ALMUSTAQBAL UNIVERSITY COLLEGE

Biomedical Engineering Department

Stage : Second year students

Subject : Chemistry 1 - Lecture 8

Lecturer: Assistant professor Dr. SADIQ . J. BAQIR

Chemical and ionic equilibrium:

There are two types of reactions:

1) Reversible reaction, $A + B \rightleftharpoons C + D$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

2) Irreversible reaction , $A + B \rightarrow C + D$

$$CaCO_{3(s)} + 2\ HCl_{(l)} \rightarrow CO_2\uparrow_{(g)} + CaCl_{2(s)} + H_2O_{(l)}$$

Generally , most of the chemical reactions are considered as reversible reactions.

There are two kinds of systems :

a) **Homogenous reactions** : chemical reactions in which the reactants and products are in the same phase (solid , liquid or gas)

$$H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$$

$$2\ KOH(l) + H_2C_2O_4(l) \rightarrow K_2C_2O_4(l) + H_2O(l)$$

b) **Heterogeneous reactions** :

Chemical reactions in which the reactants and products have more than one phase.

$$FeS(s) + HCl(l) \rightarrow FeCl_2(l) + H_2S(g)$$

Equilibrium constant (K) :

A numerical quantity that relate the concentration of reactants and products in a chemical reaction to one another.

For the chemical reaction : $aA + bB \rightleftharpoons cC + dD$

According to **mass action law** which states that **(**The rate of chemical reaction is directly proportional with formula concentration of reaction substances each raise to the power indicated by the number of ion or molecule appearing in the balanced equation of the reaction**)**. Then:

$V_f \ \alpha \ [A]^a , [B]^b$ (f= forward)

$V_f = K_f [A]^a [B]^b$

$V_b \ \alpha \ [C]^c , [D]^d$ (b= backward)

$V_b = K_b [C]^c [D]^d$

At equilibrium state : ($V_f = V_b$)

$K_f [A]^a [B]^b = K_b [C]^c [D]^d$

$$\frac{K_f}{K_b} = K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

K = equilibrium constant

Example:
Write the equilibrium constant expression for each of the reversible reactions:

a. $H_2 (g) + F_2 (g) \rightleftharpoons 2HF(g)$

b. $2NO_2 (g) \rightleftharpoons N_2 (g) + 2O_2 (g)$

solution:

a. $K_{eq} = \frac{[HF]^2}{[H_2][F_2]}$ 	b. $Keq = \frac{[N_2][O_2]^2}{[NO_2]^2}$

Example:

A container holds the following mixture at equilibrium:

$[NH_3] = 0.25$ M 	$[H_2] = 1.91$ M 	$[N_2] = 0.11$M

$3H_2 (g) + N_2 (g) \rightleftharpoons 2NH_3(g)$

Calculate the equilibrium constant of the reaction.

Solution:

$$Keq = \frac{[NH_3]^2}{[H_2]^3[N_2]} = \frac{[0.25]^2}{[1.91]^3[0.11]} = 0.082$$

Exercise:

Given the equilibrium reaction: $2HI \rightleftharpoons H_2 + I_2$

Calculate the molar concentration of I_2 in the equilibrium mixture Where $[H_2] = 1.0 \times 10^{-2}$ M and $[HI] = 4.0 \times 10^{-2}$ M and Keq = 10.

Le chatelier principle :

The position of chemical equilibrium will always shift in a direction that tends to remove the effect of the applied stress .

Factors effecting the reactions at equilibrium :

1) Nature of reactants
2) Temperature
3) Concentration
4) Pressure (in gas reactions)

Some familiar equilibrium constant expressions :

Kw = ion product (or ionization) constant for water .

Ksp = solubility product constant.

K_a = ionization (or dissociation) constant of a weak acid.

K_b = ionization (or dissociation) constant of a weak base.

Ion product constant for water (Kw) :

Aqueous solutions contains small amount of hydronium ions [H_3O^+] and hydroxide [OH^-] ions as a consequence of the dissociation reaction :

$2\,H_2O \rightleftharpoons H_3O^+ + OH^-$ or

$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

(base) (acid)

H_2O acid molecule gives H^+ to H_2O base molecule to produce H_3O^+ ions

$$K = \frac{[H3O+][OH-]}{[H2O]^2}$$

$$K\,[\,H_2O\,]^2 = [\,H_3O^+\,]\,[\,OH^-\,] = Kw$$

$$Kw = [\,H_3O^+]\,[\,OH^-\,] = 1\times10^{-14}\ mol^2 / L^2 \ \text{at}\ 25^oC$$

Kw is **temperature dependant** it increases with temperature rise , and decreases with its decrease.

Variation of Kw with temperature :

Temperature ^{o}C	Kw
0.0	1.14×10^{-15}
25	1.01×10^{-14}
40	2.92×10^{-14}
50	5.47×10^{-14}
70	2.30×10^{-13}
100	4.90×10^{-13}

Kw is used only for water.

Example :

Calculate the hydronium $[H_3O^+]$ and hydroxide ion$[OH^-]$ concentrations of pure water at 25^oC and 100^oC ?

Answer:

Because OH^- and H_3O^+ are formed from the dissociation of water only, then their concentrations are equal,

$$2\,H_2O \rightleftharpoons H_3O^+ + OH^-$$

then : $[H_3O^+] = [OH^-]$

$Kw = [H_3O^+][OH^-]$

Subsititution in the above equation gives :

$Kw = [H_3O^+]^2$ also $Kw = [OH^-]^2$

$[H_3O^+] = \sqrt{K_w}$ and $[OH^-] = \sqrt{K_w}$

At $25\ ^oC$ $[H_3O^+] = \sqrt{K_w} = \sqrt{1.01\ x\ 10^{-14}} = 1.01 \times 10^{-7}$

$pH = -\log(1.01 \times 10^{-7}) = 7.00$

$[OH^-] = \sqrt{K_w} = \sqrt{1.01\ x\ 10^{-14}} = 1.01$ x 10^-

At 100^o C

$[H_3O^+] = \sqrt{K_w} = \sqrt{49\ x 10^{-14}} = 7.0$ x 10^{-7}

pH = - log (7 x 10^{-7}) = 6.15

$[OH^-] = \sqrt{K_w} = \sqrt{49\ x 10^{-14}} = 7.0$ x 10^{-7}

Exercise:

Calculate the change in pH of pure water on heating from 25^{o}C to 50^{o}C (Kw = 5.47x10 $^{-14}$) .

Equilibrium involving sparingly soluble ionic solids :

Most sparingly soluble salts are dissociated in saturated aqueous solution .

e.g: $AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$

$$\mathbf{K} = \frac{[\boldsymbol{Ag+}][\boldsymbol{Cl-}]}{[\boldsymbol{AgCl(s)}]}$$

K [$AgCl_{(s)}$] = Ksp = [Ag^+_{aq}] [Cl^-_{aq}]

Where **Ksp = solubility product constant** (applied only for saturated solution) .

Example :

How many grams of $Ba(IO_3)_2$ (487 g / mol) can be dissolved in 500 mL of water at 25^{o}C ? Ksp for $Ba(IO_3)_2$ = 1.57x10^{-9} .

$Ba(IO_3)_2 \rightleftharpoons Ba^{2+} + 2\ IO_3^-$

S 2S

$Ksp = [\ Ba^{2+}\ ]\ [\ IO_3^-]^2$

$Ksp = (S)(2S)^2 = 1.57x10^{-9} = 4S^3$

$S = \sqrt[3]{\frac{1.57x10^{-9}}{4}}$ = $7.32x10^{-4}$ mole/ L or (M) = Solubility

No. of moles $= \frac{\text{Weight (g)}}{\text{Molar mass (g / mol)}}$

Weight = No. of moles x Molar mass (g / mol)

As Molarity (M) $= \frac{No.\ of\ moles}{Volume(liters)}$

Then **No. of moles** = Molarity x Volume (liters)

Substituting for the No. of moles gives:

$\frac{\text{Weight (g)}}{\text{Molar mass (g / mol)}}$ = Molarity x Volume (liters)

Weight (g) = Molarity x Volume (liters) x Molar mass (g / mol)

Weight in grams of $Ba(IO_3)_2$ $= 7.32x10^{-4}$ mol/liter x $\frac{500}{1000}$ Liter x 487 g /mol = 0.178 g

Then weight in grams of $Ba(IO_3)_2$ that is dissolved in 500 mL water = 0.178 g

Example :

Calculate the weight in grams of AgCl (143.3 g / mol) that can be dissolved in 600 mL of water? Ksp for AgCl = $1.8x10^{-10}$.

$$\mathbf{AgCl \rightleftharpoons Ag^+ + Cl^-}$$

S S

$Ksp = [\ Ag^+\ ]\ [\ Cl^-]$

$Ksp = (S)(\ S) = 1.8x10^{-10} = S^2$

S = $\sqrt{1.8\ x\ 10^{-10}}$ = $1.34x10^{-5}$ mole/ L or (M) = solubility

Weight(g) = Molarity x Volume (liters) x Molar mass (g / mol)

Weight in grams of AgCl = $1.34x10^{-5}$ mol/liter x $\frac{600}{1000}$ Liter x 143.32 g /mol = $1.15x10^{-3}$ g = 1.15 mg

Calculating Solubility Product Constant (Ksp) From Solubility

Example :

The weight of the sparingly soluble substance AgBr (187.8 g/mol) that dissolves in 500 mL of water to form a saturated solution is $6.65x10^{-5}$ g . Calculate the Ksp of AgBr.

Answer:

AgBr ⇌ Ag^+ + Br^-

S S

S = molar solubility = Molarity

Molarity of AgBr (M) = $\frac{wt\ (g) x\ 1000}{M.wt\ x\ Vml}$

Molarity of AgBr (M) = $\frac{6.65x10^{-5}\ x\ 1000}{187.8\ x\ 500}$ = $7.08\ x\ 10^{-7}$ = S

Ksp = [Ag^+] [Br^-]

Ksp = (S)(S) = S^2

Ksp = $(7.08x10^{-7})^2$ = $5.01\ x\ 10^{-13}$

EXAMPLE:

The solubility of barium fluoride, BaF_2, is 7.94 x 10^{-3} M at 25 °C. Calculate its solubility product constant, K_{sp},.

SOLUTION

BaF_2 (s) $\rightleftharpoons$ Ba^{2+} (aq) + 2 F^- (aq)

S 2S

Solubility = $[Ba^{2+}]$ = (S) = 7.94 x 10^{-3} M

$K_{sp} = [Ba^{2+}][F^-]^2$

$K_{sp} = (S)\ (2\ S)^2 \ = 4S^3$

$K_{sp} = 4(7.94 \times 10^{-3}\ M)^3$

$K_{sp} = 2 \times 10^{-6}$

Estimation of precipitate formation

Example:

Will a precipitate form when 20 mL of 0.01 M $AgNO_3$ solution is mixed with 2 Liter of 0.002 M K_2CrO_4 . the Ksp for Ag_2CrO_4 is 1.1 x 10^{-12}

$2AgNO_3 + K_2CrO_4 \rightarrow Ag_2CrO_4 + 2\ KNO_3$

$Ag_2CrO_4(s) \rightleftharpoons \mathbf{2}\ Ag^+ + CrO_4^{2-}$

Ksp = $[Ag^+]^2\ [CrO_4^{2-}] = 1.1\text{x}10^{-12}$

Having $AgNO_3$ gives Ag^+ and K_2CrO_4 gives CrO_4^{2-}

To calculate the ionic product (I.P) of $[Ag+]^2\ [CrO_4^{2-}]$ after mixing

M_1V_1(before mixing) = M_2V_2(after mixing)

$[Ag^+] = \frac{M1V1}{V2} = \frac{(0.01M)(20mL)}{(2000+20\ )mL} = 9.9\text{x}10^{-5}$ M

$[CrO_4^{2-}] = \frac{M1V1}{V2} = \frac{(0.002M)(2000mL)}{(2000+20\ )mL} = 0.002$ M

I.P = $[Ag+]^2\ [CrO_4^{2-}] = (9.9\text{x}10^{-5})^2\ (0.002) = 2.0 \text{ x } 10^{-11}$

As I.P > Ksp **then precipitate will form**

Notes:

1. If ionic product (I.P) < Ksp (dissolution Occurs)
2. If ionic product (I.P) = Ksp (equilibrium state) **saturation**
3. If ionic product (I.P) > Ksp (precipitation Occurs)

Example:

What pH is required to just precipitate $Fe(OH)_3$ (Ksp = $4\text{x } 10^{-38}$) from 0.1 M $FeCl_3$ solution?

Answer:

$Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3\ OH^-$

$FeCl_3 \rightarrow Fe^{3+} + 3\ Cl^-$

0.1 mole 0.1 mole

$ksp = [Fe^{3+}][OH^-]^3 = 4 \text{ x } 10^{-38}$

$[0.1][OH^-]^3 = 4 \text{ x } 10^{-38}$

$[OH^-] = \sqrt[3]{\frac{4\ x\ 10^{-38}}{0.1}} = 7 \text{ x } 10^{-13}$

pOH = - log ($7 \text{ x } 10^{-13}$) = 12.2

pH = 14 - 12.2 = 1.8