# Chemical Equilibrium

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**Chapter 13**

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Equilibrium
- Must have a reversible reaction
- Rate of the forward and reverse reactions are <u>EQUAL</u>
- Concentrations of reactants and products stay <u>constant</u> (not equal!)
(a "dynamic state" – equal but opposite change is always occurring)

Mass Action Expression (Law of Mass Action)
- A general description of the equilibrium condition
Ex. jA + kB → lC + mD

Mass action expression = $\dfrac{[C]^l [D]^m}{[A]^j [B]^k}$

- For a system at equilibrium the value of K
- If [equil]'s are known, the value of $K_{eq}$ can be calculated:

13.2 (p606)    Haber Process at 127°C

$[NH_3]=3.1 \times 10^{-2}$ M

$[N_2]=8.5 \times 10^{-1}$ M

Equilibrium Position
- a set of concentrations present when the system is at equilibrium
  (value of mass action expression = k)
- for a reaction there are an infinite number of equilibrium positions
  (Table 13.1, p527)
- for a reaction system, equilibrium will be establishes if you start with
  i.    all reactants
  ii.   all products
  iii.  any combination of reactants or products
  (ex. 13.3, p609-shows different equilibrium positions=k)

Equilibrium Expressions for <u>Gaseous</u> Systems
- concentration can be indicated in terms of <u>pressure</u>*
  ex. $N_{2\,(g)} + 3H_{2\,(g)} \leftrightarrow 2NH_{3\,(g)}$

  for []'s: $K_c = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$     $K_c \leftarrow$ means using concentrations

  for partial pressures: $K_p = \dfrac{P_{NH_3}^{\,2}}{(P_{N_2})(P_{H_2})^3}$     $K_p \leftarrow$ means using partial pressures
derived on p611-612

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

(units are usually ommited)

$\Delta n$= total # of mols of gaseous products – total # mols of gaseous reactants
- if $\Delta n$= 0, $K_p=K_c$

13.5 (p612)

Units on $K_c$ or $K_p$:
- units depend on the specific reaction
- often omitted in tables of $K_c$ & $K_p$ values

Heterogeneous Equilibrium
- equilibrium systems involving more than one phase
- the equilibrium position of a heterogeneous system <u>does not</u> depend on the amount of solid or liquid present
- [solids] & [liquids] are <u>constant</u>
- as such they do NOT appear in the mass action expression

ex. $CaCO_{3\,(s)} \leftrightarrow CaO_{(s)} + CO_{2\,(g)}$

$$K = \frac{[CaO_{(s)}][CO_{2(g)}]}{[CaCO_{3(s)}]}$$

- but the expression is evaluated with all constants together

$$\therefore \frac{K^1[CaCO_{3(s)}]}{[CaO_{(s)}]} = [CO_{2(g)}] = K_{eq}$$

ex. $2H_2O_{(l)} = 2H_{2\,(g)} + O_{2\,(g)}$        (set constant []=1)

$$K_c = \frac{[H_2]^2[O_2]}{1} = [H_2]^2[O_2]$$

$$K_p = \frac{(P_{H_2})^2(P_{O_2})}{1} = (P_{H_2})^2(P_{O_2})$$

(ex. 13.6, p614-find K & $K_p$ expressions)

Evaluating K
- The magnitude of K indicates the tendency for a reaction ($\rightarrow$or$\leftarrow$) to occur (but not how fast!)
- K much $\geq 1$

- o system consists of mostly products
- o reaction goes nearly to completion
- o equilibrium lies far to the right
  - $(R_{left} \rightarrow P_{right})$
- K <u>very small</u>
  - o system consists of mostly reactants
  - o forward reaction does not occur very much
  - o equilibrium position lies far to the left

Reaction Quotient (Q)
- the value obtained when the systems initial concentrations (before equilibrium is reached) are applied (put into) to the mass action expression
- is used to determine <u>which way</u> the system must <u>shift</u> to reach equilibrium
  - o If Q=k, the system IS in equilibrium
  - o If Q>k, then [P] is too large
    - System must shift to the left to achieve equilibrium (less[P], more [R] needed
  - o If Q<k, then [R] is too large
    - System must shift to the right to achieve equilibrium (more [P] needed, less [R])
- Ex. For the synthesis of ammonia at 500°C, the equilibrium constant is $6.0X10^{-2}$. Predict the direction in which the system will shift to reach equilibrium in each of the following cases:
  - o $[NH_3]_0 = 1.0X10^{-3}M$; $[N_2]_0 = 1.0X10^{-5}M$; $[H_2]_0 = 2.0X10^{-3}M$
  - o $[NH_3]_0 = 2.0X10^{-4}M$; $[N_2]_0 = 1.5X10^{-5}M$; $[H_2]_0 = 3.54X10^{-1}M$
  - o $[NH_3]_0 = 1.0X10^{-4}M$; $[N_2]_0 = 5.0M$; $[H_2]_0 = 1.0X10^{-2}M$

## Calculating Equilibrium Concentrations (& Pressures)
- You must have a known value of $k_c$ or $k_p$
- Using the [initial] and the direction in which the system must shift to reach equilibrium, you must set up variables to equal [equilibrium]s
- Ex. $CO_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + H_{2(g)}$ at 700K
  - K=5.10
  Calculate the [equil] of all species if 1.000mol of each gas are mixed in a 1.000L flask

- Ex. (still using a perfect square)

    $H_{2(g)} + F_{2(g)} \rightarrow 2HF_{(g)}$

    $K = 1.15 \times 10^2$
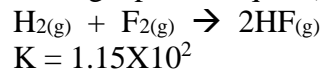
    3.000 mole of each component in a 1.500L flask [equil]'s

# What happens when [P]/[R] is not a perfect square?? Quadratic Formula

- Ex.    Suppose for a synthesis of hydrogen fluoride from hydrogen and fluorine, 3.000 mol $H_2$ and 6.000 mol $F_2$ are mixed in a 3.000L flask. Assume the equilibrium constant for the synthesis reaction at this temperature is $1.15 \times 10^2$. Calculate the equilibrium concentration for each component.

    $H_{2(g)} + F_{2(g)} \rightarrow 2HF_{(g)}$
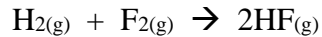
- Ex. Assume that gaseous hydrogen iodide is synthesized from hydrogen gas and iodine vapor at a temperature where the equilibrium constant is $1.00 \times 10^2$. Suppose HI at $5.000 \times 10^{-1}$ atm, $H_2$ at $1.000 \times 10^{-2}$ atm, and $I_2$ at $5.000 \times 10^{-3}$ atm are mixed in a 5.000L flask. Calculate the equilibrium pressures of all species. Calculate Kc

    $H_{2(g)} + I_{2(g)} \leftrightarrow 2HI_{(g)}$
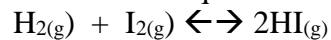
## Simplifying the Problem Solving Procedure

- For systems with small keq values shifting right
    - The shift to the right will be very small (the smaller the value of the k the more reactants you have)
    - The change in concentration of the the reactants will be so small that it will be negligible
    - Ex. [reactant] = 1M
    - [equil] = 1-X $\approx$ 1M  (this will alleviate the need for the Quadratic Equation)
- Ex.  Gaseous NOCl decomposes to form the gases NO and $Cl_2$.  At 35°C the equilibrium constant is $1.6X10^{-5}$.  In an experiment in which 1.0mol NOCl is placed in a 2.0L flask, wha ae the equilibrium concentrations?

## LeChatelier's Principle

- If a change is imposed on a system at equilibrium, the position of the equilibrium will shift in the direction that tends to reduce the change.
- Change of Concentration
    - If a reactant or product is added to a system at equilibrium, the system will shift away from the added component
    - If a reactant or product is removed from the system, the system will shift towards that component