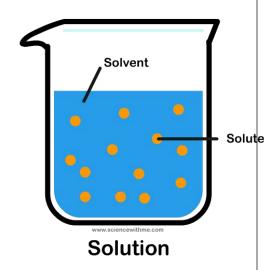
Chapter 9

Part 1
Physical properties of Solution

Solution

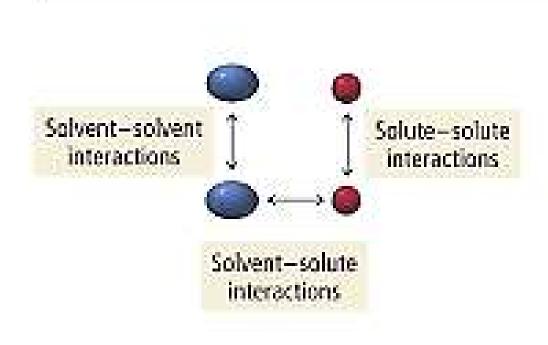
- A solution is a homogeneous mixture of two or more substances.
- The substance present in a smaller amount is called the **solute**, whereas the substance present in a larger amount is called the **solvent**.



• **Dissolution** is the process of dissolving or forming a solution. When dissolution happens, the solute separates into ions or molecules, and each ion or molecule is surrounded by molecules of solvent.

Dissolution

Solution Interactions





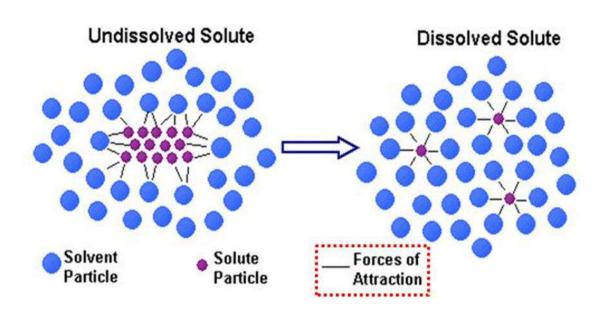
Solution

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Solvation

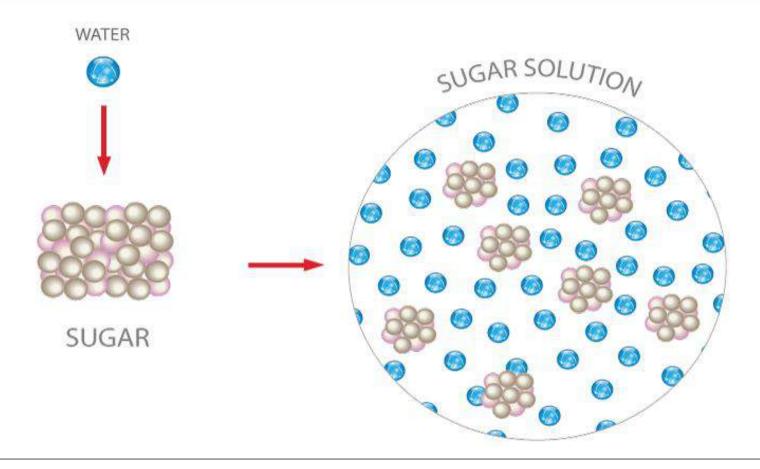
• The interactions between the solute particles and the solvent molecules is called solvation or hydration when the solvent is water).

Particles of solute will dissolve <u>IF</u> it is <u>more</u> <u>attracted</u> to the solvent particles than to itself

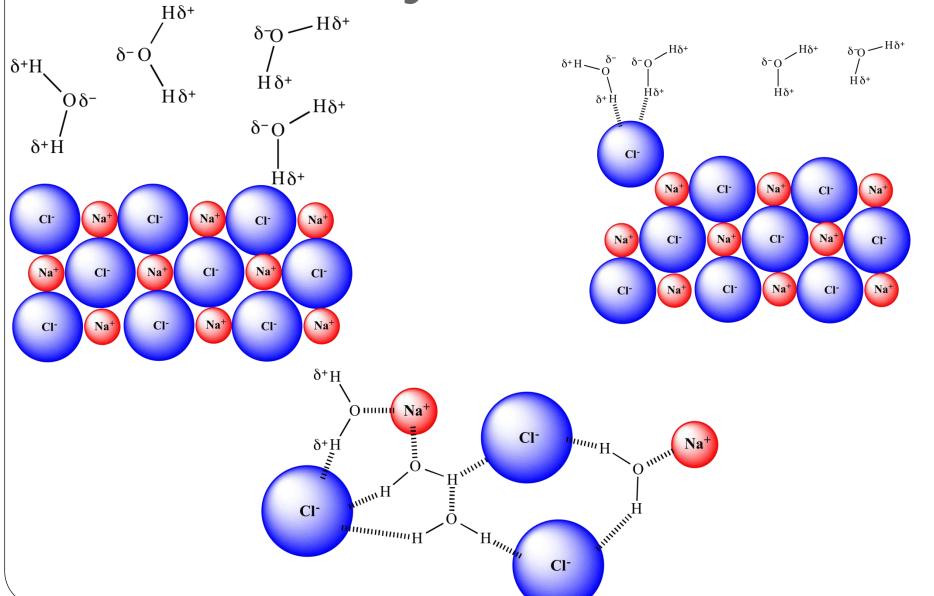


Hydration





Hydration



Types of solution according state of matter

TABLE 13.1	Types of Solutions			
Solute	Solvent	State of Resulting Solution	Examples	
Gas	Gas	Gas	Air	
Gas	Liquid	Liquid	Soda water (CO2 in water)	
Gas	Solid	Solid	$ m H_2$ gas in palladium	
Liquid	Liquid	Liquid	Ethanol in water	
Solid	Liquid	Liquid	NaCl in water	
Solid	Solid	Solid	Brass (Cu/Zn), solder (Sn/Pb)	

Types of Solutions according their capacity

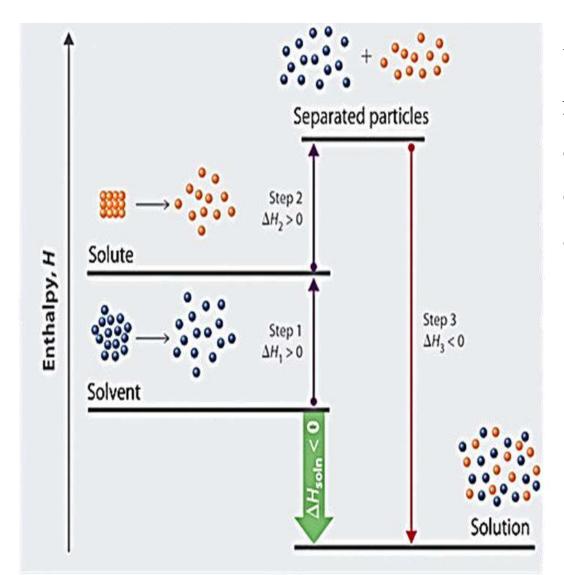
- Chemists also characterize solutions by their capacity to dissolve a solute.
- A solution that contains the maximum amount of a solute in a given solvent, at a specific temperature, is called a **saturated solution**.
- Before the saturation point is reached, the solution is said to be *unsaturated*; it contains less solute than it has the capacity to dissolve.
- A third type, a *supersaturated solution*, contains more solute than is present in a saturated solution.
- Supersaturated solutions are not very stable. In time, some of the solute will come out of a supersaturated solution as crystals. The process in which dissolved solute comes out of solution and forms crystals is called crystallization (the opposite process of dissolution).

A Molecular View of the Solution Process with enthalpy changes

- In liquids and solids, molecules are held together by intermolecular attractions. These forces also play a central role in the formation of solutions.
- In the formation of solutions, three types of interactions:
- solvent-solvent interaction
- solute-solute interaction
- solvent-solute interaction
- When a solvent is added to a solution, steps 1 and 2 are both endothermic because energy is required to overcome the intermolecular interactions in the solvent ($\Delta H_1 > 0$) and the solute ($\Delta H_2 > 0$). In contrast, energy is released in step 3, solute-solvent interaction ($\Delta H_3 < 0$).
- The overall enthalpy change in the formation of the solution (ΔH_{soln}) is the sum of the enthalpy changes in the three steps:

$$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

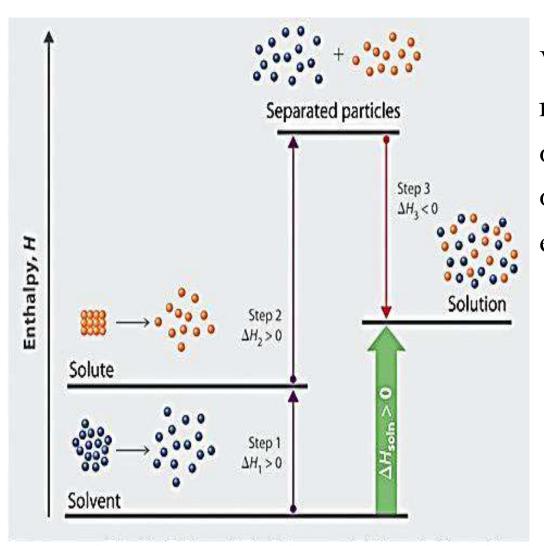
Exothermic solution formation



When ΔH_3 is larger in magnitude than the sum of ΔH_1 and ΔH_2 , the overall process is exothermic ($\Delta H_{\rm soln} < 0$).

(a) Exothermic solution formation

Endothermic solution formation

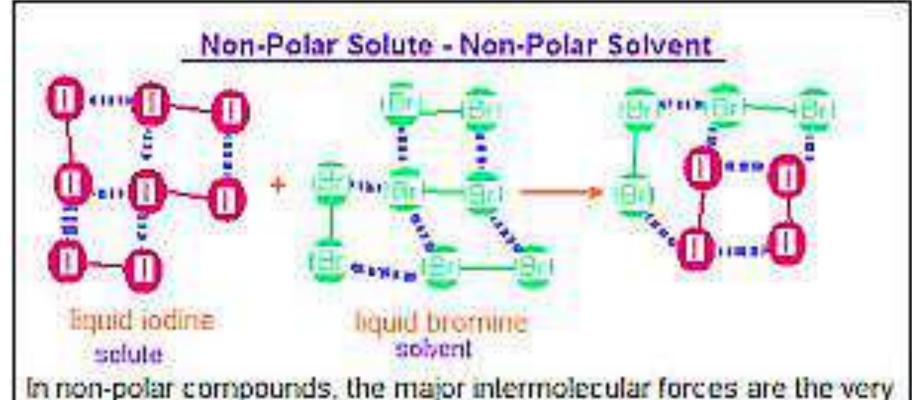


When ΔH_3 is lesser in magnitude than the sum of ΔH_1 and ΔH_2 , the overall process is endothermic ($\Delta H_{\rm soln} > 0$).

Solubility

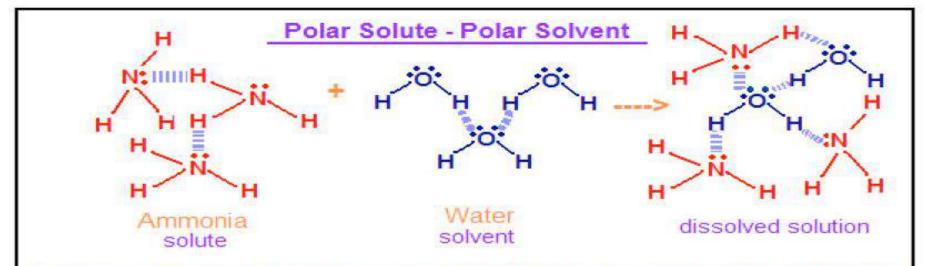
- Solubility of the solute (g/L), is defined as the maximum amount of solute that will dissolve in a given quantity of solvent at a specific temperature.
- Chemists refer to substances as soluble, slightly soluble, sparingly, or insoluble in a qualitative sense.
- The saying "like dissolves like" helps in predicting the solubility of a substance in a solvent. What this expression means is that two substances with intermolecular forces of similar type and magnitude are likely to be soluble in each other.

Like dissolves like

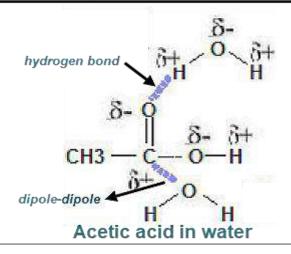


In non-polar compounds, the major intermolecular forces are the very weak induced dipoles. The weak bonds in the solution replace the weak bonds in the pure non-polar substances.

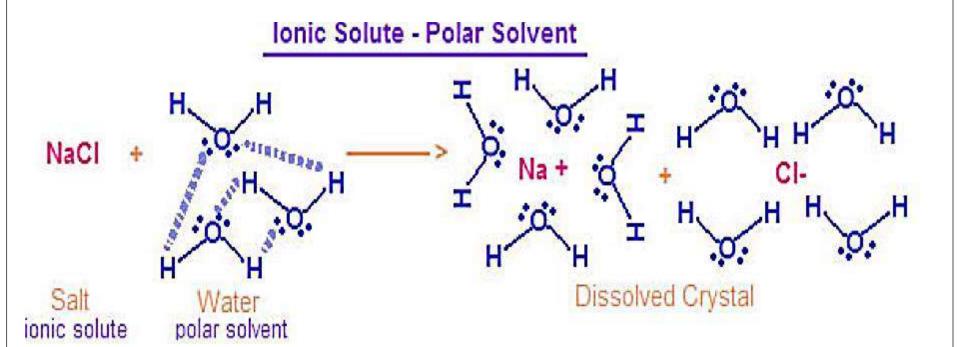
Like dissolves like



Polar ammonia molecules dissolve in polar water molecules because both types of molecules engage in H-bonding. Their intermolecular forces are relatively the same so they are able to break away from each other and form new bonds.



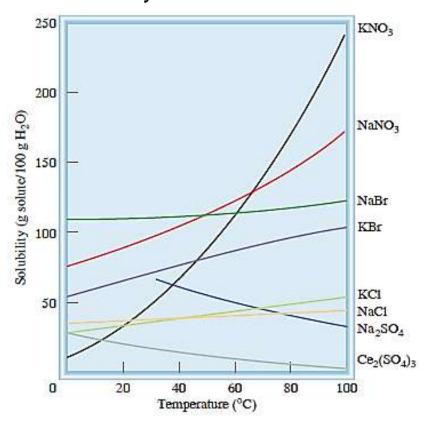
Like dissolves like

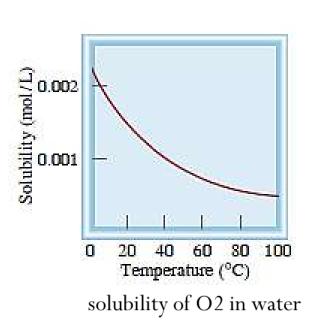


Factors affecting solubility

1- Effect of Temperature on Solubility

In most but certainly not all cases, the solubility of a solid and a liquid substance increases with temperature while the solubility of gases in water usually decreases with increasing temperature.





Factors affecting solubility

2- Effect of Pressure on the Solubility of Gases

For all practical purposes, external pressure has no influence on the solubility of liquids and solids, but it does greatly affect the solubility of gases.

The quantitative relationship between gas solubility and pressure is given by Henry's law, which states that the solubility of a gas in a liquid is proportional to the pressure of the gas over the solution:

$$c \propto P$$
 $c = kP$

Here c is the molar concentration (moles per liter) of the dissolved gas; P is the pressure (in atmospheres) of the gas over the solution; and, for a given gas, k is a constant has the units mol/L . atm.

Bends (Diver disease)

• The aqueous solubility of nitrogen gas at 25° and 1 atm is 6.8×10^{-4} mol/L. Calculate the solubility if the partial pressure of nitrogen gas N_2 increases to 5 atm.

$$c \propto P$$

$$c = kP$$

$$C_1 = \frac{C_2}{P_1} = k$$

$$C_2 = C_1 \times P_2 / P_1$$

$$= 34 \times 10^{-4} \text{ mol/L}$$

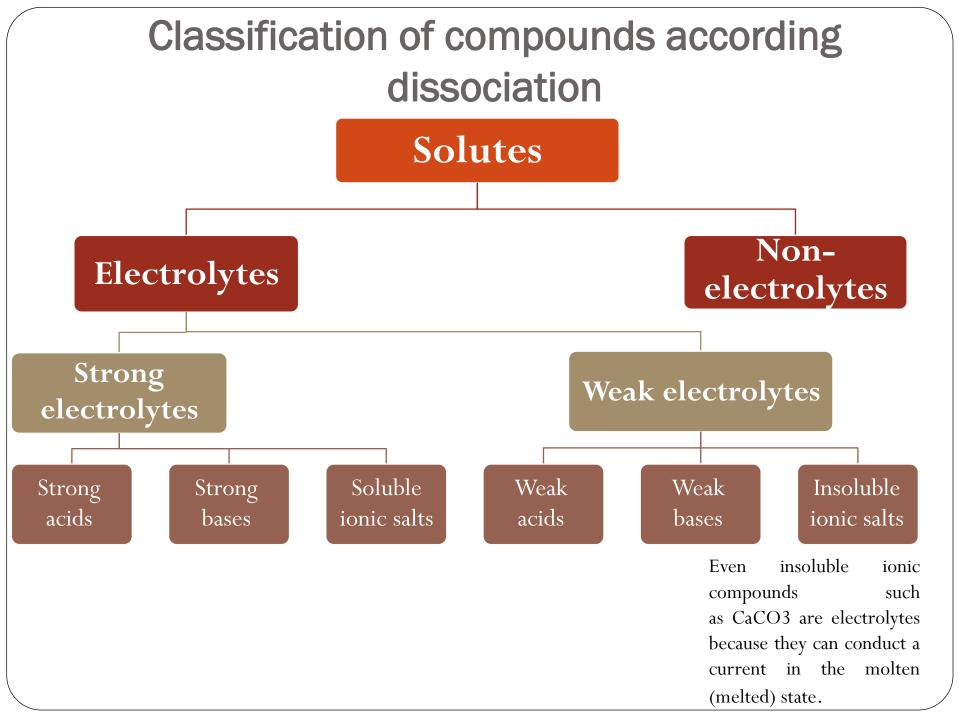
Therefore, this example show that as the pressure increases from 1 atm to 5 atm, the solubility of the N_2 gas increases from 6.8 X 10^{-4} mol/L to **34** X 10^{-4} mol/L. This supports Henry's Law.

The Bends:

- If a diver goes deeper and deeper into the water, pressure builds up in the bloodstream; as the pressure increases, the solubility of N_2 in the diver's bloodstream increases.
- Unfortunately, sometimes, the diver ascends -where pressure is low-too quickly, resulting in the rapid formation of N_2 bubbles, which causes interference with nerves, blood and lymphatic vessels, and clots

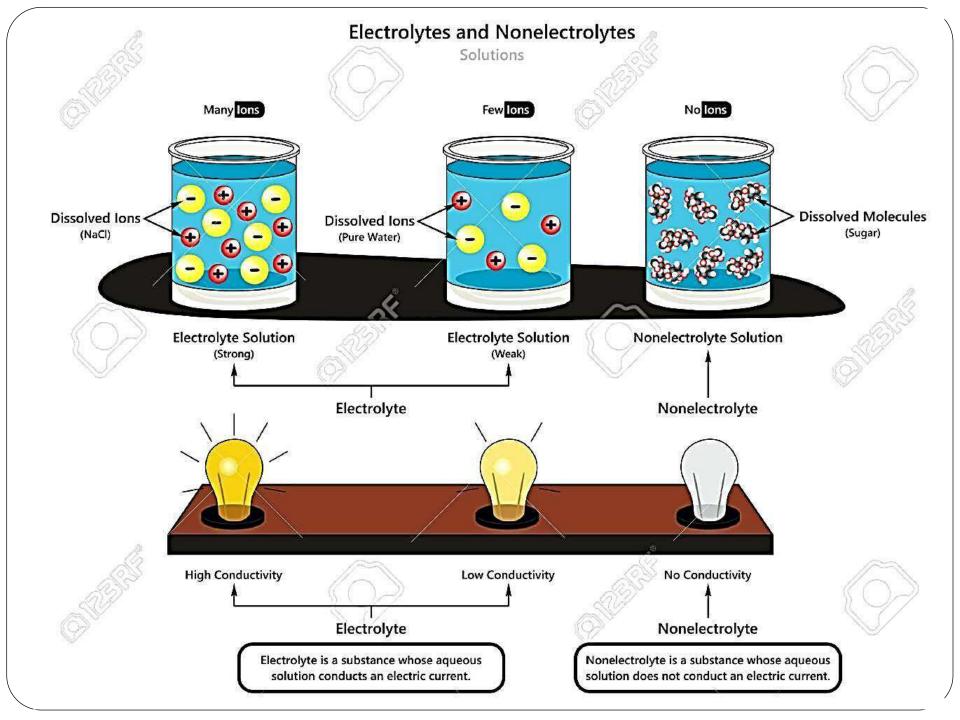
Dissociation in aqueous solution

- Solutions in which water is the dissolving medium are called **aqueous solutions**.
- **Dissociation:** is the process by which certain solutes release ions to the aqueous solution.
- These solutes are called **electrolytes** because they can conduct electricity.



Classification of compounds according dissociation

- An **electrolyte** is a compound that releases ions and thus conducts an electric current when it is in an aqueous solution or melted. It has two types:
 - 1. Strong electrolyte exist in solution completely (or nearly completely) as ions.
 - 2. Weak electrolyte produce small concentrations of ions when they dissolve.
- Do not confuse the extent to which an electrolyte dissolves with whether it is a strong or weak electrolyte. (Weak electrolytes still fully dissolve).
- **Nonelectrolyte** a substance that does **not** form ions when it dissolves in water, and so aqueous solutions of nonelectrolytes *do not conduct electricity*.



Acid and bases electrolytes

Strong Acids (Strong Electrolytes)		Strong Bases (Strong Electrolytes)	
HCI	Hydrochloric acid	LiOH	Lithium hydroxide
HNO ₃	Nitrie acid	NaOH	Sodium hydroxide
H ₂ SO ₄	Sulfuric acid	КОН	Potassium hydroxide
HCIO ₄	Perchloric acid	Ca(OH) ₂	Calcium hydroxide‡
HBr.	Hydrobromic acid	Sr(OII)2	Strontium hydroxide!
н	Hydroiodic acid	Ba(OH) ₂	Barium hydroxide‡
Weak Acids* (Weak Electrol	ytes)	Weak Bases (Weak Elect	
H ₃ PO ₄	Phosphoric acid	NH ₃	Ammonia
CH ₃ COOH	Acetic acid	CH ₃ NH ₂	Methylamine
H ₂ CO ₃	Carbonic acid		
HCN	Hydrocyanic acid		
НСООН	Formic acid		
C ₆ H ₅ COOH	Benzoic acid		

Strong electrolyte

Soluble and insoluble salts

Weak electrolyte

TΔ	RI	E 4	9
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Solubility Rules for Common Ionic Compounds in Water at 25°C

Soluble Compounds	Exceptions	
Compounds containing alkali metal ions (Li ⁺ , Na ⁺ , K ⁺ , Rb ⁺ , Cs ⁺) and the ammonium ion (NH ₄ ⁺)		
Nitrates (NO_3^-), bicarbonates (HCO_3^-), and chlorates (ClO_3^-)		
Halides (Cl ⁻ , Br ⁻ , I ⁻)	Halides of Ag^+ , Hg_2^{2+} , and Pb^{2+}	
Sulfates (SO ₄ ⁻)	Sulfates of Ag^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Hg_2^{2+} , and Pb^2	
Insoluble Compounds	Exceptions	
Carbonates (CO_3^{2-}), phosphates (PO_4^{3-}), chromates (CrO_4^{2-}), and sulfides (S^{2-})	Compounds containing alkali metal ions and the ammonium ion	
Hydroxides (OH ⁻)	Compounds containing alkali metal ions and the Ba ²⁺ ion	

Non-Electrolytes

Non-electrolyte	Chemical formu
Sucrose	C12H22O11
Glucose	C ₆ H ₁₂ O ₆
Ethanol	C ₂ H ₃ OH
Methanol	CH₃OH
Carbon tetrachloride	CC1 ₄
Carbon di sulphide	CS,
Kerosene	Hydrocarbons
Chemically pure water	H ₂ O
Urea	NH2CONH2

Chapter 9 part 2

Solution stoichiometry

Concentration Units

- Concentration is the amount of solute present in a given amount of solution.
- 1- The percent by mass (also called the percent by weight or the weight percent) is defined as $\frac{\text{mass of solute}}{\text{mass of solute}} = \frac{\text{mass of solute}}{\text{mass of solute}} \times 100\%$

$$= \frac{\text{mass of solute}}{\text{mass of soln}} \times 100\%$$

2-The percent by volume

Volume Percent
$$\left(\frac{V}{V}\right) = \frac{Volume\ Solute}{Volume\ Solution} \times 100\%$$

3-Weight by Volume percent

Weight /Volume Percent
$$\left(\frac{W}{V}\right) = \frac{\text{Weight Solute, g}}{\text{Volume Soln, m}} \times 100\%$$

4- Molality (m)

Molality has the units of mole per Kg (mol/Kg).

$$molality = \frac{moles of solute}{mass of solvent (kg)}$$

5- Molarity (M)

Molarity has the units of mole per liter (mol/L).

$$molarity = \frac{moles \text{ of solute}}{liters \text{ of soln}}$$

• Molarity of dilution: M_1V_1 Before dilution $= M_2V_2$ After dilution

6- Mole fraction (X)

For a binary solution of solute and solvent

$$X_{\text{Solute}} = \frac{\text{Moles of solute}}{\text{Total moles of solution}}$$
 $X_1 = \frac{n_1}{n_1 + n_2} = \text{mole fraction of species 1}$
 $X_{\text{Solvent}} = \frac{\text{Moles of solvent}}{\text{Total moles of solution}}$ $X_2 = \frac{n_2}{n_1 + n_2} = \text{mole fraction of species 2}$
 $X_1 = \frac{n_1}{n_1 + n_2} = \text{mole fraction of species 2}$
 $X_2 = \frac{n_2}{n_1 + n_2} = \text{mole fraction of species 2}$
 $X_1 = \frac{n_2}{n_1 + n_2} = \text{mole fraction of species 2}$
 $X_2 = \frac{n_2}{n_1 + n_2} = \text{mole fraction of species 2}$
 $X_1 = \frac{n_2}{n_1 + n_2} = \text{mole fraction of species 2}$

7- Mass fraction (W)

8- Parts per million (ppm)

$$1 \text{ ppm} = \frac{1 \text{ mg solute}}{1 \text{ kg solution}}$$
$$ppm = \frac{(mass \text{ of solute})}{(mass \text{ of solution})} x 10^6$$

As usual, both masses are in g

Ppm (m/v)=
$$\frac{\text{mass of solute (mg)}}{\text{volume of solution (L)}}$$

Problems

• How many grams of potassium dichromate $(K_2Cr_2O_7)$ are required to prepare a 250-mL solution whose concentration is 2.16 M?

$$molarity = \frac{moles of solute}{liters of soln}$$

M (Molarity not molar mass) = n (solute)/V \longrightarrow 2.16 = n/0.25 n= 2.16 x 0.25 = 0.54 moles

$$Mass = n \times molar \text{ mass} \qquad \qquad Mass = 0.54 \times 294.2 = 159 \text{ g}$$

• Describe how you would prepare 5.00 x 10^2 mL of a 1.75 M H_2SO_4 solution, starting with an 8.61 M stock solution of H_2SO_4 . Molarity of dilution: M_1xV_1 Before dilution = M_2xV_2 After dilution

$$(8.61 M)(V_i) = (1.75 M)(5.00 \times 10^2 \text{ mL})$$
$$V_i = \frac{(1.75 M)(5.00 \times 10^2 \text{ mL})}{8.61 M}$$

$$= 102 \,\mathrm{mL}$$

So, take 102 ml of the stock solution and complete to 500 ml with water.

How many milliliters (mL) of a 0.610 M NaOH solution are needed to neutralize 20.0 mL of a 0.245 M H₂SO₄ solution? 2N₂OH(qq) + H₂SO₄(qq) → N₂SO₄(qq) + 2H₂O(qq)

20.0 mL of a 0.245 M H₂SO₄ solution?
$$_{2NaOH(aq)} + _{H_2SO_4(aq)} \longrightarrow Na_2SO_4(aq) + _{2H_2O(l)}$$

 $n_{(H2SO4)} = MxV_{(H2SO4)} = 0.245 \times 20 \times 10^{-3} = 4.9 \times 10^{-3} \text{ mole}$
 $1 \text{ mole of } H_2SO_4 \cong 2 \text{ mole of NaOH}$
 $4.9 \times 10^{-3} \text{ mole} (H_2SO_4) \cong n \text{ NaOH}$
 $n_{(NaOH)} = 4.9 \times 10^{-3} \times 2 = 9.8 \times 10^{-3} \text{ mol}$
 $V_{(NaOH)} = n_{(NaOH)} / M_{(NaOH)} = 9.8 \times 10^{-3} / 0.61 = 16.1 \times 10^{-3} \text{ L}$
 $= 16.1 \text{ ml}$

• How many grams of NaOH are needed to prepare 500 ml of 0.2M aqueous solution?

$$n_{(NaOH)}=MxV_{(NaOH)=}\ 0.2\ x\ 500\ x10^{-3}=0.1\ mol$$
 Mass = n x molar mass = 0.1x 40 = 4g
So, take 4 g of NaOH and complete to 500 ml with water.

• The density of a 2.45 M aqueous solution of methanol (CH₃OH) is 0.976 g/mL. What is the molality of the solution? The molar mass of methanol is 32.04 g.

$$molarity = \frac{moles \text{ of solute}}{liters \text{ of soln}} \qquad molality = \frac{moles \text{ of solute}}{mass \text{ of solvent (kg)}}$$

2.45 M means 2.45 moles of methanol in 1 liter of solution

Density of solution = mass of solution/volume of solution 0.976 = m solution/1000

m solution = 976 g = mass solvent + mass of methanolMass of methanol = n x molar mass = $2.45 \times 32.04 = 78.498 \text{ g}$ Mass of solvent = $976 - 78.498 = 897.502 \text{ g} = 897.502 \times 10^{-3} \text{ kg}$ Molality = $2.45/897.502 \times 10^{-3} = 2.73 \text{ m}$ Calculate the molality of a 35.4 percent (by mass) aqueous solution of phosphoric acid (H_3PO_4). The molar mass of phosphoric acid is 98.00 g.

percent by mass of solute =
$$\frac{\text{mass of solute}}{\text{mass of solute} + \text{mass of solvent}} \times 100\%$$
 molality = $\frac{\text{moles of solute}}{\text{mass of solute}} \times 100\%$ (

= $\frac{\text{mass of solute}}{\text{mass of soln}} \times 100\%$ (

n phosphoric acid = mass/molar mass=
$$35.4/98$$
= 0.361 mol
Mass of solvent = mass of solution – mass of solute= $100-35.4$ = 64.6 g
So molality = $0.361/64.6$ x 10^{-3} = 5.59 m

35.4% means 35.4 g phosphoric acid in 100 g solution

• The concentrated sulfuric acid we use in the laboratory is 98.0 percent H₂SO₄ by mass. Calculate the molality and molarity of the acid solution. The density of the solution is 1.83 g/mL.

100 g of solution contains 98g H₂SO₄ solute

$$molarity = \frac{moles \text{ of solute}}{liters \text{ of soln}} \qquad molality = \frac{moles \text{ of solute}}{mass \text{ of solvent (kg)}}$$

 $n H_2SO_4 = mass / molar mass = 98/98 = 1 mole$

Density of solution = (mass/volume) for solution

V solution = 100/1.83 = 54.64 ml

Molarity = $1/(54.64 \times 10^{-3}) = 18.3 \text{ M}$

Molality = $1/(100-98)x10^{-3} = 500 \text{ m}$

• Calculate the molarity and the molality of $\rm NH_3$ for a solution of 28.0 g of NH3 in 72.0 g of water. The density of the solution is 0.898 g/mL.

$$molarity = \frac{moles \text{ of solute}}{liters \text{ of soln}} \qquad molality = \frac{moles \text{ of solute}}{mass \text{ of solvent (kg)}}$$

$$n NH_3 = mass / molar mass = 28 / 17 = 1.647 mol$$

Molality =
$$1.647/72 \times 10^{-3} = 22.875 \text{ m}$$

Mass of solution =
$$28+72=100g$$

Volume of solution=
$$(mass/density)_{solution} = 100/0.898 = 111.36 \text{ ml}$$

Molarity = 1.647/111.356 x10⁻³ = 14.8 M

N**tOtality**= 1.0+7/111.330 x10 = 14.0 M

• Calculate mole fractions in the above example.

$$X_{NH3} = 1.647/(1.647+4) = 0.291$$

$$X_{H2O} = 1-0.291=0.709$$

 $n_{H2O} = 72/18 = 4 \text{ mol}$

$$X_1 = \frac{n_1}{n_1 + n_2} = \text{mole fraction of species 1}$$

$$X_2 = \frac{n_2}{n_1 + n_2}$$
 = mole fraction of species 2

$$X_1 + X_2 = 1$$

• A 46.2-mL, 0.568 M calcium nitrate $[Ca(NO_3)_2]$ solution is mixed with 80.5 mL of 1.396 M calcium nitrate solution. Calculate the concentration of the final solution.

$$n1 = 0.568 \times 0.0462 = 0.026 \text{ mol}$$

 $n2 = 1.396 \times 0.0805 = 0.112 \text{ mol}$
 $n \text{ total} = n1 + n2 = 0.112 + 0.026 = 0.138 \text{ mol}$
 $n \text{ total} = 0.0462 + 0.0805 = 0.127 \text{ L}$

Molarity (final) = n total/V (total) = 0.138/0.127 = 1.087 M.

• What is the concentration of a solution, in parts per million, if 0.02 gram of NaCl is dissolved in 1000.grams of solution?

$$ppm = \frac{(mass \ of \ solute)}{(mass \ of \ solution)} x 10^{6}$$
As usual, both masses are in g

• A solution has a concentration of 0.5 mg/mL. What is its concentration in ppm?

 $=0.02 \times 1000 / 1 = 20 \text{ ppm}$

$$Ppm (m/v) = \frac{mass \text{ of solute } (mg)}{\text{volume of solution (L)}}$$

$$= 0.5/10^{-3} \text{ ppm} = 500 \text{ ppm}$$

$$Ppm (m/v) = \frac{mass \text{ of solute } (g)}{\text{volume of solution } (mL)} \times 10^{6}$$

$$= (0.5 \times 10^{-3}/1) \times 10^{6} = 500 \text{ ppm}$$

= 0.5/10⁻³ ppm= 500 ppm = (0.5)
• Calculate the conc. of 0.2 M Na⁺ in ppm.

 $(0.02/1000) \times 10^6 = 20$ ppm

0.2 M means 0.2 mol in 1 liter solution. Mass = $0.2 \times 23 = 4.6 \text{ g}$

 $Ppm = 4.6 \text{ x} 1000/1 = 4.6 \text{x} 10^3 \text{ ppm}$ or $ppm = (4.6/1000) \text{ x} 10^6 = 4.6 \text{x} 10^3 \text{ppm}$

9- Normality

$$Normality \; (N) = \frac{Number \; of \; gram \; equivalents \; of \; solute}{Volume \; of \; Solution \; in \; L}$$

Equivalent weight of the substance(EW)

Gram equivalent = no. of moles of solute x a

$$N = n \times a / V$$

$$N = M.a$$
 $N = Molarity \times Valency$

 $a = Number of H^+ or OH^-$ in acid- base reactions or electron transfer in redox reaction.

• What is the normality of 1.4 M H₂SO₄?

$$N = M. a$$

 $N = 1.4 \times 2 = 2.8 N$

Name	Formula	Molar mass	No. of equivalents (a)	Equival ent mass		
Hydrochloric acid	HCl	36.46	1	36.46		
Sulfuric acid	H ₂ SO ₄	98	1HSO ₄ ⁻¹ 2HSO ₄ ⁻²	98 49		
Phosphoric acid	H ₃ PO ₄	98	$1 H_2 PO_4$ $2 HPO_4$ $3 PO_4$	98 49 32.7		
Sodium hydroxide	NaOH	40	1	40		
Calcium hydroxide	Ca(OH) ₂	74	2	37		

 $H_2SO_4 + NaOH = NaHSO_4 + H_2O$ $H_2\widehat{SO}_4 + 2NaO\widehat{H} = Na_2SO_4 + 2H_2O$ $H_3PO_4 + NaOH = NaH_2PO_4 + H_2O$

 $H_3PO_4 + 2NaOH = Na_2HPO_4 + 2H_2O$

 ${\rm H_3PO_4 + 3NaOH = Na_3PO_4 + 3H_2O}$

• Equivalent mass of $KMnO_4 = molar mass/a$

158.034/5 = 31.61 g/equiv

Chapter 9 part 3+4

Oxidation-reduction reactions in aqueous solutions

Types of reactions in the aqueous medium

• **Precipitation reaction**, which results in the formation of an insoluble product, or precipitate. A precipitate is an insoluble solid that separates from the solution.

$$Pb(NO_3)_2(aq) + 2KI(aq) \longrightarrow PbI_2(s) + 2KNO_3(aq)$$

- **Acid-base reactions:** it includes transfer of H⁺ and changes of pH.
- Oxidation-reduction reactions: include transfer of electrons.

Description of reactions in aqueous solutions

• **Molecular equation:** the formulas of the compounds are written as though all species existed as molecules or whole units. It does not describe in detail what actually is happening in solution.

$$Pb(NO_3)_2(aq) + 2KI(aq) \longrightarrow PbI_2(s) + 2KNO_3(aq)$$

• Ionic equation, which shows dissolved species as free ions.

$$\mathbf{Pb}^{2+}(aq) + 2\mathbf{NO}_{3}^{-}(aq) + 2\mathbf{K}^{+}(aq) + 2\mathbf{I}^{-}(aq) \longrightarrow \mathbf{PbI}_{2}(s) + 2\mathbf{K}^{+}(aq) + 2\mathbf{NO}_{3}^{-}(aq)$$

- we see that PbI_2 is an insoluble compound and KNO_3 is soluble. Therefore, the dissolved K^+ and NO_3^- are called spectator ions, or ions that are not involved in the overall reaction.
- The **net ionic equation:** shows only the species that actually take part in the reaction.

$$Pb^{2+}(aq) + 2I^{-}(aq) \longrightarrow PbI_{2}(s)$$

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$$Pb^{2+}(aq) + 2I^{-}(aq) \longrightarrow PbI_{2}(s)$$

Oxidation-Reduction Reactions

- The class of reactions called oxidation-reduction, or redox, reactions are considered electron transfer reactions.
- Consider the formation of magnesium oxide (MgO) from magnesium and oxygen.

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$

• In this reaction, two Mg atoms give up or transfer four electrons to two O atoms (in O2). Each of these steps is called a half-reaction.

$$2Mg \longrightarrow 2Mg^{2+} + 4e^{-}$$

$$O_2 + 4e^{-} \longrightarrow 2O^{2-}$$

• The sum of the half-reactions gives the overall reaction:

$$2Mg + O_2 + 4e^- \longrightarrow 2Mg^{2+} + 2O^{2-} + 4e^-$$

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$

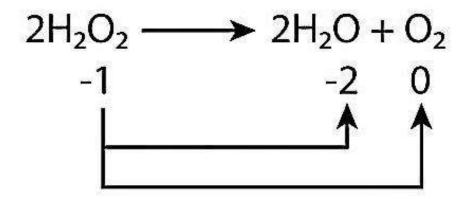
Oxidation-Reduction Reactions

• An **oxidation reaction** is a half-reaction that involves loss of electrons. In the formation of magnesium oxide, magnesium is oxidized. It is said to act as a **reducing agent or reductant** because it donates electrons to oxygen and causes oxygen to be reduced. $2Mg \longrightarrow 2Mg^{2+} + 4e^{-}$

• A reduction reaction is a half-reaction that involves gain of electrons. Oxygen is reduced and acts as an oxidizing agent or oxidant because it accepts electrons from magnesium, causing magnesium to be oxidized.

$$O_2 + 4e^- \longrightarrow 2O^{2-}$$

Disproportionation



there are reactions where a molecule, atom, or ion can at the same time be simultaneously oxidized and reduced

Oxidation Number

- An atom's oxidation number, also called oxidation state, signifies the number of charges the atom would have in a molecule (or an ionic compound) if electrons were transferred completely.
- We use the following rules to assign oxidation numbers:
- 1. In free elements (that is, in the uncombined state), each atom has an oxidation number of zero. Thus, each atom in H_2 , Br_2 , Na, Be, K, O_2 , and P_4 has the same oxidation number: zero.
- **2. For ions composed of only one atom** (that is, monatomic ions), the oxidation number is equal to the charge on the ion. Thus, Li^{+1} ion has an oxidation number of +1; Ba^{+2} ion, +2; Fe^{+3} ion, +3; I^{-1} ion, -1; O^{-2} ion, -2; and so on.
- 3- All alkali metals have an oxidation number of +1 and all alkaline earth metals have an oxidation number of +2 in their compounds. Aluminum has an oxidation number of +3 in all its compounds.
- **4. The oxidation number of oxygen** in most compounds (for example, MgO and H_2O) is -2, but in peroxide ion (O_2^{-2}) as in H_2O_2 it is -1.

- **5- The oxidation number of hydrogen** is +1, except when it is bonded to metals in binary compounds. In these cases (for example, LiH, NaH, CaH₂), its oxidation number is -1.
- **6. Fluorine has an oxidation number** of -1 in all its compounds. Other halogens (Cl, Br, and I) have negative oxidation numbers when they occur as halide ions in their compounds (as HCl). When combined with O as (ClO_4^-) they have positive oxidation numbers.
- **7- In a neutral molecule**, the sum of the oxidation numbers of all the atoms must be zero. **In a polyatomic ion**, the sum of oxidation numbers of all the elements in the ion must be equal to the net charge of the ion.
- 8- Oxidation numbers do not have to be integers. For example, the oxidation number of O in the superoxide ion, O_2^- , is -1/2 (as in KO_2).

1 1A	ľ																18 8A 2 He
1 H +1 -1	2 2A											13 3A	14 4A	15 5A	16 6A	17 7A	He
3 Li +1	4 Be +2											5 B +3	6 C +4 +2 -4	7 N +5 +4 +3 +2 +1 -3	8 0 +2 -1 -1 -2	9 F -1	10 Ne
11 Na +1	12 Mg +2	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 —8B-	10	11 1B	12 2 B	13 Al +3	14 Si +4 -4	15 P +5 +3 -3	16 S +6 +4 +2 -2	17 CI ++4-5 ++1-1	18 Ar
19 K +1	20 Ca +2	21 Sc +3	22 Ti +4 +3 +2	23 V +5 +4 +3 +2	24 Cr +6 +5 +4 +3 +2	25 Mn +7 +6 +4 +3 +2	26 Fe +3 +2	27 Co +3 +2	28 Ni +2	29 Cu +2 +1	30 Zn +2	31 Ga +3	32 Ge +4 -4	33 As +5 +3 -3	34 Se +6 +4 -2	35 Br +5 +3 +1 -1	36 Kr +4 +2

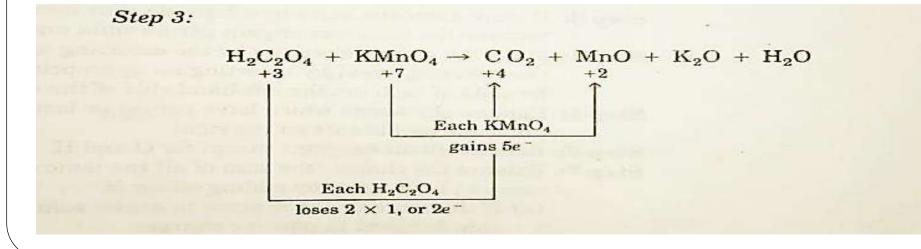
Balancing Redox Equations

- There are two methods for balancing redox reactions:
- 1- Oxidation number method.
- 2- Half reaction method.
- We consider the balancing of equations for redox reactions that occur in two situations:
- 1- When the redox equation written as molecular equation (only use the Oxidation number method).
- 2- When the redox equation written as a net ionic equation (can use the Oxidation number method and Half reaction method).

Oxidation number method for molecular equation

- Step 1: assign oxidation numbers for all atoms.
- **Step 2:** note which atom appear to lose and which atom appear to gain electrons and determine how many electrons are lost or gained for each atom.
- Step 3: determine the total loss or gain of electrons per formula unit.
- **Step 4:** make the total gain of electrons equals the total loss of electrons by multiplying a coefficient on the left side of equation.
- **Step 5:** Balance the atoms that gain or lose electrons then balance other atoms except O and H. Then, balance O atoms then hydrogen atoms.

Balance the following equation: $H_2C_2O_4 + KMnO_4 \rightarrow CO_2 + MnO + K_2O + H_2O$ Solution Step 1: +2 +6 -8 +1 +7 -8 +4 -4 +2 -2 $H_2C_2O_4 + KMnO_4 \rightarrow CO_2 + MnO + K_2O + H_2O$ +1+3-2 +1+7-2 +4-2 +2-2 +1-2 +1-2Step 2: $H_2C_2O_4 + KMnO_4 \rightarrow CO_2 + MnO + K_2O + H_2O$ Reduction: Each Mn gains 5e Oxidation: Each C loses le



Step 3:

Step 4:

$$5H_2C_2O_4 + 2KMnO_4 \rightarrow CO_2 + MnO + K_2O + H_2O$$

Step 5:

$$5H_2C_2O_4 + 2KMnO_4 \rightarrow 10CO_2 + 2MnO + K_2O + 5H_2O$$

Oxidation number method for net ionic equation

- Steps 1-4: as former
- **Step 5**: Balance the atoms that gain or lose electrons.
- **Step 6:** Balance other atoms except O and H.
- Step 7: Balance the charges:
 - A- If the reaction takes place in <u>acidic</u> medium, balance the hydrogen atoms by add H⁺ in the site deficient in positive charge.
 - B- If the reaction takes place in <u>basic</u> medium, balance the charge by adding OH⁻ in the site deficient in negative charge.
 - Step 8: add water molecules to balance oxygen atoms. So, if your balance is correct, hydrogen atom would be already balanced.

Oxidation number method for net ionic equation in acidic medium

Complete and balance the following equation for a reaction which takes in acidic solution:

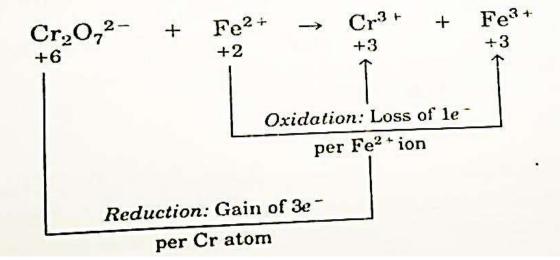
$$\operatorname{Cr}_2\operatorname{O}_7^{2-} + \operatorname{Fe}^{2+} \to \operatorname{Cr}^{3+} + \operatorname{Fe}^{3+}$$
 (acidic solution)

Solution

Step 1:

$$\text{Cr}_2\text{O}_7^{2-} + \text{Fe}^{2+} \rightarrow \text{Cr}^{3+} + \text{Fe}^{3+} + 6 - 2 + 2 + 3 + 3$$

Step 2:



Step 3:

$$Cr_2O_7^{2-}$$
 + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+}
+6 +2 +3 +3
Loss of $1e^-$ per Fe^{2+} ion

$$Total \ Gain \ of \ 2 \times 3,$$
or $6e^-$ per $Cr_2O_7^{2-}$ ion

Step 4:

$$Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+}$$

Step 5:

$$Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+}$$

Step 6: Done!

Step 7:

Total charge on left =
$$-2 + 6(+2) = +10$$

Total charge on right = $2(+3) + 6(+3) = +24$
Additional (positive) charge needed on left = $+14$
 $14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+}$

Step 8:

$$14H^{+} + Cr_{2}O_{7}^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_{2}O$$

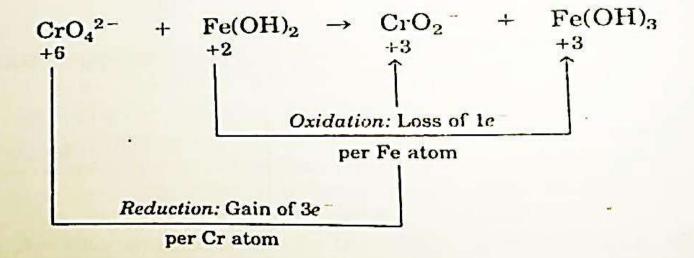
Oxidation number method for net ionic equation in basic medium

Solution

Step 1:

$$\operatorname{CrO_4^{2-}}_{+6-2}$$
 + $\operatorname{Fe}(OH)_2 \rightarrow \operatorname{CrO_2^-}_{+3-2}$ + $\operatorname{Fe}(OH)_3$
+3-2+1

Step 2:



Step 4:

$$\text{CrO}_4^{2-} + 3\text{Fe(OH)}_2 \rightarrow \text{CrO}_2^- + \text{Fe(OH)}_3$$

Sten 5

$$\text{CrO}_4^{2-} + 3\text{Fe}(\text{OH})_2 \rightarrow \text{CrO}_2^- + 3\text{Fe}(\text{OH})_3$$

Step 6: Done! Step 7:

Total charge on left =
$$-2 + 3(0) = -2$$

Total charge on right = $-1 + 3(0) = -1$
Additional (negative) charge needed on right = -1
 $CrO_4^{2-} + 3Fe(OH)_2 \rightarrow CrO_2^{-} + 3Fe(OH)_3 + OH^{-}$

Step 8:

$$2H_2O + CrO_4^{2-} + 3Fe(OH)_2 \rightarrow CrO_2^{-} + 3Fe(OH)_3 + OH^{-}$$

Half-Reaction method For net ionic equations in acidic solutions

Step 1: Separate the skeletal equation into two half-reactions, one an oxidation and the other a reduction.

Step 2: Balance each half- reaction separately, following this sequence:

- a- Balance all atoms by inspection, other than H and O.
- b- Balance O atoms by adding H2O to the appropriate side.
- c- Balance the H atoms as follows:
 - i- for acidic solutions, add H⁺ ions to the side deficient in H⁺.
- d- Balance the charge by adding electrons to the side deficient in negative charge.

Step 3: If the oxidation and reduction half-reactions contain different numbers of electrons, we need to multiply one or both half-reactions to equalize the number of electrons. Add the two half-reactions together.

Step 4: Balance the final equation by inspection. The electrons on both sides must cancel.

A final check shows that the resulting equation is "atomically" and "electrically" balanced.

Using the half-reaction method, complete and balance the following equation for a reaction occurring in acidic solution:

$$Cr_2\dot{O_7}^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+}$$
 (acidic solution)

Step 4:

$$14H^{+} + Cr_{2}O_{7}^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_{2}O_{1}^{2-}$$

 $6e^- + 14H^+ + Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O + 6e^{-}$

Half-Reaction method For net ionic equations in basic solutions

- For reactions in a basic medium, we proceed as former until step 4 as if the reaction were carried out in a acidic medium.
- **Step 5:** Then, for every H⁺ion we add an equal number of OH⁻ ions to both sides of the equation. Where H⁺ and OH⁻ ions appear on the same side of the equation, we combine the ions to give H2O.

Using the half-reaction method, complete and balance the following equation for a reaction taking place in basic solution: $MnO_4 + I \longrightarrow MnO_2 + I_2$ Step 1: $I^- \longrightarrow I_2$ Step 1: $MnO_4^- \longrightarrow MnO_2$

Step 2a: $2I^{-} \longrightarrow I_{2}$ Step 2a: Done

Step 2b: Done. Step 2b: $MnO_4^- \longrightarrow MnO_2 + 2H_2O_1$ Step 2c: $MnO_4^- + 4H^+ \longrightarrow MnO_2 + 2H_2O_1$ Step 2c: Done.

Step 2d: $2I^- \longrightarrow I_2 + 2e^-$ Step 2d: $MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O$

 $3(2I^{-} \longrightarrow I_2 + 2e^{-})$ $2(MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O)$ Step 3: $6I^{-} + 2MnO_{4}^{-} + 8H^{+} + 6e^{-} \longrightarrow 3I_{2} + 2MnO_{2} + 4H_{2}O + 6e^{-}$

Step 4: $6I^- + 2MnO_4^- + 8H^+ \longrightarrow 3I_2 + 2MnO_2 + 4H_2O_1$

Step 5: $6I^{-} + 2MnO_{4}^{-} + 8H^{+} + 8OH^{-} \longrightarrow 3I_{2} + 2MnO_{2} + 4H_{2}O + 8OH^{-}$

 $6I^- + 2MnO_4^- + 4H_2O \longrightarrow 3I_2 + 2MnO_2 + 8OH^-$