- when  $Q = K$  then the reaction is in equilibrium
- when  $Q < K$  then more reactants need to be consumed in order to reach eq
  - therefore the reaction will proceed in the forward direction
- when  $Q > K$  then more products need to be consumed in order to reach eq
  - therefore the reaction will proceed in the reverse direction
- Example: Given the data below is the reaction in equilibrium and if not in which direction will need to go in order to reach eq?



$$Q = \frac{[B]}{[A]} = \frac{2.0}{0.1} = 20 < 22 = K \quad \text{therefore it will go in the forward direction}$$

#### - Calculating Equilibrium Concentrations

- Example: The value of  $K_c = 0.0900$  at 298K for the reaction below, determine the eq concentrations if initially  $[H_2O] = 0.00432 \text{ M}$  and  $[Cl_2O] = 0.00442 \text{ M}$ .



#### 1. Write down the ICE table

	$H_2O$	$Cl_2O$	$HOCl$
Initial	0.00432	0.00442	0.0
Change	-x	-x	+2x
Eq	0.00432-x	0.00442-x	+2x

#### 2. Write down the equilibrium expression symbolically

$$K_c = \frac{[HOCl]^2}{[H_2O][Cl_2O]}$$

#### 3. Fill in the expression and get the quadratic equation

$$K_c = \frac{(2x)^2}{(0.00432 - x)(0.00442 - x)} = \frac{4x^2}{1.9094 \times 10^{-5} - 8.74 \times 10^{-2}x + x^2} = 0.0900$$

$$0.0900 \cdot (1.9094 \times 10^{-5} - 8.74 \times 10^{-2}x + x^2) = 4x^2$$

$$1.1785 \times 10^{-6} - 7.866 \times 10^{-4}x + 0.0900x^2 = 4x^2$$

$$0 = 3.9100x^2 + 7.866 \times 10^{-4}x - 1.1785 \times 10^{-6}$$

#### 4. Use the quadratic equation to find x (choose the positive value)

Recall the quadratic equation:

$$\text{for } ax^2 + bx + c = 0 \quad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

in our case,  $a = 3.9100$ ,  $b = 7.866 \times 10^{-4}$ ,  $c = 1.1785 \times 10^{-6}$

$$x = \frac{-7.866 \times 10^{-4} \pm \sqrt{(7.866 \times 10^{-4})^2 - 4 \times 3.9100 \times (-1.1785 \times 10^{-6})}}{2 \times 3.9100}$$

$$x = \frac{-7.866 \times 10^{-4} \pm \sqrt{6.187 \times 10^{-7} + 2.688 \times 10^{-5}}}{7.82}$$

$$x = \frac{-7.866 \times 10^{-4} \pm 0.005244}{7.82} \rightarrow x = 5.70 \times 10^{-4} \quad \text{or} \quad x = -7.71 \times 10^{-4}$$

5. Plug the  $x$  value into the  $E$  row of the table and find the concentrations:

$x$  must be greater than zero therefore  $x = 5.70 \times 10^{-4}$

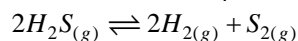
Using this value we can determine what the concentrations are at eq:

$$[\text{H}_2\text{O}] = 0.00432 - x = 0.00432 - 0.00057 = 0.00375 \text{ M}$$

$$[\text{Cl}_2\text{O}] = 0.00442 - x = 0.00385 \text{ M}$$

$$[\text{HOCl}] = 2x = 0.00114 \text{ M}$$

- Example: The value of  $K_c$  for the thermal decomposition of hydrogen sulfide is  $2.2 \times 10^{-6}$  at 1400K.



A sample of gas in which  $[\text{H}_2\text{S}] = 0.600\text{M}$  is heated to 1400K in a sealed vessel. After chemical eq has been achieved, what is the value of  $[\text{H}_2\text{S}]$ ? Assume no  $\text{H}_2$  and  $\text{S}_2$  was present in the original sample.

1. Write down the ICE table

	$\text{H}_2\text{S}$	$\text{H}_2$	$\text{S}_2$
Initial	0.600	0.0	0.0
Change	-2x	+2x	+x
Eq	0.600-2x	+2x	+x

2. Write down the equilibrium expression symbolically:

$$K_c = \frac{[\text{H}_2][\text{S}_2]}{[\text{H}_2\text{S}]^2}$$

3. Fill in the expression

$$K_c = \frac{(2x)^2(x)}{(0.600 - 2x)^2} = \frac{4x^3}{(0.600 - 2x)^2} = 2.2 \times 10^{-6}$$

4. Here we cannot use quadratic so instead we must use an assumption to find  $x$ :

$$\text{assume } 0.600 \gg 2x \therefore 0.600 - 2x \approx 0.600$$

$$\frac{4x^3}{(0.600 - 2x)^2} = 2.2 \times 10^{-6} \approx \frac{4x^3}{0.36} \rightarrow x = 0.00583\text{M}$$

5. Verify assumption:

$$\frac{0.00583 \times 2}{0.600} \times 100\% = 1.94\% < 5\% \therefore \text{valid}$$

6. Use the  $E$  row to find the equilibrium concentrations:

Using  $x = 0.00734 \text{ M}$  we can determine what the concentrations are at eq:

$$[\text{H}_2\text{S}] = 0.600 - 2x = 0.600 - 2 \times 0.00583 = 0.588 \text{ M}$$

$$[\text{H}_2] = 2x = 0.0117 \text{ M} \quad \text{and} \quad [\text{S}_2] = 0.00583 \text{ M}$$

- Example: What are the eq concentrations of each of the species in the following reaction, given the  $K_c = 5.1$  at 700K and the initial concentration of all species is 0.050 M?  $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$

	CO	H <sub>2</sub> O	CO <sub>2</sub>	H <sub>2</sub>
Initial	0.050	0.050	0.050	0.050
Change	-x	-x	+x	+x
Eq	0.050-x	0.050-x	0.050+x	0.050+x

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.050+x)(0.050+x)}{(0.050-x)(0.050-x)} = \frac{(0.050+x)^2}{(0.050-x)^2} = 5.1$$

$$\frac{(0.050+x)^2}{(0.050-x)^2} = 5.1 \rightarrow \frac{(0.050+x)}{(0.050-x)} = 2.258$$

$$2.258(0.050-x) = 0.050+x$$

$$0.1129 - 2.258x = 0.050+x \rightarrow x = 0.0193 \text{ M}$$

using this value we determine the concentrations:

$$[CO] = [H_2O] = (0.050-0.0193)\text{M} = 0.031 \text{ M}$$

$$[CO_2] = [H_2] = (0.050+0.0193)\text{M} = 0.069 \text{ M}$$

### • 15.7 Le Châtelier's Principle

- defn: when a stressor is applied to a system is at equilibrium, the system will adjust to counteract the stressor in order to re-establish eq

- stressors:

- adding or removing reactants or products
- changing the pressure/volume
- changing the temperature - we will talk about this much later

- Change in reactant or product concentration,  $A \rightleftharpoons B$

-- if we increase A then  $Q = \frac{[B]}{[A]} < K$

--- we will have to consume A and produce more B to obtain eq

--- the reaction will go in the forward direction

-- if we increase B then  $Q = \frac{[B]}{[A]} > K$

--- we will have to consume B and produce more A to obtain eq

--- the reaction will go in the reverse direction

- Change in pressure or volume,  $2A_{(g)} \rightleftharpoons B_{(g)}$

-- recall  $PV = nRT$  therefore  $P \propto n$  and  $V \propto n$

-- if we decrease the volume then  $Q = \frac{[B]}{[A]^2} < K$

--- we increase the number of collisions btwn molecules:

---- the pressure increases

---- then the no. of moles increases

--- the system will shift in the direction that reduces the no. of moles

--- the reaction will go in the forward direction toward product



-- if we increase the volume then  $Q = \frac{[B]}{[A]^2} > K$

--- we decrease the number of collisions btwn molecules:

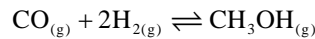
---- the pressure decreases

---- then the no. of moles decreases

--- the system will shift in the direction that increases the no. of moles

--- the reaction will go in the reverse direction toward reactant

- Example: For each scenario predict the direction the reaction goes to attain eq:



a.) CO is added ..... reaction goes toward product (forward)

b.) CH<sub>3</sub>OH is added ..... reaction goes toward reactants (reverse)

c.) Pressure is reduced .....  $\Delta n_{\text{reactants}} = 3$ ,  $\Delta n_{\text{products}} = 1$  reaction goes toward reactants (reverse)

d.) Volume is increased ..... reaction goes toward reactant (forward)

- Change in eq with T

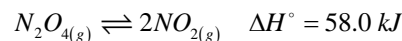
-- unlike our other changes, the value of the eq const changes with T

-- if the reaction is exothermic and we add heat then we would predict the reaction would go toward reactants: reactants  $\rightarrow$  products + heat

-- for an endothermic reaction the addition leads toward more product generation  
reactants + heat  $\rightarrow$  products

-- in each case we are treating our heat as a reactant or product

- Example: In what direction will the eq shift when each of the following changes are made to the system at eq?



(a)  $\text{N}_2\text{O}_{4(g)}$  is added ..... reaction goes toward product

(b)  $\text{NO}_{2(g)}$  is removed ..... reaction goes toward product

(c) the total pressure is increased by adding  $\text{N}_{2(g)}$  ..... reaction remains unchanged since the partial pressures of the reacting species is constant at constant volume

(d) the volume is decreased ..... reaction goes toward reactant since  
 $\Delta n_{\text{reactants}} = 1$ ,  $\Delta n_{\text{products}} = 2$

(e) the temperature is decreased ..... reaction goes toward reactant since the process is endothermic or  $\text{N}_2\text{O}_{4(g)} + 58.0 \text{ kJ} \rightleftharpoons 2\text{NO}_{2(g)}$

- The Effect of Catalysts – there is no impact on the eq constant it just allows us to reach eq faster