CHAPTER 5

REACTIONS IN AQUEOUS SOLUTIONS

A solution is a homogeneous mixture of two or more substances.

The substance present in the greatest quantity is called the solvent. And the other substances in the solution are called the solutes.

Rxn.s in aqueous solutions are important. Because:

1) water is cheap and able to solve a vast number of substances.
2) Many substances form ions in water. These ions can participate in chemical rxn.s.
3) Aqueous solutions are found everywhere, from see water to living systems.

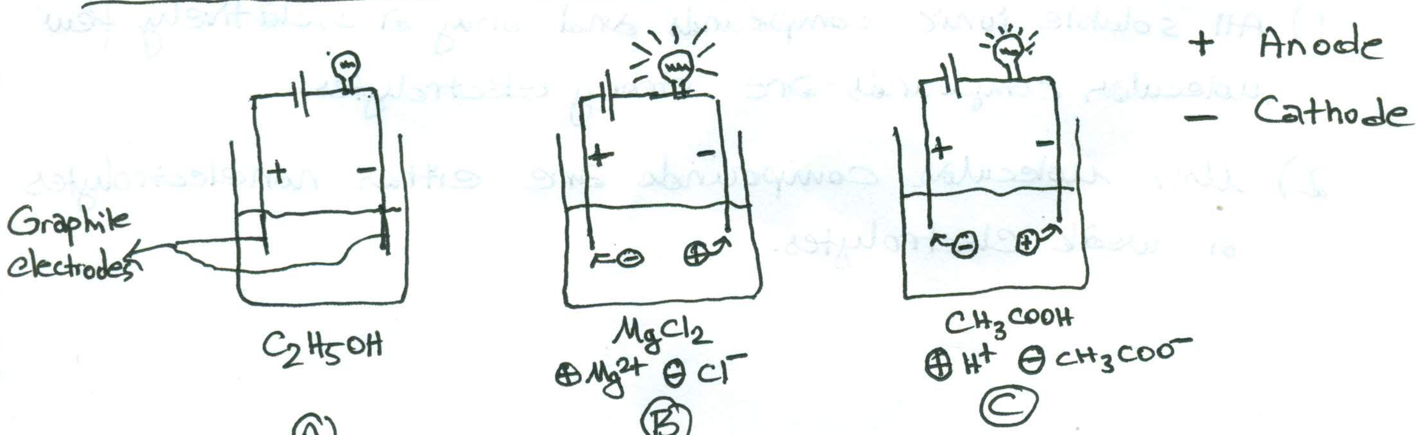
→ An important characteristic of an aqueous solution of ions is that it will conduct electricity.

In a metallic conductor electric charge is carried by e^-s.

→ In the case of aqueous solution of ions, electric charge is carried by ions. This is because the ions move independently of each other while carrying a certain quantity of charge.

Electrolyte: Solutes that provide ions when dissolved in water are called as electrolytes.

Classification of Electrolytes



Aqueous solutions of different substances

Cathode

→ In electrolytic solutions + ions are attracted to the − electrode which is called as cathode.

→ Anode : − Inons are attracted to the + electrode. This electrode is called Anode.

→ The ability of a solution to conduct electricity depends on the number of ions it contains.

In the case of A: The lamp fails to light up because there are no ions present. Molecules such as C_2H_5OH are called nonelectrolytes. A nonelectrolyte is substance that is not ionized and deos not conduct electricity.

In the case of B: The lamp lights up brightly. Because the concentration of ions in solution is high. Substances or compound like $MgCl_2$ are called strong electrolytes. A strong electrolyte is a substance that is essentially compdetely ionized in aqueous solution.

In the case of C: The lamp lights up dimly. Because the concentration of ions in solution is low. Electrolytes such as CH_3COOH are called as weak electrolytes. A weak electrolyte is substance that is only partly ionized in aqueous solution.

Generalizations based on these observations.

1) All soluble ionic compounds and only a relatively few molecular compounds are strong electrolytes.

2) Most molecular compounds are either nonelectrolytes or weak electrolytes.

Examples:

Strong electrolytes
$$MgCl_2\,(aq) \longrightarrow Mg^{2+}\,(aq) + 2Cl^-\,(aq)$$ ionic comp.

$$HCl\,(aq) \longrightarrow H^+\,(aq) + Cl^-\,(aq)$$ Molecular comp.

Weak electrolyte
$$CH_3COOH\,(aq) \rightleftharpoons H^+\,(aq) + CH_3COO^-\,(aq)$$ molecular comp.

* The equation for weak electrolyte solution is written with a doble arrow ($\rightleftharpoons$) which indicates that the process is reversable.
* For a nonelectrolyte we would write $CH_3CH_2OH\,(aq)$.

Example: What are the aluminium and sulfate ion concentrations in a 0.0165 M $Al_2(SO_4)_3$ solution? ($Al_2(SO_4)_3$ is a strong electrolyte.)

$$Al_2(SO_4)_3\,(s) \xrightarrow{H_2O} \underline{\underline{2}}\,Al^{3+}(aq) + \underline{\underline{3}}\,SO_4^{2-}\,(aq)$$

$$[Al^{3+}] = \frac{0.0165 \text{ mol } Al_2(SO_4)_3}{1\,L} \times \frac{2 \text{ mol } Al^{3+}}{1 \text{ mol } Al_2(SO_4)_3} = \frac{0.0330\ Al^{3+}}{1\,L}$$

$$= 0.0330\,M$$

$$[SO_4^{2-}] = \frac{0.0165 \text{ mol } Al_2(SO_4)_3}{1L} \times \frac{3 \text{ mol } SO_4^{2-}}{1 \text{ mol } Al_2(SO_4)_3} = 0.0495\,M$$

Precipitation Reactions

Rxn.s that result in a formation of an insoluble product is called as precipitation rxn.s. The formed insoluble ionic solid is called precipitate.

Net Ionic Equations

$$AgNO_3(aq) + NaI(aq) \rightarrow AgI(s) + NaNO_3(aq)$$

A net ionic equation is an equation that includes only the actual participants in a reaction.

→ Strong electrolytes should be represented by their separate ions.

$$Ag^+(aq) + NO_3^-(aq) + Na^+(aq) + I^-(aq) \longrightarrow AgI(s) + Na^+(aq) + NO_3^-(aq)$$

→ Notice that in equation $Na^+(aq)$ and $NO_3^-(aq)$ appear on both sides of equation.

These ions are not reactants; they go through the rxn. unchanged. These ions are called <u>spectator ions</u>.

$$Ag^+(aq) + I^-(aq) \longrightarrow AgI(s)$$

→ If we eliminate the spectator ions we obtain the net <u>ionic equation</u> above.

Predicting Precipitation Reactions

* Salts of group I cations (except Li) and NH_4^+ cations are soluble.

Soluble ionic compounds containing	Important Exceptions containing
NO_3^-	none
CH_3COO^-	none
Cl^-	Ag^+, Hg_2^{2+}, Pb^{2+}
Br^-	Ag^+, Hg_2^{2+}, Pb^{2+}
I^-	Ag^+, Hg_2^{2+}, Pb^{2+}
SO_4^-	Sr^{2+}, Ba^{2+}, Hg_2^{2+}, Pb^{2+}

Insoluble ionic compounds containing	Important Exceptions containing
S^{2-}	NH_4^+, $\boxed{Ca^{2+}, Sr^{2+}, Ba^{2+}}$, alkali metal cations
CO_3^{2-}	NH_4^+, $\boxed{Ca^{2+}, Sr^{2+}, Ba^{2+}}$, alkali metal cations
PO_4^{2-}	NH_4^+, $\boxed{Ca^{2+}, Sr^{2+}, Ba^{2+}}$, alkali metal cations
OH^-	NH_4^+, $\boxed{Ca^{2+}, Sr^{2+}, Ba^{2+}}$, alkali metal cations

Example:

a) $Mg(NO_3)_2\ (aq) + 2NaOH\ (aq) \rightarrow Mg(OH)_{2(s)} + 2NaNO_3\ (aq)$

Net ionic equation is:

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

b) $2NaOH\ (aq) + MgCl_2\ (aq) \rightarrow Mg(OH)_2(s) + 2NaCl\ (aq)$

$$2Na^+(aq) + 2OH^-\ (aq) + Mg^{2+}(aq) + 2Cl^-\ (aq) \rightarrow$$

$$Mg(OH)_2\ (s) + 2Na^+(aq) + 2Cl^-\ (aq)$$

When we eliminate the spectator ions

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

ACID-BASE REACTIONS

Acid: An Acid can be defined as a substance that provides hydrogen ions (H^+). Arrhenius acid proposition (1884).

Strong acids are molecular compounds that are almost completely ionized into $H^+(aq)$ ion.

Common strong acids are HCl, HBr, HI, $HClO_4$, HNO_3, H_2SO_4

→ Weak acids are molecular compounds that have a weak tendency for producing H^+ ions.

$HNO_3 \xrightarrow{H_2O} H^+(aq) + NO_3^-(aq)$ strong acid

$CH_3COOH\ (aq) \rightleftharpoons H^+\ (aq) + CH_3COO^-\ (aq)$ week acid

→ According to the Brønsted-Lowry theory, an acid is a proton donor.

Base: Arrhenius definition of a base is a substance that produces hydroxide ions (OH^-) in aqueous solution.

→ A strong base is a base that dissociates completely, or very nearly so, in aqueous solution.

$$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$$

→ A weak base is a base that is incompletely ionized in aqueous solution.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

NaOH : Strong base , NH_3 : Weak base

→ Brønsted-Lowry theory defines a base as a proton acceptor.

Acidic and Basic Solutions

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

Measurements show that $[H^+]_{water} = [OH^-]_{water} = 1.0 \times 10^{-7}$ M at 25 °C.

An acidic solution has $[H^+] > [H^+]_{water}$

A basic solution has $[OH^-] > [OH^-]_{water}$

Neutralization

In a neutralization rxn., an acid and a base react to form water and an aqueous solution of an ionic compound called a salt.

$$\underset{acid}{HCl(aq)} + \underset{base}{NaOH(aq)} \longrightarrow \underset{salt}{NaCl(aq)} + \underset{water}{H_2O(l)}$$

$$H^+(aq) + Cl^-(aq) + Na(aq) + OH^-(aq) \longrightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)$$

net ionization eq. $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

Examples:

* $H^+(aq) + Cl^-(aq) + \overbrace{NH_3(aq)}^{\text{weak base}} \rightarrow NH_4^+(aq) + Cl^-(aq)$

net ionic eq. is

$$H^+(aq) + NH_3(aq) \rightarrow NH_4^+(aq)$$

* $CaCO_3(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2O(l) + CO_2(g)$

* $HSO_3^- + H^+ \longrightarrow SO_2(g) + H_2O(l)$

OXIDATION-REDUCTION REACTIONS

In oxidation-reduction rxn., e⁻s are transferred between reactants. For example the rxn. of hematite with CO:

$$\overset{3+}{Fe_2}\overset{-2}{O_3}(s) + 3\overset{2+}{C}\overset{-2}{O}(g) \xrightarrow{\Delta} 2\overset{0}{Fe}(l) + 3\overset{+4}{C}\overset{-2}{O_2}(g)$$

Ion	ox. state	→	Ion	ox. state		
Fe^{3+}	+3		Fe^0	0	reducted	e^- gain
C^{2+}	+2		C^{4+}	+4	oxidized	e^- loss

Oxidation and Reduction Half-Reactions

Oxidation and reduction are two half reactions occuring at the same time. The overall redox rxn. is the some of two half-rxns.

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

The overall rxn. is the sum of two half-reactions.

Oxidation	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$
reduction	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
Overall	$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

In half-rxn of Zn, the O.S. increases from 0 to +2, corresponding to loss of 2 e^-. In half-rxn of Cu, O.S. of Cu decreased from +2 to 0, corresponding to gain of $2e^-$. So we can say that:

Zn → oxidized

Cu → reduced

→ Oxidation : O.S. of an element increases via the loss of electrons

→ Reduction : O.S. of an element decreases via the gain of electrons.

* Oxidation and reduction rxns occur together, and total number of e^-s associated with oxidation must be equal to the number of e^-s associated with reduction.

Example: Write an overall and half-rxn equations for the rxn of iron with HCl.

Oxidation	$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$
Reduction	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$
Overall	$Fe(s) + 2H^+(aq) \longrightarrow Fe^{2+}(aq) + H_2(g)$

* Behavior of some common metals with nonoxidizing Acids. (HCl, HBr, HI)

React to produce $H_2(g)$	Do not react
Alkali metals (group 1)*	Cu, Ag, Au, Hg
Alkaline earth metals (group 2)*	
Al, Zn, Fe, Sn, Pb	

* Except Be and Mg

Balancing Oxidation-Reduction Rxns. in Acidic Solution

$$\overset{+4}{S}O_3^{2-}(aq) + \overset{+7}{Mn}O_4^-(aq) \longrightarrow \overset{+6}{S}O_4^{2-}(aq) + \overset{+2}{Mn}^{2+}(aq)$$

① Write the skeleton of half rxns

$$SO_3^{2-}(aq) \longrightarrow SO_4^{2-}(aq)$$

$$MnO_4^-(aq) \longrightarrow Mn^{2+}(aq)$$

② Balance ~~each~~ each half-equations for the numbers of atoms.

a) Atoms other than H and O

b) O atoms by adding H_2O

c) H atoms by adding H^+

$$SO_3^{2-}(aq) + \underline{H_2O(l)} \longrightarrow SO_4^{2-}(aq) + \underline{2H^+}(aq)$$

$$MnO_4^-(aq) + \underline{8H^+(aq)} \longrightarrow Mn^{2+} + \underline{4H_2O}(l)$$

③ Balance each half-equation for electric charge by adding the appropriate number of e^-s.

$\times 5$ Ox. $\quad \overset{+4}{S}O_3^{2-}(aq) + H_2O(l) \longrightarrow \overset{+6}{S}O_4^{2-}(aq) + 2H^+(aq) + \underline{2e^-}$

$\times 2$ Red. $\quad \overset{+7}{Mn}O_4^-(aq) + 8H^+(aq) + \underline{5e^-} \longrightarrow \overset{+2}{Mn}^{2+} + 4H_2O(l)$

④ Obtain overall redox equation by combining the half-equations with an appropriate coefficient. Cancell out the electrons

$$5SO_3^{2-} + 5H_2O \longrightarrow 5SO_4^{2-} + 10H^+ + \cancel{10e^-}$$

$$2MnO_4^- + 16H^+ + \cancel{10e^-} \longrightarrow 2Mn^{2+} + 8H_2O$$

$$5SO_3^{2-} + 2MnO_4^- + 5H_2O + 16H^+ \longrightarrow$$

$$5SO_4 + 2Mn^{2+} + 8H_2O + 10H^+$$

⑤ Simplify the overall equation.

$$5SO_3^{2-}(aq) + 2MnO_4^-(aq) + 6H^+(aq) \longrightarrow$$
$$5SO_4^{2-}(aq) + 2Mn^{2+}(aq) + 3H_2O(l)$$

⑥ Check the overall equation to ensure that it is balanced both for number of atoms and electric charge.

$$\underline{\underline{-6}} = (5\times 2-) + (2\times 1-) + (6\times 1+) = (5\times 2-) + (2\times 2+) = \underline{\underline{-6}}$$

Balancing Redox Equation in Basic Solution

$$\overset{+7}{Mn}O_4^-(aq) + \overset{+2}{C}\overset{-3}{N}^-(aq) \longrightarrow \overset{+4}{Mn}O_2(s) + \overset{-2}{O}\overset{+4}{C}\overset{-3}{N}^-(aq)$$

① Half equations

$$MnO_4^- \longrightarrow MnO_2$$
$$CN^- \longrightarrow OCN^-$$

② Balance number of atoms

$$MnO_4^- + 4H^+ \longrightarrow MnO_2 + \underline{\underline{2H_2O}}$$
$$CN^- + \underline{\underline{H_2O}} \longrightarrow OCN^- + \underline{\underline{2H^+}}$$

③ Balance charge

Red. $MnO_4^- + 4H^+ + \underline{\underline{3e^-}} \longrightarrow MnO_2 + 2H_2O$ × 2

Ox. $CN^- + H_2O \longrightarrow OCN^- + 2H^+ + \underline{\underline{2e^-}}$ × 3

④ Obtain overall redox equation and simplify

$$2MnO_4^- + 8H^+ + \cancel{6e^-} \longrightarrow 2MnO_2 + 4H_2O$$
$$3CN^- + 3H_2O \longrightarrow 3OCN^- + 6H^+ + \cancel{6e^-}$$

$$2MnO_4^-(aq) + 3CN^-(aq) + 2H^+(aq) \longrightarrow$$
$$2MnO_2(s) + 3OCN^-(aq) + H_2O(l)$$

⑤ Change from an acidic to basic medium by adding OH^- to the both sides of the overall equation. Combine H^+ and OH^- ions to form H_2O

$$2MnO_4^-(aq) + 3CN^-(aq) + \overbrace{2H^+(aq) + \underline{\underline{2OH^-}}}^{2H_2O}(aq) \rightarrow$$

$$2MnO_2(s) + 3OCN^-(aq) + H_2O(l) + \underline{\underline{2OH^-}}$$

$$2MnO_4^-(aq) + 3CN^-(aq) + H_2O \rightarrow 2MnO_2(s) + 3OCN^-(aq) + 2OH^-$$

⑥ Verify

$$\underline{\underline{-5}} = (2\times 1-) + (3\times 1-) = (3\times 1-) + (2\times 1-) = \underline{\underline{-5}}$$

Disproportionation Reactions

In some redox rxns., same substance is both oxidized and reduced. This kind of redox rxns are called as disproportionation rxns.

For example:

$$2\overset{+1}{H_2}\overset{-1}{O_2}(aq) \longrightarrow 2H_2\overset{-2}{O}(l) + \overset{0}{O_2}(g)$$

* H_2O_2 is both oxidized and reduced.

$$\overset{+2}{S_2}O_3^{2-}(aq) + 2H^+(aq) \longrightarrow \overset{0}{S}(s) + \overset{+4}{S}O_2(g) + H_2O(l)$$

* $S_2O_3^{2-}$ is both oxidized and reduced

Oxidizing and Reducing Agents

Oxidizing agent: The substance that causes the other substances to be oxidized is called oxidizing agent or oxidant.

Reducing agent: Similarly, if a substance causes other substances to be reduced, this substance is called as an reducing agent or reductant.

An Oxidant	A Reductant
a) Contains an element whose OS decreases in a redox rxn.	a) Contains an element whose OS increases in a redox rxn.
b) Gains e^-	b) Loses e^-
c) Is reduced	c) Is oxidized

Example

$$H_2O_2\,(aq) + \underline{2Fe^{2+}}(aq) + 2H^+(aq) \rightarrow 2H_2O\,(l) + \underline{2Fe^{3+}}(aq)$$

* Fe^{2+} is oxidized to Fe^{3+}, H_2O_2 made this possible

So, H_2O_2 is an oxidant

→ MnO_4^- (permanganate) is a versatile oxidant.

→ $S_2O_3^{2-}$ (thiosulfate) is an important reductant.

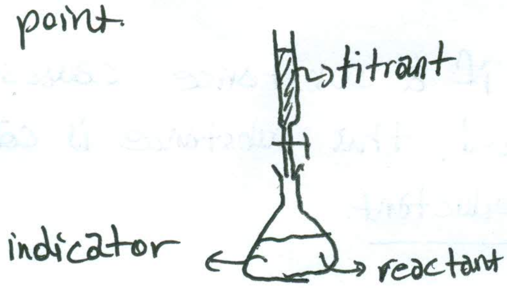
Stoichiometry of Rxns in Aqueous Solutions: Titrations

Titration is generally carried out to determine the concentration of a particular solute.

Titration: is a reaction carried out by the carefully controlled addition of one solution to another.

Equivalence Point: The point at which both reactants have reacted completely is called equivalence point.

Indicator: A very small quantity of substance that is added to the reaction mixture, and changes its color at or very near to the equivalence point.



* Indicator changes its color when the amount of titrant is equivalent to the amount of reactant.

Example: A piece of iron wire (0.1568g) is converted to $Fe^{2+}(aq)$ and requires 26.24 mL of a $KMnO_4$ solution. for its titration.

What is the molarity of $KMnO_4$ (aq)?

$$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \longrightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O$$

$$? \text{ mol } KMnO_4 = 0.1568 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.847 \text{g Fe}} \times \frac{1 \text{ mol } Fe^{2+}}{1 \text{ mol Fe}}$$

$$\times \frac{1 \text{ mol } KMnO_4^-}{5 \text{ mol } Fe^{2+}} \times \frac{1 \text{ mol } KMnO_4}{1 \text{ mol } MnO_4^-}$$

$$= 5.615 \times 10^{-4} \text{ mol } KMnO_4$$

$$[KMnO_4] = \frac{5.615 \times 10^{-4} \text{ mol}}{0.02624 \text{ L}} = 0.02140 \text{ mol/L (M)}$$