Pharmaceutical analytical chemistry I

Lecture 6

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Chemical equilibrium for reaction involving gases:

●For reactions involving gases, partial pressures of reactants and products are proportional to their molar concentrations.

Therefore equilibrium constant expression for these reactions can be written using partial pressures instead of concentration

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

$$K_p = \frac{P^2_{NH_3}}{P_{N_2}.P^3_{H_2}}$$

Equilibrium constant, Kp, describes ratio of product and reactant concentrations at equilibrium in terms of partial pressures.

- <u>N.B:</u>

● If partial pressure is used , we use Kp, to describe equilibrium constants

● If molar concentration is used , we use Kc to indicate equilibrium constants

$$K_c = \frac{[NH_3]^2}{[N_2]\ [H_2]^3} \qquad K_p = \frac{P^2NH_3}{P_{N2}.P^3_{H_2}}$$

- Relationship between Kp and Kc:

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

Where Δng =(no of moles of gas products) – (no of moles of gas reactants)

- R is gas constant = 0.0821 L. atm / K. mol
- T (absolute temperature) = 273 + °C

Example 1: For the reaction: $N_2O_4(g) \leftrightarrow 2\ NO_2(g)$

Concentrations of substances present in an equilibrium mixture at 25°C are :
$[N_2O_4] = 4.27 \times 10^{-2}$ mol/L
$[NO_2] = 1.41 \times 10^{-2}$ mol/L

What is the value of Kc for this temperature. ?

Solution:

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(1.41 \times 10^{-2}\ \text{mol/l})^2}{(4.27 \times 10^{-2}\ \text{mol/l})} = 4.66 \times 10^{-3}$$

Example 2: For the reaction

$$2\ SO_{3(g)} \rightleftharpoons 2\ SO_{2(g)} + O_{2(g)} \qquad \text{at } 1100\ K$$

Kc is 0.0271 mol/L. what is Kp at same temperature. ?

Solution: $Kp = Kc\ (RT)^{\Delta ng}$

$\Delta n = 3 - 2 = 1$

$Kp = Kc\ (RT)^{+1}$

$= 0.0271$ mol/L x (0.0821 L. atm / K. mol) (1100 K)

$= 22.45$

Homogeneous and Heterogeneous equilibria

- Homogeneous occur when all reactants and products are in the same phase.

e.g: In gas phase: $N_2(g) + H_2(g) \leftrightarrow 2NH_3(g)$

In liquid phase:

CH_3COCl + CH_3OH $\leftrightarrow$ CH_3COOCH_3 + HCl

Acetyl chloride methyl alcohol methyl acetate

- **Heterogeneous** equilibria occur when reactant or product in the equilibrium is in a different phase.

$$C + CO_2 \leftrightarrow 2CO$$

Heterogeneous Equilibria:

The concentration of a pure solid or a pure liquid **is constant** and **do not appear in the expression for the equilibrium constant**

For example

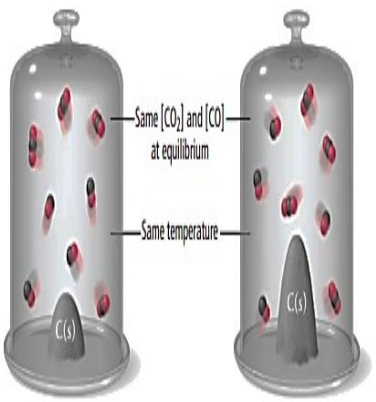
1- $CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g)$

$Kc = [CO_2]$

Since $CaCO_{3(s)}$ and $CaO_{(s)}$ are both solids, omit them from the equilibrium expression

2- $3Fe(s) + 4\,H_2O(g) \leftrightarrow Fe_3O_4(s) + 4\,H_2(g)$

$Kc = [H_2]^4 / [H_2O]^4$



Heterogeneous Equilibrium The concentration of solid carbon (the number of atoms per unit volume) is constant as long as some solid carbon is present. The same is true for pure liquids. For this reason, the concentrations of solids and pure liquids are not included in equilibrium constant expressions.

Heterogeneous Equilibria:

Example : For the reaction:

$$C_{(s)} + CO_{2(g)} \leftrightarrow 2\,CO_{(g)}$$

K_p is 167.5 atm at 1000°C. What is the partial pressure of $CO_{(g)}$ in an equilibrium system in which the partial pressure of $CO_{2(g)}$ is 0.1 atm?

Solution: reaction represents heterogeneous equilibria, so concentration of solid C(s) is a constant value , so it is neglected

$$K_p = \frac{P^2_{Co}}{P_{Co_2}} = 167.5$$

$P^2_{Co} = 167.5\ P_{Co2}$

$= 167.5 \times 0.1 = 16.7$

$P_{Co} = \sqrt{16.7} = 4.10$ atm

Homework:

1-For this heterogenous equilibrium-

$$CaCO_{3(}s) \leftrightarrow CaO(s) + CO_2(g)$$

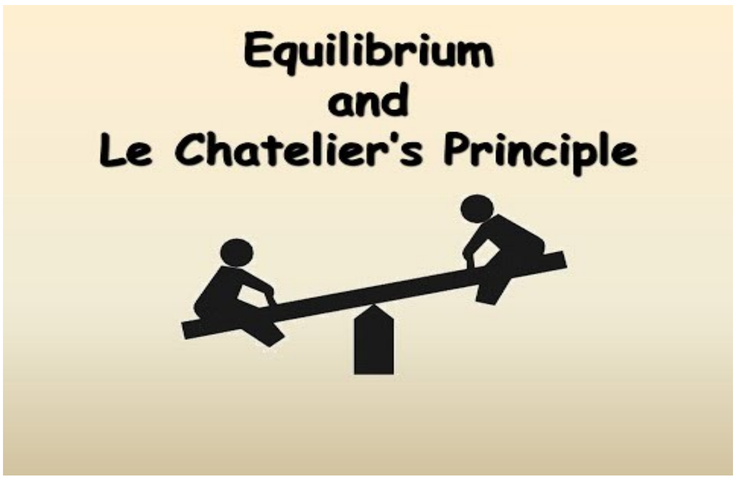
At 800°C, the pressure of **CO_2 is 0.236 atm. Calculate**

What is the value of: a) Kc and (b) Kp at this temperature.?

Summary of Guidelines for Writing Equilibrium Constant Expressions

1. The concentrations of the reacting species in solid and liquid phases are expressed in mol/L, while in the gaseous phase, the concentrations can be expressed in mol/L or in atm.
2. The concentrations of pure solids, pure liquids (in heterogeneous equilibria), and solvents (in homogeneous equilibria) do not appear in the equilibrium constant expressions.
3. The equilibrium constant (Kc or KP) is a dimensionless quantity.
4. In determining a value for the equilibrium constant, we must specify the balanced equation and the temperature.
5. If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions (e.g. H_2S)

Factors affecting chemical equilibrium
Le Chatelier's principle



Le Chatelier's Principle

When a chemical system at equilibrium is disturbed, the system shifts in a direction that minimizes the disturbance.
Disturbance means a change in concentration, pressure, volume, or temperature that removes system from the equilibrium state.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

For example :
Increase H_2 or I_2 → shift to formation of HI(forward)
Removal of H_2 or I_2 →Reaction shift to decomposition of HI (backward)

Le Chatelier's Principle

Type of stress factors:
1- Change in concentration
2- Change in pressure and volume
3- Change in temperature
4-Addition of catalyst.

Le Chatelier's Principle

1- Change in Concentration: If concentration of substance is increased, equilibrium will shift in a way that will decrease concentration of substance that was added.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Increase H_2 or I_2 → shift to formation of HI
Removal of H_2 or I_2 ¬ Reaction shift to decomposition of HI.

Le Chatelier's Principle

2- Pressure and volume changes: Increasing pressure causes a shift in the direction that will decrease number of moles of gas.

$$2\,SO_{2(g)} + O_{2(g)} \leftrightarrow 2\,SO_{3(g)}$$

3 moles **2 moles**

When pressure on an equilibrium mixture is increased (or volume of system decreased ,i.e. conc. Increased),

↓

position of equilibrium shifts to right. In this way system counteracts the change, and vise versa.

Le Chatelier's Principle

- Notes
- When pressure on an equilibrium mixture is increased (or the volume of the system decreased so conc. increased), position of equilibrium shifts to the right. In this way system counteracts change, and vise versa.
- For reactions in which $\Delta n = 0$, pressure changes have no effect on the position equilibrium.

  e.g: $N_{2(g)} + O_{2(g)} \leftrightarrow 2\ NO_{(g)}$

Le Chatelier's Principle

3- Temperature changes: examples

- $N_2(g) + 3\ H_2(g) \leftrightarrow 2\ NH_3(g)$ $\Delta H = -\ 92.4KJ$
- **Since Δ H is –ve, reaction to right , evolves heat exothermic)**

  $N_2(g) + 3\ H_2(g) \leftrightarrow 2\ NH_3(g)\ + 92.4\ KJ$

- $CO_2(g) + H_2(g) \leftrightarrow CO(g) + H_2O(g)$ $\Delta H = +\ 41.2KJ$
- **Since Δ H is + ve , reaction is endothermic, we can write equation**

  $41.2\ KJ + CO2(g) + H_{2(}g) \leftrightarrow CO(g) + H_2O(g)$

If $H_{solution} < H_{components}$ **$\Delta H = -$ ve (exothermic reaction)**
If $H_{solution} > H_{components}$ **$\Delta H = +$ ve (endothermic reaction)**

If H = heat content

$\Delta H = H_{solution} - H_{components}$

$= H_{solution} - (H_{solute} + H_{solvent})$

If $H_{solution} < H_{components}$ ΔH= - ve (exothermic reaction)

If $H_{solution} > H_{components}$ ΔH = + ve (endothermic reaction)

Le Chatelier's Principle

- In the following reaction:

$$CO_2(g) + H_2(g) \leftrightarrow CO(g) + H_2O(g) \qquad \Delta H = + 41.2KJ$$

Since Δ H is + ve , endothermic

we can write the equation

$$41.2\ KJ + CO_2(g) + H_2(g) \leftrightarrow CO(g) + H_2O(g)$$

So, increasing temperature (adding heat) of the system will favor the forward reaction. Conversely, a decrease in temperature (removing heat) will favor the reverse reaction.

- The numerical value of equilibrium constant changes when the temperature is changed.

Le Chatelier's Principle

4- Effect of catalyst: Adding a catalyst to a reaction mixture that is not at equilibrium will simply cause the mixture to reach equilibrium faster. The same equilibrium mixture could be obtained without the catalyst, but we might have to wait much longer for it to happen

5- Addition of an inert gas: If an inert gas is introduced into a reaction vessel containing other gases at equilibrium, it will not affect position of equilibrium because it will not alter partial pressures or concentrations of any of the substances already present.

Summary of Factors That May Affect the Equilibrium Position

- We have considered four ways to affect a reacting system at equilibrium. It is important to remember that:

1- Only a change in temperature changes the value of the equilibrium constant.

2- Changes in concentration, pressure, and volume can alter the equilibrium concentrations of the reacting mixture, but they cannot change the equilibrium constant **as long as** the temperature does not change.

3- A catalyst can speed up the process, but it has no effect on the equilibrium constant or on the equilibrium concentrations of the reacting species.