Mustansiryah University

College of Science

Department of Chemistry

First Grade

Analytical Chemistry

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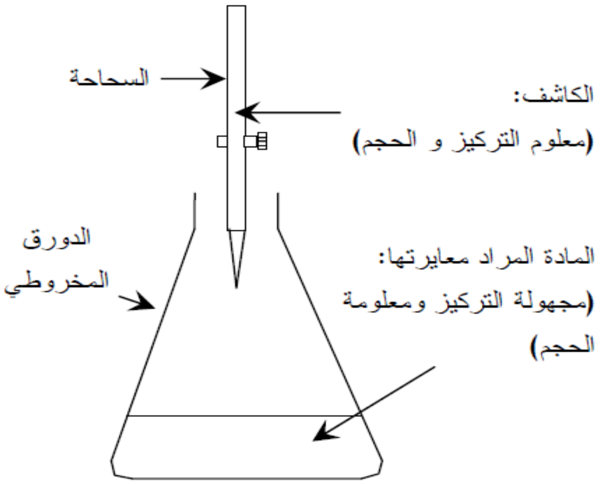

Analytical Chemistry

First grade (2020-2021)

References:-

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(2) “Fundamental of Analytical Chemistry” by Doglas A.Skooge, Donald M.West and James Holler, 8th Edition, 2004.

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Analytical Chemistry

The science seeks ever improved means of measuring the chemical composition of natural and artificial materials by using techniques to identify the substances which may be present in a material and to determine the exact amounts of the identified substance. Analytical chemistry involves the analysis of matter to determine its composition and the quantity of each kind of matter that is present. Analytical chemists detect traces of toxic chemicals in water and air. They also develop methods to analyze human body fluids for drugs, poisons, and levels of medication.

Analytical chemistry consists of:

(A) Qualitative analysis which deals with the identification of elements, ions, or compounds present in a sample (tells us what chemicals are present in a sample).

(B) Quantitative analysis which is dealing with the determination of how much of one or more component is present (tells how much amounts of chemicals are present in a *sample*). This analysis can be divided into three branches.

(1) Volumetric analysis (Titrimetric analysis): The analyte reacts with a measured volume of reagent of known concentration, in a process called titration.

(2) Gravimetric analysis: usually involves the selective separation of the analyte by precipitation, followed by the very non-selective measurement of mass (of the precipitate).

(3) Instrumental analysis: They are based on the measurement of a physical property of the sample, for example, an electrical property or the absorption of electromagnetic radiation. Examples are spectrophotometry (ultraviolet, visible, or infrared), fluorimetry, atomic spectroscopy (absorption, emission), mass spectrometry, nuclear magnetic resonance spectrometry (NMR), X-ray spectroscopy (absorption, fluorescence).

Solutions

Solution: Homogeneous mixture of two or more substance produce from dissolved (disappeared) solute particle (ions, atoms, molecules) (lesser amount) between solvent particle (larger amount).

Solute (lesser amount) + Solvent (larger amount) → Solution

$$\mathbf{NaCl_{(s)} + H_2O_{(l)} \rightarrow Salt\ Solution}$$

Concentrated Solution has a large amount of solute.

Dilute Solution has a small amount of solute.

Solute	**Solvent**		
	Gas	**Liquid**	**Solid**
Gas	$O_{2(g)}$ in $N_{2(g)}$, Air	$CO_{2(g)}$ in $H_2O_{(L)}$, Soda	$H_{2(g)}$ in $Pd_{(s)}$, H_2 catalyst
Liquid	Perfume	$Alcohol_{(L)}$ in $H_2O_{(L)}$	$Hg_{(L)}$ in $Ag_{(s)}$, Dental filling
Solid	Dust air, Smoke industry	$NaCl_{(s)}$ in $H_2O_{(L)}$, salt water, saline sol.	$Zn_{(s)}$ in $Cu_{(s)}$, Brass alloy

Classification of solutions according to amount of solute:

(1) Unsaturated solutions: if the amount of solute dissolved is less than the solubility limit, or if the amount of solute is less than capacity of solvent.

(2) Saturated solutions: is one in which no more solute can dissolve in a given amount of solvent at a given temperature, or if the amount of solute equal to capacity of solvent.

(3) Super saturated solutions: solution that contains a dissolved amount of solute that exceeds the normal solubility limit (saturated solution). Or a solution contains a larger amount of solute than capacity of solvent. This it's occurs when the solution is heated to a high temperature.

Classification of solution based on solute particle size:

(1) True solution: A homogeneous mixture of two or more substance in which substance (solute) has a particle size less than 1 nm dissolved in solvent. Particles of true solution cannot be filtered through filter paper and are not visible to naked eye (NaCl in water).

(2) Suspension solution: heterogeneous mixtures which settles on standing and its components can be separated by filtrating (Amoxcycilline Antibiotics), particle of solute visible to naked eye.

(3) Colloidal solution: homogeneous mixture which does not settle on standing, nor are their components filterable, solute particle visible with electron microscope (milk).

Stoichiometric Calculations

Gram atomic weight:

(gAw some time Awt): Is the weight of a specified number of atoms of that element (contains exactly the same number of atoms of that element as there are carbon atoms in exactly 12g of carbon 12 (this number is Avogadro's number = 6.022×10^{23} atoms).

Gram molecular weight:

(gMw some times M.wt): Defined as the sum of the atomic weight of the atoms that make up a molecular compound. Or the weight of Avogadro's number of molecules of any compound.

Gram formula weight:

(gFw some time F.wt): The sum of the atomic weight of the atoms that make up an ionic formula. (is the more accurate description for substances that do not exist as molecules but exist as ionic compounds e.q strong electrolytes-acids, bases, salts). Sometimes use the term molar mass (Molecular weight, M.wt) in place of gram formula weight, gFw).

Example (1):- Calculate the number of grams in one mole of $CaSO_4.7H_2O$ (calculate gram molecular or formula weight).

Solution:

One mole is the formula weight expressed in grams. The formula weight is **(Ca=40.08, S=32.06, O=16.00, H=1.01)**

$$\mathbf{CaSO_4.7H_2O = 40.08 + 32.06 + (16.0 \times 4) + 7[(2 \times 1.01) + 16.00]}$$

$$\mathbf{= 262.25\ gm/mol}.$$

Mole Concept: Mole

which is Avogadro's number (6.022×10^{23}) of atoms, molecules, ions or other species. Numerically: it is the atomic, molecular, or formula weight of a substance expressed in grams.

$$\mathbf{mole = \frac{weight\ (g)}{formula\ weight\ \left(\frac{g}{mole}\right)}}$$

$$\mathbf{mmole = \frac{weight\ (mg)}{formula\ weight\ \left(\frac{mg}{mmole}\right)}} \qquad \mathbf{(1\ mole = 1000\ mmole)}$$

Where formula weight represents the atomic or molecular weight of the substance.

Example (2):-Calculate the number of moles in 500 mg Na_2WO_4.

Solution (A.wt W= 183,84 g/mole , Na = 23 g/mole, O = 16 g/mol)

$$\mathbf{mmole = \frac{wt\ (mg)}{M.wt\ (\frac{mg}{mmole})} = \frac{500\ (mg)}{293.8\ (\frac{mg}{mmole})} = 1.706\ mmole}$$

$$\mathbf{mole = \frac{mmole}{1000} = \frac{1.706}{1000} = 0.00170\ mol}$$

Example (3): How many molecules are contained in 25.0 g H_2**.**

Solution: (A.wt H= 1.008 g/mole)

$$\mathbf{moles\ H_2 = \frac{wt\ (g)}{Fwt} = \frac{25.0\ g}{2.016\,\frac{g}{mole}} = 12.40\ mole}$$

No. Molecules = No. moles × Avogadro number

= 12.40 × $6.022X10^{23}$ = 7.74×10^{24} molecule

Example (4):-How many milligrams are in 0.250 mmole Fe_2O_3 (ferric oxide).

Solution: (A.wt O= 16 g/mole , Fe = 56 g/mole)

$$\mathbf{wt\ (mg) = mmole \times M.wt\ \left(\frac{mg}{mmol}\right)}$$

$$\mathbf{= 0.250\ mmole\ \times 159.7\,\frac{mg}{mmol}\ \ = 39.9\ mg}$$

Example (5):- Calculate the number of mole of NaCl required to prepare 1Kg of AgCl according to the equation: (Na=23, Cl=35.5, N=14 , Ag =107.86, O = 16 g/mole)

Solution: $$\mathbf{AgNO_3 + NaCl \longrightarrow NaNO_3 + AgCl}$$

$$\mathbf{No\ of\ mols(AgCl) = \left(\frac{\mathit{wt}}{\mathit{Mwt}}\right) = \left(\frac{1Kg}{143.36(\frac{\mathit{g}}{\mathit{mol}})}\right) = \left(\frac{1000g}{143.36(\frac{\mathit{g}}{\mathit{mol}})}\right) = 6.98\mathit{mol}}$$

according to the balance equation the mole ratio between NaCl & AgCl equal 1:1 therefore we need 6.98 mol of NaCl .

Example (6):Calculate the number of mole of $Ca(HCO_3)_2$ required to prepare 1.5 mol of CO_2 according to the equation.

$$Ca(HCO_3)_2 + 2HCl \longrightarrow CaCl_2 + 2CO_2 + 2H_2O$$

solution:

No. of mol of $Ca(HCO_3)_2$ = No. of mol of $CO_2 \times 0.5$

$= 1.5 \times 0.5 = 0.75$ mol of $Ca(HCO_3)_2$

Example (7): What mass of KI is needed to produce 69.6 gm of K_2SO_4 by the reaction :

$$8KI + 5H_2SO_4 \longrightarrow 4K_2SO_4 + 4I_2 + H_2S + 4H_2O$$

solution :

No. of mol of K_2SO_4= wt / M.wt $\longrightarrow$ 69.6 gm / 174 (gm /mol) = 0.4 mol

No. of mol of KI = 2×0.4= 0.8 mol

wt of KI = mol × M.wt = 0.8×166 = 133gm

Problems 1

Q1: Find the number of Na^+ ions in 2.92 g of Na_3PO_4?

Q2: Find the number of K^+ ions in 3.41 mol of K_2HPO_4?

Q3: Find the amount of the indicated element (in moles) in

(a) 8.75 g of $\underline{B_2}O_3$. (b) 167.2 mg of $Na_2B_4\underline{O_7} \cdot 10H_2O$.

(c) 4.96 g of $\underline{Mn_3}O_4$. (d) 333 mg of $Ca\underline{C_2}O_4$.

Q4: Find the amount in millimoles of the indicated species in.

(a) 850 mg of $\underline{P}_2O_5$. (b) 40.0 g of $\underline{C}O_2$.

(c) 12.92 g of $NaHC\underline{O_3}$. (d) 57 mg of $\underline{Mg}NH_4PO_4$.

Q5- What is the mass in grams of

a- 7.1 mol of KBr b- 20.1 mmol of PbO c- 3.76 mol of $MgSO_4$

How do we express concentrations of solutions

1-The Molarity Concentration: -

Also called (Molarity, amount of concentration or substances concentration) is a measure of the concentration of a chemical species in a particular of a solute in a solution, in terms of amount of substance per unit volume of solution. In chemistry, the most commonly used unit for molarity is the number of moles per litre, having the unit symbol (mol./L). A solution with a concentration of 1 mol./L is said to be 1 Molar, commonly designated as 1M.

A-Molarity concentration for solutions prepared from dissolving solid solute in liquid solvent

defined as a number of solute moles dissolved in solution volumes in litre.

$$\boldsymbol{Molarity\ (M) = \frac{No.of\ mole\ solute}{solution\ volume\ (L)} = (\frac{mole}{L})}$$

$$\boldsymbol{Molarity\ (M) = \left(\frac{mole}{L}\right) \Rightarrow \quad mole = M \times V}(\mathrm{L})$$

$$\boldsymbol{Molarity\ (M) = \frac{No.of\ mmole\ solute}{solution\ volume\ (mL)} = (\frac{mmole}{mL})}$$

$$\boldsymbol{Molarity\ (M) = \left(\frac{mmole}{mL}\right) \Rightarrow \quad mmole = M \times V(mL)}$$

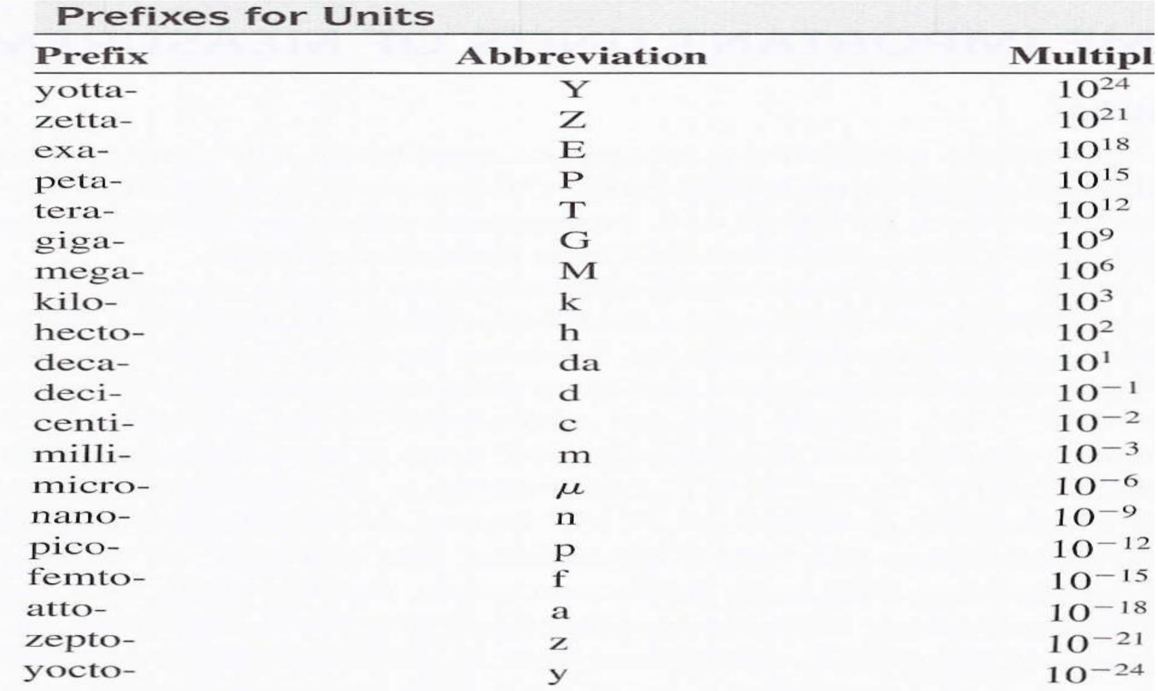
$$\boxed{\boldsymbol{M = \frac{No\ of\ mole\ solute}{Volume\ solution\ (L)} = \frac{\frac{wt\ (g)}{M.wt\ (\frac{g}{mole})}}{\frac{V\ (mL)}{1000\ (\frac{mL}{L})}} = \frac{wt\ (g)}{M.wt\ (\frac{g}{mole})} \times \frac{1000}{V\ (mL)}}}$$

Example (8):-A solution is prepared by dissolving 1.26 gm $AgNO_3$ in a 250 mL volumetric flask and diluting to volume. Calculate the molarity of the silver nitrate solution. How many millimoles $AgNO_3$ were dissolved?

Solution:

$$\boldsymbol{M = \frac{wt\ (g)}{M.wt\ (\frac{g}{mol})} \times \frac{1000}{V\ (mL)} = \frac{1.26\ (g)}{169.9\ (\frac{g}{mol})} \times \frac{1000}{250\ (mL)} = 0.0297\ mol/L}$$

$$mmole = M\left(\frac{mmol}{mL}\right) \times V\,(mL) \quad = 0.0297\left(\frac{mmol}{mL}\right) \times 250\,mL = 7.42\,mmole$$



Prefixes for Units

Prefix	Abbreviation	Multipl
yotta-	Y	10^{24}
zetta-	Z	10^{21}
exa-	E	10^{18}
peta-	P	10^{15}
tera-	T	10^{12}
giga-	G	10^{9}
mega-	M	10^{6}
kilo-	k	10^{3}
hecto-	h	10^{2}
deca-	da	10^{1}
deci-	d	10^{-1}
centi-	c	10^{-2}
milli-	m	10^{-3}
micro-	μ	10^{-6}
nano-	n	10^{-9}
pico-	p	10^{-12}
femto-	f	10^{-15}
atto-	a	10^{-18}
zepto-	z	10^{-21}
yocto-	y	10^{-24}

Example (9):- How many grams per millilitre of NaCl are contained in a 0.250 M solution.

Solution :

$$\mathrm{M} = \frac{wt\,(g)}{M.wt\,(\frac{g}{mol})} \times \frac{1000}{V\,(mL)}$$

$$0.250\,M = \frac{wt\,(g)}{58.4\,(\frac{g}{mol})} \times \frac{1000}{1\,(mL)}\,, \qquad wt\,(g) = 0.0146\,(\frac{g}{mL})$$

Example (10):-How many grams Na_2SO_4 should be weight out to prepare 500 mL of a 0.100 M solution.

Solution :

$$M = \frac{wt\,(g)}{M.wt\,\left(\frac{g}{mol}\right)} \times \frac{1000\,\left(\frac{mL}{L}\right)}{V\,(mL)} \quad ,$$

$$\mathbf{0.10}\left(\frac{mol}{L}\right)=\frac{wt\ (g)}{142\ \left(\frac{g}{mol}\right)}\times\frac{1000\ \left(\frac{mL}{L}\right)}{500\ (mL)}$$

$$wt\ (g)=\frac{0.10\ \left(\frac{mol}{L}\right)\times 142\ \left(\frac{g}{mol}\right)\times 500\ (mL)}{1000\ \left(\frac{mL}{L}\right)}=7.1\ g$$

Example (11):- Calculate the concentration of potassium ion in grams per litre after mixing 100 mL of 0.250 M KCl and 200 mL of 0.100 M K_2SO_4.

Solution : $mmol\ (K^+)\ =mmol\ (KCl)+2\times mmol\ (K_2SO_4)$

$$mmol\ (K^+)=V\ (mL)\times M\ \left(\frac{mmol}{mL}\right)+2\left[V\ (mL)\times M\ \left(\frac{mmol}{mL}\right)\right]$$

$$=100\ (mL)\times 0.250\ \left(\frac{mmol}{mL}\right)+\ 2\left[200\ (mL)\times 0.1\ \left(\frac{mmol}{mL}\right)\right]$$

$$=25\ mmol+2\ [20\ mmol]$$

$$=25\ mmol+40\ mmol=65\ mmol\ in\ 300\ mL$$

$$mmole=\frac{wt\ (mg)}{M.wt\ (\frac{mg}{mmol})}$$

$$wt=65\ (mmol)\times 39.1\ \left(\frac{mg}{mmol}\right)=2541.5\ mg$$

$$=\frac{2541.5\ (mg)}{1000\ \left(\frac{mg}{g}\right)}=2.541\ gm\ in\ 300\ mL$$

$$V\ in\ \ L=\frac{300\ (mL)}{1000\ (\frac{mL}{L})}=\ 0.3\ L\ ,\ \ Conc.of\ Sol.=\frac{2.541\ gm}{0.3\ L}=8.47\ (\frac{gm}{L})$$

Problems 2

Q1- How many grams of K_2SO_4 are contained in 50 ml of 0.200 M**,**

Q2- How many millimoles of K_2SO_4 are present?

Q3- Calculate the molar concentration of a brine solution obtained
by mixing equal volumes of two solutions of the same substance,
the first 0.1 M and the second 0.5 M

Q4-Calculate the molar concentrations of 1.00 mg/L solutions of each of the following.

(a) $AgNO_3$, (b) $Al_2(SO_4)_3$, (c) CO_2, (d) $(NH_4)_4Ce(SO_4)_4.\ 2H_2O$, (e) HCl, (f) $HClO_4$.

B -Molarity concentration for solution prepared from dissolved liquid solute in liquid solvent.

$$\boxed{M = \frac{\% \times \mathbf{density} \times 1000}{\mathbf{M.wt}} = \frac{\% \times \mathbf{sp.gr.} \times 1000}{\mathbf{M.wt}} =}$$

$$\% = (wt/wt\%) = \frac{wt\ solute\ (g)}{wt\ solution\ (g)} \times 100$$

$$\% = (wt/wt\%) = \frac{wt\ solute\ (\cancel{g})}{wt\ solution\ (g)} \times \left(\frac{100cg}{\cancel{g}}\right)$$

$$\% = (wt/wt\%) = \left(\frac{cg}{g}\right)$$

Density: is the weight per unit volume at the specified temperature, usually (gm/mL) or (gm/cm^3) or (gm.cm^{-3}) in 20°C (is the ratio of the mass in (gm) and volume (mL).

Specific gravity (sp. gr.): defined as the ratio of the mass of a body (e.g. a solution) usually at 20°C to the mass of an equal volume of water at 4°C (or sometimes 20°C) or (is the ratio of the densities of the two substances).

Notice -The Specific gravity (sp. gr.) its without unit.

(sp. gr.) =[d(substance)/d(water)] ⟶ d(substance) = (sp. gr.) × d(water) (g/mL) = d(substance) (g/mL)

Example (12):- Calculate the molarity of 28.0% NH_3, density 0.898 = (sp. gr.).

Solution:

$$M.wt\ NH_3 = 14 + (3 \times 1) = 17$$

$$M = \frac{\%\ (wt/wt) \times (density)\left(\frac{g}{mL}\right)\ or\ (sp.gr.) \times\ 1000}{M.wt}$$

$$M = \frac{\frac{28}{100} \times 0.898\ \times 1000}{17} = 16.470\left(\frac{mol}{L}\right) = 16.470\left(\frac{mmol}{mL}\right) = 16.470\ M$$

$$M = \frac{28\left(\frac{cg}{g}\right) \times \left(\frac{1g}{100cg}\right)\ \times 0.898\left(\frac{g}{mL}\right)\ \times 1000\left(\frac{mL}{L}\right)}{17\left(\frac{g}{moL}\right)} = 16.470\left(\frac{moL}{L}\right) = 16.470\ M$$

$$M = \frac{28\left(\frac{\cancel{cg}}{\cancel{g}}\right) \times \left(\frac{1\cancel{g}}{100\cancel{cg}}\right) \times 0.898\left(\frac{\cancel{g}}{\cancel{mL}}\right) \times 1000\left(\frac{\cancel{mL}}{L}\right)}{17\left(\frac{\cancel{g}}{moL}\right)} = 16.470\left(\frac{moL}{L}\right) = 16.470\ M$$

Example (13):-How many millilitres of concentrated sulphuric acid, 94.0% (g/100g solution), density 1.831 g/cm^3, are required to prepare 1 liter of a 0.100 M solution.

Solution:

$$\mathbf{M} = \frac{\frac{94}{100} \times 1.831 \times 1000}{98.1} = 17.5\left(\frac{\mathbf{mol}}{\mathbf{L}}\right) \mathbf{or} \left(\frac{\mathbf{mmol}}{\mathbf{mL}}\right)$$

$$\mathbf{no.\ of\ mmol\ (conc.) = no.\ mmol\ (dilu.)}$$

$$(\mathbf{M_1} \times \mathbf{V_1})_{\mathbf{conc.}} = (\mathbf{M_2} \times \mathbf{V_2})_{\mathbf{dilu.}}$$

$$17.5 \times \mathbf{V_1} = 0.1 \times 1000$$

$$\mathbf{V_1} = 5.71\ \mathbf{mL}$$

Of concentrated H_2SO_4 must be diluted to 1L (1000mL) to prepare (become) 0.1M.

Another solution*:* $\mathrm{no.\ of\ mmol\ (conc.) = no.\ mmol\ (dilu.)}$

$$(\mathbf{M_1} \times \mathbf{V_1})_{\mathbf{conc.}} = (\mathbf{M_2} \times \mathbf{V_2})_{\mathbf{dilu.}}$$

$$\left(\frac{\% \times \mathbf{sp.gr.\ or\ (density)} \times 1000}{\mathbf{M.wt}} \times \mathbf{V_1}\right)_{\mathbf{conc.}} = (\mathbf{M_2} \times \mathbf{V_2})_{\mathbf{dilu.}}$$

$$\frac{\frac{94}{100} \times 1.831 \times 1000}{98.1} \times \mathbf{V_1} = 0.1 \times 1000$$

$$\mathbf{V_1} = 5.71\ \mathbf{mL}$$

Diluting Solutions

We often must prepare dilute solutions from more concentrated stock solutions. For example, we may prepare a dilute HCl solution from concentrated HCl to be used for titration .Or, we may have a stock standard solution from which we wish to prepare a series of more dilute standards. The millimoles of stock solution taken for dilution will be identical to the millimoles in the final diluted solution

$$\boxed{\mathbf{M_{stock}} \times \mathbf{V_{stock}} = \mathbf{M_{diluted}} \times \mathbf{V_{diluted}}}$$

Example (14):-You wish to prepare a calibration curve for the spectrophotometric determination of permanganate. You have a stock 0.100 M solution of $KMnO_4$ and a series of 100 mL volumetric flasks. What volumes of the stock solution will you have to pipet into the flasks to prepare standards of 1.00, 2.00, 5.00, and $10.0\text{x}10^{-3}$ M $KMnO_4$ solutions?

Solution: **$1.0\text{x}10^{-3}$ M**

$$(\mathbf{M_1 \times V_1})_{\mathbf{conc.}} = (\mathbf{M_2 \times V_2})_{\mathbf{dilu.}}$$

$$\mathbf{0.1\left(\frac{mmol}{mL}\right) \times V_1 = 1.0 \times 10^{-3}\left(\frac{mmol}{mL}\right) \times 100\ (mL)}$$

$\mathbf{V_1 = 1.0\ mL\ stock\ solution\ (conc.)}$,**Also to prepare 2.0, 5.0, 10.0 $\mathbf{x10^{-3}}$ M**

Example (15):-You wish to prepare 500 mL of 0.1 M $K_2Cr_2O_7$ solution from a 0.250 M solution. What volume of the 0.250 M solution must be diluted to 500 mL.

Solution:

$$\boldsymbol{(no.of\ mmol)_{conc.} = (no.of\ mmol)_{dilu.}}$$

$$\boldsymbol{(M_1 \times V_1)_{conc.} = (M_2 \times V_2)_{dilu.}}$$

$$\boldsymbol{0.250\left(\frac{mmol}{mL}\right) \times V_1(mL) = 0.1\left(\frac{mmol}{mL}\right) \times 500\ mL, \qquad V_1 = 200\ mL}$$

Example (16):- What is the molarity of a 13.0% solution of H_2SO_4? and What is the volume should be diluted to prepare a 1.25 M solution in 100mL volumetric flask?

Solution:

From specific gravity table in the appendix, the specific gravity of the acid is 1.090.

$$\mathbf{M = \frac{\% \times SP.gr \times 1000}{M.wt} = \frac{0.13 \times 1.090 \times 1000}{98} = 1.45}$$

$$(\mathbf{M_1 \times V_1})_{\mathbf{conc.}} = (\mathbf{M_2 \times V_2})_{\mathbf{dilu.}} \quad \longrightarrow \quad \mathbf{1.45 \times V_1 = 1.25 \times 100\ mL}$$

$$\mathbf{V_1 = 86.20mL.}$$

Example (17):- How many mL of permanganate $KMnO_4$ (0.100 M) should be used to prepare 100 mL of 1.0×10^{-3} M solution.

Solution:

$$(\mathbf{M_1 \times V_1})_{\mathbf{conc.}} = (\mathbf{M_2 \times V_2})_{\mathbf{dilu.}}$$

$$\mathbf{0.1\left(\frac{mmol}{mL}\right) \times V_1 = 1.0 \times 10^{-3}\left(\frac{mmol}{mL}\right) \times 100\ (mL)}$$

$$\mathbf{V_1 = 1.0\ mL}\ \text{stock solution (conc.)},$$

Example (18):- What volume of the 0.250 M of $K_2Cr_2O_7$ solution must be diluted to prepare 500 mL of 0.1 M solution.

$$(\mathbf{M_1} \times \mathbf{V_1})_{\mathbf{conc.}} = (\mathbf{M_2} \times \mathbf{V_2})_{\mathbf{dilu.}}$$

$$\mathbf{0.250}\left(\frac{\mathbf{mmol}}{\mathbf{mL}}\right) \times \mathbf{V_1(mL)} = \mathbf{0.1}\left(\frac{\mathbf{mmol}}{\mathbf{mL}}\right) \times \mathbf{500\ mL} \quad , \mathbf{V_1} = \mathbf{200\ mL}$$

Example (19):- What volume of 0.40 M $Ba(OH)_2$ must be added to 50 mL of 0.30 M NaOH to give a solution 0.50 M in $[OH^-]$

Solution:

mmol of **Solution$_3$** = **2×mmol** of **Solution$_1$** + **mmol** of **Solution$_2$**

Solution$_1$ = 0.40 M $Ba(OH)_2$, v = (x mL)

Solution$_2$ = 0.30 M NaOH , v = (50 mL)

Solution$_3$ = Mix ($Ba(OH)_2$+NaOH) , v = (x + 50) mL

$$\textbf{(Solution}_3\textbf{)}\ \mathbf{mmole\ OH^-(M \times V) = 2 \times mmol\ Ba(OH)_2 + mmole\ NaOH}$$

$$\mathbf{0.5\ M \times (50 + x)mL = 2 \times (0.40\ M \times (x)\ mL) + 0.30\ M \times 50\ mL}$$

$$\mathbf{x = 33\ mL\ Ba(OH)_2}$$

Problems 3

Q1: How many milliliters of concentration hydrochloric acid, 38 %(wt/wt), specific gravity 1.19, are required to prepare 1L of a 0.1 M solution?

Q2: Calculate the molarity of each of the following commercial acid or base solutions: (a) 70% $HClO_4$, sp. gr. 1.668, (b) 69% HNO_3, sp. gr. 1.409.

Equivalent weight (Eq.wt)

Is the formula weight divided by the number of reacting units (**H^+** or **OH^-** for acid-base and electron for oxidation-reduction reaction).

Equivalent weight: ***of a compound is defined as ratio between molecular weight and total charge on cation or total charge on anion.***

$$\mathbf{(Eq.wt)}\left(\frac{\mathbf{gm}}{\mathbf{Eq}}\right)\ \mathbf{for\ (acid - base)\ reaction} = \frac{\mathbf{formula\ weight\ (F.wt)}}{\mathbf{No.of\ H^+\ or\ OH^-}}$$

$$(\mathbf{Eq.\,wt})\left(\frac{\mathbf{gm}}{\mathbf{Eq}}\right)\ \mathbf{for\ (oxidation-reduction)\ reaction} = \frac{\mathbf{formula\ weight\ (F.wt)}}{\mathbf{No.\,of\ electrons}}$$

$$(\mathbf{Eq.\,wt})\left(\frac{\mathbf{gm}}{\mathbf{Eq}}\right)\mathbf{for\ salts}\ = \frac{\mathbf{formula\ weight\ (F.wt)}}{\mathbf{No.\,of\ (cations\ or\ anions)} \times \mathbf{charge\ of\ ion}}$$

Example (24):- Calculate the equivalent weight of the following substances:

$$\mathbf{1-(Bases)\ NH_3 + H_2O = NH_4{}^+ + OH^-, Eq\ wt} = \frac{\mathbf{Mwt}}{\mathbf{No.of\ H^+\ or\ OH^-}} = \frac{\mathbf{17.03}}{\mathbf{1}} = \mathbf{17.03}\left(\frac{\mathbf{gm}}{\mathbf{Eq.}}\right)$$

2- (Acids) $H_2C_2O_4$ (in reaction with NaOH) $H_2C_2O_4 + 2NaOH = Na_2C_2O_4 + 2H_2O$

$$\mathbf{Eq\ wt} = \frac{\mathbf{90.049}\left(\frac{\mathbf{gm}}{\mathbf{mol}}\right)}{\mathbf{2}\ \left(\frac{\mathbf{eq}}{\mathbf{mol}}\right)} = \mathbf{45.02}\ \left(\frac{\mathbf{gm}}{\mathbf{Eq}}\right)$$

3- (Oxidizing agents) $KMnO_4$ [Mn^{7+} is reduced to Mn^{2+}]

$$\mathbf{MnO_4^- + 8H^+ + 5e = Mn^{+2} + 4H_2O}$$

$$\mathbf{Eq\ wt} = \frac{\mathbf{M.\,wt}}{\mathbf{No.\,of\ electron}} = \frac{\mathbf{158.04}}{\mathbf{5}} = \mathbf{31.608}\ \left(\frac{\mathbf{gm}}{\mathbf{Eq}}\right)$$

4- (Salts) $Al_2(SO_4)_3$.

$$\mathbf{Al_2(SO_4)_3 \ \rightarrow\ 2Al^{+3} + 3\ SO_4{}^{-2}}$$

$$Eq\ wt = \frac{M.wt}{No.\,of\ (cations\ or\ anions) \times charge\ of\ ion}$$

$$= \frac{\mathbf{342.15}}{|\mathbf{2\times3}|} = \frac{\mathbf{342.15}}{\mathbf{6}} = \mathbf{57}\left(\frac{\mathbf{gm}}{\mathbf{Eq}}\right)$$

5- NaCl - Eq wt = $\frac{M.wt\ (\mathbf{NaCl})}{\mathbf{1}}$

6- $CaCl_2$ - Eq wt = $\frac{M.wt\ (\mathbf{CaCl_2})}{\mathbf{2}}$

7-$AlCl_3$ - Eq wt = $\frac{M.wt\ (\mathbf{AlCl_3})}{\mathbf{3}}$

8 - Na_2CO_3 - Eq wt = $\frac{M.wt\ (\mathbf{Na_2CO_3})}{\mathbf{2}}$

9 – $NaHCO_3$ - Eq wt = $\frac{M.wt\ (NaHCO_3)}{1}$

Normal concentration

Normality (N): ***Number of equivalent solute in solution volume in litre.***

$$Normality\ (N) = \frac{No.of\ equivalent\ solute(eq.)}{Solution\ Volumn\ (L)}$$

$$Normality\ (N) = \frac{\frac{wt(gm)}{Eq.wt\ (\frac{gm}{eq})}}{\frac{V\ (mL)}{1000\ (\frac{mL}{L})}}$$

$$Normality\ (N) = \frac{wt(gm)}{Eq.wt(\frac{gm}{eq.})} \times \frac{1000(\frac{mL}{L})}{V\ (mL)} = \left(\frac{Eq.}{L}\right)$$

$$Normality\ (N) = \left(\frac{Eq.}{L}\right) \Rightarrow \quad Eq. = N \times V(\mathrm{L})$$

$$Normality\ (N) = \frac{No.of\ meq\ solute(meq)}{solution\ volume\ (mL)} = (\frac{meq}{mL})$$

$$Normality\ (N) = \left(\frac{meq}{mL}\right) \Rightarrow \quad meq = N \times V(mL)$$

$$N = (\frac{Eq.}{L}) = (\frac{meq.}{mL})$$

$$\text{Number of equivalent } (Eq) = \frac{\text{wt (gm)}}{\text{Eq. wt} \left(\frac{\text{gm}}{\text{Eq}}\right)}$$

$$\text{Number of equivalent } (Eq) = \text{N} \left(\frac{\text{Eq}}{\text{L}}\right) \times \text{V (L)}$$

$$\text{Number of milliequivalent } (meq) = \frac{\text{wt (mg)}}{\text{Eq. wt } (\frac{\text{mg}}{\text{meq}})}$$

$$\text{Number of milliequivalent } (meq) = \text{N} \left(\frac{\text{meq.}}{\text{mL}}\right) \times \text{V (mL)}$$

Example (25):- Calculate the normality of the solutions containing the following:

(a) 5.300gm/L Na_2CO_3 (when the CO_3^{-2} reacts with two protons),

(b) 5.267 gm/L $K_2Cr_2O_7$ (the Cr^{6+} is reduced to Cr^{3+}).

Solution :(a)

$$Na_2CO_3 \rightarrow 2Na^+ + CO_3^{-2}$$

$$N = \frac{wt}{Eq.wt} \times \frac{1000}{V\ (mL)} = \frac{5.3}{\frac{105.99}{2}} \times \frac{1000}{1000} = 0.10\ Eq/L.$$

(b)

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

$$= \frac{5.267}{\frac{294.19}{6}} \times \frac{1000}{1000} = 0.1074\ Eq/L$$

Example (26):- How many millilitres of a 0.25M solution of H_2SO_4 will react with 10mL of a 0.25M solution of NaOH.

Solution: $H_2SO_4 \longrightarrow 2H^+ + SO_4^{-2} + 2NaOH = Na_2SO_4 + 2H_2O$

$$N = nM\ \left(n = No.\ of\ mol\ equivalent\ \left(\frac{eq}{mol}\right),\ H^+, OH^-, or\ electron\right)$$

$$N_{H_2SO_4} = 2\left(\frac{eq}{mol}\right) \times 0.25\ M\left(\frac{mol}{L}\right) = 0.5\ N\ \left(\frac{Eq}{L}\right) or\ \left(\frac{meq}{mL}\right)$$

$$N_{NaOH} = 1\left(\frac{eq}{mol}\right) \times 0.25\ M\left(\frac{mol}{L}\right) = 0.25\ N\ \left(\frac{Eq}{L}\right) or\ \left(\frac{meq}{mL}\right)$$

$$(N \times V)_{H_2SO_4} = (N \times V)_{NaOH}$$

$$(0.5 \times V)_{H_2SO_4} = (0.25 \times 10)_{NaOH}, \qquad V_{H_2SO_4} = 5.0\ mL$$

Example (27):- A solution contains 3.30 gm of $Na_2CO_3.10H_2O$ in each 15 ml.

1- What is its molarity?

2- What is its normality?

3- How many millilitres of 3.1N acetic acid CH_3COOH will react with 25 ml of the carbonate solution, the reaction doing according to this equation

$$\mathbf{2CH_3COOH \longrightarrow 2CH_3COO^- + 2H^+}$$

$$\mathbf{Na_2CO_3 \longrightarrow 2Na^+ \quad + \quad CO_3^=}$$

$$\mathbf{2H^+ + CO_2^= \longrightarrow H_2O + CO_2}$$

4- How many millilitres of 3.1N H_2SO_4 will react with 25 ml of the carbonate solution, the reaction doing according to this equation

$$\mathbf{H_2SO_4 \longrightarrow SO_4^- + 2H^+}$$

$$\mathbf{Na_2CO_3 \longrightarrow 2Na^+ + CO_3^=}$$

$$\mathbf{2H^+ + CO_2^= \longrightarrow H_2O + CO_2}$$

Solution:

1 – $$\mathbf{M = \frac{wt\ (g)}{M.wt\ (\frac{g}{mol})} \times \frac{1000}{V\ (mL)}}$$

$$\mathbf{M = \frac{3.30}{286\ (\frac{g}{mol})} \times \frac{1000}{15\ (mL)} \quad , \quad M = 0.77M}$$

2- $\mathbf{N = a(eq/mol)\ M(mol/L) = 2 \times 0.77 = 1.53N\ (eq/L)}$

3- $\mathbf{N_1 V_1 = N_2 V_2 \quad , \quad 3.1 \times V_1 = 1.53 \times 25}$

$\mathbf{V_1 = 12.4}$ **ml acetic acid.**

4- $\mathbf{N_1 V_1 = N_2 V_2 \quad , \quad 3.1 \times V_1 = 1.53 \times 25}$

$\mathbf{V_1 = 12.4}$ **ml** $\mathbf{H_2SO_4}$**.**

Example (28):- A solution of sodium carbonate is prepared by dissolving 0.212 gm Na_2CO_3 and diluting to 100mL. Calculate the normality of the solution

(a) if it is used as a monoacidic base.

(b) if it is used as a diacidic base.

Solution:

(**a**) – $$\mathbf{N = \frac{wt}{Eq.wt} \times \frac{1000}{V\,(mL)} = \frac{0.212}{\frac{106.0}{1}} \times \frac{1000}{100} = 0.020\,\frac{meq}{mL}}$$

(**b**) – $$\mathbf{N = \frac{0.212}{\frac{106.0}{2}} \times \frac{1000}{100} = 0.040\ meq/mL}$$

Example (29)*:-* Iodine (I_2) is an oxidizing agent that in reactions with reducing agent is reduced to iodide (I^-). How many grams I_2 would you weigh out to prepare 100mL of a 0.10N I_2 solution?

Solution: $$\mathbf{I_2 + 2e^- \rightarrow 2I^-}$$

$$\mathbf{N = \frac{wt}{Eq.wt} \times \frac{1000}{V\,(mL)}\ , \qquad 0.1 = \frac{wt}{\frac{254}{2}} \times \frac{1000}{100}\ , \qquad wt = 1.27g}$$

Example (30)*:-*Calculate the normality of a solution of 0.25 g/L $H_2C_2O_4$, both as an acid and as a reducing agent.

Solution: **as an acid** $$\mathbf{H_2C_2O_4 + 2NaOH \rightarrow Na_2C_2O_4 + H_2O}$$

as a reducing agent $$\mathbf{{C_2O_4}^{-2} \rightarrow 2CO_2 + 2e^-}$$

$$\mathbf{N = \frac{wt}{Eq.wt} \times \frac{1000}{V\,(mL)} = \frac{0.25g}{\frac{90.04}{2}} \times \frac{1000}{1000} = 0.00555\ \left(\frac{eq}{L}\right) or\ (\frac{meq}{mL})}$$

Example (31)*:-* How many milliequivalents are involved in 43.50 mL of 0.1379 N $K_2Cr_2O_7$?

Solution: $\mathbf{no.\ of\ milliequivalents = N \times V = 0.1379\frac{meq}{mL} \times 43.50\ mL = 5.9987\ meq}$.

Example (32)*:-* What is normality of 0.3 M H_3PO_3 when it undergoes the following reaction ? $\mathbf{H_3PO_3 + 2OH^- \longrightarrow HPO_3^{-2} + 2H_2O}$

Solution: **Normality = a × molarity = 2 × 0.3 = 0.6 N .**

Example (33)*:-* calculate the number of mg present in 1 mL of

a) – 0.3 N H_2SO_4 (Mwt = 98 g/mol) solution.
b) – 0.4 N $Ca(OH)_2$ (Mwt = 74 g/mol) solution.

Solution a-

$$\boldsymbol{Normality\ (N) = \frac{wt(gm)}{Eq.wt(\frac{gm}{eq})} \times \frac{1000}{V\ (mL)} = \left(\frac{Eq.}{L}\right)}$$

$$\boldsymbol{0.3 = \frac{wt(gm)}{(\frac{98}{2})} \times \frac{1000}{1\ mL} \quad \Rightarrow \quad wt(gm) = \frac{49 \times\ 0.3 \times\ 1\ mL}{1000} \quad = 0.0147gm}$$

0.0147 gm × 1000 (mg/gm) = 14.7 mg

Solution another way: $\boldsymbol{Normality\ (N) = \left(\frac{meq}{mL}\right) \Rightarrow \quad meq = N\times V(mL)}$

$$\boldsymbol{meq = N\times V(mL) = 0.3\ \times 1 = 0.3\ meq}$$

$$\mathbf{meq} \ = \left(\frac{\boldsymbol{wt(mg)}}{\boldsymbol{Eq.wt(\frac{mg}{meq})}}\right) \Rightarrow \boldsymbol{wt(mg)} = \mathbf{meq} \times \boldsymbol{Eq.wt\left(\frac{mg}{meq}\right)} = \mathbf{0.3} \times \left(\frac{\mathbf{98}}{\mathbf{2}}\right) = \mathbf{14.7\ mg}$$

In the same way, branch b can be resolved.

Example (34): What volume of a 0.232 N solution contains **(a)** 3.17 meq of solute **(b)** 6.5 eq of solute?

Solution:

(a)

$$\mathbf{N = \frac{No.of\ milliequivalent}{Solution\ Volumn\ (ml)}}$$

$$\mathbf{Solution\ Volumn\ (ml) = \frac{No.\ of\ milliequivalent}{N} = \frac{3.17}{0.232} = 13.7\ ml}$$

$$\mathbf{(b)\quad Solution\ Volumn\ (L) = \frac{No.\ of\ equivalent}{N} = \frac{6.5}{0.232} = 28.0\ L}$$

molal concentration

molality(m):-The solution concentration produce from dissolved solute (mole) in solvent (kg***), molality does not change with temperature and used for physicochemical measurements.***

molality(m):- ***Number moles of solute in mass of solvent by kg.***

$$\mathbf{molality(m)} = \frac{\boldsymbol{No.of\ moles\ solute(moL)}}{\boldsymbol{mass\ of\ solvent\ by\ (kg)}} = \frac{\dfrac{\boldsymbol{wt(gm)}}{\boldsymbol{M.wt}\ (\frac{\boldsymbol{gm}}{\boldsymbol{moL}})}}{\dfrac{\boldsymbol{wt\ (gm)}}{\mathbf{1000}\ (\frac{\boldsymbol{gm}}{\boldsymbol{Kg}})}}$$

$$\mathbf{molality\ (m)} = \frac{\boldsymbol{wt(gm)}}{\boldsymbol{M.wt}\ (\frac{\boldsymbol{gm}}{\boldsymbol{moL}})} \times \frac{\mathbf{1000}(\frac{\boldsymbol{gm}}{\boldsymbol{Kg}})}{\mathbf{wt\ (gm)}}$$

$$\mathbf{molality\ (m)} = \left(\frac{\boldsymbol{No.of\ moL\ solute(moL)}}{\boldsymbol{mass\ of\ solvent(Kg)}}\right) \Rightarrow \boldsymbol{moL = m \times mass\ of\ solvent(Kg)}$$

$$\mathbf{molality\ (m)} = \left(\frac{\boldsymbol{No.of\ mmoL\ solute(mmoL)}}{\boldsymbol{mass\ of\ solvent(g)}}\right) \Rightarrow \boldsymbol{mmoL = m \times mass\ of\ solvent(g)}$$

$$\boldsymbol{m} = \left(\frac{\boldsymbol{mol}}{\boldsymbol{Kg(solvent)}}\right) = \left(\frac{\boldsymbol{mmoL}}{\boldsymbol{gm(solvent)}}\right)$$

Example (41)*:-* Calculate the molal concentration of solution its prepared by dissolve 4 g of NaOH in 500 g of solvent (distilled water).

$$\mathbf{Molality\ (m)} = \frac{\mathbf{wt}}{\mathbf{M.wt}} \times \frac{\mathbf{1000}}{\mathbf{wt\ (g)}} = \frac{\mathbf{4\ g}}{\mathbf{40\ g/mol}} \times \frac{\mathbf{1000}}{\mathbf{500}} = \mathbf{0.2\ m\ (mol/kg)}$$

The relationship between Molarity concentration, molality concentration and density :

$$\left[\mathbf{M} = \frac{\mathbf{md}}{\mathbf{1} + \frac{\mathbf{Mwt}}{\mathbf{1000}}}\right] \quad , \quad \left[\mathbf{m} = \frac{\mathbf{M}}{\mathbf{d} - \frac{\boldsymbol{Mwt}}{\mathbf{1000}}}\right]$$

$$[\mathbf{d} = \mathbf{M}\left(\frac{\mathbf{1}}{\mathbf{m}} + \frac{\mathbf{Mwt}}{\mathbf{1000}}\right)]$$

M = Molarity **,** **m** = molality **, d** = density of solution**, Mwt** = molecular weight of solute

Example (42):- calculate the molality and Molarity concentration of solution consist of 0.5 mole solute in 200 gm of solvent, density of solution is 1.02 (g/mL) and the Mwt of solute (67gm/mol.).

Solution:-

$$\mathbf{molality\ (m)} = \frac{\boldsymbol{wt(gm)}}{\boldsymbol{M.wt}\ (\frac{\boldsymbol{gm}}{\boldsymbol{moL}})} \times \frac{\mathbf{1000}(\frac{\boldsymbol{gm}}{\boldsymbol{Kg}})}{\mathbf{wt\ (gm)}} = \mathbf{0.5} \times \frac{\mathbf{1000}}{\mathbf{200}} = \mathbf{2.5}\ (\frac{\boldsymbol{mol}}{\boldsymbol{kg}})$$

$$\mathbf{(Molarity)M} = \frac{\mathbf{md}}{\mathbf{1+}\frac{\mathbf{Mwt}}{\mathbf{1000}}} = \frac{\mathbf{2.5\times1.02}}{\mathbf{1+(67/1000)}} = \frac{\mathbf{2.55}}{\mathbf{1.067}} = \mathbf{2.39}\ (\frac{\boldsymbol{mol}}{\boldsymbol{L}})$$

Example (43):- calculate the density of solution consist of 15 g solute in 400 gm of solvent, the Molarity of this solution 0.4 M, the Mwt of solute (100 g/moL).

Solution:-

$$\mathbf{molality\ (m)} = \frac{\boldsymbol{wt(gm)}}{\boldsymbol{M.wt}\ (\frac{\boldsymbol{gm}}{\boldsymbol{moL}})} \times \frac{\mathbf{1000}(\frac{\boldsymbol{gm}}{\boldsymbol{Kg}})}{\mathbf{wt\ (gm)}} = \frac{\mathbf{15}}{\mathbf{100}} \times \frac{\mathbf{1000}}{\mathbf{400}} = \mathbf{0.375}(\frac{\boldsymbol{mol}}{\boldsymbol{kg}})$$

$$\mathbf{d} = \mathbf{M}\left(\frac{\mathbf{1}}{\mathbf{m}} + \frac{\mathbf{Mwt}}{\mathbf{1000}}\right) = \mathbf{0.4}\left(\frac{\mathbf{1}}{\mathbf{0.375}} + \frac{\mathbf{100}}{\mathbf{1000}}\right) = \mathbf{1.1067}\ (\frac{\boldsymbol{g}}{\boldsymbol{mL}})$$

Example (44):- The molality of a solution of ethanol, C_2H_5OH, in water is 1.54 m. How many gm of ethanol is dissolved in 2.50 kg water?

Solution:-

Molality $= \left(\frac{\text{mole}}{\text{wt(kg)}}\right)$ → **mole = 2.50 × 1.54 = 3.85 mol**

and mass of ethanol = mole × M.wt → **3.85 × 46.1 = 177 gm**

Formal concentration

(Formality) F: - Chemists sometime use the term formality for solutions of ionic salts that do not exist as molecules in the solid or in solution. The concentration is given as formal (F). Formality is numerically the same as molarity.

$$F = \frac{wt\ (g)}{F.wt\ (\frac{g}{mol})} \times \frac{1000}{V\ (mL)}$$

The term use for solutions of ionic salts that do not exist as molecules in the solid or in solution. ***Operationally, formality is identical to molarity.***

Example (20): Exactly **4.57** g of **$BaCl_2.2H_2O$** are dissolved in sufficient water to give **250mL** of solution. Calculate the formal concentration of **$BaCl_2$** and **Cl^-** in this solution.

Solution:

$$F_{BaCl_2} = \frac{wt}{Fwt} \times \frac{1000}{V\ (mL)} = \frac{4.57}{244} \times \frac{1000}{250} = 0.0749\ F\ \mathrm{BaCl_2.2H_2O}$$

$$BaCl_2 \quad \rightarrow \quad Ba^{2+} \quad + \quad 2Cl^-$$

$$0.0749F \qquad 0.0749F \qquad 0.0749F \times 2 = 0.149F\ Cl^-$$

Example (21):-Prepare **500**mL of **0.010 F** solution of **Na^+** from **Na_2CO_3**.

Solution:

$$Na_2CO_3 \rightarrow 2Na^+ + CO_3^{2-}$$

$$(0.05)F = \frac{0.01}{2} \qquad 0.01F$$

$$F_{Na_2CO_3} = \frac{wt}{F.wt} \times \frac{1000}{V(mL)} \quad , \quad 0.005 = \frac{wt}{106} \times \frac{1000}{500}$$

$$2 \times wt = 0.005 \times 106 \quad , \quad wt = \frac{0.005 \times 106}{2} = 0.265\ g\ Na_2CO_3$$

Equilibrium Molarity

Equilibrium Molarity **:**The equilibrium molarity expresses the molar concentration of a particular species in a solution at equilibrium. To state the species molarity, it is necessary to know how the solute behaves when it is dissolved in a solvent. For example, the species molarity of **H_2SO_4** in a solution with an analytical concentration of **1.0 M** is **0.0** M because the sulfuric acid is entirely dissociated into a mixture of **H^+**, **HSO_4^-**, and **SO_4^{2-}** ions; essentially no H_2SO_4 molecules as such are present in this solution. The equilibrium concentrations and thus the species molarity of these three ions are **1.01**, **0.99**, and **0.01** M, respectively.

Example (22):- Calculate the formal concentration of: (a) an aqueous solution that contains **1.80g of ethanol** in **750mL**. (b) An aqueous solution that contains **365mg** of iodic acid **HIO_3** in **20.0mL** (the acid is **71.0%** ionized in this solution).

Solution: **(a)**

$$F_{ethanol} = \frac{wt}{Fwt} \times \frac{1000}{(V)\ mL} = \frac{1.80}{46.1} \times \frac{1000}{750} = 0.0521\ F\ C_2H_5OH$$

The only solute species present in significant amount in an aqueous solution of ethanol is **C_2H_5OH**, therefore; $M = F = 0.0521$

(b)

$$F = \frac{wt(g)}{Fwt} \times \frac{1000}{(V)\ mL} = \frac{\frac{365(mg)}{1000(\frac{mg}{g})}}{176} \times \frac{1000}{20} = 0.104\ F$$

Here, only **29.0%** (**100% - 71.0%** = **29.0%**) of the solute exists as un dissociated **HIO_3**. Thus, the molar concentration of this species will be:

$$\frac{29.0}{100} \times 0.104F = 0.0302M\ HIO_3$$

Example (23):- Calculate the analytical and equilibrium molar concentration of the solute species in an aqueous solution that contains 285 mg of trichloroacetic acid, Cl_3CCOOH (Fwt=163.4) in 10.0mL (the acid is 73% ionized in water). Employing HA as the symbol for Cl_3CCOOH, we substitute into equation (law) to obtain the analytical or total concentration of the acid.

Solution:

$$(\mathbf{Total\ conc.\ of\ HA})\ \mathbf{C_{HA}} = \frac{\mathbf{wt(g)}}{\mathbf{F.wt}} \times \frac{\mathbf{1000}}{\mathbf{(V)\ mL}} = \frac{\frac{\mathbf{285(mg)}}{\mathbf{1000(\frac{mg}{g})}}}{\mathbf{163.4}} \times \frac{\mathbf{1000}}{\mathbf{10}} = \mathbf{0.174\ F\ (HA)}$$

Because all but 27% of the acid is undissociated into H_3O^+ and A^-, the species concentration of HA is:

$$\mathbf{[HA] = C_{HA}(0.174\ F) \times \frac{27.0}{100} = 0.047M}$$

The molarity of H_3O^+ as well as that of A^- equal to the analytical concentration of the acid minus the species concentration of dissociated acid.

$$\mathbf{[H_3O^+] = [A^-] = 0.174 - 0.047 = 0.127\ M}$$

Note: the analytical concentration of HA is the sum of the species concentration of HA and A^- $\mathbf{C_{HA} = [HA] + [A^-] = [HA] + [H_3O^+]}$

Concentration by percent

A – $$\mathbf{\left(\frac{wt}{wt}\%\right) = \frac{wt\ solute\ (g)}{wt\ solution\ or\ sample\ (g)} \times 100}$$

$$\mathbf{\left(\frac{wt}{wt}\%\right) = \frac{wt\ solute\ (\cancel{g})}{wt\ solution\ or\ sample\ (g)} \times \left(\frac{100cg}{\cancel{g}}\right) = (\frac{cg}{g})}$$

$$\mathbf{\left(\frac{wt}{wt}\%\right) = \frac{wt\ solute\ (mg)}{wt\ solution\ or\ sample\ (mg)} \times 100}$$

$$\mathbf{\left(\frac{wt}{wt}\%\right) = \frac{wt\ solute\ (kg)}{wt\ solution\ or\ sample\ (kg)} \times 100}$$

B – $$\mathbf{\left(\frac{wt}{V}\%\right) = \frac{wt\ solute\ (g)}{V\ solution\ or\ sample\ (mL)} \times 100}$$

$$\mathbf{\left(\frac{wt}{V}\%\right) = \frac{wt\ solute\ (\cancel{g})}{V\ solution\ or\ sample\ (mL)} \times \left(\frac{100cg}{\cancel{g}}\right) = (\frac{cg}{mL})}$$

$$\left(\frac{\mathbf{wt}}{\mathbf{V}}\%\right)=\frac{\mathbf{wt\ solute\ (mg)}}{\mathbf{V\ solution\ or\ sample\ (\mu L)}}\times\mathbf{100}$$

$$\mathbf{C}-\qquad\left(\frac{\mathbf{V}}{\mathbf{V}}\%\right)=\frac{\mathbf{V\ solute\ (mL)}}{\mathbf{V\ solution\ or\ sample\ (mL)}}\times\mathbf{100}$$

$$\left(\frac{\mathbf{V}}{\mathbf{V}}\%\right)=\frac{\mathbf{V\ solute\ (L)}}{\mathbf{V\ solution\ or\ sample\ (L)}}\times\left(\frac{\mathbf{100cL}}{\mathbf{L}}\right)=\left(\frac{\mathbf{cL}}{\mathbf{L}}\right)$$

$$\left(\frac{\mathbf{V}}{\mathbf{V}}\%\right)=\frac{\mathbf{V\ solute\ (\cancel{L})}}{\mathbf{V\ solution\ or\ sample\ (L)}}\times\left(\frac{\mathbf{100cL}}{\cancel{\mathbf{L}}}\right)=\left(\frac{\mathbf{cL}}{\mathbf{L}}\right)$$

$$\left(\frac{\mathbf{V}}{\mathbf{V}}\%\right)=\frac{\mathbf{V\ solute\ (\mu L)}}{\mathbf{V\ solution\ or\ sample\ (\mu L)}}\times\mathbf{100}$$

Example(35)*:-*Calculate the weight percentage of solution prepare by mixing 5.0g $AgNO_3$ with 100mL water (density of water $1g/cm^3$).

Solution:

$$\left(\frac{\mathbf{wt}}{\mathbf{wt}}\%\right)=\frac{\mathbf{wt\ solute\ (g)}}{\mathbf{wt\ solution\ (g)}}\times\mathbf{100}$$

$$\left(\frac{\mathbf{wt}}{\mathbf{wt}}\%\right)=\frac{\mathbf{wt\ solute\ (AgNO_3)(g)}}{\mathbf{wt\ solute+wt\ solvent\ (H_2O)\ (g)}}\times\mathbf{100}$$

$$\left(\frac{\mathbf{wt}}{\mathbf{wt}}\%\right)=\frac{\mathbf{5\ g}}{\mathbf{5\ g+(100\ mL\times 1\frac{g}{mL})}}\times\mathbf{100}=\frac{\mathbf{5\ g}}{\mathbf{105\ g}}\times\mathbf{100}=\mathbf{4.76}\%\left(\frac{\mathbf{wt}}{\mathbf{wt}}\right)=\mathbf{4.76}\left(\frac{\mathbf{cg}}{\mathbf{g}}\right)$$

Example (36)*:-* Calculate number of grams in 500mL silane solution (wt/v%)= (0.859%).

Solution:

$$\left(\frac{\mathbf{wt}}{\mathbf{V}}\%\right)=\frac{\mathbf{wt\ solute\ (g)}}{\mathbf{V\ solution\ (mL)}}\times\mathbf{100}$$

$$\mathbf{0.859}\ \%=\frac{\mathbf{wt\ NaCl\ (g)}}{\mathbf{500mL}}\times\mathbf{100}$$

$$\mathbf{wt\ NaCl}=\frac{\mathbf{0.859\times 500}}{\mathbf{100}}=\mathbf{4.295\ g\ NaCl}$$

Solution another way: **The percent concentration = 0.859 $\left(\frac{cg}{mL}\right)$ × V(mL)**

$$= \mathbf{0.859} \left(\frac{cg}{mL}\right) \times \mathbf{500(mL) = 429.5\ cg} \times \left(\frac{1g}{100cg}\right) = \mathbf{4.295\ g\ NaCl}$$

Example (37):-Calculate the weight of glucose in litter solution (wt /v %) = 5 %.

Solution:

$$\left(\frac{\mathbf{wt}}{\mathbf{V}}\%\right) = \frac{\mathbf{wt\ solute\ (g)}}{\mathbf{V\ solution\ (mL)}} \times \mathbf{100} = \frac{\mathbf{wt\ glucose\ (g)}}{\mathbf{V\ solution\ (mL)}} \times \mathbf{100}$$

$$\mathbf{5\%} = \frac{\mathbf{wt\ glucose\ (g)}}{\mathbf{1000\ (mL)}} \times \mathbf{100} \quad , \quad \mathbf{wt\ glucose} = \frac{\mathbf{5 \times 1000}}{\mathbf{100}} = \mathbf{50\ gm}$$

Solution another way: **The percent concentration** = $\mathbf{5} \left(\frac{cg}{mL}\right) \times \mathbf{V(mL)}$

$$= \mathbf{5} \left(\frac{cg}{mL}\right) \times \mathbf{1000(mL) = 5000\ cg} \times \left(\frac{1g}{100cg}\right) = \mathbf{50\ gm}$$

Example (38)*:-* Calculate the volume percentage of solution preparing by mixing 50mL methyl alcohol with water to give 250mL of solution.

Solution:

$$\left(\frac{\mathbf{V}}{\mathbf{V}}\%\right) = \frac{\mathbf{V\ solute\ (mL)}}{\mathbf{V\ solution\ or\ sample\ (mL)}} \times \mathbf{100}$$

$$= \frac{\mathbf{50\ mL}}{\mathbf{250mL}} \times \mathbf{100} = \mathbf{20} \left(\%\frac{\mathbf{V}}{\mathbf{V}}\right) = \mathbf{20} \left(\frac{cL}{L}\right)$$

Example (39):-Calculate the volume of ethanol in litter solution cconsists of ethanol and water **0.9** (%$\frac{\mathbf{V}}{\mathbf{V}}$**)**.

Solution:

$$\left(\frac{\mathbf{V}}{\mathbf{V}}\%\right) = \frac{\mathbf{V\ solute\ (mL)}}{\mathbf{V\ solution\ (mL)}} \times \mathbf{100} = \frac{\mathbf{V\ ethanol(mL)}}{\mathbf{V\ solution\ (mL)}} \times \mathbf{100}$$

$$\mathbf{0.9\%} = \frac{\mathbf{V\ ethanol(mL)}}{\mathbf{1000\ (mL)}} \times \mathbf{100} \quad , \quad \mathbf{V\ ethanol} = \frac{\mathbf{0.9 \times 1000}}{\mathbf{100}} = \mathbf{9\ mL}$$

Solution another way: **The volume percent concentration** = $\mathbf{0.9} \left(\frac{cL}{L}\right) \times \mathbf{V(L)}$

$$\mathbf{V\ ethanol = 0.9} \left(\frac{cL}{L}\right) \times \mathbf{1\ (L) = 0.9\ cL} \times \left(\frac{10mL}{1cL}\right) = \mathbf{9\ mL}$$

Example (40):- A 12.5% (w/w) $NiCl_2$ (Mwt = 129.61 g/mol) solution has a density of 1.149 g/mL Calculate **(a)** the molar concentration of $NiCl_2$ in this solution.

(b) The mass in grams of $NiCl_2$ contained in each liter of this solution.

Solution (a) –

$$M = \frac{\% \left(\frac{wt}{wt}\right) \times (density) \times 1000}{M.wt} = \frac{\frac{12.5}{100} \times 1.149 \times 1000}{129.61} = 1.1081\ M$$

Solution another way: $M = \dfrac{12.5\left(\frac{cg}{g}\right)\times\left(\frac{1g}{100cg}\right)\times 1.149\ \left(\frac{g}{mL}\right)\times 1000\left(\frac{mL}{L}\right)}{129.61\left(\frac{g}{mol}\right)} = 1.1081\left(\frac{mol}{L}\right)$

$$M = \frac{12.5\left(\frac{\cancel{cg}}{\cancel{g}}\right)\times\left(\frac{1\cancel{g}}{100\cancel{cg}}\right)\times 1.149\ \left(\frac{\cancel{g}}{\cancel{mL}}\right)\times 1000\left(\frac{\cancel{mL}}{L}\right)}{129.61\left(\frac{\cancel{g}}{mol}\right)} = 1.1081\left(\frac{mol}{L}\right)$$

Solution (b) –

$$wt\ (g) in\ Liteer\ of\ solution\ = M \times M.wt\ =$$

$$wt\left(\frac{g}{L}\right) = M\left(\frac{mol}{L}\right) \times 129.61\left(\frac{g}{mol}\right) == 143.625\left(\frac{g}{L}\right)$$

Solution another way: $C\left(\frac{g}{L}\right) = \left(\frac{wt}{wt}\right)\% \times \left(\frac{1}{100}\right) \times\ \mathbf{d}\left(\frac{g}{mL}\right) \times \left(\frac{1000}{1}\right)\ =$

$$wt_{(g)} = 12.5\left(\frac{cg}{g}\right) \times \left(\frac{1g}{100cg}\right) \times\ 1.149\left(\frac{g}{mL}\right) \times \left(\frac{1000ml}{1L}\right) = 143.625\ g\ /L$$

$$wt_{(g)} = 12.5\left(\frac{\cancel{cg}}{\cancel{g}}\right) \times \left(\frac{1\cancel{g}}{100\cancel{cg}}\right) \times\ 1.149\left(\frac{g}{\cancel{mL}}\right) \times \left(\frac{1000\cancel{ml}}{1L}\right) = 143.625\ g\ /L$$

Problems 4

Q1- Change 0.1 M NaCl to wt/v%.

Q2- Change 0.2 N NaCl to, g/mL.

Q3- Change 0.3 M NaCl to mg/Kg, (Mwt Na = 23g/mol , Cl = 35.5 g/mol).

Mole fraction concentration (X)

Mole fraction concentration (X):- The ratio between number of mole for solute or solvent to solution, the terms used in physical chemistry (phases equilibrium for example). **Note** the molar fraction without units.

$$\textbf{Mole fraction for solute } (\mathbf{X_1}) = \frac{\textbf{no. mole solute } (\mathbf{n_1})}{\textbf{no. mole solute } (\mathbf{n_1}) + \textbf{no. mole solvent } (\mathbf{n_2})}$$

$$\textbf{Mole fraction for solvent } (\mathbf{X_2}) = \frac{\textbf{no. mole solvent}}{\textbf{no. mole solute } (\mathbf{n_1}) + \textbf{no. mole solvent } (\mathbf{n_2})}$$

Example (45):- One litter of acetic acid solution contain 80.8 g of acetic acid, the solution density 1.00978 **g/cm^3** or **g/mL**. (**cm^3 = mL**) calculate the mole fraction (X_1) for the solute and mole fraction (X_2) for the solvent in this solution

Solution:

$$\textbf{Mole fraction for solute } (\mathbf{X_1}) = \frac{\textbf{no. mole solute } (\mathbf{n_1})}{\textbf{no. mole solute } (\mathbf{n_1}) + \textbf{no. mole solvent } (\mathbf{n_2})}$$

$$= \frac{\left(\frac{\mathbf{wt(g)}}{\mathbf{M.wt}(\frac{\mathbf{g}}{\mathbf{mol}})}\right)_{\mathbf{CH_3COOH}}}{\left(\frac{\mathbf{wt(g)}}{\mathbf{M.wt}(\frac{\mathbf{g}}{\mathbf{mol}})}\right)_{\mathbf{CH_3COOH}} + \frac{\left(\textbf{density of solution } \left(\frac{\mathbf{g}}{\mathbf{mL}}\right) \times \textbf{volume of solution}(\mathbf{mL}) - \textbf{wt of solute}(\mathbf{g})\right)}{(\textbf{Mwt of Solvent } (\frac{\mathbf{g}}{\mathbf{mol}}))}}$$

$$= \frac{\frac{80.8}{60}}{\frac{80.8}{60} + \left(\frac{(1.009791 \times 1000) - 80.8}{18}\right)} = \frac{\frac{80.8}{60}}{\frac{80.8}{60} + \left(\frac{1009.791 - 80.8}{18}\right)} = \frac{\frac{80.8}{60}}{\frac{80.8}{60} + \left(\frac{929}{18}\right)}$$

$$= \frac{\mathbf{1.35}}{\mathbf{1.35 + 51.6}} = \frac{\mathbf{1.35}}{\mathbf{52.95}} = \mathbf{0.025}$$

$$\textbf{Mole fraction for solvent } (\mathbf{X_2}) = \frac{\textbf{no. mole solvent}}{\textbf{no. mole solute } (\mathbf{n_1}) + \textbf{no. mole solvent } (\mathbf{n_2})}$$

$$\frac{\left(\frac{1.009791\left(\frac{g}{mL}\right) \times 1000mL - 80.8\,g}{18\left(\frac{g}{mol}\right)}\right)}{\frac{80.8(g)}{60\left(\frac{g}{mol}\right)} + \left(\frac{1.009791\left(\frac{g}{mL}\right) \times 1000mL - 80.8\,g}{18\left(\frac{g}{mol}\right)}\right)} = \frac{\left(\frac{(1.009791 \times 1000) - 80.8}{18}\right)}{\frac{80.8}{60} + \left(\frac{(1.009791 \times 1000) - 80.8}{18}\right)} =$$

$$= \frac{\left(\frac{1009.791 - 80.8}{18}\right)}{\frac{80.8}{60} + \left(\frac{1009.791 - 80.8}{18}\right)} = \frac{\left(\frac{929}{18}\right)}{\frac{80.8}{60} + \left(\frac{929}{18}\right)} = \frac{\mathbf{51.6}}{\mathbf{1.35 + 51.6}} = \frac{\mathbf{51.6\ mol}}{\mathbf{52.95\ mol}} = \mathbf{0.975}$$

$$\mathbf{X_1 + X_2 = 1\ unit = 0.025 + 0.975 = 1.00\ unit}$$

The mole fraction - for a homogeneous solution consisting of three compounds A, B, and C is (X_1) for compound A and (X_2) for compound B and (X_3) for compound C .

Example (46):-A solution contains 116 gm acetone (CH_3COCH_3) , 138 gm ethyl alcohol (C_2H_5OH) , and 126 gm water . Determine the mole fraction of each ?

Solution -

$\textbf{Mol}_{\text{acetone}} = \textbf{wt / M.wt} \longrightarrow \textbf{116 / 58.0 = 2.0 mol}$

$\textbf{Mol}_{\text{C2H5OH}} = \textbf{wt / M.wt} \longrightarrow \textbf{138 / 46.0 = 3.0mol}$

$\textbf{Mol}_{\text{water}} = \textbf{wt / M.wt} \longrightarrow \textbf{126 / 18 = 7.0 mol}$

Sum of mole = 2.0 + 3.0 + 7.0 = 12.0 mole

$$\textbf{Mole fraction for } (\mathbf{X}) = \frac{\textbf{no.mole solute}}{\textbf{sum of mole}}$$

$$\textbf{Mole fraction for acetone}(\mathbf{X_1}) = \frac{\mathbf{2.0\ mole}}{\mathbf{12.0\ mole}} = \mathbf{0.167}$$

$$\textbf{Mole fraction for } \mathbf{C_2H_5OH(X_2)} = \frac{\mathbf{3.0\ mole}}{\mathbf{12.0\ mole}} = \mathbf{0.250}$$

$$\textbf{Mole fraction for water}(\mathbf{X_3}) = \frac{\mathbf{7.0\ mole}}{\mathbf{12.0\ mole}} = \mathbf{0.583}$$

$$\mathbf{X_1+X_2+X_3= 1 \quad , \qquad 0.167 + 0.250 + 0.583 = 1}$$

The relationship between molarity and normality with percentage concentration

Example (47):-Calculate the molar and normal concentration for 0.85% (w/v%) sodium chloride solution.

$$\mathbf{M} = \frac{\textbf{wt (g)}}{\textbf{M.wt}} \times \frac{\mathbf{1000}}{\textbf{V mL}} = \frac{\textbf{wt (g)}}{\textbf{M.wt}} \times \frac{\mathbf{1000}}{\mathbf{100}} = \frac{\textbf{wt}}{\textbf{V}}\% \times \frac{\mathbf{1000}}{\textbf{M.wt}}$$

$$\mathbf{M} = \frac{\mathbf{0.85}}{\mathbf{100}} \times \frac{\mathbf{1000}}{\mathbf{58.5}} = \mathbf{0.145M}$$

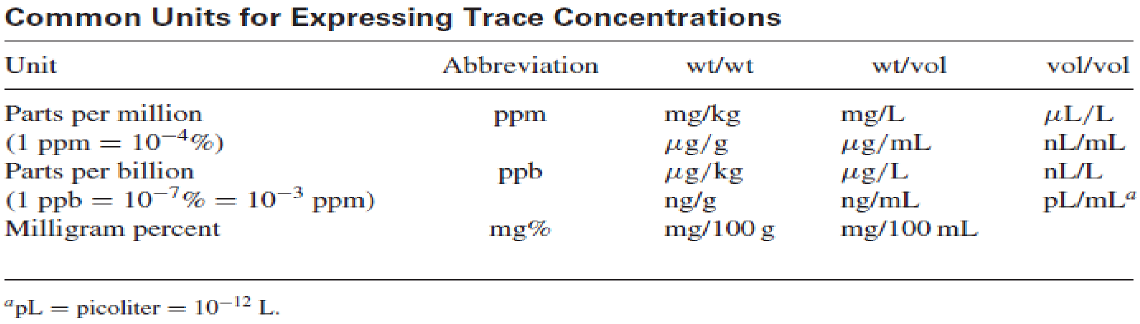
$$\mathbf{N = n \times M = 1 \times 0.145 = 0.145\ N}$$

- Concentration in parts per thousand or million or billion:-

$$\text{part per thousand (ppt)}\left(\frac{\text{wt}}{\text{wt}}\right)=\frac{\text{wt solute (g)}}{\text{wt solution (sample)(g)}}\times 10^{3}=\frac{\text{wt (mg)}}{\text{wt (g)}}=\frac{\text{wt (g)}}{\text{wt (kg)}}$$

$$\text{part per million (ppm)}\left(\frac{\text{wt}}{\text{wt}}\right)=\frac{\text{wt solute (g)}}{\text{wt solution (sample)(g)}}\times 10^{6}=\frac{\text{wt (μg)}}{\text{wt (g)}}=\frac{\text{wt (mg)}}{\text{wt (kg)}}$$

$$\text{part per billion (ppb)}\left(\frac{\text{wt}}{\text{wt}}\right)=\frac{\text{wt solute (g)}}{\text{wt solution (sample)(g)}}\times 10^{9}=\frac{\text{wt (ng)}}{\text{wt (g)}}=\frac{\text{wt (μg)}}{\text{wt (kg)}}$$



Common Units for Expressing Trace Concentrations

Unit	Abbreviation	wt/wt	wt/vol	vol/vol
Parts per million (1 ppm = 10^{-4}%)	ppm	mg/kg μg/g	mg/L μg/mL	μL/L nL/mL
Parts per billion (1 ppb = 10^{-7}% = 10^{-3} ppm)	ppb	μg/kg ng/g	μg/L ng/mL	nL/L pL/mL[a]
Milligram percent	mg%	mg/100 g	mg/100 mL	

[a] pL = picoliter = 10^{-12} L.

Divisions of volume unit

$$1\text{L} = 10\text{dL} = 10^{2}\text{cL} = 10^{3}\text{mL} = 10^{6}\mu\text{L} = 10^{9}\text{nL} = 10^{12}\ \text{pL}$$

Divisions of mass unit

$$1\text{g} = 10\text{dg} = 10^{2}\ \text{cg} = 10^{3}\text{mg} = 10^{6}\mu\text{g} = 10^{9}\text{ng} = 10^{12}\ \text{pg}$$

Example (48):- A 2.6 g sample of plant tissue was analyzed and found to contain 3.6 μg zinc, what is the concentration of zinc in the plant in ppm? in ppb?

$$\text{ppm}=\frac{\text{wt (μg)}}{\text{wt (g)}}=\frac{3.6\ \text{μg}}{2.6\ \text{g}}=1.4\frac{\text{μg}}{\text{g}}=1.4\ \text{ppm}$$

$$\text{ppb}=\frac{\text{wt (ng)}}{\text{wt (g)}}=\frac{3.6\ \times 10^{3}\text{ng}}{2.6\ \text{g}}=1.4\times 10^{3}\frac{\text{ng}}{\text{g}}=1400\ \text{ppb}$$

$$\text{part per thousand (ppt)}\ \left(\frac{\text{wt}}{\text{V}}\right)=\frac{\text{wt solute (g)}}{\text{V solution (sample)(mL)}}\times 10^{3}=\frac{\text{wt (mg)}}{\text{V (mL)}}=\frac{\text{wt (g)}}{\text{V (L)}}$$

$$\textbf{part per million (ppm)}\ (\frac{\text{wt}}{\text{V}}) = \frac{\text{wt solute (g)}}{\text{V solution (sample)(mL)}} \times 10^{6} = \frac{\text{wt }(\mu\text{g})}{\text{V (mL)}} = \frac{\text{wt (mg)}}{\text{V (L)}}$$

$$\textbf{part per billion (ppb)}\ \left(\frac{\text{wt}}{\text{V}}\right) = \frac{\text{wt solute (g)}}{\text{V solution (sample)(mL)}} \times 10^{9} = \frac{\text{wt (ng)}}{\text{V (mL)}} = \frac{\text{wt }(\mu\text{g})}{\text{V (L)}}$$

$$\textbf{part per trillion (ppt)}\ \left(\frac{\text{wt}}{\text{V}}\right) = \frac{\text{wt solute (g)}}{\text{V solution (sample)(mL)}} \times 10^{12} = \frac{\text{wt (pg)}}{\text{V (mL)}} = \frac{\text{wt (ng)}}{\text{V (L)}}$$

Example (49-A):- A 25.0 μL serum sample was analyzed for glucose content and found to contain 26.7 μg. Calculate the concentration of glucose in ppm and in mg/dL.

Solution: *Note: 1dL = 100 mL*

$$\text{ppm} = \frac{\text{wt }(\mu\text{g})}{\text{V (mL)}} = \frac{26.7\ (\mu\text{g})}{\frac{25.0\ (\mu\text{L})}{1000\ (\frac{\mu\text{L}}{\text{mL}})}} = \frac{26.7\ (\mu\text{g})}{0.025\ (\text{mL})}$$

$$= 1.07 \times 10^{3}\ (\frac{\mu\text{g}}{\text{mL}}) = 1.07 \times 10^{3}\ \text{ppm}$$

$$\frac{\text{wt (mg)}}{\text{V (dL)}} = \frac{26.7\ \mu\text{g} \times 10^{-3}\,\frac{\text{mg}}{\mu\text{g}}}{25\ \mu\text{L} \times 10^{-5}\,\frac{\text{dL}}{\mu\text{L}}} = 107\ \text{mg/dL}$$

Example (49-B):- prove the

$$\textbf{part per million (ppm)}\ \left(\frac{\text{wt}}{\text{V}}\right) = \frac{\text{wt solute (g)}}{\text{V solution (sample)(mL)}} \times 10^{6} = \frac{\text{wt }(\mu\text{g})}{\text{V (mL)}} = \frac{\text{wt (mg)}}{\text{V (L)}}$$

Solution:

$$\textbf{part per million (ppm)}\ \left(\frac{\text{wt}}{\text{V}}\right) = \frac{\text{wt solute (g)}}{\text{V solution (sample)(mL)}} \times 10^{3} \times 10^{3} =$$

$$(\text{ppm})\left(\frac{\text{wt}}{\text{V}}\right) = \frac{\text{wt solute (g)}}{\text{V solution (sample)(mL)}} \times (\frac{10^{3}\text{mg}}{\text{g}}) \times (\frac{10^{3}\mu\text{g}}{\text{mg}}) = \frac{\text{wt }(\mu\text{g})}{\text{V (mL)}}$$

$$(\text{ppm})\left(\frac{\text{wt}}{\text{V}}\right) = \frac{\text{wt solute }\cancel{(\text{g})}}{\text{V solution (sample)(mL)}} \times (\frac{10^{3}\cancel{\text{mg}}}{\cancel{\text{g}}}) \times (\frac{10^{3}\mu\text{g}}{\cancel{\text{mg}}}) = \frac{\text{wt }(\mu\text{g})}{\text{V (mL)}}$$

$$(\text{ppm})\left(\frac{\text{wt}}{\text{V}}\right) = \frac{\text{wt solute (g)}}{\text{V solution (sample)(mL)}} \times (\frac{10^{3}\text{mg}}{\text{g}}) \times (\frac{10^{3}\text{mL}}{\text{L}}) = \frac{\text{wt (mg)}}{\text{V (L)}}$$

$$(\text{ppm})\left(\frac{\text{wt}}{\text{V}}\right) = \frac{\text{wt solute }\cancel{(\text{g})}}{\text{V solution (sample)}\cancel{(\text{mL})}} \times (\frac{10^{3}\text{mg}}{\cancel{\text{g}}}) \times (\frac{10^{3}\cancel{\text{mL}}}{\text{L}}) = \frac{\text{wt (mg)}}{\text{V (L)}}$$

$$part\ per\ thousand\ (ppt)\ (\frac{\mathrm{v}}{\mathrm{V}}) = \frac{v\ solute\ (mL)}{V\ solution\ (sample)(mL)} \times 10^3 = \frac{V\ (\mu L)}{V\ (mL)} = \frac{V\ (mL)}{V\ (L)}$$

$$part\ per\ million\ (ppm)\ (\frac{\mathrm{v}}{\mathrm{V}}) = \frac{v\ solute\ (mL)}{V\ solution\ (sample)(mL)} \times 10^6 = \frac{V\ (nL)}{V\ (mL)} = \frac{V\ (\mu L)}{V\ (L)}$$

$$part\ per\ billion\ (ppb)\ (\frac{\mathrm{v}}{\mathrm{V}}) = \frac{v\ solute\ (mL)}{V\ solution\ (sample)(mL)} \times 10^9 = \frac{V\ (pL)}{V\ (mL)} = \frac{V\ (nL)}{V\ (L)}$$

The relationship between molarity, normality and part per million

$$M = \frac{ppm(\frac{wt}{v})}{M.wt\ \times 1000} = \frac{ppm(\frac{mg}{L})}{M.wt(\frac{g}{mol})\ \times 1000(\frac{mg}{g})} = \left(\frac{mol}{L}\right) = (\frac{mmol}{mL})$$

$$M = \frac{ppm(\frac{wt}{v})}{M.wt\ \times 1000} = \frac{ppm(\frac{\cancel{mg}}{L})}{M.wt(\frac{\cancel{g}}{mol})\ \times 1000(\frac{\cancel{mg}}{\cancel{g}})} = \left(\frac{mol}{L}\right) = (\frac{mmol}{mL})$$

$$N = \frac{ppm(\frac{wt}{v})}{Eq.wt\ \times 1000} = \frac{ppm(\frac{mg}{L})}{Eq.wt\ (\frac{g}{eq})\ \times 1000(\frac{mg}{g})} = \left(\frac{eq}{L}\right) = (\frac{meq}{mL})$$

$$N = \frac{ppm(\frac{wt}{v})}{Eq.wt\ \times 1000} = \frac{ppm(\frac{\cancel{mg}}{L})}{Eq.wt\ (\frac{\cancel{g}}{eq})\ \times 1000(\frac{\cancel{mg}}{\cancel{g}})} = \left(\frac{eq}{L}\right) = (\frac{meq}{mL})$$

$$\mathbf{ppm\ =\ M \times\ } M.wt\ \times 1000$$

$$ppm\left(\frac{mg}{L}\right) = M\left(\frac{mol}{L}\right) \times\ M.wt\ \left(\frac{g}{mol}\right) \times 1000\left(\frac{mg}{g}\right) = \left(\frac{mg}{L}\right)$$

$$ppm\left(\frac{mg}{L}\right) = M\left(\frac{\cancel{mol}}{L}\right) \times M.wt\left(\frac{\cancel{g}}{\cancel{mol}}\right) \times 1000\left(\frac{mg}{\cancel{g}}\right) = \left(\frac{mg}{L}\right)$$

$$\mathbf{ppm = N \times \mathit{Eq.wt} \times 1000}$$

$$ppm\left(\frac{mg}{L}\right) = N\left(\frac{Eq}{L}\right) \times Eq.wt\left(\frac{g}{Eq}\right) \times 1000\left(\frac{mg}{g}\right) = \left(\frac{mg}{L}\right)$$

$$ppm\left(\frac{mg}{L}\right) = N\left(\frac{\cancel{Eq}}{L}\right) \times Eq.wt\left(\frac{\cancel{g}}{\cancel{Eq}}\right) \times 1000\left(\frac{mg}{\cancel{g}}\right) = \left(\frac{mg}{L}\right)$$

Example (50):- (a) Calculate the molar conc. of 1.0 ppm solutions each of Li^+ and Pb^{+2}.(b) What weight of $Pb(NO_3)_2$ will have to be dissolved in 1 liter of water to prepare a 100 ppm Pb^{+2} solution.

Solution:

$$\mathbf{M = \frac{ppm}{M.wt \times 1000}}$$

(a)

$$\mathbf{M_{Li^+} = \frac{1.0}{6.94 \times 1000} = 1.44 \times 10^{-4}\ mole/L}$$

$$\mathbf{M_{Pb^{+2}} = \frac{1.0}{207 \times 1000} = 4.83 \times 10^{-6}\ mole/L}$$

(b)

$$\mathbf{M = \frac{100}{207 \times 1000} = 4.83 \times 10^{-4}\ mole/L}$$

$$\mathbf{M = \frac{wt}{M.wt} \times \frac{1000}{V\ (mL)}}$$

$$\mathbf{4.83 \times 10^{-4} = \frac{wt}{283.2} \times \frac{1000}{1000} \qquad wt = 0.137g\ Pb(NO_3)_2}$$

Example (51):-The concentration of Zinc ion (Zn^{+2}) in blood serum is about (1ppm). Express this as meq/L.

$$N = \frac{ppm}{Eq.wt \times 1000} = \frac{ppm}{\frac{A.wt}{2} \times 1000} = \frac{1}{\frac{65.4}{2} \times 1000} = 3.06 \times 10^{-5}\ Eq/L$$

$$= 3.06 \times 10^{-5}\left(\frac{Eq}{L}\right) \times 1000\left(\frac{meq}{Eq}\right) = 3.06 \times 10^{-2}\ meq/L$$

Problems

Q1:- Calculate the molar concentration of 1 ppm solutions of each of the following?

a) $AgNO_3$ b) $Al_2(SO_4)_3$ c) CO_2 d) $HClO_4$

Q2: Calculate the ppm conc. Of 2.5×10^{-4} M solutions of each of the following ?

a) Ca^{+2} b) $CaCl_2$ c) HNO_3 d) KCN

Q3: You want to prepare 1L of a solution containing 1ppm Fe^{+2} . How many grams ferrous ammonium sulfate, $FeSO_4(NH_4)_2SO_4.6H_2O$, must be dissolved and diluted in 1L ? What would be the molarity of this solution?

Q4: How many grams NaCl should be weighed out to prepare 1L of a 100 ppm solution of (a) Na^+ and (b) Cl^-

Q5- One liter of a 500 ppm solution of $KClO_3$ contains how many grams of K^+?

p- Functions

Scientists frequently express the concentration of a species in terms of its p-function, or p-value. The p-value is the negative logarithm (to the base 10) of the molar concentration of that species. Thus, for the species X,

$$\boxed{pX = -\log [X]}$$

As shown by the following examples, p-values offer the advantage of allowing concentrations that vary over ten or more orders of magnitude to be expressed in terms of small positive numbers.

Example (52):- Calculate the p-value for each ion in a solution that is 2.00 X 10^{-3} M in NaCl and 5.4 X 10^{-4} M in HCl.

$$\mathbf{NaCl \longrightarrow Na^{+} + Cl^{-}\ , \qquad HCl \longrightarrow H^{+} + Cl^{-}}$$

Solution

$$\mathbf{pH = -\log [H^{+}] = -\log (5.4 \times 10^{-4}) = 3.27}$$

$$\mathbf{pNa = -\log (2.00 \times 10^{-3}) = -\log 2.00 \times 10^{-3} = 2.699}$$

$$\mathbf{[Cl^{-}] = 2.00 \times 10^{-3}\ M + 5.4 \times 10^{-4}\ M}$$

$$\mathbf{=2.00 \times 10^{-3}\ M + 0.54 \times 10^{-3}\ M = 2.54 \times 10^{-3}\ M}$$

$$\mathbf{pCl = -\log 2.54 \times 10^{-3}\ M = 2.595}$$

Example (53):- Calculate the molar concentration of Ag^{+} in a solution that has a pAg of 6.372.

Solution:

$$\mathbf{pAg = -\log [Ag^{+}] = 6.372, \quad \log [Ag^{+}] = -6.372}$$

$$\mathbf{[Ag^{+}] = \frac{-6.372}{Log} = Log^{-1} (-6.372) = 4.246 \times 10^{-7} = 4.25 \times 10^{-7}\ M}$$

Acid-Base Equilibria

Acid-base theories:-

1) Arrhenius Theory (H^{+} and OH^{-}):-

Acid:-any substance that ionizes (partially or completely) in water to give hydrogen ion (which associate with the solvent to give hydronium ion H_3O^{+}):

$$\mathbf{HA + H_2O \leftrightarrow H_3O^{+} + A^{-}}$$

Base:-any substance that ionizes in water to give hydroxyl ions. Weak (partially ionized) to generally ionize as follows:-

$$\mathbf{B + H_2O \leftrightarrow BH^{+} - OH^{-}}$$

While strong bases such as metal hydroxides (e.g. NaOH) dissociate as

$$\mathbf{M(OH)_n \leftrightarrow M^{n+} + nOH^{-}}$$

This theory is obviously restricted to water as the solvent.

2) Bronsted-Lowry Theory (taking and giving protons, H^{+}):-

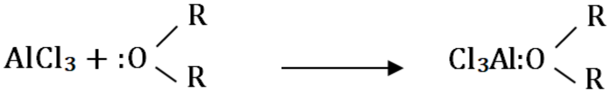
Acid:-any substance that can donate a proton.

Base:-any substance that can accept a proton. Thus, we can write a half reaction:

$$\textbf{Acid} = \textbf{H}^+ + \textbf{Base}$$

3) Lewis Theory (taking and giving electrons):-

Acid:-a substance that can accept an electron pair.



Base:-a substance that can donate an electron pair.

$$\mathbf{H_2O{:} + H^+ \leftrightarrow H_2O{:}H^+(H_3O^+)} \qquad \mathbf{HO{:}^- + H^+ \leftrightarrow H{:}OH}$$

Strong acids: - H_2SO_4, $HClO_4$, HNO_3, HI and HCl .

Strong bases: - LiOH, KOH, NaOH and $Ca(OH)_2$.

Acid-Base Equilibria in water

when an acid or base is dissolved in water, it will dissociate, or ionize, the amount of ionization being dependent on the strength of the acid or base. A strong electrolyte is completely dissociated, while a weak electrolyte is partially dissociated.

$$\mathbf{HCl + H_2O \rightarrow H_3O^+ + Cl^-}\ (\textbf{strong acid, completely ionized})$$

$$\mathbf{HOAC + H_2O \longleftrightarrow H_3O^+ + OAC^-}\ \ (\textbf{weak acid, partially ionized})$$

Thermodynamic acidity constant K°

$$\mathbf{K^\circ = \frac{aH_3O^+ \times aOAc^-}{aH_2O \times aHOAc}}$$

In dilute solutions, the activity of water remains essentially constant, and is taken as unity at standard state:

$$\mathbf{K_a^\circ = \frac{aH_3O^+ \times aOAc^-}{aHOAc}}$$

Pure water ionizes slightly, or undergoes auto protolysis (self-ionization of solvent to give a cation and anion):-

$$\mathbf{2H_2O \leftrightarrow H_3O^+ + OH^-}$$

The equilibrium constant for this is:

$$\mathbf{K_w^\circ = \frac{aH_3O^+ \times aOH^-}{aH_2O^2}}$$

Again, the activity of water is constant in dilute solution (its concentration is essentially constant at ~ 55.3M), so:-

$$\mathbf{K_w^\circ = aH_3O^+ \times aOH^-}$$

K_w° (thermodynamic auto protolysis or self - ionization constant)

We will use H^+ in place of H_3O^+ for simplification, also, molar concentration will generally be used instead of activities and represented by square brackets [ ] around the species).

$$\mathbf{HCl \leftrightarrow H^+ + Cl^-}$$

$$\mathbf{HOAC \leftrightarrow H^+ + OAC^-, K_a = \frac{[H^+][OAC^-]}{HOAc}}$$

$$\mathbf{H_2O \leftrightarrow H^+ + OH^-, K_w = [H^+][OH^-]}$$

$$\mathbf{1.0 \times 10^{-14} = [H^+][OH^-]\ at\ 25°C}$$

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

***Example* (55):-**A 1.0×10^{-3} M solution of HCl prepared. What is the hydroxyl ion concentration $[OH^-]$ & pH?

Solution:

$$\mathbf{K_w = [H^+][OH^-] = 1.0 \times 10^{-14}}$$

$$\mathbf{1.0 \times 10^{-3} \times [OH^-] = 1.0 \times 10^{-14}}$$

$$\mathbf{[OH^-] = 1.0 \times 10^{-11}\ M\ , \qquad pOH = 11}$$

The pH scale: $\mathbf{pH = 14 - 11 = 3}$

Buffer solution

A buffer is defined as a solution that resists change in pH when a small amount of an acid or base is added or when the solution is diluted. A buffer solutions consist of a weak base and their salt (conjugate acid) or a weak acid and its salt (conjugate base).

Types of Buffer Solution

The two primary types into which buffer solutions are broadly classified into are acidic and alkaline buffers.

Acidic Buffers:

As the name suggests, these solutions are used to maintain acidic environments. Acid buffer has acidic pH and is prepared by mixing a weak acid and its salt with a strong acid. An aqueous solution of an equal concentration of acetic acid and sodium acetate has a pH of 4.74.

- pH of these solutions is below seven
- These solutions consist of a weak acid and a salt of a weak acid.
- An example of an acidic buffer solution is a mixture of sodium acetate and acetic acid (pH = 4.75).

Alkaline (basic) Buffers:

These buffer solutions are used to maintain basic conditions. Basic buffer has a basic pH and is prepared by mixing a weak base and its salt with strong base. The aqueous solution of an equal concentration of ammonium hydroxide and ammonium chloride has a pH of 9.25.

- The pH of these solutions is above seven
- They contain a weak base and a salt of the weak base.
- An example of an alkaline buffer solution is a mixture of ammonium hydroxide and ammonium chloride (pH = 9.25).

Significance of Handerson –H, Equation:- Handerson-H, Equation can be used to:

1. Calculate the pH of the buffer prepared from a mixture of the salt and weak acid/base.
2. Calculate the pKa value.
3. Prepare buffer solution of needed pH.

Derivation of Henderson-H, equation for acidic buffer solutions

$$\mathbf{HA + H_2O \leftrightarrow A^- + H_3O^+ \quad , \qquad Ka' = \frac{\{A^-\}\{H_3O^+\}}{\{HA\}\{H_2O\}},}$$

$$\mathbf{Ka} = \frac{\{A^-\}\{H_3O^+\}}{\{HA\}}\,, \qquad \{H_3O^+\} = \{H^+\}$$

$$\{A^-\}\{H^+\} = \mathbf{Ka} \times \{HA\}, \qquad \{H^+\} = \frac{\mathbf{Ka} \times \{HA\}}{\{A^-\}}$$

$$\{H^+\} = \mathbf{Ka} \times \frac{\{HA\}}{\{A^-\}} = -log\{H^+\} = -\log \mathbf{Ka} - \log\frac{\{HA\}}{\{A^-\}}$$

$$pH = \mathbf{pKa} + \log\frac{\{A^-\}}{\{HA\}}\quad , \quad \{A^-\} = \{salt\}\,, \{HA\} = \{acid\}$$

$$pH = \mathbf{pKa} + \log\frac{\{salt\}}{\{acid\}}\ \text{(Handerson} - \text{H, Equation for acidic Buffer solutions).}$$

In same way we can to derivation of Henderson-H, equation for alkaline (basic) buffer solutions

$$\mathbf{B + H_2O \leftrightarrow BH^+ + OH^-}\quad , \quad K_b{}' = \frac{\{OH^-\}\{BH^+\}}{\{B\}\{H_2O\}}$$

$$K_b = \frac{\{OH^-\}\{BH^+\}}{\{B\}}\,,$$

$$\{OH^-\}\{BH^+\} = K_b \times \{B\}, \qquad \{OH^-\} = \frac{K_b \times \{B\}}{\{BH^+\}}$$

$$\{OH^-\} = K_b \times \frac{\{B\}}{\{BH^+\}} = -log\{OH^-\} = -\log K_b - \log\frac{\{B\}}{\{BH^+\}}$$

$$pOH = pK_b + \log\frac{\{BH^+\}}{\{B\}}\quad , \quad \{BH^+\} = \{salt\}\,, \{B\} = \{base\}$$

$$pOH = pK_b + \log\frac{\{salt\}}{\{base\}}\ \textbf{(Handerson} - \textbf{H, Equation for basic Buffer solutions)}$$

Example (56):- Calculate the pH of a buffer prepared by adding 10mL of 0.1M acetic acid to 20mL of 0.1M sodium acetate ?

Henderson-Hasselbalch equation:-

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

$$\mathbf{pH = -\log 1.75 \times 10^{-5} + \log \frac{\left(\frac{0.1\times20}{30}\right)}{\left(\frac{0.1\times10}{30}\right)} = 4.76 + \log 2.0 = 5.06}$$

We can use millimoles of acids and salt in place of molarity.

Buffer capacity (β) is defined as the moles of an acid or base necessary to change the pH of a solution by 1, divided by the pH change and the volume of **buffer** in liters; it is a unitless number.

Buffer capacity (β) = $\left(\frac{n(mol)}{dpH}\right)$

β is buffer capacity

n is the number of moles of an acid or a base added per liter of buffer solution

dpH is the change in pH: dpH = final pH - initial pH

Example (57):- A buffer solution is 0.2M of acetic acid and sodium acetate. Calculate the change in pH upon adding 1.0mL of 0.1M hydrochloric acid to 10mL of this solution and Buffer capacity (β) of this solution.

Solution: $$\mathbf{pH = pK_a + \log \frac{[salt]-[adding\ acid]}{[acid]+[adding\ acid]}}$$

$$\mathbf{(pH)_2 = 4.76 + \log \frac{[0.2\times10]-[0.1\times1]}{[0.2\times10]+[0.1\times1]} = 4.71}$$

$$\mathbf{(pH)_1 = 4.76 + \log \frac{[0.2]}{[0.2]} = 4.76}$$

$$\mathbf{\Delta pH = (pH) - (pH)_2 = 4.76 - 4.71 = 0.05}$$

The change in pH is (0.05). This is rather small especially if we consider that had the HCl been added to unbuffered neutral solution the final concentration would have been approximately 10^{-2}M, and the pH would be 2.0.

Buffer capacity (β) = $$\left(\frac{\frac{n(mol)}{V_L(Buffer\ solutio)}}{dpH}\right) = \left(\frac{\frac{M\times V(L)(acid)}{V_L(Buffer\ solutio)}}{0.05}\right)$$

$$= \left(\frac{\frac{\frac{0.1\times0.001}{10}}{1000}}{0.05}\right) = \left(\frac{\frac{0.0001}{0.01}}{0.05}\right) = \left(\frac{0.01}{0.05}\right) = \mathbf{0.2}$$

Example (58):- You have acidic solution with pH = 4 it was diluted 100 times. Calculate the pH value of this solution after dilution.

Solution:

pH = 4 (before dilution), pH = -log [H^+], 4 = - log [H^+],

$$[H^+] = \frac{-4}{Log} = Log^{-1}(-4) = 1 \times 10^{-4}\ M$$

$$(M_1 \times V_1)_{\text{before dilution}} = (M_2 \times V_2)_{\text{after dilution}}$$

$$(1 \times 10^{-4} \times V) = (M_2 \times 100V),\ M_2 = \left(\frac{1 \times 10^{-4} \times V}{100V}\right) = 1 \times 10^{-6}\ M$$

$$pH = -Log(H^+),\ pH = -Log(1 \times 10^{-6}) = 6\ (\text{after dilution})$$

Example (59):- You have acidic Buffer solution with pH = 4 it was diluted 100 times. Calculate the pH value of this solution after dilution.

Solution: The equation of acidic Buffer solution

$$pH = pKa + \log\frac{\{salt\}}{\{acid\}}$$

$$4 = pKa + \log\frac{\{X\}}{\{Y\}}\ (\text{before dilution})$$

$$\{salt\} = \{X\}_{(\text{before dilution})},\ \{salt\} = \left\{\frac{X}{100}\right\} = \{0.01X\}_{(\text{after dilution})},$$

$$\{acid\} = \{Y\}_{(\text{before dilution})},\ \{acid\} = \left\{\frac{Y}{100}\right\} = \{0.01Y\}_{(\text{after dilution})},$$

$$pKa_{(\text{before dilution})} = pKa_{(\text{after dilution})},$$

$$\log\frac{\{X\}}{\{Y\}} = \log\frac{\{0.01X\}}{\{0.01Y\}}$$

$$pH = pKa + \log\frac{\{0.01X\}}{\{0.01Y\}}\ (\text{after dilution}) = 4$$

This result means that the pH of this solution did not change due to dilution because it is a buffer solution.

Volumetric analysis (titration analysis)

Are the most useful and accurate analytical techniques, especially for millimole amounts of analyte. They are rapid and can be automated, and they can be applied to smaller amounts of analyte when combined with a sensitive instrumental technique for detecting the completion of the titration reaction, for example, pH measurement. In a titration the test substance (analyte) in a flash react with a reagent added from a buret as a solution of known concentration. This is referred to as a standard solution and is called the titrant. The volume of titrant required to just completely react with the analyte is measured. Since we know the concentration as well as the reaction between the analyte and the reagent, we can calculate the amount of analyte.

The requirements of a titration are as follows

(1) The reaction must be stoichiometric: That is, there must be a well-defined and known reaction between the analyte and the titrant..

$$\mathbf{CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O}$$

(2) The reaction should be rapid. Most ionic reactions.

(3) There should be no side reaction, and the reaction should be specific.

(4) There should be a marked change in some property of the solution when the reaction is complete. This may be a change in color of the solution or in some electrical or other physical property of the solution (by used indicator or pH meter).

(5) The point at which an equivalent or stoichiometric amount of titrant is added is called the equivalence point. The point at which the reaction is observed to be complete is called the end point, that is, when a change in some property of the solution.

(6) The reaction should be quantitative. That is, the equilibrium of the reaction should be far to the right so that a sufficiently sharp change will occur at the end point to obtain the desired accuracy. The equivalence point is the theoretical end of the titration where the number of moles of titrant = number of moles of analyte. The end point is the observed end of the titration.

Standard solution

A solution is prepared by dissolving an accurately weighed quantity of a highly pure material called a primary standard and diluting to an accurately known volume in a volumetric flask.

A primary standard should fulfil these requirements

(1) It should be 100.00% pure, although 0.01 to 0.02% impurity is tolerable if it is accurately known.

(2) It should be stable to drying temperature, and it should be stable indefinitely at room temperature. The primary standard is always dried before weighing.

(3) It should be readily available and fairly inexpensive.

(4) Although not necessary, it should have a high formula weight.

(5) If it is to be used in titration, it should possess the properties required for a titration listed above. In particular, the equilibrium of the reaction should be far to the right so that a very sharp end point will be obtained.

A solution standardized by titrating a primary standard is itself a secondary standard. It will be less accurate than a primary standard solution due to the errors of titrations. A high formula weight means a larger weight must be taken for a given number of moles. This reduces the error in weighing.

Classification of volumetric or titration methods

(1) Neutralization (acid-base) titrations: Many compounds, both inorganic and organic, are either acids or bases can be titrated with a standard solution of a strong base or a strong acid. The end point of these titrations are easy to detect, either by means of indicator or by following the change in pH with a pH meter.

(2) Precipitation titrations: In the case of precipitation, the titrant forms an insoluble product with the analyte. An example is the titration of chloride ion with silver nitrate solution to form silver chloride precipitate.

(3) Complexometric titrations : In Complexometric titrations ,the titrant is a reagent that forms a water-soluble complex with the analyte , a metal ion .The titrant is often a chelating.

(4) Reduction-Oxidation titrations: These (redox) titrations involve the titration of an oxidizing agent with a reducing agent, or vice versa .An oxidizing agent gains electrons and a reducing agent loses electrons in a reaction between them.

Acid-Base Titrations

An Acid-Base titration involves a neutralization reaction in which an acid is reacted with an equivalent amount of base at equivalence point or endpoint. The titration is always a strong acid or strong base

A) Titration of strong acid versus strong base.

For Example:

$$\mathbf{HCl + NaOH \rightarrow NaCl + H_2O}$$

$$\mathbf{H^+Cl^- + Na^+OH^- \rightarrow Na^+Cl^+ + H_2O}$$

The equivalent point is where the reaction is theoretically complete while the endpoint where the colour of indicator were changed.

Example (60):- Calculate the pH at (0, 5, 45, 50, 55 mL) titration of 50.0mL of 0.10M HCl with 0.10M NaOH?

Solution:

(1) At 0 titration: before addition of 0.1M NaOH

$$\mathbf{pH = -\log[H^+] = -\log 0.1 = 1.0}$$

(2) At 5 mL titration: before equivalence point

$$\mathbf{mmol\ NaOH\ added = M \times V = 0.1 \times 5 = 0.5}$$

$$\mathbf{mmol\ HCl\ = M \times V = 0.1 \times 50 = 50}$$

$$\mathbf{mmol\ HCl\ remaining = mmol\ HCl\ total - mmol\ NaOH\ added}$$

$$\mathbf{= 5.0 - 0.5 = 4.5}$$

$$\mathbf{M_{HCl} = \frac{mmol}{V} = \frac{4.5}{50+5} = 0.0818M}$$

$$\mathbf{pH = -\log 0.0818 = 1.09}$$

(3) At 45 mL titration: before equivalence point

$$\mathbf{mmol.\ NaOH\ added = M \times V = 0.1 \times 45 = 4.5}$$

$$\mathbf{mmol.\ HCl\ remaining\ (unreacted) = 5.0 - 4.5 = 0.5}$$

$$\mathbf{M_{HCl} = \frac{mmol}{V} = \frac{0.5}{50+45} = 0.00526M}$$

$$\mathbf{pH = -\log 0.00526 = 2.28}$$

(4) At 50 mL titration: Equivalence Point

$$\mathbf{mmol.\ NaOH\ added = M \times V = 0.1 \times 50 = 5}$$

$$\mathbf{mmol.\ NaOH\ added\ (5.0) = mmol\ HCl\ (5.0)}$$

$$\mathbf{2H_2O \leftrightarrow H_3O^+ + OH^-}$$

$$\mathbf{Kw = 1 \times 10^{-14} = [H^+][OH^-]}$$

$$\mathbf{\sqrt{1 \times 10^{-14}} = [H^+] = [OH^-] = 1 \times 10^{-7}M}$$

$$\mathbf{pH = -\log 10^{-7} = 7\ (neutrilization\ step)}$$

(5) At 55 mL titration: after equivalence point

$$\mathbf{mmol.\ NaOH\ added = M \times V = 0.1 \times 55 = 5.5}$$

$$\mathbf{mmol\ NaOH\ remaining\ (excess) = 5.5 - 5 = 0.5}$$

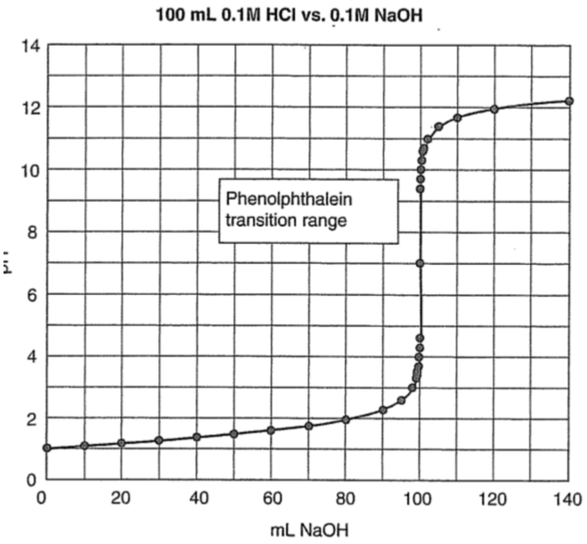
$$\mathbf{M_{NaOH} = \frac{mmol}{V} = \frac{0.5}{50+55} = 0.00476M}$$

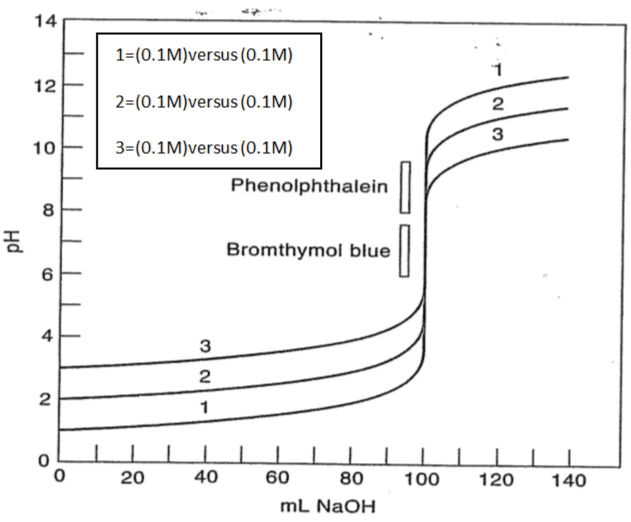
$$\mathbf{pOH = -\log 0.00476 = 2.32}$$

$$\mathbf{pH = 14 - 2.32 = 11.68}$$

Construction (plot) titration curve of strong acid versus strong base:-

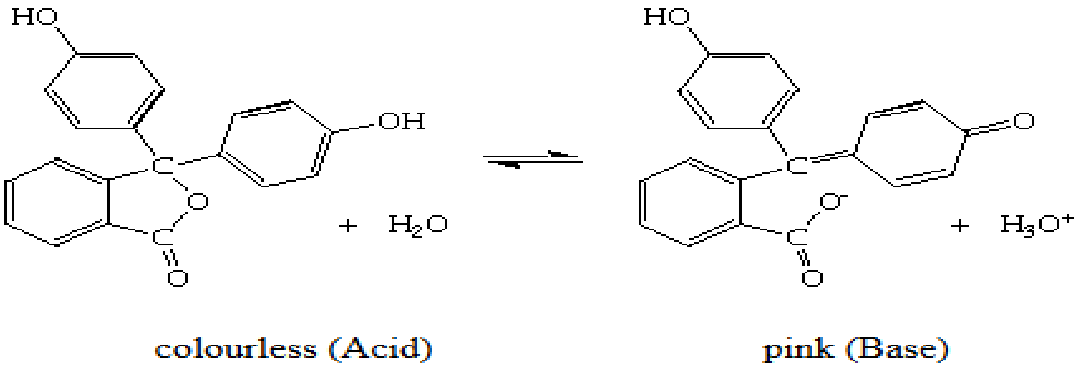
The relationship between pH calculated for HCl remaining or unreacted (excess) or NaOH on Y axis and the volume of titrant (0.1M NaOH) added on X axis, this curve called titration curve. This curve used for estimation the equivalence point (theoretically) and selection of the indicator for detecting the endpoint reaction by the colour change of the indicator.





Note: The selection of the indicator become more critical as the solution become more dilute and the sharpness endpoint decrease as the concentration. The point at which the reaction is observed to be complete at the indicator colour where changed is called endpoint.

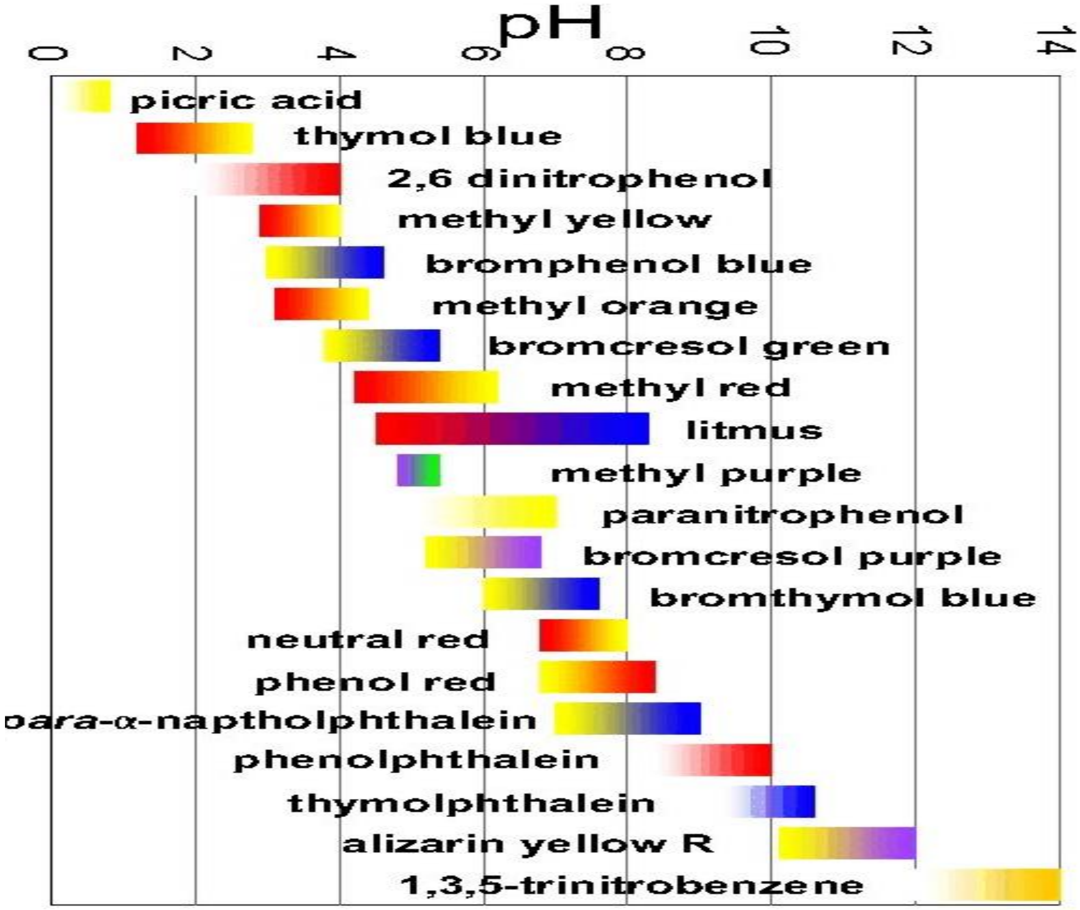
Indicators (Acid-Base):- are substances which change colour with change pH.



They are usually weak acids or bases, which when dissolved in water dissociate slightly and form ions. Phenolphthalein is a colourless, weak acid which dissociates in water forming pink anions. Under acidic conditions, the equilibrium is to the left, and the concentration of the anions is too low for the pink colour to be observed. However, under alkaline conditions, the equilibrium is to the right, and the concentration of the anion becomes sufficient for the pink colour to be observed.

Common Acid – Base Indicators

Indicator	Approximate pH Range for Color Change	Color Change
Methyl Orange	3.2-4.4	Red to yellow
Bromthymol blue	6.0-7.6	Yellow to blue
Phenolphthalein	8.2-10	Colorless to pink
Litmus	5.5-8.2	Red to blue
Bromcresol green	3.8-5.4	Yellow to blue
Thymol blue	8.0-9.6	Yellow to blue



B) Titration of weak acid versus strong base:-

Acetic acid with sodium hydroxide

$$\mathbf{HOAC + Na^{+}OH^{-} \leftrightarrow Na^{+}OAC^{-} + H_2O}$$

***Example (61)*:-** Calculate the pH at 0, 10, 25, 50, and 60mL titrant in the titration of 50mL of 0.1M acetic acid (Ka=1.75×10^{-5}) with 0.10M NaOH?

Solution:

(1) At 0mL titrant (0.1M NaOH): HOAC solution only

$$[\mathbf{H^{+}}] = \sqrt{\mathbf{K_a C_{HA}}} = \sqrt{\mathbf{1.75 \times 10^{-5} \times 0.1}} = \mathbf{1.32 \times 10^{-3} M}$$

$$\mathbf{pH = -log[H^{+}] = -log1.23 \times 10^{-3} = 2.88}$$

(2)At 10mL titrant (0.1M NaOH):before equivalence point (buffer formation region)

$$\mathrm{HOAC + Na^{+}OH^{-} \leftrightarrow Na^{+}OAC^{-} + H_2O}$$

$$\text{mmol NaOH added} = \mathrm{M \times V} = 0.1 \times 10 = 1.0 = \text{mmol of NaOAc (salt) formed}$$

$$\text{mmol of HOAC (total)} = \mathrm{M \times V} = 0.1 \times 50 = 5.0$$

$$\text{mmol of HOAc remaining (unreacted)} = 5.0 - 1.0 = 4.0$$

$$\mathbf{pH = pKa + \log\frac{[Salt]}{[Acid]} = 4.76 + \log\frac{1.0}{4.0} = 4.16}$$

(3) At 25mL titrant (0.1M NaOH): before equivalence point (buffer formation region)

$$\mathbf{mmol\ NaOH\ added = M \times V = 0.1 \times 25 = 2.5mmol.}$$
$$\mathbf{= mmol\ of\ NaOAC\ (salt)\ formed}$$

$$\mathbf{mmol\ of\ HOAc\ remaining\ (unreacted) = 5.0 - 2.5 = 2.5mmol}$$

$$\mathbf{pH = pKa + \log\frac{[Salt]}{[Acid]} = 4.76 + \log\frac{2.5}{2.5} = 4.76}$$

$$\mathbf{pH = pKa\ (mid - point)}$$

(4) At 50mL titrant (0.1M NaOH): equivalence point

$$\text{mmol NaOH added} = \mathrm{M \times V} = 0.1 \times 50 = 5.0 = \text{mmol of NaOAC (salt) formed}$$

All NaOH reacted with all HOAC and converted it to its salt sodium acetate.

$$\mathrm{OAC^{-} + H_2O \leftrightarrow HOAC + OH^{-}}$$

$$\mathrm{[OH^{-}]} = \sqrt{\mathrm{K_b C_{OAC^-}}} = \sqrt{\frac{\mathrm{K_w}}{\mathrm{K_a}}\mathrm{C_{OAC^-}}} = \sqrt{\frac{10^{-14}}{1.75 \times 10^{-5}} \times 0.05} = 5.35 \times 10^{-6}\mathrm{M}$$

$$\mathbf{pOH = -\log[OH^{-}] = -\log 5.35 \times 10^{-6} = 5.27}$$

$$\mathbf{pH = 14 - 5.27 = 8.73}$$

(5) At 60mL titrant (0.1M NaOH): after equivalence point (NaOH solution alone)

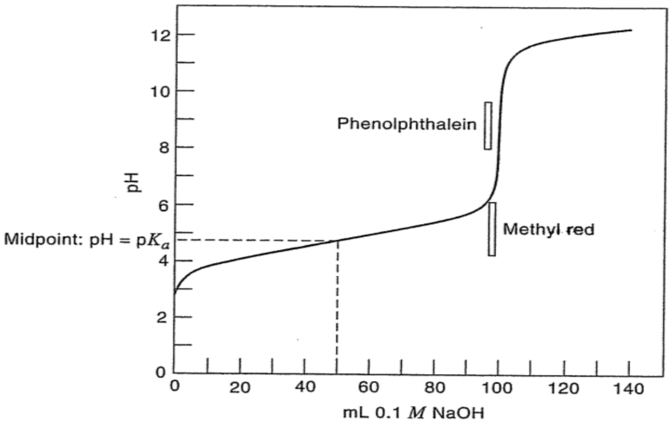
$$\mathbf{mmol\ NaOH\ added = M \times V = 0.1 \times 60 = 6.0mmol}$$

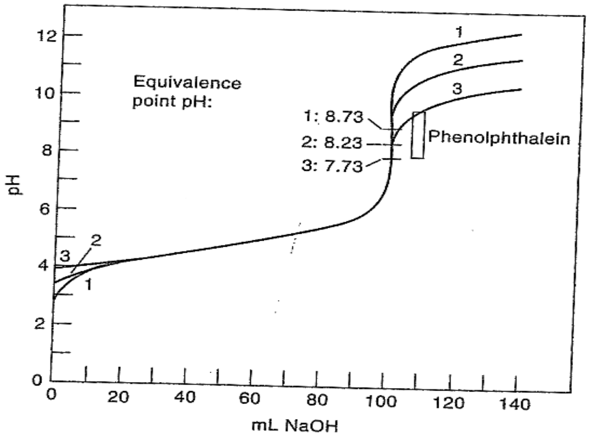
$$\mathbf{mmol\ of\ NaOH\ remaining\ (excess) = 6.0 - 5.0 = 1.0mmol}$$

$$\mathbf{pOH = -\log\frac{1.0mmol}{50mL + 60mL} = 2.04}$$

$$\mathbf{pH = 14 - 2.04 = 11.96}$$

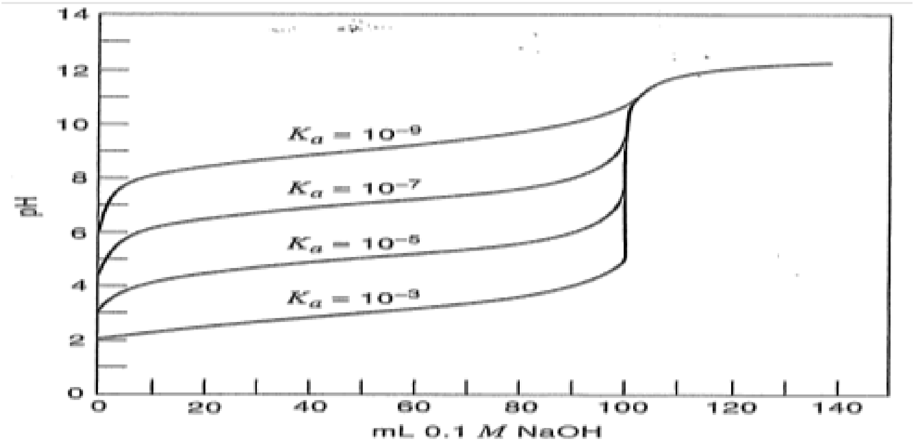
Construction (plotting) titration curve of weak acid versus strong base:-





The sharpness endpoint decreases as the concentration decreases.

Titration curves for 50mL 0.1M weak acids of different Ka value versus 0.1M NaOH



The sharpness of the endpoint decreases as Ka decreases.

(C) Titration of weak base versus strong acid:-Titration of ammonia solution versus hydrochloric acid.

***Example (62)*:-** Calculate the pH at 0, 10, 25, 50, and 60mL of titrant of 50mL of 0.1M NH_3 (K_b=1.75×10^{-5}) with 0.1M HCl?

(1) At 0mL titrant (0.1M HCl): NH_3 solution alone

$$[\mathbf{OH^-}] = \sqrt{\mathbf{K_b C_{B^-}}} = \sqrt{\mathbf{1.75 \times 10^{-5} \times 0.1}} = \mathbf{0.00130M}$$

$$\mathbf{pOH = -\log[OH^-] = -\log 0.00130 = 2.88}$$

$$\mathbf{pH = 14 - 2.88 = 11.12}$$

(2) At 10mL titrant (0.1M HCl): before equivalence point (buffer formation region)

$$\text{mmol HCl added} = M \times V = 0.1 \times 10 = 1.0 = \text{mmol of } NH_4Cl \text{ (salt) formed}$$

$$\mathbf{mmol\ NH_3\ total = M \times V = 0.1 \times 50 = 5.0}$$

$$\mathbf{mmol\ NH_3\ remaining\ (unreacted) = 5.0 - 1.0 = 4.0}$$

$$\mathbf{pOH = pK_b + \log\frac{[Salt]}{[Base]} = 4.75 + \log\frac{1.0}{4.0} = 4.15}$$

$$\mathbf{pH = 14 - 4.15 = 9.85}$$

(3) At 25mL titrant (0.1M HCl): before equivalence point (buffer formation region)

$$\text{mmol HCl added} = M \times V = 0.1 \times 25 = 2.5\text{mmol}$$
$$= 2.5\text{mmol of } NH_4Cl \text{ (salt) formed}$$

$$\text{mmol } NH_3 \text{ remaining (unreacted)} = 5.0 - 2.5 = 2.5$$

$$pOH = pK_b + \log\frac{[Salt]}{[Base]} = 4.75 + \log\frac{2.5}{2.5} = 4.75 \qquad pOH = pK_b \text{ mid} - \text{point}$$

(4) At 50mL titrant (0.1M HCl): equivalence point region

$$\text{mmol HCl added} = M \times V = 0.1 \times 50 = 5.0\text{mmol}$$

The all HCl added converted all NH_3 to its salt NH_4Cl

$$NH_4^+ + H_2O \leftrightarrow NH_4OH + H^+$$

$$[H^+] = \sqrt{K_a C_{BH^+}} = \sqrt{\frac{K_w}{K_b} C_{BH^+}} = \sqrt{\frac{10^{-14}}{1.75 \times 10^{-5}} \times 0.05} = 5.35 \times 10^{-6}M$$

$$pH = -\log 5.35 \times 10^{-6} = 5.27$$

(5) At 60mL titrant (0.1M HCl): after equivalence point

$$\text{mmol HCl added} = \text{M} \times \text{V} = 0.1 \times 60 = 6.0\text{mmol}$$

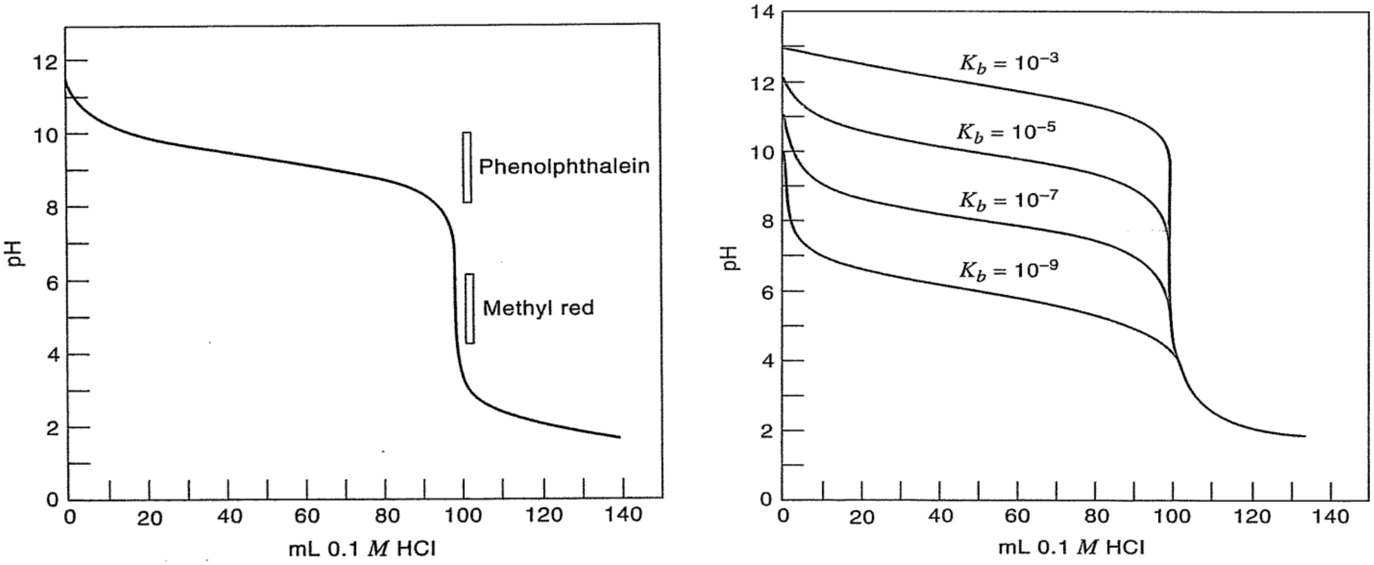
$$\mathbf{mmol\ HCl\ remaining\ (excess) = 6.0 - 5.0 = 1.0}$$

$$\mathbf{M_{HCl} = \frac{1.0mmol}{50mL + 60mL} = 0.00909M}$$

$$\mathbf{pH = -log0.00909 = 2.05}$$

Construction (plotting) titration curve:-

Titration curve for 50mL 0.1M weak base of different K_b values versus 0.1M HCl.



The sharpness of the endpoint decreases as K_b decreases of weak bases.

Back titration (indirect titration)

Sometimes

1 - a reaction is slow to go to completion.

2 - a sharp end point cannot be obtained.

A back titration will often yield useful results. In this technique, a measured amount of the reagent, which would normally be the tritrant, is added to the sample so that there is a slight excess. After the reaction with the analyte is allowed to go to completion, the amount of excess (unreacted) reagent is determined by titration with another standard solution. In back-titration, a known number of millimoles of reaction it is taken, in excess of the analyte. The unreacted portion is titrated. A back titration is a titration method where the concentration of an analyte is determined by reacting it with a known amount of excess reagent. The remaining excess reagent is then titrated with another, second reagent. The second titration's result shows how much of the excess reagent was used in the first titration, thus allowing the original analyte's concentration to be calculated. A back titration may also be called an indirect titration.

mmol of analyte = mmol first titrant – mmol back titrant

Example (54):- A 0.50 g sample containing Na_2CO_3 plus inert matter in analyzed by adding 50.0mL of 0.1M HCl, a slight excess, boiling to remove CO_2, and then back-titrating the excess acid with 0.1M NaOH. If 5.6mL of NaOH is required for the back-titration, what is the percent Na_2CO_3 in the sample.

Solution:

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2CO_3$$

$$H_2CO_3 \longrightarrow H_2O + CO_2 \uparrow$$

$$(\text{Excess})\ HCl + NaOH \longrightarrow NaCl + H_2O$$

$$\text{mmol } Na_2CO_3 = (\text{mmol HCl} \times \frac{1mmol.Na_2CO_3}{2mmol.HCl}) - mmol\ NaOH$$

$$(\frac{wt}{M.wt} \times 1000)_{Na_2CO_3} = (M \times V \times \frac{1}{2})_{HCl} - (M \times V)_{NaOH}$$

$$(\frac{wt}{106} \times 1000) = (0.1 \times 50 \times \frac{1}{2}) - (0.1 \times 5.6)$$

$$\frac{wt \times 1000}{106} = (2.5) - (0.56)\ ,\quad \frac{wt \times 1000}{106} = (1.94)$$

$$wt \times 1000 = (1.94\times 106) \quad , \quad wt_{Na_2CO_3} = \frac{206}{1000}$$

$$wt_{Na_2CO_3} = 0.206 \text{ gm} \quad , \quad \%Na_2CO_3 = \frac{wt\ Na_2CO_3}{wt\ sample}\times 100$$

$$= \frac{0.206}{0.500}\times 100 = 41.2\ \%$$

Precipitation Reactions and Titrations

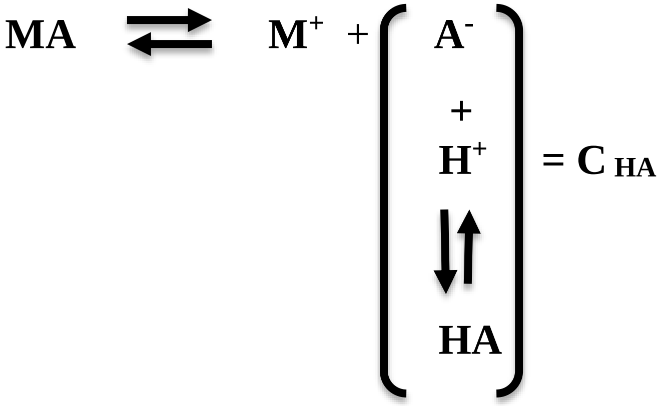
A number of anions form slightly precipitates with certain ions and can be titrated with the metal solutions.

$$Ag^{+} + Cl^{-} \longrightarrow AgCl\downarrow$$

$$Ba^{+2} + SO4^{-2} \longrightarrow BaSO_4\downarrow$$

Effect of acidity on solubility of precipitates Conditional solubility product [Ksp'].

The solubility of a precipitate whose anion is derived from a weak acid will increase in the presence of added acid because the acid will lead to combine with the anion and thus remove the anion from solution for example the precipitate MA that partially dissolves to give M+ and A- ions will exhibit the following.



The anion **[A⁻]** can combine with protons to increase the solubility of the precipitates. The combined equilibrium concentrations of **A^-** and **HA** make up the total analytical concentration, **C_{HA}**, which will be equal to **[M^+]** from the dissolved precipitate (**M^+** or **A^-** excess).

$$Ca_2C_2O_4 \rightleftharpoons Ca^{+2} + C_2O_4^{-2} \qquad Ksp = [Ca^{+2}][C_2O_4^{-2}] = 2.6x\ 10^{-9} \quad (1)$$

$$C_2O_4^{-2} + H^+ \rightleftharpoons HC_2O_4^- \qquad K_{a2} = \frac{[H+][C2O4-2]}{[\ HC2O4-]} = 6.1x\ 10^{-5} \quad (2)$$

$$HC_2O_4^- + H^+ \leftrightharpoons H_2C_2O_4 \qquad K_{a1} = \frac{[H+][HC2O4-]}{[H2C2O4]} = 6.5x\ 10^{-2} \quad (3)$$

The solubility **S** of **$Ca_2C_2O_4$** is equal to **[Ca^{+2}] = C_{H2C2O4}**, where **C_{H2C2O4}** represents the concentration of all the oxalate species in equilibrium **=[$H_2C_2O_4$] + [$HC_2O_4^-$]+[$C_2O_4^{-2}$].** We can substitute **$C_{H2C2O4}\ \alpha_2$** for **[$C_2O_4^{-2}$]** in the **K_{sp}** expression:-

$$C_{H_2C_2O_4} = [H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{-2}]$$

$$\alpha_0 = \frac{[H_2C_2O_4]}{[H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{-2}]} = \frac{[H_2C_2O_4]}{C_{H_2C_2O_4}} \Longrightarrow [H_2C_2O_4] = \alpha_0 \times C_{H_2C_2O_4}$$

$$\alpha_1 = \frac{[HC_2O_4^{\;-}]}{[H_2C_2O_4] + [HC_2O_4^{\;-}]+[C_2O_4^{\;-2}]} = \frac{[HC_2O_4^{\;-}]}{C_{H_2C_2O_4}} \Longrightarrow [HC_2O_4^{\;-}] = \alpha_1 \times C_{H_2C_2O_4}$$

$$\alpha_2 \frac{[C_2O_4^{\;-2}]}{[H_2C_2O_4] + [HC_2O_4^{\;-}]+[C_2O_4^{\;-2}]} = \frac{[C_2O_4^{\;-2}]}{C_{H_2C_2O_4}} \Longrightarrow [C_2O_4^{\;-2}] = \alpha_2 \times C_{H_2C_2O_4}$$

$$\boxed{Ksp = [Ca^{+2}][C_2O_4^{\;-2}] = [Ca^{+2}] \times C_{H_2C_2O_4} \times \alpha_2}$$

We can write then

$$\boxed{\frac{K_{sp}}{\alpha_2} = K_{sp}{}' = [Ca^{+2}] \times C_{H_2C_2O_4} = S^2}$$

$$\boxed{\alpha_2 = \frac{Ka_1Ka_2}{[H^+]^2 + [H^+]Ka_1 + Ka_1Ka_2}}$$

Where $K_{sp}{}'$ is the conditional solubility product.

Note: - The conditional solubility product value holds for only a **specified pH**

Example 1 : Calculate the solubility of **CaC_2O_4** in water and in a solution containing 0.001M HCl and compare them**?** $CaC_2O_4 \rightleftharpoons Ca^{+2} + C_2O_4^{-2}$

$$Ksp(CaC_2O_4) = 2.6 \times 10^{-9}\,, Ka_1 = 6.5 \times 10^{-2}\,, Ka_2 = 6.1 \times 10^{-5}$$

Solubility of **CaC_2O_4 in water** $Ksp_{(CaC2O4)} = [Ca^{+2}][C_2O_4^{-2}] = S^2$

$$S^2 = \sqrt{Ksp_{(CaC_2O_4)}}\ \sqrt{2.6 \times 10^{-9}} = 5.09 \times 10^{-5}\ M$$

Solubility of **CaC_2O_4** in a solution containing 0.001M HCl, (acid solution).

$$\alpha_2 = \frac{Ka_1Ka_2}{[H^+]^2 + [H^+]Ka_1 + Ka_1Ka_2}$$

$$\alpha_2 = \frac{(6.5 \times 10^{-2}) \times (6.1 \times 10^{-5})}{(1.0 \times 10^{-3})^2 + (1.0 \times 10^{-3}) \times (6.5 \times 10^{-2}) + (6.5 \times 10^{-2}) \times (6.1 \times 10^{-5})}$$

$\alpha_2 = 5.7 \times 10^{-2}$ → $S = \sqrt{\frac{Ksp}{\alpha_2}} = \sqrt{\frac{2.6 \times 10^{-9}}{5.7 \times 10^{-2}}} = 2.1 \times 10^{-4}\ \mathrm{M}$

$$S_{\text{in acid solution}} > S_{\text{in water}}$$

$$\text{The Comparison} = \frac{S_{\text{in acid solution}}}{S_{\text{in water}}} \times 100$$

$$= \frac{2.1\times10^{-4}}{5.09\times10^{-5}} \times 100 = 412.6\% \ (\textit{incrase in solubility})$$

Method of driving values of α_0 ,α_1 and α_2

$$HA \leftrightarrow A^- + H^+ \quad , \quad Ka = \frac{\{A^-\}\{H^+\}}{\{HA\}} \ \ldots\ldots\ldots\ldots\ldots(1)$$

$$\{HA\}_T = \{HA\} + \{A^-\}\ , \quad \alpha_0 = \frac{\{HA\}}{\{HA\} + \{A^-\}}\ , \alpha_1 = \frac{\{A^-\}}{\{HA\} + \{A^-\}}$$

From equation no 1 $\{HA\} = \frac{\{A^-\}\{H^+\}}{Ka}$

$$\alpha_0 = \frac{\frac{\{A^-\}\{H^+\}}{Ka}}{\frac{\{A^-\}\{H^+\}}{Ka} + \{A^-\}} \times \frac{\frac{Ka}{\{A^-\}}}{\frac{Ka}{\{A^-\}}} = \frac{\{H^+\}}{\{H^+\} + Ka}$$

In the same way $\alpha 1 = \frac{\{A^-\}}{\{HA\} + \{A^-\}} = \frac{Ka}{\{H^+\} + Ka}$

$$H_2A \leftrightarrow HA^- + H^+ \quad , Ka_1 = \frac{\{HA^-\}\{H^+\}}{\{H_2A\}} \ \ldots\ldots\ldots\ldots\ldots(1)$$

$$HA^- \leftrightarrow A^{-2} + H^+ \quad , \quad Ka_2 = \frac{\{A^{-2}\}\{H^+\}}{\{HA^-\}} \ \ldots\ldots\ldots\ldots\ldots(2)$$

$$\{H_2A\}_T = \{H_2A\} + \{HA^-\} + \{A^{-2}\}$$

$$\alpha_0 = \frac{\{H_2A\}}{\{H_2A\} + \{HA^-\} + \{A^{-2}\}}$$

$$\alpha_1 = \frac{\{HA^-\}}{\{H_2A\} + \{HA^-\} + \{A^{-2}\}}$$

$$\alpha_2 = \frac{\{A^{-2}\}}{\{H_2A\} + \{HA^-\} + \{A^{-2}\}}$$

From equation no 1 $\{H_2A\} = \frac{\{HA^-\}\{H^+\}}{Ka_1}$

$$\alpha_0 = \frac{\frac{\{HA^-\}\{H^+\}}{Ka_1}}{\frac{\{HA^-\}\{H^+\}}{Ka_1} + \{HA^-\} + \{A^-\}},$$

From equation no 2 $\{HA^-\} = \frac{\{A^{-2}\}\{H^+\}}{Ka_2}$

$$\alpha_0 = \frac{\frac{\frac{\{A^{-2}\}\{H^+\}}{Ka_2}\{H^+\}}{Ka_1}}{\frac{\frac{\{A^{-2}\}\{H^+\}}{Ka_2}\{H^+\}}{Ka_1} + \frac{\{A^{-2}\}\{H^+\}}{Ka_2} + \{A^{-2}\}},$$

$$\alpha_0 = \frac{\dfrac{\{A^{-2}\}\{H^+\}^2}{Ka_1Ka_2}}{\dfrac{\{A^{-2}\}\{H^+\}^2}{Ka_1Ka_2} + \dfrac{\{A^{-2}\}\{H^+\}}{Ka_2} + \{A^{-2}\}} \times \frac{\dfrac{Ka_1Ka_2}{\{A^{-2}\}}}{\dfrac{Ka_1Ka_2}{\{A^{-2}\}}}$$

$$\alpha_0 = \frac{\{H^+\}^2}{\{H^+\}^2 + \{H^+\}Ka_1 + Ka_1Ka_2}$$

In the same way $\alpha_1 = \dfrac{\{H^+\}Ka_1}{\{H^+\}^2 + \{H^+\}Ka_1 + Ka_1Ka_2}$

and $\alpha_2 = \dfrac{Ka_1Ka_2}{\{H^+\}^2 + \{H^+\}Ka_1 + Ka_1Ka_2}$

Example 2 :- Calculate the solubility of CaF_2 in 0.1 M HCl. Also calculate equilibrium concentration of F- and HF. **$Ksp_{(CaF2)} = 3.9\times10^{-11}$, $Ka_{(HF)} = 6.8\times10^{-4}$,**

solution

$CaF_2 \leftrightarrow [Ca^{+2}] + 2[F^-]$, $Ksp_{(CaF2)} = [Ca^{+2}]\,[F^-]\,[F^-] = [Ca^{+2}]\,[F^-]^2$

$HCl \rightarrow H^+ + Cl^-$, $H^+ + F^- \leftrightarrow HF$, $C_{HF} = [HF] + [F^-]$

$Ksp_{(CaF2)} = [Ca^{+2}]\,[F^-]^2$ $[F^-]=\alpha_1 C_{HF}$

$Ksp_{(CaF2)} = [Ca^{+2}]\,[\alpha_1 C_{HF}]^2$, $Ksp_{(CaF2)} = [Ca^{+2}]\,[\alpha_1^2 C^2_{HF}]$,

$\frac{Ksp}{\alpha_1^2} = K'_{sp} = [Ca^{+2}]\,[C^2_{HF}]$, $C_{HF} = 2S$ S = solubility , $[Ca^{+2}] = S$

$\frac{Ksp}{\alpha_1^2} = K'_{sp} = [S]\,[2S]^2 \rightarrow 4S^3$,

$$\alpha_1 = \frac{Ka}{[H+]+Ka} = \frac{6.8\times10^{-4}}{0.1 + 6.8\times10^{-4}} = \frac{6.8\times10^{-4}}{0.100068} = 6.75\times10^{-3}$$

$$K'_{sp} = \frac{Ksp}{\alpha_1^2} = \frac{3.9\times10^{-11}}{(6.75\times10^{-3})^2} = 8.559\times10^{-7}\,,\quad K'_{sp} = [S]\,[2S]^2 \rightarrow 4S^3$$

$$S = \sqrt[3]{\frac{K'_{sp}}{4}}\ , \quad S = \sqrt[3]{\frac{8.559\times10^{-7}}{4}} = \sqrt[3]{2.139\times10^{-7}} = 5.98\times10^{-3}\ M$$

$$C_{HF} = 2S = 5.98\times10^{-3}\times 2 = 0.01196\ M$$

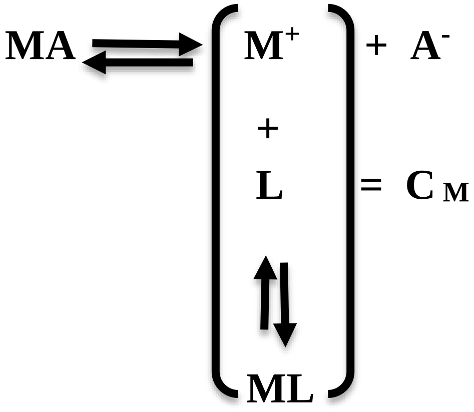
$$[F^-]_{eq.} = \alpha_1\, C_{HF} = 6.75\times10^{-3} \times 0.01196 = 8.073\times10^{-5}\ M$$

$$[HF]_{eq.} = C_{HF} - [F^-] = 0.01196 - 8.073\times10^{-5} = 1.1879\times10^{-2}\ M$$

OR -- $[HF]_{eq.} = \alpha_0\, C_{HF} = (1-\alpha_1)\, C_{HF} = (1- 6.75\times10^{-3}) \times 0.01196 = 1.1879\times10^{-2}\ M$

Effect of Complexation on solubility (Conditional solubility product)

The Complexing agent can compete for the metal ion in a precipitate, just as acids compete for the anion. A precipitate [**MA]** that dissociate to give [**M**$^+$] and [**A**$^-$**]** and whose metal complexes with the ligand L to form [**ML**$^+$**]** would have the following equilibria:-



The sum of **M**$^+$ and [**ML**$^+$**]** is the analytical concentration C_M in equilibrium, which is equal to **[A**$^-$**].** Calculation for such a situation are handled in a manner completely analogous to those for the effects of acids on solubility Consider the solubility of **AgBr** in the presence of **NH$_3$**. The equilibria are:-

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

$$Ag^+ + NH_3 \rightleftharpoons Ag(NH_3)^+ \ , \qquad K_{f_1} = \frac{\{Ag(NH_3)^+\}}{\{Ag+\}\{NH_3\}}$$

$$Ag(NH_3)^+ + NH_3 \rightleftharpoons Ag(NH_3)_2^+ \ , \quad K_{f_2} = \frac{\{Ag(NH_3)_2{}^+\}}{\{Ag(NH_3)^+\}\{NH_3\}}$$

$$K_{sp} = [Ag^+][Br^-] = C_{Ag} \times \beta_0 \times [Br^-] = 4 \times 10^{-13}$$

$$\frac{\mathbf{Ksp}}{\boldsymbol{\beta_0}} = \mathbf{K'_{sp} = C_{Ag}\ [Br^-] = S^2}$$

The solubility **S** of **[AgBr]** is equal to **[Br $^-$]** = **C_{Ag},** where **C_{Ag}** represents the concentrations of all the silver species in equilibrium = **[Ag $^+$] + [Ag (NH$_3$)$^+$] +[Ag(NH$_3$)$_2$$^+$].** we can substitute **C_{Ag} β_0** for **[Ag $^+$]** in the **Ksp** expression**.** Where **β_0** is the fraction of silver species present as **[Ag $^+$].**

$$C_{Ag} = [Ag^+] + [Ag\,(NH_3)^+] + [Ag\,(NH_3)_2{}^+]$$

$$\beta_0 = \frac{[Ag^+]}{[Ag^+] + [Ag\,(NH_3)^+] + [Ag\,(NH_3)_2{}^+]} = \frac{[Ag^+]}{C_{Ag}} \Longrightarrow [Ag^+] = \beta_0 \times C_{Ag}$$

$$\beta_1 = \frac{[Ag\,(NH_3)^+]}{[Ag^+] + [Ag\,(NH_3)^+] + [Ag\,(NH_3)_2{}^+]} = \frac{[Ag\,(NH_3)^+]}{C_{Ag}} \Longrightarrow [Ag\,(NH_3)^+] = \beta_1 \times C_{Ag}$$

$$\beta_2 = \frac{[Ag\,(NH_3)_2{}^+]}{[Ag^+] + [Ag\,(NH_3)^+] + [Ag\,(NH_3)_2{}^+]} = \frac{[Ag\,(NH_3)_2{}^+]}{C_{Ag}} \Longrightarrow [Ag\,(NH_3)_2{}^+] = \beta_2 \times C_{Ag}$$

$$\boxed{Ksp = [Ag^+][Br^-] = C_{Ag}\ \beta_0\ [Br^-]}$$

We can write then

$$\boxed{\frac{K_{sp}}{\beta_0} = K_{sp}{}' = C_{Ag}\ [Br^-] = S^2}$$

$$\boxed{B_0 = \frac{1}{1 + K_{f_1}\{NH_3\} + K_{f_1}\,K_{f_2}\{NH_3\}^2}}$$

Where **K'sp** is again the **conditional solubility product**, whose value depends on the **concentration of Ammonia**.

Example 3:- Calculate the molar solubility of **AgBr** (silver bromide) in water and in (0.1M) of **Ammonia solution** and compare them? **Ksp = 4 ×10 $^{-13}$, K$_{f1}$ = 2.5×10^{3}, K$_{f2}$ = 1.0× 10^{4}** .

Solubility of **AgBr in water Ksp$_{(AgBr)}$ = [Ag^{+}][Br^{-}]** = S^{2}

$$S^2 = \sqrt{Ksp_{(AgBr)}}\ \sqrt{4\times10^{-13}} = 6.3\times10^{-7} M$$

Solubility of **AgBr** in a solution containing 0. 1M NH$_3$.

$$B_0 = \frac{1}{1+K_{f_1}\{NH_3\}+K_{f_1}\,K_{f_2}\{NH_3\}^2} \qquad B_0 =$$

$$\frac{1}{1+(2.5\times10^3)\times(0.1)+(2.5\times10^3)\times(1\times10^4)\times(0.1)^2} = 1\times\ 10^{-6}$$

$$S = \sqrt{\frac{K_{sp}}{\beta_0}} = \sqrt{\frac{4\times\ 10^{-13}}{4\times\ 10^{-6}}} = 3.2\times\ 10^{-4}\ M$$

$$S_{\text{in ammonia solution}} > S_{\text{in water}}$$

$$\textbf{The Comparison} = \frac{S_{\text{in ammonia solution}}}{S_{\text{in water}}} = \frac{3.2\times10^{-4}}{6.3\times10^{-7}} = (508\ \textit{times more soluble})$$

Method of deriving values of B_0 , B_1 and B_2

$$Ag^{+} + NH_3 \leftrightarrow Ag(NH_3)^{+}\ ,\ K_{f_1} = \frac{\{Ag(NH_3)^{+}\}}{\{Ag+\}\{NH_3\}} \ \ldots\ldots\ldots\ldots(1)$$

Ag $(NH_3)^+$ +NH_3 $\leftrightarrow$ Ag $(NH_3)_2^+$, $\mathrm{K_{f_2}} = \frac{\{\mathrm{Ag\ (NH_3)_2}^+\}}{\{\mathrm{Ag\ (NH_3)^+}\}\{\mathrm{NH_3}\}}$**..(2)**

$$\{\mathrm{Ag^+}\}_\mathrm{T} = \{\mathrm{Ag^+}\} + \{\mathrm{Ag\ (NH_3)^+}\} + \{\ \mathrm{Ag\ (NH_3)_2}^+\}$$

$$B_0 = \frac{\{\mathrm{Ag^+}\}}{\{\mathrm{Ag^+}\}+ \{\mathrm{Ag\ (NH_3)^+}\}+ \{\ \mathrm{Ag\ (NH_3)_2}^+\}}\ ,$$

$$B_1 = \frac{\{\mathrm{Ag\ (NH_3)^+}\}}{\{\mathrm{Ag^+}\}+ \{\mathrm{Ag\ (NH_3)^+}\}+ \{\ \mathrm{Ag\ (NH_3)_2}^+\}}$$

$$B_2 = \frac{\{\ \mathrm{Ag\ (NH_3)_2}^+\}}{\{\mathrm{Ag^+}\}+ \{\mathrm{Ag\ (NH_3)^+}\}+ \{\ \mathrm{Ag\ (NH_3)_2}^+\}}\ ,$$

From equation no 2 $\left\{\ \mathrm{Ag\ (NH_3)_2}^+\right\} = \mathrm{K_{f_2}}\ \{\mathrm{Ag\ (NH_3)^+}\}\ \{\mathrm{NH_3}\}$

$$B_0 = \frac{\{\mathrm{Ag^+}\}}{\{\mathrm{Ag^+}\} + \{\mathrm{Ag\ (NH_3)^+}\} + \{\ \mathrm{Ag\ (NH_3)_2}^+\}}$$

$$B_0 = \frac{\{\mathrm{Ag^+}\}}{\{\mathrm{Ag^+}\}+ \{\mathrm{Ag\ (NH_3)^+}\}+ \mathrm{K_{f_2}}\{\mathrm{Ag\ (NH_3)^+}\}\{\mathrm{NH_3}\}}\ ,$$

From equation no 1 $\{\mathrm{Ag\ (NH_3)^+}\} = \mathrm{K_{f_1}}\ \{\mathrm{Ag\ +}\}\ \{\mathrm{NH_3}\}$

$$B_0 = \frac{\{\mathrm{Ag^+}\}}{\{\mathrm{Ag^+}\} + \mathrm{K_{f_1}}\{\mathrm{Ag^+}\}\{\mathrm{NH_3}\} + \mathrm{K_{f_1}}\ \mathrm{K_{f_2}}\{\mathrm{Ag^+}\}\{\mathrm{NH_3}\}\{\mathrm{NH_3}\}}$$

$$B_0 = \frac{\{\mathrm{Ag^+}\}}{\{\mathrm{Ag^+}\}\left(1+ \mathrm{K_{f_1}}\{\mathrm{NH_3}\}+\mathrm{K_{f_1}}\ \mathrm{K_{f_2}}\{\mathrm{NH_3}\}^2\right)}\ ,$$

$$B_0 = \frac{1}{1 + K_{f_1}\{NH_3\} + K_{f_1} K_{f_2}\{NH_3\}^2}$$

In the same way

$$B_1 = \frac{K_{f_1}\{NH_3\}}{1 + K_{f_1}\{NH_3\} + K_{f_1} K_{f_2}\{NH_3\}^2}$$

$$and$$

$$B_2 = \frac{K_{f_1} K_{f_2}\{NH_3\}^2}{1 + K_{f_1}\{NH_3\} + K_{f_1} K_{f_2}\{NH_3\}^2}$$

Precipitation Titration (Argenometric Titration)

Example 4:- Calculate **pCl** for the titration of 100 mL of 0.10 M **NaCl** with (**0.1 M) $AgNO_3$** after addition of **[0.0, 20.0, 99.0, 99.50, 100.0, 100.50 and 110.0 mL] $AgNO_3$?**

Ksp (AgCl) =1.0×10^{-10}

$$NaCl + AgNO_3 \longrightarrow AgCl \downarrow + NaNO_3$$

At 0.00 mL

pCl = - log [Cl^-] ⟶ - log [0.1] ⟶ pCl^- = 1.00

At 20.0 mL

mmol Cl^- = M × V = 0.1 mmol/mL × 100 mL =10.0 mmol

mmolAg^+ = M × V = 0.1 mmol/mL × 20 mL =2.0 mmol

Cl^- left = 10 -2 = 8 mmol ⟶ [Cl^-] = (mmol/V_T)= 8/120 = 0.0667M

pCl^- = - Log [0.0667] = 1.18

At 99.0 mL

mmolAg^+ = 99 mL × 0.1 mmol/mL = 9.9 mmol

Cl^- left = 10 -9.9 = 0.1 mmol ➡ $[Cl^-]$ = (mmol/V_T)= 0.1/199 = 5 × 10^{-4}M

pCl^- = - Log [5 × 10^{-4}] = 3.26

At 99.5 mL

mmolAg^+ = 99.5 mL × 0.1 mmol/mL=9.95 mmol

Cl^- left = 10 -9.95 = 0.05 mmol ➡ $[Cl^-]$ = (mmol/V_T)= 0.05/199.5 = 2.5 × 10^{-4}M

pCl^- = - Log [2.5 × 10^{-4}] = 3.6

At 100 mL

All the Cl^- is reacted with Ag^+:- [Equivalent point]

$$[\mathrm{Cl}^-] = \sqrt[2]{\boldsymbol{ksp}_{(\boldsymbol{AgCl})}} = \sqrt[2]{\mathbf{1.0\ x10^{-10}}} = 1.0\ \text{x}10^{-5}\ \text{M}$$

pCl^- = - Log [1.0 x10^{-5}] = 5

At 100.5 mL

mmolAg^+ = 100.5 mL × 0.1 mmol/mL=10.05 mmol

Ag^+ left = 10.05 -10 = 0.05 mmol ➡ $[Ag^+]$ = (mmol/V_T)= 0.05/200.5 = 2.5 ×10^{-4} M

$$[\mathrm{Cl}^-] = \frac{\boldsymbol{ksp}_{(\boldsymbol{AgCl})}}{[\mathrm{Ag+}]} = \frac{1.0 \times 10^{-10}}{2.5 \times 10^{-4}} = 4 \times 10^{-7}\ \text{M}$$

pCl^- = - Log [4 ×10^{-7}] = 6.4

At 110 mL

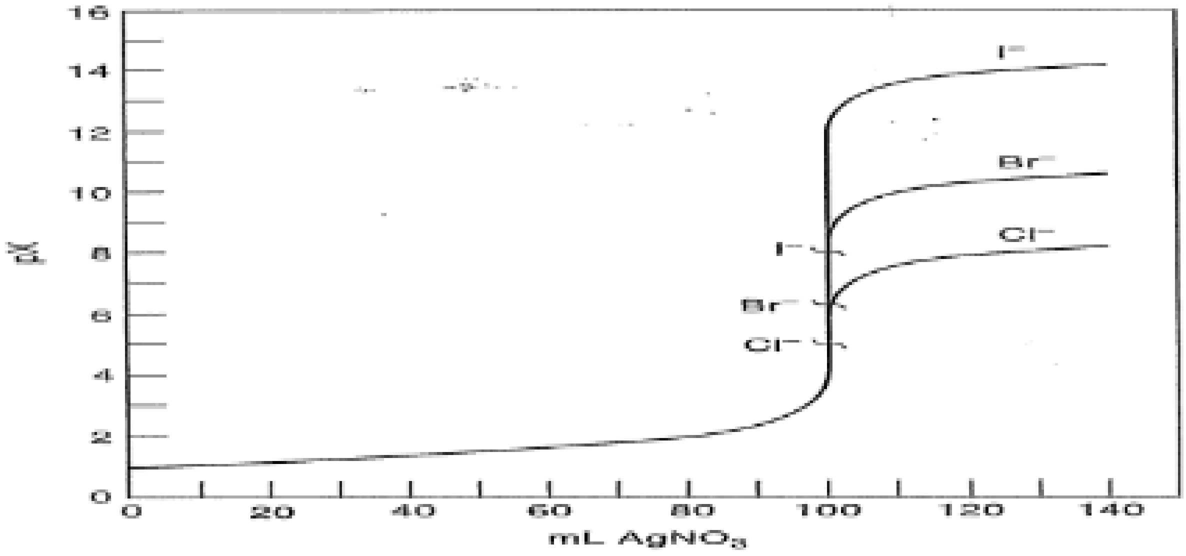
mmolAg^+ = 110 mL × 0.1 mmol/mL= 11 mmol

Ag^+ left = 11 -10 = 1 mmol ➡ $[Ag^+]$ = (mmol/V_T)= 1/210 = 4.76 ×10^{-3} M

$$[\mathrm{Cl}^-] = \frac{\boldsymbol{ksp}_{(\boldsymbol{AgCl})}}{[\mathrm{Ag+}]} = \frac{1.0 \times 10^{-10}}{4.76 \times 10^{-3}} = 2.1 \times 10^{-8}\ \text{M}$$

pCl^- = - Log [2.1 × 10^{-8}] = 7.67

Titration curves for 100mL 0.1M Cl^-, Br^-, and I^- solutions versus 0.1M $AgNO_3$.



Note: The smaller the K_{sp}, the sharper the endpoint (or the smaller the K_{sp}, the larger the break at the equivalence point).

The detection of the endpoint (indicators):

We can detect the endpoint by measuring either pCl or pAg with two types of indicators:

(1) Indicators Reacting with the Titrant:

There are several examples of an indicator forming a colored compound with a titrant, two common method were:

(a) Mohr Method

used for determining chloride ion, after chloride ion consumed by reacting with equal mmol of $AgNO_3$, the excess (after drops) of $AgNO_3$ than reacting with the indicator (K_2CrO_4) to form red precipitate Ag_2CrO_4.

$$Cl^- + Ag^+ \longrightarrow AgCl\downarrow \qquad K_{sp} = 1.0 \times 10^{-10}$$

Analyte **titrant** **white precipitate**

$$CrO_4^{-2} + 2Ag^+ \longrightarrow Ag_2CrO_4\downarrow \qquad K_{sp} = 1.1 \times 10^{-12}$$

Analyte **titrant** **red precipitate**

The concentration of the indicator is important. The $\mathbf{Ag_2CrO_4}$ should just start precipitating at the equivalent point, where we have a saturated solution of **AgCl.** From Ksp, the concentration of $\mathbf{Ag^+}$ at the equivalent point is $\mathbf{10^{-5}M}$. (It is less than this before the equivalent point). So, $\mathbf{Ag_2CrO_4}$ should precipitate just when $\mathbf{Ag^+ = 10^{-5}M}$. The solubility product of $\mathbf{Ag_2CrO_4}$ is $\mathbf{1.1\ x10^{-12}}$. By inserting the $\mathbf{Ag^+}$concentration in the K_{sp} equation for $\mathbf{Ag_2CrO_4}$**,**we calculate that, for this to occur,[$\mathbf{CrO_4^{-2}}$]should be **0.011M**.

$$[10^{-5}]^2 \times [CrO_4^{-2}] = 1.1 \times 10^{-12}$$

$$[CrO_4^{-2}] = 1.1 \times 10^{-2}\ M$$

If the concentration is greater than $\mathbf{Ag_2CrO_4}$ will begin to precipitate when $\mathbf{[Ag^+]}$ is less than $\mathbf{10^{-5}\ M}$ (before the equivalent point). If it is less than 0.011M, then the $\mathbf{[Ag^+]}$ will have exceed $\mathbf{10^{-5}\ M}$ (beyond the equivalent point) before precipitation of $\mathbf{Ag_2CrO_4}$ begins**.** In actual practice, the indicator concentration is kept at 0.002 to 0.005 M. If it is much higher than this, the intense yellow color of the Chromate ion obscures the red $\mathbf{Ag_2CrO_4}$ precipitate color, and an excess of $\mathbf{Ag^+}$ is required to produce enough precipitate to be seen. An indicator blank should always be run and subtracted from the titration to correct for errors.

The Mohr titration must be performed at a **pH** of about **8.** If the solution is too acid (**pH < 6**), then part of the indicator is present as [$\mathbf{HCrO_4^-}$**]**, and more [$\mathbf{Ag^+}$**]** will be required to form the [$\mathbf{Ag_2CrO_4}$] precipitate. Above (**pH 8),** silver hydroxide may be precipitated at (**pH > 10**). The pH is properly maintained by adding solid calcium carbonate to the solution. (While the carbonate ion is a fairly strong Brønsted base, the concentration in a saturated calcium carbonate solution is just sufficient to give a **pH** about **8.)** The Mohr titration is useful for determining chloride in neutral or unbuffered solutions, such as drinking water.

(b)Volhard Titration (Back Titration)

This is an indirect titration procedure for determining anions that precipitate with silver **(**$\mathbf{Cl^-}$ **,** $\mathbf{Br^-}$**, and** $\mathbf{SCN^-}$**)** and it is performed in acid ($\mathbf{HNO_3}$) solution. In this procedure, we add a measured excess of $\mathbf{AgNO_3}$ to precipitate the anion and then determine the excess $\mathbf{Ag^+}$ by back titration with standard potassium thiocyanate solution:-

$$\boxed{\begin{array}{l} X^- + Ag^+ \longrightarrow AgX + \text{excess } Ag^+ \\ \text{excess } Ag^+ + SCN^- \longrightarrow AgSCN \end{array}}$$

We detect the End Point by adding iron **(III)** as a **(Ferric ammonium sulfate),** which forms a soluble red complex with the first excess of titrant:-

$$\boxed{Fe^{+3} + SCN^- \longrightarrow Fe(SCN)^{+2}}$$

If the precipitate AgX is less soluble than **AgSCN**, we do not have to remove the precipitate before titrating. Such is the case with **(Br^-, and SCN^-).** In the case of **I^-** we do not add the indicator until all the **I^-** is precipitated, since it would be oxidized by the **iron (III).** If the precipitate is more soluble than **AgSCN**, it will react with the titrant to give a high and diffuse end point. Such is the case with **AgCl:-**

$$\boxed{Ag^+ + SCN^- \longrightarrow AgSCN + Cl^-}$$

Therefore, we remove the precipitate by filtration before titrating. Obviously, these indicators must not form a compound with the titrant that is more stable than the precipitate, or the color reaction would occur when the first drop of titrant is added.

(2) Adsorption Indicators (Fajan's Methods)

With adsorption indicators, the indicator reaction takes place on the surface of the precipitate. The Fluorescein indicators such as fluorescein, methyl violet and Rhodamine and Bromophenol blue are dyes, exists in solution as ionized form, usually anion **In^-.** Consider the titration of **Cl^-** with **Ag^+**, before the equivalent point, **Cl^-** is in excess, and the primary adsorbed layer is **Cl^-**.This repulses the indicator anion, and the more loosely held secondary layer (counter ion) of adsorbed ions is cations, such as **Na^+.**

$$\boxed{AgCl : Cl^- :: Na^+}$$

Beyond the equivalent point, **Ag^+** is excess and the surface of the precipitate become positively charged, with the primary layer being **Ag^+.** This will now attract the indicator anion and adsorb it in the secondary layer.

$$\boxed{AgCl : Ag^+ :: In^-}$$

The color of the adsorbed indicator is different from that of the unabsorbed indicators, and the difference signals the completion of the titration. The more insoluble precipitate can be titrated in more strongly adsorbed indicators. We want the maximum surface area for adsorption in contrast to gravimetry. Coagulate decreases the surface area for absorption of the indicator, which in turn decrease the sharpness of the end point, we can prevent coagulation of silver chloride by adding some **Dextrin** to solution.

Problems

1- Explain the Volhard Titration of Chloride, the Fajan's titration which is used for acid solutions. Why?

2- Explain the principles of adsorption indicators.

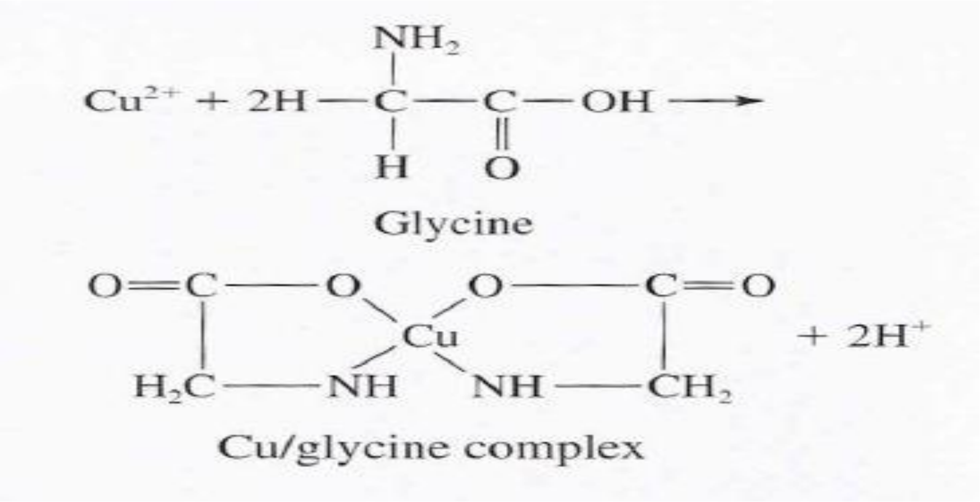
3- Calculate the solubility of PbS in (0.01M) HCl? And calculate the equilibrium concentrations of S^{-2}, HS^- and H_2S**.** $\mathbf{K_{sp(PbS)}= 3\times10^{-28}, K_{a1}=9.6\times10^{-8}, K_{a2}=1.3\times10^{-14}}$**.**

Complexometric Reactions and Titrations

Many metal ions form slightly dissociated with various ligand (complexing agents). Complexometric titration is useful for determining a large number of metals. Selectivity can be achieved by appropriate use of masking agents (addition of other complexing agents that react with interfering metal ions) and by pH control.

Complexes and formation constant:-

Complexes play an important role in many chemical and biochemical processes, for example, the heme molecule in blood holds the iron atom tightly because the nitrogen atoms of the heme form strong ligand or complexing bonds, which means nitrogen is a good complexer.



$$\mathbf{M} + \mathbf{L} \rightleftharpoons \mathbf{ML} \qquad \beta_1 = \frac{[ML]}{[M][L]} = K_1$$

$$\mathbf{M} + 2\mathbf{L} \rightleftharpoons \mathbf{ML_2} \qquad \beta_2 = \frac{[\mathbf{ML_2}]}{[M][L]^2} = K_1K_2$$

$$\mathbf{M} + 3\mathbf{L} \rightleftharpoons \mathbf{ML_3} \qquad \beta_3 = \frac{[\mathbf{ML_3}]}{[M][L]^3} = K_1K_2K_3$$

$$\mathbf{M} + n\mathbf{L} \rightleftharpoons \mathbf{ML}_n \qquad \beta_n = \frac{[\mathbf{ML}_n]}{[M][L]^n} = K_1K_2K_3 \ldots . K_n$$

For a given species like ML, we can calculate an alpha value, which is the fraction of the total metal concentration existing in that form. Thus, α_M is the fraction of the total metal present at equilibrium as the free metal, α_{ML} is the fraction present as ML, and so on. the alpha values are given by:

Calculation of Alpha Values for Metal complexes

The alpha values for metal ligand complexes can be derived in the same way that we derived values for polyfunctional acids . The alphas are defined as

$$\alpha_M = \frac{[M]}{c_M} \qquad \alpha_{ML_2} = \frac{[ML_2]}{c_M}$$

$$\alpha_{ML} = \frac{[ML]}{c_M} \qquad \alpha_{ML_n} = \frac{[ML_n]}{c_M}$$

The total metal concentration $c_M = [M] + [ML] + [ML_2] + \cdots + [ML_n]$

From the overall formation constants the concentration of the complexes can be expressed in the terms of the free metal concentration **[M],** to give

$$c_M = [M] + \beta_1 [M][L] + \beta_2 [M][L]^2 + \cdots + \beta_n [M][L]^n$$

$$= [M]\{1 + \beta_1 [L] + \beta_2 [L]^2 + \cdots + \beta_n [L]^n\}$$

Now α_M can be found as:

$$\alpha_M = \frac{[M]}{c_M} = \frac{[M]}{[M] + \beta_1[M][L] + \beta_2[M][L]^2 + \beta_3[M][L]^3 \ldots\ldots..\beta_n[M][L]^n}$$

$$\alpha_M = \frac{[M]}{c_M} = \frac{[M]}{[M]\{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 \ldots\ldots..\beta_n[L]^n\}}$$

$$\alpha_M = \frac{[M]}{c_M} = \frac{1}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 \ldots\ldots..\beta_n[L]^n}$$

From above Equations. We can find α_{ML} from

$$\alpha_{ML} = \frac{[ML]}{c_M} = \frac{\beta_1[M][L]}{[M] + \beta_1[M][L] + \beta_2[M][L]^2 + \beta_3[M][L]^3 \ldots\ldots..\beta_n[M][L]^n}$$

$$\alpha_{ML} = \frac{[ML]}{c_M} = \frac{\beta_1[M][L]}{[M]\{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 \ldots\ldots..\beta_n[L]^n\}}$$

$$= \frac{\beta_1[L]}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 \dots \dots .. \beta_n[L]^n}$$

$$\alpha_M = \frac{1}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 \dots \dots .. \beta_n[L]^n}$$

$$\alpha_{ML} = \frac{\beta_1[L]}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 \dots \dots .. \beta_n[L]^n}$$

$$\alpha_{ML_2} = \frac{\beta_2[L]^2}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 \dots \dots .. \beta_n[L]^n}$$

$$\alpha_{ML_n} = \frac{\beta_n[L]^n}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 \dots \dots .. \beta_n[L]^n}$$

Many cations will form complexes in solution with a variety of substances have a pair of unshared electron (e.g. on N, O, S atoms in molecule) capable of satisfying the coordination number of the metal. The metal ion is a Lewis acid (electron pair acceptor), and the complexer is a Lewis base (electron pair donor). The number of molecules of the complexing agent, called the ligand, will depend on the coordination number of the metal and on the number of complexing group on the ligand molecules.

$$\mathbf{Ag^+ + NH_3 \leftrightarrow Ag(NH_3)^+ \quad , \quad Kf_1 = \frac{[Ag(NH_3)^+]}{[Ag^+][NH_3]} = 2.5 \times 10^3}$$

$$\mathbf{Ag(NH_3)^+ + NH_3 \leftrightarrow Ag(NH_3)_2^+ \; , \; Kf_2 = \frac{[Ag(NH_3)_2^+]}{[Ag(NH_3)^+][NH_3]} = 1.0 \times 10^4}$$

$$\mathbf{Ag^+ + 2NH_3 \leftrightarrow Ag(NH_3)_2^+ \quad , \; Kf = Kf_1 . Kf_2 = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = 2.5 \times 10^7}$$

Formation constant (K_f):- the formation constant is also called the stability constant Ks or Ksp.

$$\mathbf{K_f = K_s = \frac{1}{K_i} = \frac{1}{K_d}}$$

$$\mathbf{Ag(NH_3)_2^+ \leftrightarrow Ag^+ + 2NH_3 \quad , \; K_d = \frac{1}{K_f} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = 4.0 \times 10^{-8}}$$

Example (1) :- A divalent metal M^{+2} reacts with a ligand L to form 1:1 complex.

$$\mathbf{M^{+2} + L = ML^{+2}}\ ,\ \ \mathbf{K_f = \frac{[ML^{+2}]}{[M^{+2}][L]} = 1.0 \times 10^{8}}$$

Calculate the conc. of M^{+2} in a solution prepared by mixing equal volume of 0.2M (M^{+2}) and 0.2M (L), $\mathbf{K_f = 1.0 \times 10^{8}}$**.**

Solution:

The concentration of complex =

$$\frac{\mathbf{M^{+2}}}{\mathbf{mmol(m \times V)}} + \frac{\mathbf{L}}{\mathbf{mmol(m \times V)}} = \frac{\mathbf{ML^{+2}}}{\mathbf{[ML^{+2}] = \frac{(m\times V)M^{+2}}{(\ v_T\ =2v\ )\mathit{mix}}}}$$

$$\mathbf{[ML^{+2}] = \frac{(m \times V)}{2v} = \frac{0.2\ v}{2v} = \frac{0.2}{2} = 0.1M}$$

$$\mathbf{K_f = \frac{[ML^{+2}]}{[M^{+2}][L]} = 1.0 \times 10^{8} = \frac{0.1\ M}{(x)(x)}}$$

$$\mathbf{0.1M\ =\ 1.0 \times 10^{8}\ \times \boldsymbol{x}^{2}\quad ,\quad \boldsymbol{x}^{2} = \left(\frac{0.1\mathit{M}}{1.0 \times 10^{8}}\right) = 1.0 \times 10^{-9}}$$

$$\mathbf{\boldsymbol{x} = \sqrt[2]{1.0 \times 10^{-9}}\quad ,\quad \boldsymbol{x} = [M^{+2}] = 3.2 \times 10^{-5}M}$$

Example(2) :- Silver ion forms a stable 1:1 complex with triethylene tetramine (**trien**) $[NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2]$. Calculate the silver ion conc. at equilibrium when 25mL of 0.01M silver nitrate is added to 50mL of 0.015M trien, $\mathbf{K_f = 5.0 \times 10^{7}}$?

Solution

$$\mathbf{Ag^{+} + trien \leftrightarrow Ag(trien)^{+}}\ ,\ \ \mathbf{K_f = \frac{[Ag(trien)^{+}]}{[Ag^{+}][trien]} = 5.0 \times 10^{7}}$$

$[Ag^{+}]$ unreacted = x

$$\mathbf{mmol\ Ag^{+} = M \times V = 0.01 \times 25 = 0.25mmol}$$

$$\mathbf{mmol\ trien = M \times V = 0.015 \times 50 = 0.75mmol}$$

$$\mathbf{mmol\ trien\ unreacted = 0.75 - 0.25 = 0.5mmol}$$

$$\mathbf{M_{trien} = \frac{mmol}{V} = \frac{0.5}{50+25} = 6.7 \times 10^{-3}M}$$

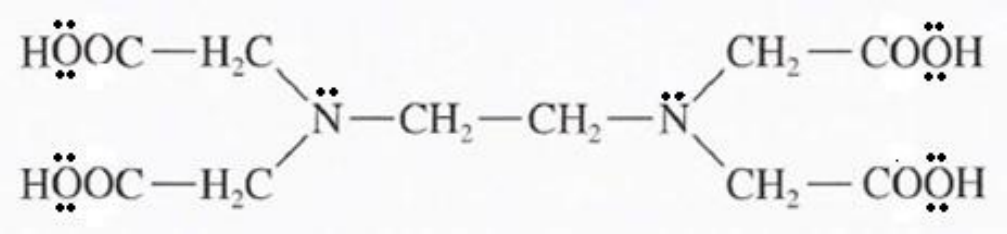
$$\mathbf{K_f = \frac{[Ag(trien)^+]}{[Ag^+][trien]} = 5.0 \times 10^7 = \frac{\frac{0.25mmol}{50+25}}{x(6.7 \times 10^{-3})} = \frac{3.3 \times 10^{-3}}{x(6.7 \times 10^{-3})}}$$

$$\mathbf{x = \frac{3.3 \times 10^{-3}}{5.0 \times 10^7 \times 6.7 \times 10^{-3}} = [Ag^+] = 9.8 \times 10^{-9}M}$$

Chelates:-EDTA (the ultimate titrating agent for metals): An organic agent that has two or more groups capable of complexing with a metal ion is called a chelating agent, the complex formed is called a chelate. The chelating agent is called the ligand. Titration with a chelating agent is called a chelometric titration.

The term chelate is derived from the Greek term meaning (claw like) chelating agents literally wrap themselves around a metal ion.

EDTA equilibrium:-The protons in EDTA Ethylene Diamine Tetra Acetic acid are displaced upon complexing with a metal ion. Negatively charged chelate results



Tetraprotic acid (H_4Y): six complexing groups (hexadentate) multidentate

Formation constant:-Lets EDTA =

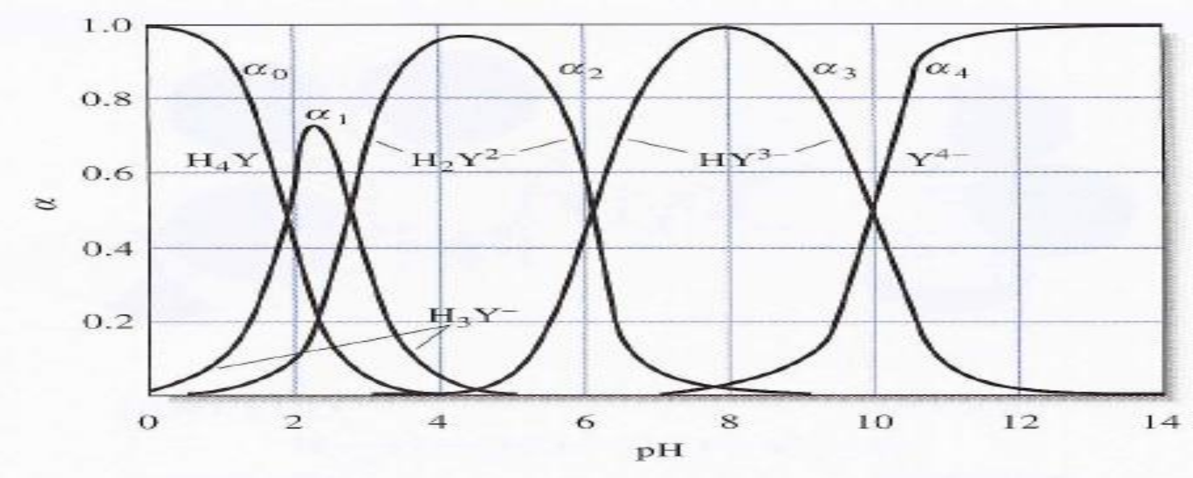
$$\mathbf{H_4Y \ \rightleftharpoons\ H^+ + H_3Y^- \qquad K_{a1} = 1.0 \times 10^{-2} = \frac{[H^+][H_3Y^-]}{H_4Y}}$$

$$\mathbf{H_3Y^- \rightleftharpoons H^+ + H_2Y^{-2}} \qquad K_{a2} = 2.2 \times 10^{-3} = \frac{[\mathbf{H^+}][\mathbf{H_2Y^{-2}}]}{[\mathbf{H_3Y^-}]}$$

$$\mathbf{H_2Y^{-2} \rightleftharpoons H^+ + HY^{-3}} \qquad K_{a3} = 6.9 \times 10^{-7} = \frac{[\mathbf{H^+}][\mathbf{HY^{-3}}]}{[\mathbf{H_2Y^{-2}}]}$$

$$\mathbf{HY^{-3} \rightleftharpoons H^+ + Y^{-4}} \qquad K_{a4} = 5.5 \times 10^{-11} = \frac{[\mathbf{H^+}][\mathbf{Y^{-4}}]}{[\mathbf{HY^{-3}}]}$$

Effect of pH on EDTA equilibria :-



Composition of EDTA solutions as a function of pH

α_0 **= fraction of the total EDTA species that exists as** H_4Y

α_1 **= fraction of the total EDTA species that exists as** H_3Y^-

α_2 **= fraction of the total EDTA species that exists as** H_2Y^{2-}

α_3 **= fraction of the total EDTA species that exists as** HY^{3-}

α_4 **= fraction of the total EDTA species that exists as** Y^{4-}

$$C_T = [\mathbf{Y^{4-}}] + [\mathbf{HY^{3-}}] + [\mathbf{H_2Y^{2-}}] + [\mathbf{H_3Y^-}] + [\mathbf{H_4}Y]$$

$$\alpha_4 = \frac{\mathbf{Y^{-4}}}{C_T}\ ,\quad \alpha_3 = \frac{HY^{3-}}{C_T}\ ,\ \alpha_2 = \frac{H_2Y^{2-}}{C_T}\ ,\ \alpha_1 = \frac{H_3Y^-}{C_T}\ ,\ \alpha_0 = \frac{H_4Y}{C_T}$$

Example 3:- A solution has 0.1 M of EDTA Calculate the approximate concentration of this species $[\mathbf{Y^{4-}}], [\mathbf{HY^{3-}}], [\mathbf{H_2Y^{2-}}], [\mathbf{H_3Y^-}], [\mathbf{H_4Y}]$ **at pH** $\mathbf{2.4, 6, 8, 10.}$

Solution: - the concentration of $[\mathbf{Y^{4-}}]\boldsymbol{at\ pH\ 2} = \boldsymbol{\alpha_4} \times \boldsymbol{C_T}$ **= 0 × 0.1 = 0 M**

the concentration of $[\mathbf{HY^{3-}}]\boldsymbol{at\ pH\ 2} = \boldsymbol{\alpha_3} \times \boldsymbol{C_T}$ **= 0 × 0.1 = 0 M**

the concentration of $[\mathbf{H_2Y^{2-}}]\boldsymbol{at\ pH\ 2} = \boldsymbol{\alpha_2} \times \boldsymbol{C_T}$ **= ~ 0.1 × 0.1= ~ 0.01 M**

the concentration of $[\mathbf{H_3Y^{-}}]\boldsymbol{at\ pH\ 2} = \boldsymbol{\alpha_1} \times \boldsymbol{C_T}$ **= ~ 0.6 × 0.1= ~ 0.06 M**

the concentration of $[\mathbf{H_4}\boldsymbol{Y}]\boldsymbol{at\ pH\ 2} = \boldsymbol{\alpha_0} \times \boldsymbol{C_T}$ **= ~ 0.4 × 0.1= ~ 0.04 M**

In the same way, we can calculate the species concentration at different pH values.

Example 4:- Calculate the fraction of EDTA that exists as Y^{-4} at pH 10, and from this calculate pCa in 100mL of solution of 0.1M Ca^{+2} at pH 10 (α_4 = 0.35) after adding 100mL of 0.1M EDTA. $\mathbf{K_f = 4.943 \times 10^{10}}$

The fraction of **$[Y^{-4}]$ at pH = 10** , $\boldsymbol{\alpha_4} = \frac{[\mathrm{Y^{-4}}]}{\boldsymbol{C_T}}$, $[\mathbf{Y^{-4}}] = \boldsymbol{\alpha_4}\ \boldsymbol{C_T}$,

$$[\mathrm{Y^{-4}}] = \mathbf{0.35 \times 0.1}\boldsymbol{M} = \mathbf{0.035}\boldsymbol{M}$$

- **The pCa** $\mathbf{mmol\ Ca^{2+} = M \times V = 0.1 \times 100 = 10.0mmol}$

$$\mathbf{mmol\ EDTA = M \times V = 0.1 \times 100 = 10.0mmol}$$

We have formed 10.0mmol CaY^{-2} in 200mL, or 0.050M

$$\mathbf{K_f = \frac{[CaY^{-2}]}{[Ca^{+2}]\alpha_4[C_{H_4Y}]} = \frac{0.05}{(x)(0.35)(x)} = \frac{0.05}{(0.35) \times x^2}}$$

$$\mathbf{4.943{\times}10^{10} = \frac{0.05}{(0.35) \times x^2}\ ,\quad 0.05 = 4.943{\times}10^{10} \times 0.35 \times x^2}$$

$$\mathbf{x^2 = \frac{0.05}{4.943{\times}10^{10} \times 0.35} = 2.9 \times 10^{-12}}$$

$$\mathbf{x = \sqrt[2]{2.9 \times 10^{-12}} = 1.7 \times 10^{-6}M}$$

$$\mathbf{pCa = -\log 1.7 \times 10^{-6} = 5.77}$$

Conditional formation constant (used for a fixed pH):

$$\mathbf{K_f^{`}} = \text{conditional formation constant} = \mathbf{K_f \alpha_4} = \frac{[\mathbf{CaY^{-2}}]}{[\mathbf{Ca^{+2}}][\mathbf{C_{H_4Y}}]}$$

The conditional formation constant value holds for only a specified pH.

Example 5: **-** Calculate the equilibrium concentration of **Ni^{2+}** in a solution with an analytical **Niy^{2-}** concentration of **0.0150 M** at pH (a) **3.0** and (b) **8.0** (**α_4 is 2.5×10^{-11}** at **pH 3** and **5.4×10^{-3}** at **pH 8**). **$K_f = 4.2 \times 10^{18}$**

$$\mathbf{Ni^{2+} + Y^{4-} \rightleftharpoons NiY^{2-}}, \qquad \mathbf{K_{f_{NiY}}} = \frac{[\mathbf{NiY^{2-}}]}{[\mathbf{Ni^{2+}}][\mathbf{Y^{4-}}]} = \mathbf{4.2 \times 10^{18}}$$

Since the complex is the only source of both **Ni^{+2}** and the **EDTA** species,

$$[\mathbf{Ni^{2+}}] = [\mathbf{Y^{4-}}] + [\mathbf{HY^{3-}}] + [\mathbf{H_2Y^{2-}}] + [\mathbf{H_3Y^{-}}] + [\mathbf{H_4Y}] = \mathbf{C_T}$$

$$\mathbf{K_{f\ NiY}} = \frac{[\mathbf{NiY^{2-}}]}{[\mathbf{Ni^{2+}}]\propto_4 \mathbf{C_T}} = \frac{[\mathbf{NiY^{2-}}]}{[\mathbf{Ni^{2+}}]^2 \propto_4}$$

a) At pH 3

$$\mathbf{K_{f\ NiY}} = \frac{[\mathbf{NiY^{2-}}]}{[\mathbf{Ni^{2+}}]^2 \propto_4} = \mathbf{4.2 \times 10^{18}} = \frac{\mathbf{0.015}}{[\mathbf{Ni^{2+}}]^2 \times \mathbf{2.5 \times 10^{-11}}}$$

$$\mathbf{2.5 \times 10^{-11} \times 4.2 \times 10^{18}} = \frac{\mathbf{0.0150}}{[\mathbf{Ni^{2+}}]^2} = \mathbf{1.05 \times 10^{8}}$$

$$[\mathbf{Ni^{2+}}]^2 \times \mathbf{1.05 \times 10^{8}} = \mathbf{0.0150},$$

$$[\mathbf{Ni^{2+}}]^2 = \frac{\mathbf{0.0150}}{\mathbf{1.05 \times 10^{8}}} = \mathbf{1.43 \times 10^{-10}}$$

$$[\mathbf{Ni^{2+}}] = \sqrt[2]{\mathbf{1.43 \times 10^{-10}}} = \mathbf{1.2 \times 10^{-5}\ M}$$

b) At pH 8

$$\mathbf{K_{f\ NiY}} = \frac{[\mathbf{NiY^{2-}}]}{[\mathbf{Ni^{2+}}]^2 \propto_4} = \mathbf{4.2 \times 10^{18}} = \frac{\mathbf{0.015}}{[\mathbf{Ni^{2+}}]^2 \times \mathbf{5.4 \times 10^{-3}}}$$

$$\mathbf{5.4 \times 10^{-3} \times 4.2 \times 10^{18}} = \frac{\mathbf{0.0150}}{[\mathbf{Ni^{2+}}]^2} = \mathbf{2.268 \times 10^{16}}$$

$$[\mathbf{Ni^{2+}}]^2 \times \mathbf{2.268 \times 10^{16} = 0.0150},$$

$$[\mathbf{Ni^{2+}}]^2 = \frac{\mathbf{0.0150}}{\mathbf{2.268 \times 10^{16}}} = \mathbf{6.6 \times 10^{-19}}$$

$$[\mathbf{Ni^{2+}}] = \sqrt[2]{\mathbf{6.6 \times 10^{-19}}} = \mathbf{8.1 \times 10^{-10}\ M}$$

Example 6:- The formation constant for CaY^{2-} is 1.8×10^{10} at pH10. Calculate pCa in 100mL of a solution of 0.10M Ca^{+2} at pH10 after addition of a 0mL, 50mL, 100mL and 150mL of 0.1M EDTA?

(1) At 0mL: (0.10M Ca^{+2} alone) $\mathbf{pCa = -\log[Ca^{2+}] = -\log 0.1 = 1.0}$

(2) At 50mL: before equivalence point

$$\mathbf{mmol\ Ca^{2+} = M \times V = 0.1 \times 100 = 10.0 mmol}$$

$$\mathbf{mmol\ EDTA = M \times V = 0.1 \times 50 = 5.0 mmol}$$

$$\mathbf{mmol\ Ca^{2+} unreacted = 10.0 - 5.0 = 5.0 mmol}$$

$$\mathbf{pCa = -\log[Ca^{2+}] = -\log\frac{5.0 mmol}{100mL + 50mL} = 1.48}$$

(3) At 100mL: equivalence point

$$\mathbf{K_f} = \frac{[\mathbf{CaY^{-2}}]}{[\mathbf{Ca^{+2}}][\mathbf{C_{H_4Y}}]} = \mathbf{1.8 \times 10^{10}} = \frac{\frac{\mathbf{10mmol}}{\mathbf{100mL+100mL}}}{(\mathbf{x})(\mathbf{x})}$$

$$\mathbf{1.8 \times 10^{10}} = \frac{\mathbf{0.05}}{(\mathbf{x})^2}, \quad (\mathbf{x})^2 = \frac{\mathbf{0.05}}{\mathbf{1.8\times10^{10}}} = \mathbf{2.8 \times 10^{-12}},$$

$$\mathbf{x} = \sqrt[2]{2.8 \times 10^{-12}} = 1.7 \times 10^{-6}\mathrm{M}$$

$$\mathrm{pCa} = -\log[\mathrm{Ca}^{2+}] = -\log 1.7 \times 10^{-6} = 5.77$$

(4) At 150mL: after equivalence point

$$\text{mmol EDTA} = \mathrm{M} \times \mathrm{V} = 0.1 \times 150 = 15.0\text{mmol}$$

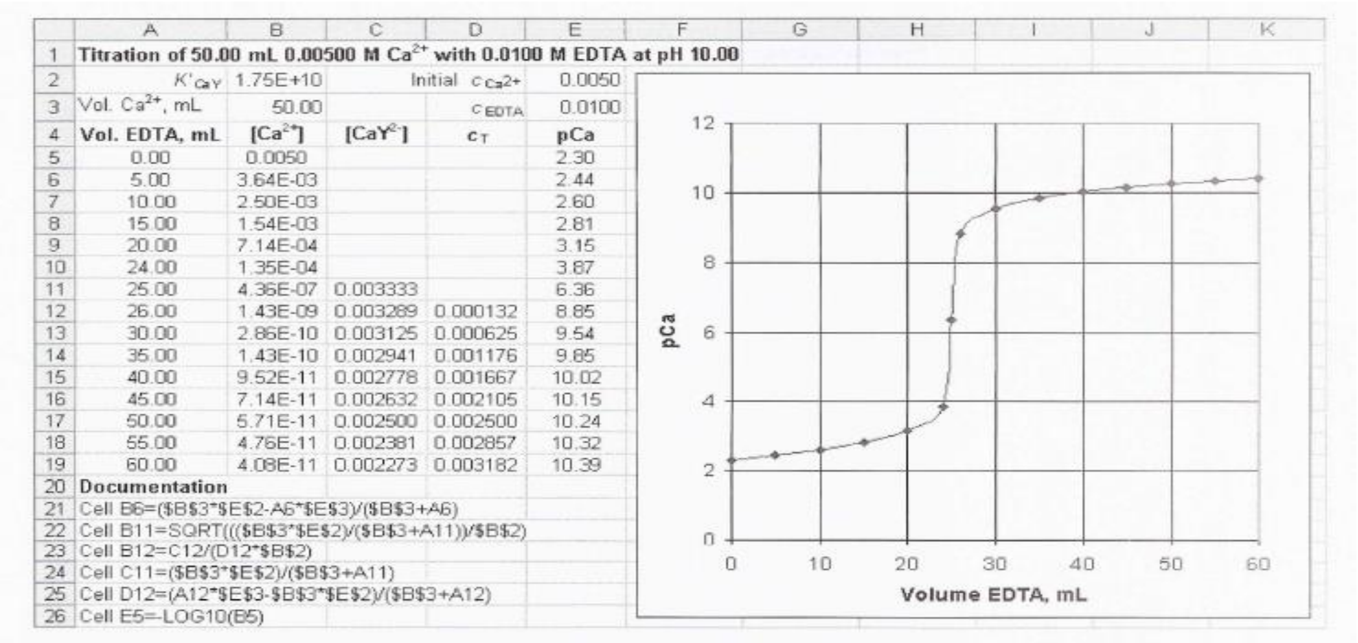
$$\text{mmol EDTA unreacted} = 15.0 - 10.0 = 5.0\text{mmol}$$

$$\mathrm{M_{EDTA}} = \frac{5\text{mmol}}{100\text{mL} + 150\text{mL}} = 0.02\mathrm{M}, \quad [\mathrm{CaY}^{-2}] = \frac{10\text{mmol}}{100\text{mL} + 150\text{mL}} = 0.04\mathrm{M}$$

$$\mathrm{K_f} = \frac{[\mathrm{CaY}^{-2}]}{[\mathrm{Ca}^{+2}][\mathrm{C_{H_4Y}}]} = \frac{0.04}{[\mathrm{Ca}^{+2}](0.02)} = 1.8 \times 10^{10}$$

$$0.04 = [\mathrm{Ca}^{+2}] \times 0.02 \times 1.8 \times 10^{10}\,, \quad [\mathrm{Ca}^{+2}] = \frac{0.04}{0.02 \times 1.8 \times 10^{10}} =$$

$$[\mathrm{Ca}^{+2}] = 1.1 \times 10^{-10}\mathrm{M}\,, \quad \mathrm{pCa} = -\log 1.1 \times 10^{-10} = 9.95$$

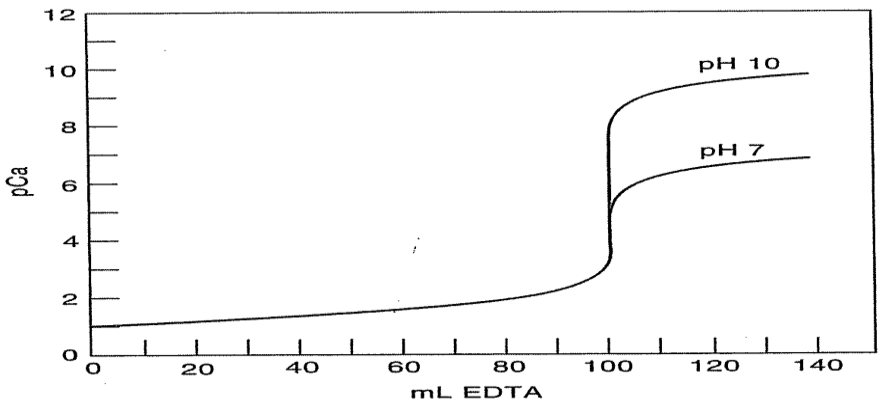


	A	B	C	D	E
1	**Titration of 50.00 mL 0.00500 M Ca^{2+} with 0.0100 M EDTA at pH 10.00**				
2	K'_{CaY}	1.75E+10		Initial c_{Ca2+}	0.0050
3	Vol. Ca^{2+}, mL	50.00		c_{EDTA}	0.0100
4	**Vol. EDTA, mL**	**$[Ca^{2+}]$**	**$[CaY^{2-}]$**	**c_T**	**pCa**
5	0.00	0.0050			2.30
6	5.00	3.64E-03			2.44
7	10.00	2.50E-03			2.60
8	15.00	1.54E-03			2.81
9	20.00	7.14E-04			3.15
10	24.00	1.35E-04			3.87
11	25.00	4.36E-07	0.003333		6.36
12	26.00	1.43E-09	0.003289	0.000132	8.85
13	30.00	2.86E-10	0.003125	0.000625	9.54
14	35.00	1.43E-10	0.002941	0.001176	9.85
15	40.00	9.52E-11	0.002778	0.001667	10.02
16	45.00	7.14E-11	0.002632	0.002105	10.15
17	50.00	5.71E-11	0.002500	0.002500	10.24
18	55.00	4.76E-11	0.002381	0.002857	10.32
19	60.00	4.08E-11	0.002273	0.003182	10.39
20	**Documentation**				
21	Cell B6=(B3*E2-A6*E3)/(B3+A6)				
22	Cell B11=SQRT(((B3*E2)/(B3+A11))/B2)				
23	Cell B12=C12/(D12*B2)				
24	Cell C11=(B3*E2)/(B3+A11)				
25	Cell D12=(A12*E3-B3*E2)/(B3+A12)				
26	Cell E5=-LOG10(B5)				

Spreadsheet for the titration of 50.00 mL of 0.00500 M Ca^{2+} with 0.01 M EDTA in a solution buffered at pH 10

Metal-EDTA titration curves:-Only some metal chelates are stable enough to allow titration in acid solution, others require alkaline solution. Titration curves for 100mL 0.1M Ca^{+2} versus 0.1M Na_2EDTA at pH7 and pH10.

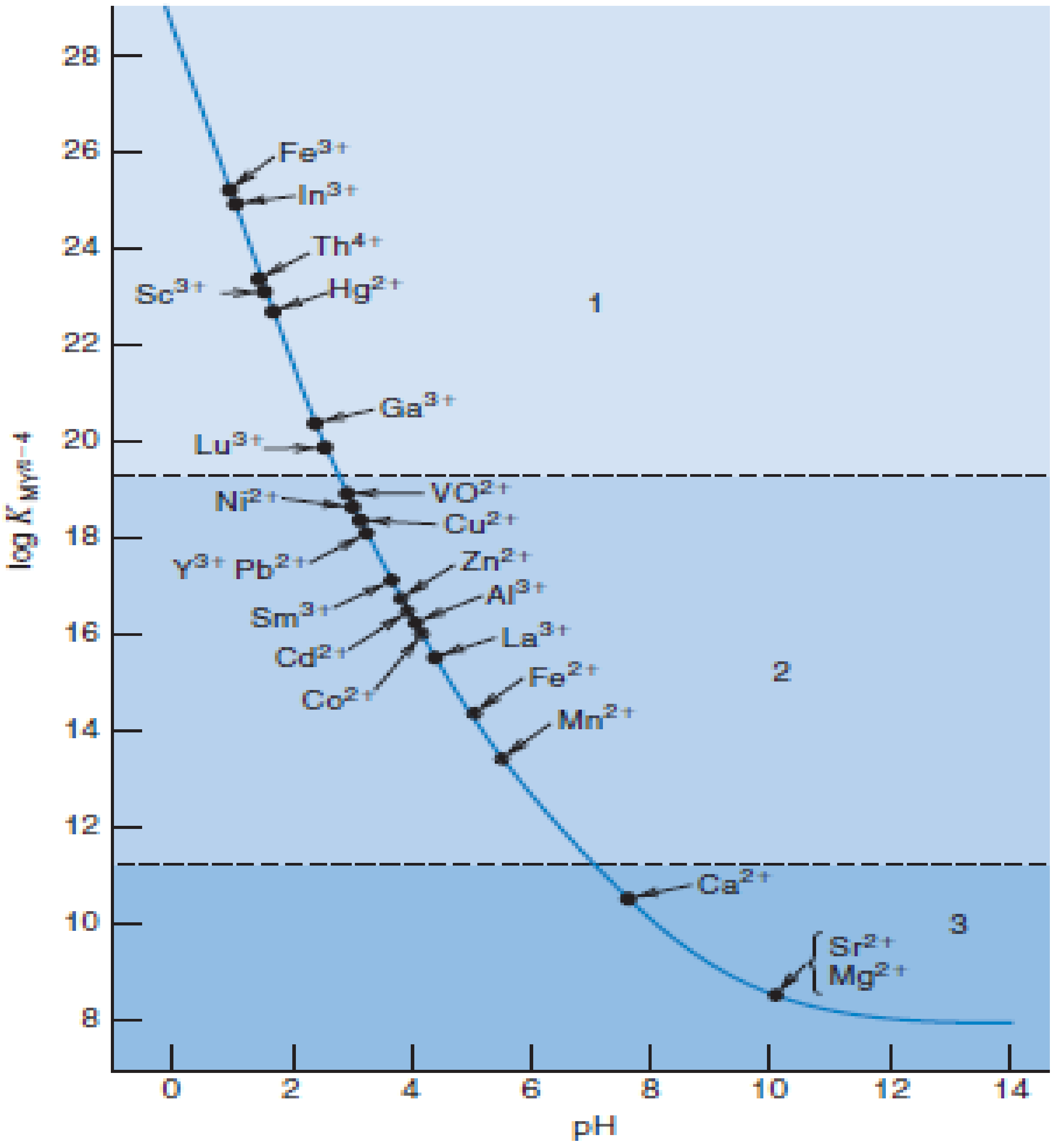
Detection of the endpoint (indicators: they are chelating agents indicators used for chelometric titrations are themselves chelating agents. They are usually dyes of the o,o'-dihydroxyazo type.: is a typical indicator it contains three ionisable protons, so we will represent it by **H_3In**. This indicator can be used for the titration of **Mg^{+2}** with **EDTA**. A small amount of indicator is added to the sample solution, and its forms a red complex with part of the **Mg^{+2}**, the colour of the uncomplexed indicator is blue, as soon as all the **Mg^{+2}** is titrated, the **EDTA** displaces the indicator from the magnesium, causing a change in the colour from red to blue.



$$\boxed{\underset{\text{(red)}}{MgIn^-} + \underset{\text{(colorless)}}{H_2Y^{2-}} \rightarrow \underset{\text{(colorless)}}{MgY^{2-}} + \underset{\text{(blue)}}{HIn^{2-}} + H^+}$$

This will occur over a pMg range, and the change will be sharper if the indicator is kept as dilute as possible and will still give a good colour.

Figure below shows the minimum **pH** at which different metals can be titrated with **EDTA**. The points on the curve represent the **pH** at which the conditional formation constant **K_f** for each metal is **10^6 (log K_f = 6)**, which was arbitrarily chosen as the minimum needed for a sharp end point. Note that the smaller the **K_f** , the more alkaline the solution must be to obtain a **Kf of 10^6** (i.e., the larger α_4 must be). Thus, **Ca^{2+}** with **K_f** only about **10^{10}** requires a **pH of ~≥ 8**. The dashed lines in the figure divide the metals into separate groups according to their formation constants. One group is titrated in a highly acidic **(pH < ~3)** solution, a second group at **pH ~3 to 7**, and a third group at **pH > 7**. At the highest pH range, all the metals will react, but not all can be titrated directly due to precipitation of hydroxides. For example, titration of **Fe^{3+}** or **Th^{4+}** is not possible without the use of back-titration or auxiliary complexing agents to prevent hydrolysis. At the intermediate pH range, the third group will not titrate, and the second group of metals can be titrated in the presence of the third group. And finally, in the most acidic pH range, only the first group will titrate and can be determined in the presence of the others. Note that a moderately acidic environment is satisfactory for many divalent heavy-metal cations and that a strongly acidic medium can be tolerated in the titration of such ions as **iron (Ill) and indium(Ill)**.



Minimum pH needed for satisfactory titration of various cations with EDTA.

REDUCTION - OXIDATION TITRATION
REDOX TITRATION

Oxidation is defined as a loss of electrons to give a higher oxidation state (more positive).

Reduction is defined as a gain of electrons to give a lower oxidation state (more negative).

OXIDATION NUMBERS The following rules predict the oxidation number for each of the atoms/ions in a compound or ion.

General Rules (Always applicable–No exceptions)

1. For any uncombined element, the oxidation number is zero.

Examples: Fe, Xe, O_2, H_2 (0 for all of these)

2. For any monatomic ion, the oxidation number is equal to the charge on the ion. Examples: Fe^{2+}, F^-, O^{2-}, H^+ (+2, -1, -2, and +1 respectively)

3. For any compound, the sum of the oxidation numbers must be zero.

Examples: $NaCl = Na^+ + Cl^- = +1 + (-1) = 0$

$MgF_2 = Mg^{2+} + 2\ F^- = +2 + 2(-1) = 0$

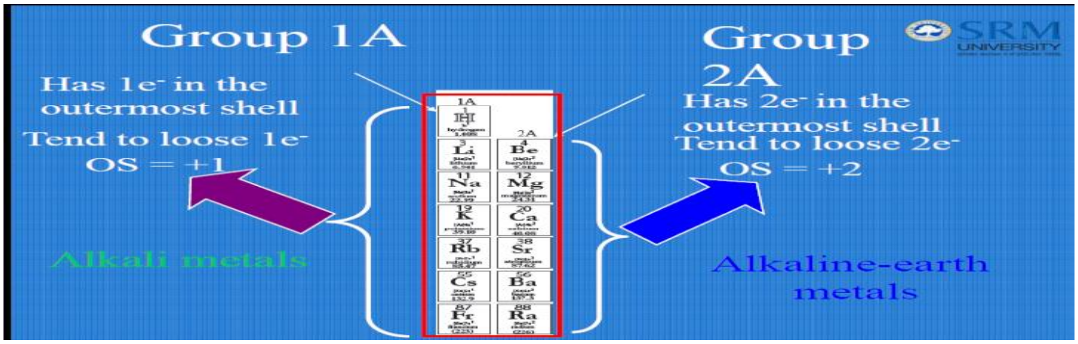
$K_2Cr_2O_7 = 2\ K^+ + 2\ Cr + 7\times O^{2-}$

$= 2(+1) + 2(X) + 7\times(-2) = 0$ ---- $X = +6$

Special Rules These rules only apply to certain columns on the Periodic Table.

1. Column IA +1 (Except H with a metal, then H = -1)
2. Column IIA +2
3. Column IIIA +3 (Normally, however +1 possible near the bottom of the table)
4. Column IVA +4
5. Column VA +5 to -3
6. Column VIA -2 (Oxygen is -2 except when combined with F, or in O_2^{2-})
7. Column VIIA -1 (Fluorine is -1 in compounds)
8. Column VIIIA (Usually only 0)

9. Transition Metals (3-12)



Group 1A

Has $1e^-$ in the outermost shell

Tend to loose $1e^-$

OS = +1

Alkali metals

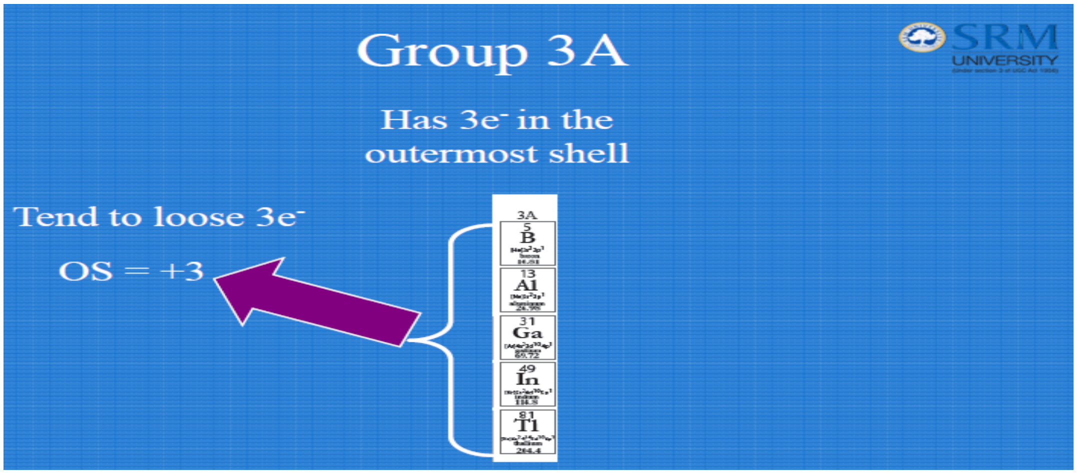
Group 2A

Has $2e^-$ in the outermost shell

Tend to loose $2e^-$

OS = +2

Alkaline-earth metals

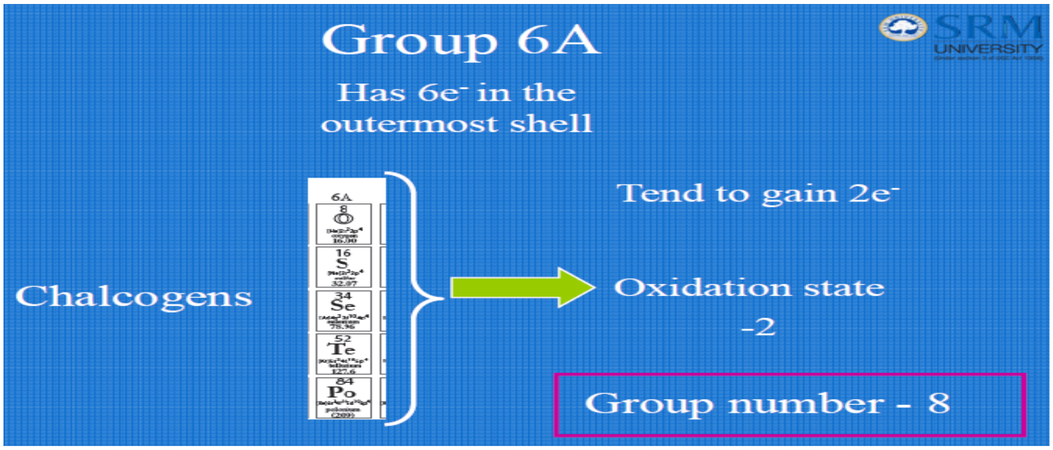


Group 3A

Has $3e^-$ in the outermost shell

Tend to loose $3e^-$

OS = +3



Group 6A

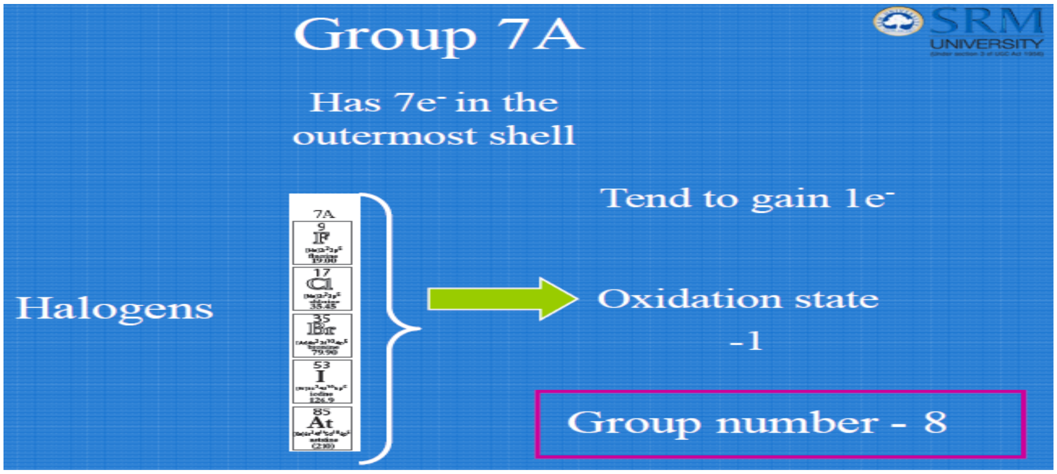
Has $6e^-$ in the outermost shell

Chalcogens

Tend to gain $2e^-$

Oxidation state -2

Group number - 8



Group 7A

Has $7e^-$ in the outermost shell

Halogens

Tend to gain $1e^-$

Oxidation state -1

Group number - 8

Oxidizing agent an oxidizing substance which tend to take on an electron or electrons and be reduced to a lower oxidation state. For example -

$$\mathbf{Ce^{4+} + e^- \longrightarrow Ce^{3+}}$$

- Oxidizing ability depends strongly on pH value.

$KMnO_4$ in presence of dil. H_2SO_4

$$\mathbf{MnO_4^{-1} + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O \quad E^0_{red} = +1.52\ V}$$

Reducing agent an reducing substance which tend to give up an electron or electrons and be oxidized to a higher oxidation state. For example -

$$\mathbf{Fe^{2+} \longrightarrow Fe^{3+} + e^- \qquad E^o_{red} = +0.771V}$$

Oxalic acid $H_2C_2O_4{\bullet}2H_2O$ ::: $C_2O_4^{2-} = 2CO_2 + 2e^-$

Q – Calculate the oxidation number for the central atom in the following compounds.

$KMnO_4$, $K_2Cr_2O_7$, H_2O_2, HNO_3, H_2SO_4, KIO_3, $H_2C_2O_4{\bullet}2H_2O$, H_2S, $SnCl_2$

H_2SO_4 : $(+1\times2)+(S)+(-2\times4) = 0 \longrightarrow S = +6$

REDUCTION - OXIDATION REACTION

Is one that occurs between a reducing and an oxidizing agent,

For example $\mathbf{Ox_1 + Red_2 \longrightarrow Red_1 + Ox_2}$

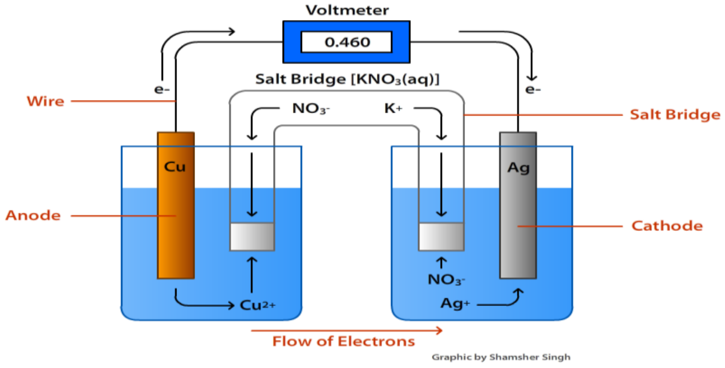
$$\mathbf{Ce^{4+} + Fe^{2+} \longrightarrow Ce^{3+} + Fe^{3+}}$$

$$\mathbf{2H^+ + Zn_{(s)} \longrightarrow H_{2(g)} + Zn^{2+}}$$

Electro chemical cells:

There are two kinds of electrochemical cells, galvanic (voltaic) and electrolytic cell.

1- galvanic cells In this type of cells the chemical reaction spontaneously occurs to produce electrical energy for example , zinc - copper cell, lead storage battery , copper - silver cell.



Graphic by Shamsher Singh

Copper - Silver cell

2- Electrolytic cell electrical energy is used to force a nonspontaneous chemical reaction to occur, that is to go in the reverse direction it would in a galvanic cell. An example is the electrolysis of water

$$2H_2O \longrightarrow H_{2(g)}\uparrow + 2O_{2(g)}\uparrow \quad \text{(acid solution)}$$

An electrochemical cell consists of two conductors called **electrodes** each of which is immersed in an electrolyte solution.

Anode is the electrode at which oxidation occurs.

Cathode is the electrode at which reduction occurs.

The solutions surrounding the two electrodes are different and must be separated to avoid direct reaction between the reactants.

The most common way of avoiding mixing is to insert a salt bridge.

Salt bridge allows charge transfer through the solution but prevent mixing of the solution .

Q- The equation that is not represented as a redox reaction is,

a- $AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$

b- $2H_2 + O_2 \longrightarrow 2H_2O$

c- $2H_2O_2 \longrightarrow 2H_2O + O_2\ (g)$

d- $Cu_{(s)} + 2\,AgNO_3 \longrightarrow Cu(NO_3)_2 + 2Ag_{(s)}$

Redox reaction as two half reaction As a redox reaction involves both oxidation and reduction components, it is possible to divide the total reaction , these clearly demonstrate which species gains electrons and which losses them .

This can be suitably illustrated by the reaction between iron (III) and tin (II).

$$2Fe^{3+} + Sn^{2+} \longrightarrow Sn^{4+} + 2\,Fe^{2+}$$

This reaction can be divided into two half reactions show below

$$2Fe^{3+} + 2e^{-} \longrightarrow 2\,Fe^{2+} \quad \text{(reduction)}$$

$$Sn^{2+} \longrightarrow Sn^{4+} + 2e^{-} \quad \text{(oxidation)}$$

Total $2Fe^{3+} + Sn^{2+} + \cancel{2e^{-}} \longrightarrow Sn^{4+} + 2\,Fe^{2+} + \cancel{2e^{-}}$

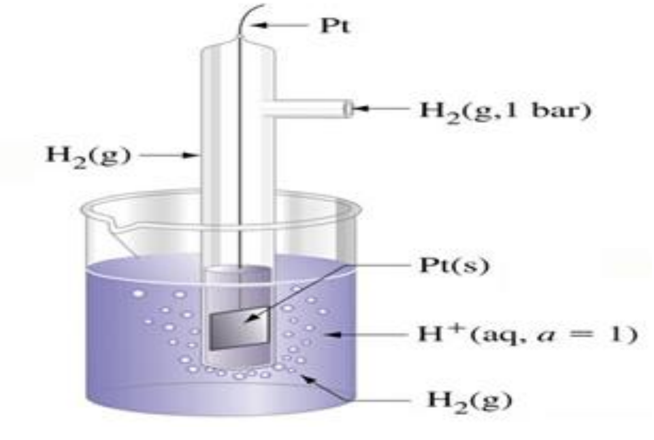
This method of expressing a redox reaction as two half reactions provide a kind of flexibility to the concept of redox reaction.

No half reaction occur by itself there must be an electron donor (reducing agent) and an electron accepter (an oxidizing agent) **Fe^{3+}** oxidizing agent **Sn^{2+}** reducing agent .

(SHE) standard hydrogen electrode:

the electrode potential of the half reaction

$$2H^{+} + 2e^{-} \leftrightarrow H_2 \quad E^{0} = 0.00\ V$$



This figure show the (SHE)

The potential have differences between this half reaction and other half reactions have been measured and arranged in increasing order.

Table - standard potentials of some element

standard potentials at 25 C ^{0}	V
$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$	-0.76
$Cr^{3+}_{(aq)} + 3e^- \rightarrow Cr_{(s)}$	-0.74
$Fe^{2+}_{(aq)} + 2e^- \rightarrow Fe_{(s)}$	-0.41
$Cd^{2+}_{(aq)} + 2e^- \rightarrow Cd_{(s)}$	-0.40
$Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)}$	-0.23
$Sn^{2+}_{(aq)} + 2e^- \rightarrow Sn_{(s)}$	-0.14
$Fe^{3+}_{(aq)} + 3e^- \rightarrow Fe_{(s)}$	-0.04
$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$	0.00
$Sn^{4+}_{(aq)} + 2e^- \rightarrow Sn^{2+}_{(aq)}$	0.15
$Cu^{2+}_{(aq)} + e^- \rightarrow Cu^+_{(aq)}$	0.16
$ClO_4{}^-_{(aq)} + H_2O_{(l)} + 2e^- \rightarrow ClO_3{}^-_{(aq)} + 2OH^-_{(aq)}$	0.17
$AgCl_{(s)} + e^- \rightarrow Ag(s) + Cl^-_{(aq)}$	0.22
$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$	0.34
$ClO_3{}^-_{(aq)} + H_2O_{(l)} + 2e^- \rightarrow ClO_2{}^-_{(aq)} + 2OH^-_{(aq)}$	0.35
$IO^-_{(aq)} + H_2O_{(l)} + 2e^- \rightarrow I^-_{(aq)} + 2OH^-_{(aq)}$	0.49
$Cu^+_{(aq)} + e^- \rightarrow Cu_{(s)}$	0.52
$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$	0.80
$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)}$	1.23
$Cr_2O_7{}^{2-}_{(aq)} + 14H^+_{(aq)} + 6e^- \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$	1.33
$Ce^{4+}_{(aq)} + e^- \rightarrow Ce^{3+}_{(aq)}$	1.44
$MnO_4{}^-_{(aq)} + 8H^+_{(aq)} + 5e^- \rightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}$	1.49
$H_2O_{2(aq)} + 2H^+_{(aq)} + 2e^- \rightarrow 2H_2O_{(l)}$	1.78

Expression of cells the electrochemical cell by convention a cell is written with the anode on the left

anode /solution /cathode

For example $\mathbf{Ce^{4+} + Fe^{2+} \longleftrightarrow Ce^{3+} + Fe^{3+}}$

$$\mathbf{Pt/\ Fe^{2+}(C_1),\ Fe^{3+}(C_2)\ //\ Ce^{4+}(C_3),\ Ce^{3+}(C_4)\ /Pt}$$

C_1 C_2 C_3 and C_4 represent the concentration of the different species , the double line represents the salt bridge.

Since oxidation occurs at the anode and reduction occurs at the cathode, the stronger reducing agent is placed on the left and the stronger oxidizing agent is placed on the right.

The potential of the cell is given by

$$\mathbf{E_{cell} = E_{cathode} - E_{anode}}$$

So a positive potential difference provides the necessary negative free energy and the chemical reaction spontaneously. For example Electro chemical cells

$$\mathbf{Fe^{3+}} + e^- = \mathbf{Fe^{2+}} \qquad \mathbf{E^o_{red} = +0.771V}$$

$$\mathbf{Sn^{4+} + 2e^- = Sn^{2+}} \qquad \mathbf{E^o_{red} = +0.154V}$$

$$\mathbf{E^o_{cell} = E^o_{cathode} - E^o_{anode} = E^o_{Fe^{3+}/Fe^{2+}} - E^o_{Sn^{4+}/Sn^{2+}}}$$

$$\mathbf{= 0.771 - (0.154) = 0.617V}$$

$$\mathbf{2Fe^{3+}} + \mathbf{Sn^{2+}} = \mathbf{2Fe^{2+} + Sn^{4+}}$$

Example (1) - determine the reaction between the following half-reaction and calculate the corresponding cell voltage:

$$\mathbf{Fe^{3+}} + e^- = \mathbf{Fe^{2+}} \qquad \mathbf{E^o_{red} = +0.771V}$$

$$\mathbf{I_3^- + 2e^- = 3I^-} \qquad \mathbf{E^o_{red} = +0.5355V}$$

Solution: since the $\mathbf{Fe^{3+}}$ / $\mathbf{Fe^{2+}}$ potential is the more positive, $\mathbf{Fe^{3+}}$ is a better oxidizing agent than $\mathbf{I_3^-}$. $\mathbf{Fe^{3+}}$ will oxidize $\mathbf{I^-}$ to give $\mathbf{I_3^-}$ (Triiodide ion) and

$$\mathbf{E^o_{cell} = E^o_{cathode} - E^o_{anode}} = \mathbf{E^o_{cell}} = \mathbf{E^o_{Fe^{3+}/Fe^{2+}} - E^o_{I_3^-/I^-}}$$

In the some fashion, the second half-reaction must be subtracted from the first (multiplied by 2) to give the overall cell reaction,

$\mathbf{2Fe^{3+} + 3I^- = 2Fe^{2+} + I_3^- \quad E^o_{cell} = 0.771\ V - 0.536\ V = +0.235\ V}$

* That multiplying a half-reaction by any number does not change its potential.

Balancing Redox Equations

Knowing how to balance oxidation- reduction reactions is essential to understanding all the concepts covered in this course .

Q- Complete and balance the following equation after adding H^+ OH^-, or H_2O as needed

$$MnO_4^- + NO_2^- \longleftrightarrow Mn^{2+} + NO_3^-$$

1- We write and balance the two half-reaction involved.

For **MnO_4^-**, we write $MnO_4^- \longleftrightarrow Mn^{2+}$

To account for the 4 oxygen atoms on the left-hand side of the equation we add **$4H_2O$** on the right-hand side of the equation, which means that we must provide **$8H^+$** on the left.

$$MnO_4^- + 8H^+ \longleftrightarrow Mn^{2+} + 4H_2O$$

$$MnO_4^- = Mn \times 1 + O \times 4 = -1, \quad Mn + (-2) \times 4 = -1, \quad Mn = +7$$

To balance the charge, we need to add 5 electrons to the left side of the equation. Thus

$$MnO_4^- + 8H^+ + 5e^- \longleftrightarrow Mn^{2+} + 4H_2O$$

For the other half-reaction

$$NO_2^- \longleftrightarrow NO_3^-$$

We add one H_2O to the left side of the equation to supply the needed oxygen and $2H^+$ on the right to balance hydrogen

$$NO_2^- + H_2O \longleftrightarrow NO_3^- + 2H^+$$

$$NO_2^- = N \times 1 + O \times 2 = -1, \ N + (-2) \times 2 = -1, \ N = +3$$

$$NO_3^- = N \times 1 + O \times 3 = -1, \ N + (-2) \times 3 = -1, \ N = +5$$

Then we add two electrons to the right-hand side to balance the charge

$$NO_2^- + H_2O \longleftrightarrow NO_3^- + 2H^+ + 2e^-$$

Before combining the two equation, we must multiply the first by 2 and the second by 5 so that the number of electrons lost will be equal to the number of electrons gained. We then add the two half-reactions to obtain

$$\mathbf{2MnO_4^- + 16H^+ + 10e^- + 5NO_2^- + 5\,H_2O \longleftrightarrow 2Mn^{2+} + 8H_2O + 5NO_3^- + 10\,H^+ + 10e^-}$$

Which then rearranges to the balanced equation

$$\mathbf{2MnO_4^- + 6H^+ + 5NO_2^- \longleftrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O}$$

Q - Complete and balance the following equation after adding H^+ OH^-, or H_2O as needed

$$\mathbf{MnO_4^- + Fe^{2+} \longleftrightarrow Mn^{2+} + Fe^{3+}}$$

Nernst equation

The effect of concentration on electrode potential . A mathematical expression that related the potential of an electrode to the activities of those species in solution that is responsible for potential. For a cell with the following general equation

$$\mathbf{aA + bB + \text{------} + ne \longleftrightarrow cC + dD + \text{-------}}$$

The electrode potential for this reaction is given by the equation

$$\boxed{E = E^0 - \frac{RT}{nF}\, ln \frac{[C]^c[D]^d - -}{[A]^a[B]^b —}}$$

Where $\mathbf{E^0}$ = the standard electrode potential which is characteristic for each half-reaction, **R**= the gas constant **8.314** K^{-1} mol^{-1} ,**T**= temperature K, **n** = number of moles of electrons that appear in the half –reaction for the electrode process as written, **F** = faraday constant = **96485 C**, **In** = natural logarithm = 2.303 log,

If we substitute numerical values for the constants convert to bas 10 logarithms and specify 25 ^{0}C for the temperature, we gat

$$\boxed{E = E^0 - \frac{0.0592}{n}\, log \frac{[C]^c[D]^d - -}{[A]^a[B]^b —}}$$

Examples : Typical half-cell reactions and their corresponding nernst expressions follow. **1-** $\mathbf{Zn^{2+} + 2e \longleftrightarrow Zn_{(s)}}$ $\quad E = E^0 - \frac{0.0592}{2} \log \frac{1}{[Zn^{2+}]}$

$Zn_{(s)}$ is not included in the logarithmic because it is a pure solid. Thus, the electrode potential varies linearly with the logarithm of the reciprocal of the zinc ion concentration **$[Zn^{2+}]$**.

2- $\mathbf{Fe^{3+} + e \longleftrightarrow Fe^{2+}}$ $\quad E = E^0 - \frac{0.0592}{1} \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$

The potential for this couple can be measured with an inert metallic electrode immersed in a solution containing both iron species.
The potential depends on the logarithm of the ratio between the molar concentrations of these ions.

3- $\mathbf{2H^+ + 2e \longleftrightarrow H_{2\,(g)}}$ $\quad E = E^0 - \frac{0.0592}{2} \log \frac{pH_2}{[H^+]^2}$

In this example ***PH₂*** is the pressure of hydrogen (in atm) at the surface of the electrode.

4- $\mathbf{MnO_4^- + 5e + 8H^+ \longleftrightarrow Mn^{2+} + 4H_2O}$, $E = E^0 - \frac{0.0592}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$

Here, the potential depends not only on the concentration of manganese species but also on the pH of the solution.

5- $\mathbf{AgCl_{(s)} + e \longleftrightarrow Ag_{(s)} + Cl^-}$ $\quad E = E^0 - \frac{0.0592}{1} \log [Cl^-]$ This half-cell reaction describes the behavior of silver electrode immersed in a chloride solution that is saturated with AgCl**.**

Example (2) : Calculate the electrode potential of a silver electrode immersed in a solution containing 0.05 M NaCl and saturated with AgCl.using **$K_{sp(AgCl)} = 1.82 \times 10^{-10}$**.

(a) $E^0_{Ag+/Ag}$ = 0.776 V $\quad \mathbf{Ag^+ + e \longleftrightarrow Ag_{(s)}}$

(b) $E^0_{AgCl/Ag}$ = 0.222 V $\quad \mathbf{AgCl_{(s)} + e \longleftrightarrow Ag_{(s)} + Cl^-}$

Solution : **(a) $Ag^+ + e \longleftrightarrow Ag_{(s)}$** $\quad$ **$E^0_{Ag+/Ag}$ = 0.776** V

$$\mathbf{E = E^0_{Ag^+/Ag} - \frac{0.0592}{1} \log \frac{1}{[Ag^+]}}$$

The **[Ag⁺**] concentration of this solution is given by

$$[\mathbf{Ag^+}] = \frac{K_{sp}}{[Cl^-]} = \frac{1.82 \text{ x } 10^{-10}}{0.05} = \mathbf{3.64 \times 10^{-9} M}$$

Substitution into Nernst expression gives:

$$\mathbf{E = 0.776 - 0.0592 \log \frac{1}{3.64 \times 10^{-9}} = 0.299 \text{ V}}$$

(b) - $\mathbf{AgCl_{(s)} + e \longleftrightarrow Ag_{(s)} + Cl^-}$ $\quad \mathbf{E^0_{AgCl/Ag} = 0.222 \text{ V}}$

$\mathbf{E = E^0_{AgCl/Ag} - \frac{0.0592}{1} \log [Cl^-]}$ **Concentration of** $[Cl^-]$ = **0.05 M**

Here we may write

$\mathbf{E = 0.222 - 0.0592 \log [Cl^-] = 0.222 - 0.0592 \log 0.05 = 0.299 \text{ V}}$

Oxidation-reduction (redox) Titration: In redox titrations the concentration of the substances or ions involved in the reaction continuously keeps changing in the course of the titration. Hence the redox potential of the solution must also change (the phenomenon may be compared to the change of the pH of solution during acid-base titration) by plotting the redox potential corresponding to different points in the titration, a titration curve similar to the curve obtained in an acid-base method is obtained. The titration curve in redox reactions can be drawn by plotting the potential of half cell against the volume in millimeter of the titrant.

Points in the redox titration

1- Before titration

2- Prior to the equivalence point

3- At the equivalence point

3- After the equivalence point

Example (3): consider the titration of **50.0 ml** of **0.05 M Fe^{2+}** with **0.10 M Ce^{4+}** in a medium that is **1.0 M in H_2SO_4** at all time.

$$Ce^{4+} + e^- \longleftrightarrow Ce^{3+} \quad E^o = 1.44\ V\ (1M\ H_2SO_4)$$

$$Fe^{3+} + e^- \longleftrightarrow Fe^{2+} \quad E^o = 0.68\ V\ (1M\ H_2SO_4)$$

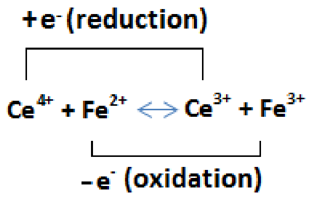
Solution:

At all times during the titration this reaction is rapid and reversible and in equilibrium hence .

E_{system} is the potential of the titration and is the value plotted on the y-axis.

E_{system} represents the potential of the electrochemical cell:

$$Ce^{4+} + Fe^{2+} \longleftrightarrow Ce^{3+} + Fe^{3+}$$



$$SHE//\ Ce^{4+}, Ce^{3+}, Fe^{3+}, Fe^{2+}/Pt$$

We can follow either $E_{Ce^{4+},Ce^{3+}}$ or $E_{Fe^{3+},Fe^{2+}}$

$$E_{system} = E_{Ce^{4+},Ce^{3+}} = E_{Fe^{3+},Fe^{2+}}$$

(a) At Volume [Ce^{4+}]solution = 0 mL

In the beginning of the titration the solution would contain only **Fe^{2+}** ions and may have traces of **Fe^{3+}** due the aerial oxidation of the solution.

As the concentration of the **Fe^{3+}** ion is too small the calculation of the potential has no meaningful significance.

(b) At Volume [Ce^{4+}] solution = 5 mL

Excess of **Fe^{2+}** concentration of (Fe^{2+}/Fe^{3+}) are measurable.

$$E_{system} = E_{Fe^{3+},Fe^{2+}} = E^o_{Fe^{3+},Fe^{2+}} - \frac{0.0592}{n}\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$[Fe^{2+}] = \frac{50\times0.05 - 5\times0.1}{50+5} + [Ce^{4+}] \approx \frac{50\times0.05-5\times0.1}{50+5} = \frac{2.0}{55}\,M$$

$$[Fe^{3+}] = \frac{5\times0.1}{50+5} - [Ce^{4+}] \approx \frac{0.5}{50+5} = \frac{0.5}{55}\ M$$

$$\mathbf{E_{system}} = \mathbf{E_{Fe^{3+},Fe^{2+}}} = \mathbf{0.68} - \frac{\mathbf{0.0592}}{\mathbf{1}}\ \mathbf{log}\frac{\left(\frac{2.0}{55}\right)}{\left(\frac{0.5}{55}\right)} = \mathbf{0.64\ V}$$

(c)- At Volume [Ce^{4+}] solution = 25 mL at the eq. point : no excess of [Fe^{2+}]

[Ce^{4+}]×V_{total} = [Fe^{2+}] ×V_{total} and [Ce^{3+}]×V_{total} = [Fe^{3+}] ×V_{total}

The reaction takes place in one vessel

[Ce^{4+}] = [Fe^{2+}] and [Ce^{3+}] = [Fe^{3+}]

$$\mathbf{E_{eq}} = \mathbf{E_{Fe^{3+},Fe^{2+}}} = \mathbf{E^{o}{}_{Fe^{3+},Fe^{2+}}} - \frac{\mathbf{0.0592}}{\boldsymbol{n}}\ \mathbf{log}\frac{[\mathbf{Fe^{2+}}]}{[\mathbf{Fe^{3+}}]}\ \text{------}(1)$$

$$\mathbf{E_{eq}} = \mathbf{E_{Ce^{4+},Ce^{3+}}} = \mathbf{E^{o}{}_{Ce^{4+},Ce^{3+}}} - \frac{\mathbf{0.0592}}{\boldsymbol{n}}\ \mathbf{log}\frac{[\mathbf{Ce^{3+}}]}{[\mathbf{Ce^{4+}}]}\ \text{------}(2)$$

Summation of eq(1) and eq(2)

$$\mathbf{2E_{eq}} = \mathbf{E^{o}{}_{Fe^{3+},Fe^{2+}}} + \mathbf{E^{o}{}_{Ce^{4+},Ce^{3+}}} - \frac{\mathbf{0.0592}}{\boldsymbol{n}}\ \mathbf{log}\frac{[\mathbf{Fe^{2+}}][\mathbf{Ce^{3+}}]}{[\mathbf{Fe^{3+}}][\mathbf{Ce^{4+}}]}$$

$$= \mathbf{E^{o}{}_{Fe^{3+},Fe^{2+}}} + \mathbf{E^{o}{}_{Ce^{4+},Ce^{3+}}}$$

$$\mathbf{E_{eq}} = \frac{\mathbf{E^{o}{}_{Fe^{3+},Fe^{2+}}} + \mathbf{E^{o}{}_{Ce^{4+},Ce^{3+}}}}{\mathbf{2}} = \frac{\mathbf{0.68+1.44}}{\mathbf{2}} = \mathbf{1.06\ V}$$

(d)- At Volume [Ce^{4+}]solution = 25.10 mL > Veq = 25 mL

After the eq. point : excess of **[Ce^{4+}]** and concentration of **[Ce^{3+}]/ [Ce^{4+}]**

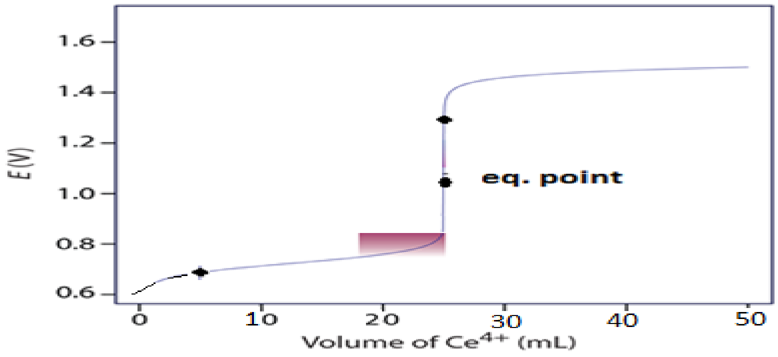
Are measurable. Hence **E_{system}** post-eq = $\mathbf{E_{Ce^{4+},Ce^{3+}}}$

$$\mathbf{E_{system}} = \mathbf{E_{Ce^{4+},Ce^{3+}}} = \mathbf{E^{o}{}_{Ce^{4+},Ce^{3+}}} - \frac{\mathbf{0.0592}}{\boldsymbol{n}}\ \mathbf{log}\frac{[\mathbf{Ce^{3+}}]}{[\mathbf{Ce^{4+}}]}$$

$$[\mathbf{Ce^{4+}}] = \frac{\mathbf{25.1\times0.1-50\times0.05}}{\mathbf{50+25.1}} + [\mathbf{Fe^{2+}}] \approx \frac{\mathbf{25.1\times0.1-50\times0.05}}{\mathbf{50+25.1}} = \frac{\mathbf{0.01}}{\mathbf{75.1}}\ \mathbf{M}$$

$$[\mathbf{Ce^{3+}}] = \frac{\mathbf{25\times0.1}}{\mathbf{50+25.1}} - [\mathbf{Fe^{2+}}] \approx \frac{\mathbf{2.5}}{\mathbf{75.1}} = \frac{\mathbf{2.5}}{\mathbf{75.1}}\ \mathbf{M}$$

$$\mathbf{E_{system}} = \mathbf{1.44} - \frac{\mathbf{0.0592}}{\mathbf{1}}\ \mathbf{log}\frac{\mathbf{2.5}}{\mathbf{0.01}} = \mathbf{1.3\ V}$$



Redox titration methods :

1- Permanganometry
2- Dichromatometry
3- Cerimetry
4- Iodometry and Iodimetry
5- Iodametry
6- Bromatometry

Permanganometrc Titration :

This method is based on reactions of oxidation by permanganate ion.

Oxidation may proceed in acid or in alkaline or neutral solution. When KMnO4 acts as an oxidizing agent in acidic solution the septivalent Mn in it reduced to Mn^{2+} ions and a manganous salt of the acid used formed.

For example if $FeSO_4$ is the reducing agent and if it is oxidized in the presence of H_2SO_4 the reaction is represented by the equation;

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O$$

Or in ionic form

$$5Fe^{2+} + MnO_4^- + 8H^+ = 5Fe^{3+} + Mn^{2+} + 4H_2O$$

The decrease of the valence of manganese by **5** shows that the **$KMnO_4$** molecule gains 5 electrons this is also very clear from the following equation:

$$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$$

It follows that in this case the gram-equivalent of **$KMnO_4$** is

g/eq =158.03/5 =31.61 g/eq

during oxidation in alkaline or neutral solution the **Mn^{7+}** ion is reduced to **Mn^{4+}** with the formation of manganese oxide **MnO_2** in the form of a brown precipitate for example

$$Cr_2(SO_4)_3 + 2KMnO_4 + 8KOH = 2K_2CrO_4 + 2MnO_2 + 2K_2SO_4 + 4H_2O$$

$$MnO_4^- + 4H^+ + 3e^- = MnO_2 + 2H_2O$$

Therefore in this case the gram-equivalent of **$KMnO_4$** has a different value namly

$$g/eq = 158.03/3 = 52.68\ g/eq$$

A redox indicator

(Also called an **oxidation-reduction indicator**) is an indicator which undergoes a definite color change at a specific electrode potential. The requirement for fast and reversible color change means that the oxidation-reduction equilibrium for an indicator redox system needs to be established very quickly. Therefore, only a few classes of organic redox systems can be used for indicator purposes.

There are two common types of redox indicators:

- metal-organic complexes (Ex. phenanthroline)
- true organic redox systems (Ex. Methylene blue)

Sometimes colored inorganic oxidants or reductants (Ex. Potassium permanganate, Potassium dichromate) are also ***incorrectly*** called redox indicators. They can’t be classified as **true** redox indicators because of their irreversibility. Almost all redox indicators with true organic redox systems involve a proton as a participant in their electrochemical reaction. Therefore, sometimes redox indicators are also divided into two general groups: independent or dependent on pH.

Questions:

1- What is an oxidizing agent? A reducing agent?

2- What is the Nernst equation?

3- What is the standard potential?

4- What is the redox indicator?

4- Complete and balance the following equation after adding H^+ OH^-, or H_2O as needed

(a) - $IO_3^- + I^- \longrightarrow I_2$

(b) - $MnO_4^- + H_2SO_3 \longrightarrow Mn^{2+} + SO_4^{2-}$

(c) - $MnO_4^- + H_2S \longrightarrow Mn^{2+} + S$

(d) – $Al + NO_3^- \longrightarrow AlO_2^- + NH_3$

(e) - $2ClO_3^- + SO_2 = SO_4^{-2} + Cl_2$ **,**

(f) - $2ClO_3^- + H_2S = SO_4^{-2} + Cl_2$

(g)- $Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

5- What is the potential of a solution containing **10.0 ml** of **0.1 M** Fe^{2+} with **10 mL of 0.05 M** Ce^{4+} in a medium that is **1.0 M in** H_2SO_4 at all time?

6- Prove the $$-\frac{RT}{nF}\ ln\ \frac{[C]^c[D]^d--}{[A]^a[B]^b-} = -\frac{0.0592}{n}\ log\ \frac{[C]^c[D]^d--}{[A]^a[B]^b-}$$

Knowing that **R** = **8.314** K^{-1} mol^{-1} and **F** = faraday constant = **96485 C**

7- Describe the types of electrochemical cells with examples.

8- What are the types of electrochemical cells and then explain the difference between them.

9- Determine the reaction between the following half-reaction and calculate the corresponding cell voltage:

$$Cu^{2+} + 2e^- = Cu \qquad E^o_{red} = +0.34V$$

$$Zn^{2+} + 2e^- = Zn \qquad E^o_{red} = -0.76V$$

10 - The element that undergoes oxidation is: $H_2 + O_2 \longrightarrow H_2O$

11- The element that undergoes reduction is: $N_2 + 3H_2 \longrightarrow 2NH_3$

اسماء وشحنات بعض الجذور الكيميائية

Nitrate	NO_3	-1
Nitrite	NO_2	-1
Chloride ,Bromide, & Iodide	(Cl, Br, & I)	-1
Acetate	CH_3COO	-1
Chlorate, Bromate, & Iodate	(ClO_3, BrO_3, & IO_3)	-1
Hypochlorite	ClO	-1
Chlorite	ClO_2	-1
Perchlorate	ClO_4	-1
Hydroxyl	HO	-1
Cyanide	CN	-1
Cyanate	CNO	-1
Thiocyanate	SCN	-1
Ammonium	NH_4	+1
Bicarbonate	HCO_3	-1
Carbonate	CO_3	-2
Sulfate	SO_4	-2
Sulfite	SO_3	-2
Sulfide	S	-2
Thiosulfate	S_2O_3	-2
Oxalate	C_2O_4	-2
Chromate	CrO_4	-2
Dichromate	Cr_2O_7	-2
Phosphate	PO_4	-3
Phosphite	PO_3	-3

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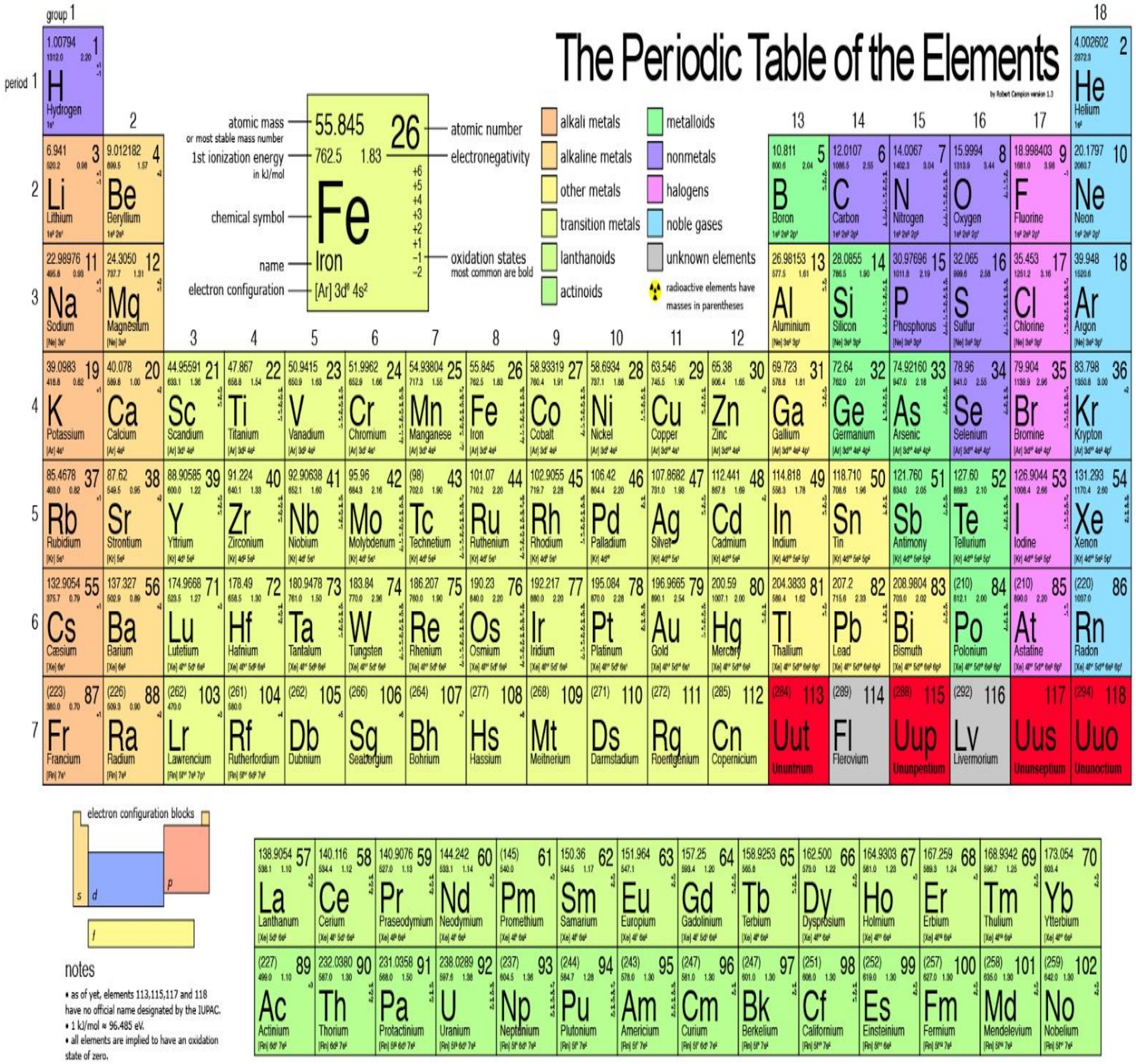

The Periodic Table of the Elements

by Robert Campion version 1.3

Key (example cell): 55.845 — atomic mass or most stable mass number; 26 — atomic number; 762.5 — 1st ionization energy in kJ/mol; 1.83 — electronegativity; Fe — chemical symbol; Iron — name; +6 +5 +4 +3 +2 +1 −1 −2 — oxidation states most common are bold; [Ar] 3d⁶ 4s² — electron configuration

Legend: alkali metals; alkaline metals; other metals; transition metals; lanthanoids; actinoids; metalloids; nonmetals; halogens; noble gases; unknown elements; radioactive elements have masses in parentheses

period	group 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H Hydrogen 1.00794 1312.0 2.20																	2 He Helium 4.002602 2372.3
2	3 Li Lithium 6.941 520.2 0.98	4 Be Beryllium 9.012182 899.5 1.57											5 B Boron 10.811 800.6 2.04	6 C Carbon 12.0107 1086.5 2.55	7 N Nitrogen 14.0067 1402.3 3.04	8 O Oxygen 15.9994 1313.9 3.44	9 F Fluorine 18.998403 1681.0 3.98	10 Ne Neon 20.1797 2080.7
3	11 Na Sodium 22.98976 495.8 0.93	12 Mg Magnesium 24.3050 737.7 1.31											13 Al Aluminium 26.98153 577.5 1.61	14 Si Silicon 28.0855 786.5 1.90	15 P Phosphorus 30.97696 1011.8 2.19	16 S Sulfur 32.065 999.6 2.58	17 Cl Chlorine 35.453 1251.2 3.16	18 Ar Argon 39.948 1520.6
4	19 K Potassium 39.0983 418.8 0.82	20 Ca Calcium 40.078 589.8 1.00	21 Sc Scandium 44.95591 633.1 1.36	22 Ti Titanium 47.867 658.8 1.54	23 V Vanadium 50.9415 650.9 1.63	24 Cr Chromium 51.9962 652.9 1.66	25 Mn Manganese 54.93804 717.3 1.55	26 Fe Iron 55.845 762.5 1.83	27 Co Cobalt 58.93319 760.4 1.91	28 Ni Nickel 58.6934 737.1 1.88	29 Cu Copper 63.546 745.5 1.90	30 Zn Zinc 65.38 906.4 1.65	31 Ga Gallium 69.723 578.8 1.81	32 Ge Germanium 72.64 762.0 2.01	33 As Arsenic 74.92160 947.0 2.18	34 Se Selenium 78.96 941.0 2.55	35 Br Bromine 79.904 1139.9 2.96	36 Kr Krypton 83.798 1350.8 3.00
5	37 Rb Rubidium 85.4678 403.0 0.82	38 Sr Strontium 87.62 549.5 0.95	39 Y Yttrium 88.90585 600.0 1.22	40 Zr Zirconium 91.224 640.1 1.33	41 Nb Niobium 92.90638 652.1 1.60	42 Mo Molybdenum 95.96 684.3 2.16	43 Tc Technetium (98) 702.0 1.90	44 Ru Ruthenium 101.07 710.2 2.20	45 Rh Rhodium 102.9055 719.7 2.28	46 Pd Palladium 106.42 804.4 2.20	47 Ag Silver 107.8682 731.0 1.93	48 Cd Cadmium 112.441 867.8 1.69	49 In Indium 114.818 558.3 1.78	50 Sn Tin 118.710 708.6 1.96	51 Sb Antimony 121.760 834.0 2.05	52 Te Tellurium 127.60 869.3 2.10	53 I Iodine 126.9044 1008.4 2.66	54 Xe Xenon 131.293 1170.4 2.60
6	55 Cs Cæsium 132.9054 375.7 0.79	56 Ba Barium 137.327 502.9 0.89	71 Lu Lutetium 174.9668 523.5 1.27	72 Hf Hafnium 178.49 658.5 1.30	73 Ta Tantalum 180.9478 761.0 1.50	74 W Tungsten 183.84 770.0 2.36	75 Re Rhenium 186.207 760.0 1.90	76 Os Osmium 190.23 840.0 2.20	77 Ir Iridium 192.217 880.0 2.20	78 Pt Platinum 195.084 870.0 2.28	79 Au Gold 196.9665 890.1 2.54	80 Hg Mercury 200.59 1007.1 2.00	81 Tl Thallium 204.3833 589.4 1.62	82 Pb Lead 207.2 715.6 2.33	83 Bi Bismuth 208.9804 703.0 2.02	84 Po Polonium (210) 812.1 2.00	85 At Astatine (210) 890.0 2.20	86 Rn Radon (220) 1037.0
7	87 Fr Francium (223) 380.0 0.70	88 Ra Radium (226) 509.3 0.90	103 Lr Lawrencium (262) 470.0	104 Rf Rutherfordium (261) 580.0	105 Db Dubnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (264)	108 Hs Hassium (277)	109 Mt Meitnerium (268)	110 Ds Darmstadium (271)	111 Rg Roentgenium (272)	112 Cn Copernicium (285)	113 Uut Ununtrium (284)	114 Fl Flerovium (289)	115 Uup Ununpentium (288)	116 Lv Livermorium (292)	117 Uus Ununseptium	118 Uuo Ununoctium (294)

57 La Lanthanum 138.9054 538.1 1.10	58 Ce Cerium 140.116 534.4 1.12	59 Pr Praseodymium 140.9076 527.0 1.13	60 Nd Neodymium 144.242 533.1 1.14	61 Pm Promethium (145) 540.0	62 Sm Samarium 150.36 544.5 1.17	63 Eu Europium 151.964 547.1	64 Gd Gadolinium 157.25 593.4 1.20	65 Tb Terbium 158.9253 565.8	66 Dy Dysprosium 162.500 573.0 1.22	67 Ho Holmium 164.9303 581.0 1.23	68 Er Erbium 167.259 589.3 1.24	69 Tm Thulium 168.9342 596.7 1.25	70 Yb Ytterbium 173.054 603.4
89 Ac Actinium (227) 499.0 1.10	90 Th Thorium 232.0380 587.0 1.30	91 Pa Protactinium 231.0358 568.0 1.50	92 U Uranium 238.0289 597.6 1.38	93 Np Neptunium (237) 604.5 1.36	94 Pu Plutonium (244) 584.7 1.28	95 Am Americium (243) 578.0 1.30	96 Cm Curium (247) 581.0 1.30	97 Bk Berkelium (247) 601.0 1.30	98 Cf Californium (251) 608.0 1.30	99 Es Einsteinium (252) 619.0 1.30	100 Fm Fermium (257) 627.0 1.30	101 Md Mendelevium (258) 635.0 1.30	102 No Nobelium (259) 642.0 1.30

notes

- as of yet, elements 113,115,117 and 118 have no official name designated by the IUPAC.
- 1 kJ/mol ≈ 96.485 eV.
- all elements are implied to have an oxidation state of zero.

امنياتنا بالتوفيق