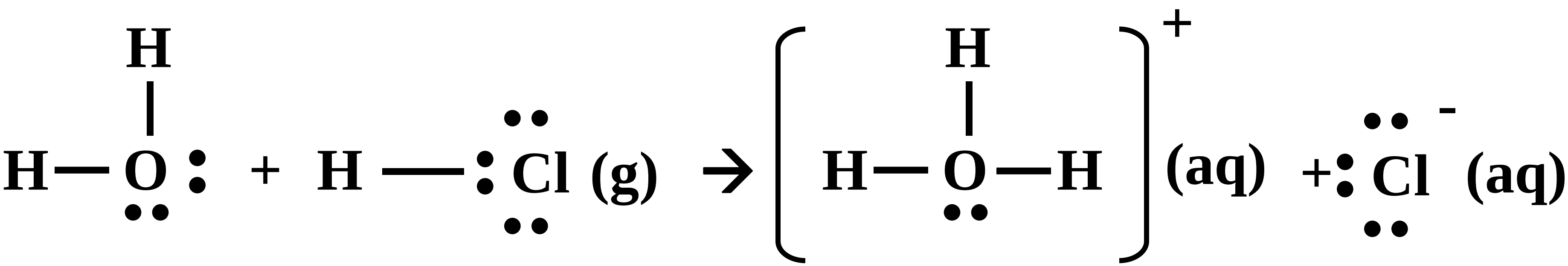
Acids and Bases

The Arrhenius concept

Acid: a substance that dissociates in water to produce H_3O^+ ions

H_3O^+ some times shown as H^+ (aq)



Oxides may be incorporated into the Arrhenius scheme

$$N_2O_5\ (s) + H_2O \rightarrow 2H^+\ (aq) + 2NO_3^-\ (aq)$$

Note: The Arrhenius concept is based on presence of water

The BrØnsted-Lowry Concept

Acid : a substance that can donate a proton

Base: a substance that can accept a proton

$$CH_3COOH\ (aq) + H_2O\ (aq) \rightleftharpoons H_3O^+\ (aq) + CH_3COO^-\ (aq)$$

CH_3COOH: is the acid (lost a proton)

H_2O: is the base (accepted a proton)

Now look at the reverse reaction:

CH_3COO^- : is the base (accepted a proton)

H_3O^+ : is the acid (lost a proton)

Pairs that are related through the loss or gain of a proton are

Conjugate pairs

$$\underset{\textit{Acid}_1}{CH_3COOH\ (aq)} + \underset{\textit{Base}_2}{H_2O\ (aq)} \rightleftharpoons \underset{\textit{Acid}_2}{H_3O^+\ (aq)} + \underset{\textit{Base}_1}{CH_3COO^-\ (aq)}$$

H_2O is the conjugate base of H_3O^+

H_3O^+ is the conjugate acid of H_2O

Water can also act as an acid

$$\underset{\textit{Acid}_1}{H_2O\,(aq)} + \underset{\textit{Base}_2}{NH_3\,(aq)} \rightleftharpoons \underset{\textit{Acid}_2}{NH_4^+\,(aq)} + \underset{\textit{Base}_1}{OH^-\,(aq)}$$

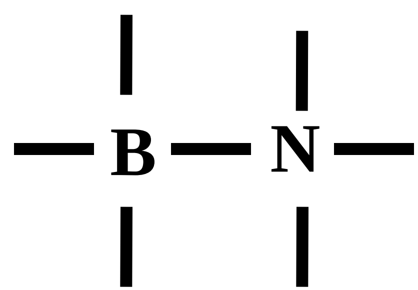
H_2O is the conjugate acid of OH^-

OH^- is the conjugate base of H_2O

The Lewis definition

Acid: a substance that can form a covalent bond by accepting an electron pair from a base

Base: a substance that have an unshared electron pair with which it can form a covalent bond with an atom, molecule or ion.

$BF_3 \quad + \quad :NH_3 \quad \rightarrow$ 

Accepts e's **Donates e's**

Acid **Base**

Electrolytes

Strong electrolytes are completely ionized in water solution

NaOH is a strong electrolyte

$$NaOH \rightarrow Na^+ + OH^-$$

0.2M solution of NaOH contains:
0.2M of Na^+ ions and
0.2M of OH^- ions

Weak electrolytes are incompletely ionized in water solution

Dissolved molecules exist in equilibrium with their ions in weak electrolytes solutions

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

Water dissociation

Pure water is a very weak electrolyte

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

In simplified form

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

Ionization constant

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

In dilute solutions the concentration of water is constant

$$K[H_2O] = [H^+][OH^-]$$

$$K[H_2O] = K_w$$

Water dissociation constant, at 25°C, K_w = 1.0×10^{-14}

$$[H^+][OH^-] = 1.0\times10^{-14}$$

$$[H^+] = [OH^-] = x$$

$$x^2 = 1.0\times10^{-14}$$

$$x = 1.0\times10^{-7}$$

In pure water

$$[H^+] = 1.0 \times 10^{-7} M$$

$$[OH^-] = 1.0 \times 10^{-7} M$$

In acidic solutions

$$[H^+] > 1.0 \times 10^{-7} M$$

In basic solutions

$$[OH^-] > 1.0 \times 10^{-7} M$$

Example

What are [H^+] and [OH^-] in a 0.020M solution of HCl?

HCl is a strong electrolyte

$$HCl \rightleftharpoons H^+ + Cl^-$$

[H^+] = 0.020M

$$\left[H^+\right]\left[OH^-\right] = 1.0\times10^{-14}$$

$$0.020\times\left[OH^-\right] = 1.0\times10^{-14}$$

$$\left[OH^-\right] = \frac{1.0\times10^{-14}}{0.020} = 5.0\times10^{-13}M$$

pH

$$pH = \log\frac{1}{[H^+]} = -\log[H^+]$$

The pH is the negative logarithm of the hydrogen ion concentration

For pure water

$$[H^+] = 1.0\times10^{-7}M$$

$$\log = 1.0\times10^{-7} = -7$$

$$pH = 7$$

pOH of a solution is defined in the same terms

$$pH = \log\frac{1}{[OH^-]} = -\log[OH^-]$$

The relationship between pH and pOH can be derived from the water dissociation constant

$$\left[H^+\right]\left[OH^-\right] = 1.0\times10^{-14}$$

Take the logarithm of each term

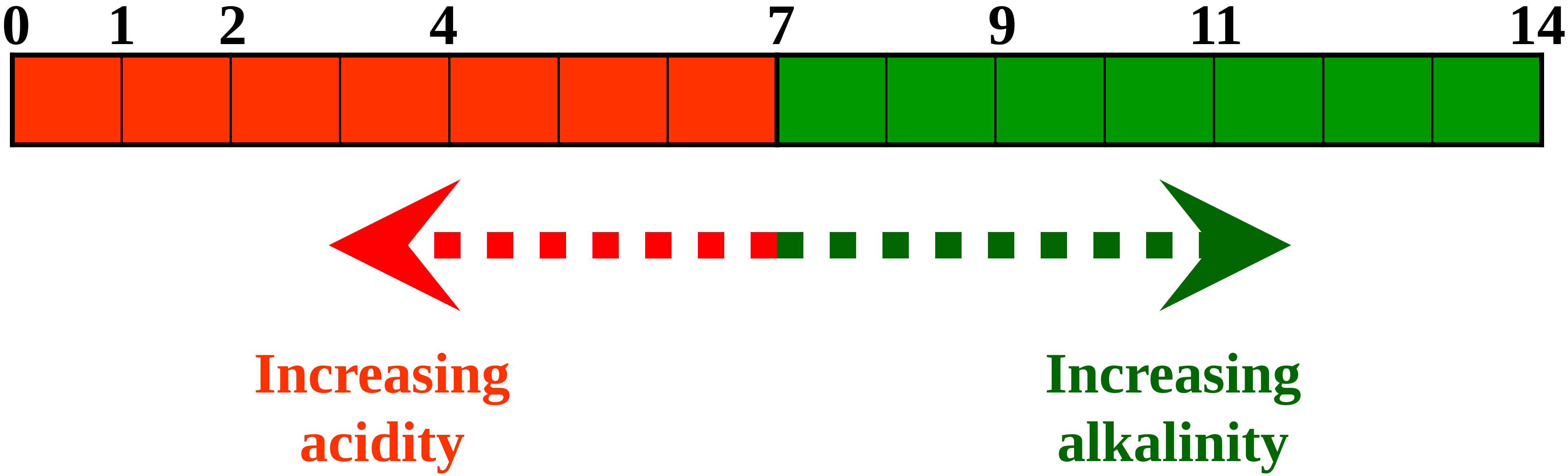
$$\log\left[H^+\right] + \log\left[OH^-\right] = \log\left(1.0\times10^{-14}\right)$$

Multiply by -1

$$-\log\left[H^+\right] - \log\left[OH^-\right] = -\log\left(1.0\times10^{-14}\right)$$

$$pH + pOH = 14$$

The pH scale



Example

For a 0.05M HCl solution

a. Calculate $[H^+]$ **&** $[OH^-]$

b. Calculate pH

c. Calculate pOH

a.

$[H^+]$ = 0.05M

$$\left[H^+\right]\left[OH^-\right] = 1.0\times10^{-14}$$

$$0.05\times\left[OH^-\right] = 1.0\times10^{-14}$$

$$\left[OH^-\right] = \frac{1.0\times10^{-14}}{0.05} = 2.0\times10^{-13}M$$

b. $$pH = -\log[H^+]$$

$$pH = -\log(5.0\times10^{-13}) = 1.30$$

c. $$pH + pOH = 14$$

$$pOH = 14 - pH = 14 - 1.30$$

$$pOH = 12.7$$

Example

If pH for a solution =10.60
Determine [H$^+$]

$$pH = -\log[H^+]$$

$$10.60 = -\log[H^+]$$

$$-10.60 = \log[H^+]$$

$$[H^+] = 10^{-10.60} = 2.5\times10^{-11} M$$

Weak electrolytes

Acetic acid as an example

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

C_a	0	0
$C_a - x$	x	x

$$[H^+] = [CH_3COO^-] = x$$

$$K_a = \frac{[H^+]^2}{C_a - x} \longrightarrow K_a = \frac{[H^+]^2}{C_a} \longrightarrow \boxed{[H^+] = \sqrt{K_a C_a}}$$

Assume x:too small

For a weak base

$$BOH \rightleftharpoons B^{+} + OH^{-}$$

$$K_b = \frac{[B^{+}][OH^{-}]}{[BOH]}$$

$$K_b = \frac{[OH^{-}]^2}{C_b} \longrightarrow \boxed{[OH^{-}] = \sqrt{K_b C_b}}$$

Example

What is the pH for a 0.080M solution of acetic acid? (K_a=1.80×10^{-5})

$$\boxed{\left[H^+\right] = \sqrt{K_a C_a}}$$

$$\left[H^+\right] = \sqrt{1.80\times10^{-5}\times0.080} = 1.2\times10^{-3}\text{ M}$$

$$\boxed{pH = -\log[H^+]}$$

$$pH = 2.92$$

Example

What is the pH for a 0.200M solution of NH_3?(K_b=1.80×10^{-5})

$$\boxed{\left[OH^-\right] = \sqrt{K_b C_b}}$$

$$\left[OH^-\right] = \sqrt{1.80 \times 10^{-5} \times 0.200} = 1.90 \times 10^{-3}\ \mathrm{M}$$

$$\boxed{pOH = -\log[OH^-]}$$

$$pOH = 2.72$$

$$\boxed{pH + pOH = 14}$$

$$pH = 14 - 2.72 = 11.28$$

Buffer solutions

Are solutions capable of maintaining their pH at some fairly constant value even when small amounts of acids or base are added

A buffer solution can be prepared from

Both a weak acid and a salt of the acid

Or Both a weak base and a salt of the base

Examples of buffer solutions

Acetic acid + sodium acetate $CH_3COOH + CH_3COO^-$

Ammonia +ammonium chloride $NH_3 + NH_4Cl$

Calculating the pH of buffer solutions

weak acid + salt of the acid $$pH = pK_a + \log\frac{[salt]}{[acid]}$$

weak base + salt of the base $$pOH = pK_b + \log\frac{[salt]}{[base]}$$

***Henderson-Hasselbalch* equations**

In general, the ratio of ionic species to molecular species for an effective buffer should be between 1/10 and 10/1.

Applying the equation to get the pH range :

$$pH = pK_a + \log\frac{1}{10} \xrightarrow{\text{to}} pH = pK_a + \log\frac{10}{1}$$

$$pH = pK_a - 1 \xrightarrow{\text{to}} pH = pK_a + 1$$

A buffer solution can be prepared with a pH of any value between (*pK_a+1*) and (*pK_a - 1*)

Example

What is the pH of a solution made by adding 2.05g of Sodium acetate (CH_3COONa) into one liter of 0.09M acetic acid (CH_3COOH)? $K_{\text{acetic acid}} = 1.80\times10^{-5}$

M.wt. of CH_3COONa = 82.0 g/mol

$$\#moles_{salt} = \frac{2.05g}{82g/mol} = 0.025mol$$

$$C_{salt} = \frac{0.025mol}{1L} = 0.025M$$

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

$$pH = -\log\left(1.80\times10^{-5}\right) + \log\left(\frac{0.025}{0.09}\right) = 4.2$$

Example

What weight of CH_3COONa should be added to 1.0L of 0.1M CH_3COOH to prepare a buffer solution with a pH of 5.0

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

$$5.0 = -\log\left(1.80\times10^{-5}\right) + \log\frac{[salt]}{0.1}$$

$$[salt] = 0.18M$$

$$M = \frac{n}{V} \longrightarrow n = 0.18M \times 1.0L = 0.18mol$$

$$n = \frac{wt(g)}{M.wt.(g/mol)} \longrightarrow wieght = 0.18mol \times 82.0g/mol = 14g$$

Example

2.45×10^{-3}g of NaCN is added to 500mL of 0.1M HCN.
The pH of the solution =6.4
Determine K_{HCN}

$$Mwt_{NaCN} = 49g/mol$$

$$n = \frac{wt(g)}{M.wt.(g/mol)} = \frac{2.45\times10^{-3}g}{49g/mol} = 5.0\times10^{-5}mol$$

$$M_{NaCN} = \frac{5.0\times10^{-5}mol}{0.500L} = 1.0\times10^{-4}M$$

$$6.4 = pK_a + \log\frac{1.0\times10^{-4}}{0.10} \longrightarrow K_a = 4.0\times10^{-10}$$

Solubility product

If an "insoluble" or "slightly soluble" salt is placed in water, An equilibrium is established

$$AgCl\,(s) \rightleftharpoons Ag^{+}\,(aq) + Cl^{-}\,(aq)$$

The equilibrium constant is

$$K = \frac{[Ag^{+}][Cl^{-}]}{[AgCl]}$$

Since the concentration of a pure solid is a constant, we can write

$$K_{SP} = K[AgCl] = [Ag^{+}][Cl^{-}]$$

K_{SP} is called a solubility product

$$Mg(OH)_2\ (s) \rightleftharpoons Mg^{2+}\ (aq) + 2OH^-\ (aq)$$

$$K_{SP} = [Mg^{2+}][OH^-]^2$$

$$Bi_2S_3\ (s) \rightleftharpoons 2Bi^{3+}\ (aq) + 3S^{2-}\ (aq)$$

$$K_{SP} = [Bi^{3+}]^2[S^{2-}]^3$$

The solubility of a salt usually varies widely with temperature, the numerical value of K_{SP} for a salt changes with temperature.

Example

At 25^{o}C, 0.00188g of AgCl dissolves in 1L of water. What is the solubility product of AgCl?

$$Mwt_{AgCl} = 143 g/mol$$

$$n_{AgCl} = \frac{wt(g)}{M.wt.(g/mol)} = \frac{0.00188g}{143 g/mol} = 1.31 \times 10^{-5} mol$$

$$\mathbf{AgCl\ (s) \rightleftharpoons Ag^{+}\ (aq) + Cl^{-}\ (aq)}$$

$$1.31 \times 10^{-5} \quad 1.31 \times 10^{-5}$$

$$K_{SP} = [Ag^{+}][Cl^{-}] = \left(1.31 \times 10^{-5}\right) \times \left(1.31 \times 10^{-5}\right) = 1.72 \times 10^{-10}$$

Example

At 25°C, 7.8×10^{-5} mol of Ag_2CrO_4 dissolves in 1L of water. What is the solubility product of Ag_2CrO_4?

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

$$2(7.8\times10^{-5}) \qquad 7.8\times10^{-5}$$

$$K_{SP} = [Ag^+]^2[CrO_4^{2-}] = \left[2\left(7.8\times10^{-5}\right)\right]^2 \times \left[7.8\times10^{-5}\right]$$

$$K_{SP} = 1.9\times10^{-12}$$

Molar solubility: number of moles dissolved per liter

At 25^{o}C, 0.00188g of AgCl dissolves in 1L of water.

$$n_{AgCl} = \frac{wt(g)}{M.wt.(g/mol)} = \frac{0.00188g}{143g/mol} = 1.31\times10^{-5}mol$$

$$AgCl\,(s) \rightleftharpoons Ag^{+}\,(aq) + Cl^{-}\,(aq)$$

$$1.31\times10^{-5}M \qquad 1.31\times10^{-5}M$$

S **S**

$$CaCO_3\,(s) \rightleftharpoons Ca^{2+}\,(aq) + CO_3^{2-}\,(aq)$$

S **S**

$$K_{SP} = [Ca^{2+}][CO_3^{2-}] = S \times S = S^2$$

$$S = \sqrt{K_{SP}}$$

Example

What is the relation between solubility, S, and K_{SP} for $Ca_3(PO_4)_2$?

$$Ca_3(PO_4)_2\ (s) \rightleftharpoons 3Ca^{2+}\ (aq) + 2PO_4^{3-}\ (aq)$$

3S **2S**

$$K_{SP} = [Ca^{2+}]^3[PO_4^{3-}]^2$$

$$= [(3S)]^3 \times [(2S)]^2$$

$$= 108S^5$$

Example

What is the solubility, S, of BaF_2?

$$K_{SP(BaF_2)} = 1.8\times10^{-7}$$

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

$$K_{SP} = [Ba^{2+}][F^-]^2 = S\times(2S)^2 = 4S^3$$

$$4S^3 = 1.8\times10^{-7} \longrightarrow S^3 = \frac{1.8\times10^{-7}}{4}$$

$$S = \sqrt[3]{\frac{1.8\times10^{-7}}{4}}$$

$$S = 3.56\times10^{-3}\,M$$

Example

What is the relation between solubility, S, and K_{SP} for Ag_3PO_4?

$$Ag_3PO_4\,(s) \rightleftharpoons 3Ag^+\,(aq) + PO_4^{3-}\,(aq)$$

3S **S**

$$K_{SP} = [Ag^+]^3[PO_4^{3-}]$$

$$= (3S)^3 \times (S)$$

$$= 27S^4$$

Example

The solubility of $CaSO_4$ is 0.67g/L at certain temperature. What is K_{SP} for $CaSO_4$?

Determine S in units of M

$$S = \frac{0.67g/L}{136.2g/mol} = 4.9\times10^{-3} mol/L$$

$$CaSO_4\ (s) \rightleftharpoons Ca^{2+}\ (aq) + SO_4^{2-}\ (aq)$$

$$K_{SP} = [Ca^{2+}][SO_4^{2-}] = S\times S$$

$$K_{SP} = \left(4.9\times10^{-3}\right)^2 = 2.4\times10^{-5}$$

Example

What is pH and pOH for a solution of $Fe(OH)_2$? given that K_{SP}= 1.6×10^{-14}.

$$Fe(OH)_2\ (s) \rightleftharpoons Fe^{2+}(aq) + 2OH^-(aq)$$

S **2S**

$$K_{SP} = [Fe^{2+}][OH^-]^2 = (S)(2S)^2 = 4S^3$$

$$4S^3 = 1.6\times10^{-14} \longrightarrow S^3 = \frac{1.6\times10^{-14}}{4}$$

$$S = \sqrt[3]{\frac{1.6\times10^{-14}}{4}}$$

$$S = 1.6\times10^{-5}M$$

$$[OH^-] = 2S = 2\left(1.6\times10^{-5}\right) = 3.2\times10^{-5}\,M$$

$$pOH = -\log[OH^-] = -\log(3.2\times10^{-5}) = 4.5$$

$$\boxed{pH + pOH = 14} \longrightarrow \boxed{pH = 14 - 4.5 = 9.5}$$