ALMUSTAQBAL UNIVERSITY

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Medical Laboratories Techniques Department

Stage : First year students
Subject : General Chemistry 1 - Lecture 5

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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.

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.

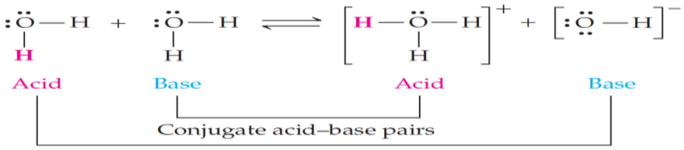
Ion product constant for water (Kw) :

DISSOCIATION OF WATER

One of the most important properties of water is its ability to act both as an acid and as a base.

In the presence of an acid, water acts as a base, whereas in the presence of a base, water acts as an acid.

It's not surprising, therefore, that in pure water one molecule can donate a proton to another in a reaction in which water acts as both an acid and a base in the same reaction:



Aqueous solutions contain a 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

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

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

$$Kw = [H_3O^+][OH^-] = 1 \times 10^{-14}\ mol^2 / L^2 \text{ at } 25^oC$$

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

Variation of Kw with temperature :

Temperature °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°C and 100°C.

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 °C $[H_3O^+] = \sqrt{K_w} = \sqrt{1.01\ x\ 10^{-14}} = 1.01 \times 10^{-7}$

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

$[\ OH^-\ ] = \sqrt{K_w} = \sqrt{1.01\ x\ 10^{-14}} = 1.01 \text{ x } 10^{-7}$

At 100^o C

$[\ H_3O^+\ ] = \sqrt{K_w} = \sqrt{49\ x10^{-14}} = 7.0 \text{ x } 10^{-7}$

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

$[\ OH^-\ ] = \sqrt{K_w} = \sqrt{49\ x10^{-14}} = 7.0 \text{ x } 10^{-7}$

Exercise:

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

Equilibrium involving sparingly soluble ionic solids :

Most sparingly soluble salts are dissociated in saturated aqueous solution.

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

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

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

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

Example:

The solubility product of $Mg(OH)_2$ (58 g/ mol) is 10^{-11} . Calculate its solubility in g/L .

$$\mathbf{Mg(OH)_2 \rightleftarrows \underset{S}{Mg^{2+}} + \underset{2S}{2OH^-}}$$

$Ksp = [Mg^{2+}]\ [2OH^-]^2$

The molar solubility (S) = $[Mg^{2+}]$

$Ksp = [S][2S]^2 = 4[S]^3 = 10^{-11}$

$S = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{10^{-11}}{4}} = 1.35x10^{-4}$

Solubility (g / L) = molar solubility(S) x M.wt

Solubility (g / L) = $1.35x10^{-4}$ x 58 = 0.0078 g/L

Example :

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

$AgCl \rightleftharpoons Ag^+ + Cl^-$

S S

Ksp = $[Ag^+] [CI^-]$

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

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

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

Weight in grams of AgCl = $1.34x10^{-5}$ mole/liter x $\frac{600}{1000}$ Liter x 143.5 g /mole = $1.15x10^{-3}$ g = 1.15 mg

Example :

How many grams of $Ba(IO_3)_2$ (487 g / mole) can be dissolved in 500 mL of water at 25°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

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

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

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

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 6.65×10^{-5} g . Calculate the Ksp of AgBr.

Answer:

$AgBr \rightleftharpoons Ag^{+} + Br^{-}$

S S

S = molar solubility = Molarity

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

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

Ksp = $[\ Ag^{+}\ ]\ [\ Br^{-}]$

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

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

Example:

The solubility of AgCl (143.5 g/mol) is 0.0015 g/L at 25 ^{o}C. Calculate its solubility product constant (Ksp).

Answer:

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

S S

S = molar solubility = Molarity = S = $\frac{solubility\ (g/L)}{M.wt}$

$S = \frac{0.0015\ (g/L)}{143.5} = 1.05 \times 10^{-5}$ M

$S = [Ag^{+}] = [Cl^{-}] = 1.05 \times 10^{-5}$ M

$Ksp_{AgCl} = [Ag^{+}][Cl^{-}]$

$Ksp = [1.05 \times 10^{-5}][1.05 \times 10^{-5}] = 1.1 \times 10^{-10}$

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:

$$\begin{array}{lcl} BaF_2\ (s) & \rightleftharpoons & Ba^{2+}\ (aq) + 2\ F^{-}\ (aq) \\ & & \quad S \qquad\qquad 2S \end{array}$$

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

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

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

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

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

Estimation of precipitate formation

Notes:

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

Example:

Will a precipitate is formed when 100 mL of 0.035 M $Pb(NO_3)_2$ is added to 100 mL of 0.045 M NaCl ? K_{sp} for $PbCl_2 = 1.6 \times 10^{-5}$.

$Pb(NO_3)_2(aq) + 2NaCl(aq) \rightarrow PbCl_2(s) + 2NaNO_3(aq)$

Solution:

$Pb(NO_3)_2(aq) \rightarrow \mathbf{Pb^{2+}}(aq) + 2NO_3^-(aq)$
$NaCl\ (aq) \rightarrow \mathbf{Na^+}(aq) + Cl^-(aq)$

$Pb(NO_3)_2(aq) + 2NaCl(aq) \rightarrow PbCl_2(s) + 2NaNO_3(aq)$

$\mathbf{PbCl_2(s) \leftrightarrows Pb^{2+}(aq) + 2Cl^-(aq)}$

$K_{sp} = [Pb^{2+}][Cl^-]^2$

the concentration of the two compounds when the solutions are mixed.

$V_2 = 100 + 100 = 200\ mL = 0.2\ L$

$M_1V_1(\text{before mixing}) = M_2V_2(\text{after mixing})$

$[Pb(NO_3)_2\ ] = [Pb^{2+}] = \frac{M1V1}{V2} = \frac{(0.035M)(100mL)}{(200\ )mL} = 0.0175M$

$[NaCl] = [Cl^-] = \frac{M1V1}{V2} = \frac{(0.045M)(100mL)}{(200\ )mL} = 0.0225\ M$

$I.P\ (Q) = [Pb^{2+}]\ [Cl^-]^2 = (0.0175)\ (0.0225)^2 = 8.9 \times 10^{-6}$

As I.P < Ksp then precipitate will not form

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