

Mustansiriyah University

College of Science

Department of Chemistry

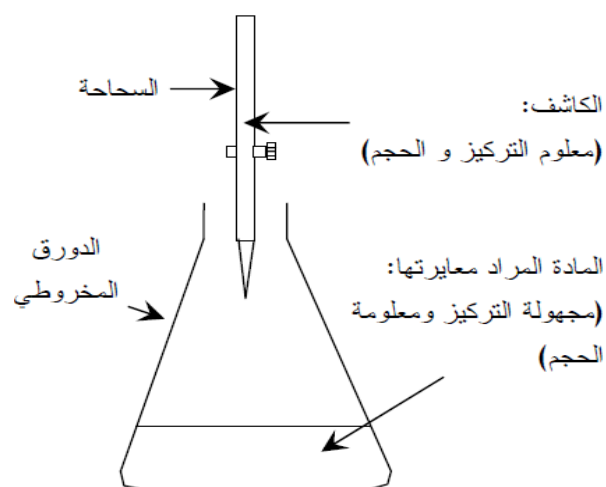
First Grade



Analytical Chemistry

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Analytical Chemistry

First grade (2020-2021)

References:-

- (1) "Analytical Chemistry" by Gary D. Christian, 6th Edition, 2004, John Wiley and Sons, Inc.
- (2) "Fundamental of Analytical Chemistry" by Douglas A. Skooge, Donald M. West and James Holler, 8th Edition, 2004.
- (3) "An Introduction to Analytical Chemistry" by Douglas A. Skooge & Donald M. West, 4th Edition, 1986.
- (4) - الاساسيات النظرية للكيمياء التحليلية اللاعضوية التحليل الكمي الوزني و الحجمي، تأليف د. هادي كاظم عوض واخرون، 1986.

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.

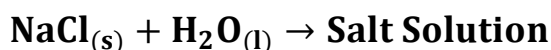
(2) Gravimetric analysis: usually involves the selective separation of the analyte by precipitation, followed by the very non-selective measurement of mass (of the precipitate).

(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



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 ₂ O _(L) , Soda	H _{2(g)} in Pd _(s) , H ₂ catalyst
Liquid	Perfume	Alcohol _(L) in H ₂ O _(L)	Hg _(L) in Ag _(s) , Dental filling
Solid	Dust air, Smoke industry	NaCl _(s) in H ₂ O _(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 (Amoxycycline 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.g 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 $\text{CaSO}_4 \cdot 7\text{H}_2\text{O}$ (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)

$$\begin{aligned}\text{CaSO}_4 \cdot 7\text{H}_2\text{O} &= 40.08 + 32.06 + (16.0 \times 4) + 7[(2 \times 1.01) + 16.00] \\ &= 262.28 \text{ gm/mol.}\end{aligned}$$

$$\text{Mwt of CaSO}_4 \cdot 7\text{H}_2\text{O} = \text{Ca} \times 1 = 40.08 \times 1 = 40.08$$

$$\text{S} \times 1 = 32.06 \times 1 = 32.06$$

$$\text{O} \times 4 = 16 \times 4 = 64.00$$

$$\text{H} \times 14 = 1.01 \times 14 = 14.14$$

$$\text{O} \times 7 = 16 \times 7 = 112.00$$

262.28 (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.

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

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

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

Example (2):-Calculate the number of moles in 500 mg Na₂WO₄.

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

$$\text{mmole} = \frac{\text{wt (mg)}}{\text{M. wt } \left(\frac{\text{mg}}{\text{mmole}}\right)} = \frac{500 \text{ (mg)}}{293.8 \left(\frac{\text{mg}}{\text{mmole}}\right)} = 1.706 \text{ mmole}$$
$$\text{mole} = \frac{\text{mmole}}{1000} = \frac{1.706}{1000} = 0.00170 \text{ mol}$$

Example (3): How many molecules are contained in 25.0 g H₂.

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

$$\text{moles H}_2 = \frac{\text{wt (g)}}{\text{Fwt}} = \frac{25.0 \text{ g}}{2.016 \frac{\text{g}}{\text{mole}}} = 12.40 \text{ mole}$$

No. Molecules = No. moles × Avogadro number

$$= 12.40 \times 6.022 \times 10^{23} = 7.74 \times 10^{24} \text{ molecule}$$

Example (4):-How many milligrams are in 0.250 mmole Fe₂O₃ (ferric oxide).

Solution: (A.wt O= 16 g/mole , Fe = 56.85 g/mole)

$$\text{Mwt of Fe}_2\text{O}_3 = \text{Fe} \times 2 = 55.85 \times 2 = 111.7$$

$$\text{O} \times 3 = 16 \times 3 = 48.0$$

$$\begin{array}{r} \text{-----} \\ 159.7 \end{array}$$

$$\text{wt (mg)} = \text{mmole} \times \text{M. wt} \left(\frac{\text{mg}}{\text{mmol}}\right)$$
$$= 0.250 \text{ mmole} \times 159.7 \frac{\text{mg}}{\text{mmol}} = 39.9 \text{ mg}$$

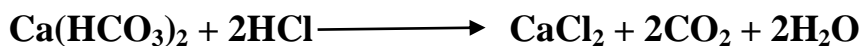
Example (5):- Calculate the number of mole of NaCl required to prepare 1Kg of AgCl according to the equation: (Na=23, Cl=35.5, N=14 , Ag =107.86, O = 16 g/mole)

Solution: $\text{AgNO}_3 + \text{NaCl} \longrightarrow \text{NaNO}_3 + \text{AgCl}$

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

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 $\text{Ca}(\text{HCO}_3)_2$ required to prepare 1.5 mol of CO_2 according to the equation.



solution: **No. of mol of $\text{Ca}(\text{HCO}_3)_2$ = No. of mol of $\text{CO}_2 \times 0.5$**
= $1.5 \times 0.5 = 0.75$ mol of $\text{Ca}(\text{HCO}_3)_2$

Example (7): What mass of KI is needed to produce 69.6 gm of K_2SO_4 by the reaction : (**Mwt, K= 39.1 , S = 32 , O = 16 , I = 127**)



We divide the equation by 4



solution :

No. of mol of $\text{K}_2\text{SO}_4 = \text{wt} / \text{M.wt} \longrightarrow 69.6 \text{ gm} / 174 (\text{gm} / \text{mol}) = 0.4 \text{ mol}$

No. of mol of KI = $2 \times 0.4 = 0.8 \text{ mol}$

wt of KI = mol \times M.wt = $0.8 \times 166 = 133 \text{ gm}$

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 B_2O_3 . (b) 167.2 mg of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.

(c) 4.96 g of Mn_3O_4 . (d) 333 mg of CaC_2O_4 .

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

(a) 850 mg of P_2O_5 . (b) 40.0 g of CO_2 .

(c) 12.92 g of NaHCO_3 . (d) 57 mg of MgNH_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.

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

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

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

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

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

Example (8):-A solution is prepared by dissolving 1.26 gm AgNO₃ in a 250 mL volumetric flask and diluting to volume. Calculate the molarity of the silver nitrate solution. How many millimoles AgNO₃ were dissolved?

Solution:

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

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

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 :

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

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

Example (10):-How many grams Na₂SO₄ should be weight out to prepare 500 mL of a 0.100 M solution.

Solution :

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

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

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

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 K₂SO₄.

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

$$\begin{aligned} \text{mmol} (K^+) &= V (mL) \times M \left(\frac{\text{mmol}}{\text{mL}} \right) + 2 \left[V (mL) \times M \left(\frac{\text{mmol}}{\text{mL}} \right) \right] \\ &= 100 (mL) \times 0.250 \left(\frac{\text{mmol}}{\text{mL}} \right) + 2 \left[200 (mL) \times 0.1 \left(\frac{\text{mmol}}{\text{mL}} \right) \right] \\ &= 25 \text{ mmol} + 2 [20 \text{ mmol}] \\ &= 25 \text{ mmol} + 40 \text{ mmol} = 65 \text{ mmol in } 300 \text{ mL} \end{aligned}$$

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

$$\begin{aligned} \text{wt} &= 65 (mmol) \times 39.1 \left(\frac{mg}{mmol} \right) = 2541.5 \text{ mg} \\ &= \frac{2541.5 (mg)}{1000 \left(\frac{mg}{g} \right)} = 2.541 \text{ gm in } 300 \text{ mL} \end{aligned}$$

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

Problems 2

Q1- How many grams of K₂SO₄ are contained in 50 ml of 0.200 M,

Q2- How many millimoles of K₂SO₄ 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) AgNO₃, (b) Al₂(SO₄)₃, (c) CO₂, (d) (NH₄)₄Ce(SO₄)₄ · 2H₂O, (e) HCl, (f) HClO₄.

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

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

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

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

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

Density: is the weight per unit volume at the specified temperature, usually (gm/mL) or (gm/cm³) 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% NH₃, density 0.898 = (sp. gr.).

Solution:

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

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

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

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

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

Example (13):-How many millilitres of concentrated sulphuric acid, 94.0% (cg/g) solution, density 1.831 g/cm³, are required to prepare 1 liter of a 0.100 M solution.

Solution:

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

no. of mmol (conc.) = no. mmol (dilu.)

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

$$17.5 \times V_1 = 0.1 \times 1000$$

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

Of concentrated H₂SO₄ must be diluted to 1L (1000mL) to prepare (become) 0.1M.

Another solution: no. of mmol (conc.) = no. mmol (dilu.)

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

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

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

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

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

$$M_{\text{stock}} \times V_{\text{stock}} = M_{\text{diluted}} \times V_{\text{diluted}}$$

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 10.0×10^{-3} M KMnO_4 solutions?

Solution: 1.0×10^{-3} M

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

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

$V_1 = 1.0$ mL stock solution (conc.), Also to prepare 2.0, 5.0, 10.0×10^{-3} M

Example (15):-You wish to prepare 500 mL of 0.1 M $\text{K}_2\text{Cr}_2\text{O}_7$ solution from a 0.250 M solution. What volume of the 0.250 M solution must be diluted to 500 mL.

Solution:

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

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

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

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 100 mL of 1.25 M H_2SO_4 solution?

Solution:

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

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

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

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

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:

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

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

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

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.

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

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

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:

$$\text{mmol of Solution}_3 = 2 \times \text{mmol of Solution}_1 + \text{mmol of Solution}_2$$

$$\text{Solution}_1 = 0.40 \text{ M } Ba(OH)_2 \quad , \quad v = (x \text{ mL})$$

$$\text{Solution}_2 = 0.30 \text{ M NaOH} \quad , \quad v = (50 \text{ mL})$$

$$\text{Solution}_3 = \text{Mix } (Ba(OH)_2 + NaOH) \quad , \quad v = (x + 50) \text{ mL}$$

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

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

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

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.

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.

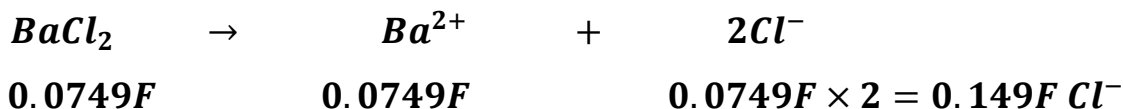
$$F = \frac{\text{wt (g)}}{F.\text{wt } \left(\frac{\text{g}}{\text{mol}} \right)} \times \frac{1000}{V (\text{mL})}$$

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 $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ are dissolved in sufficient water to give 250mL of solution. Calculate the formal concentration of BaCl_2 and Cl^- in this solution.

Solution:

$$F_{\text{BaCl}_2} = \frac{wt}{Fwt} \times \frac{1000}{V(\text{mL})} = \frac{4.57}{244} \times \frac{1000}{250} = 0.0749 F \text{ BaCl}_2 \cdot 2\text{H}_2\text{O}$$



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

Solution:

$$\begin{array}{l} \text{Na}_2\text{CO}_3 \rightarrow 2\text{Na}^+ + \text{CO}_3^{2-} \\ (0.05)F = \frac{0.01}{2} \quad 0.01F \\ F_{\text{Na}_2\text{CO}_3} = \frac{wt}{F \cdot wt} \times \frac{1000}{V(\text{mL})} \quad , \quad 0.005 = \frac{wt}{106} \times \frac{1000}{500} \end{array}$$

$$2 \times wt = 0.005 \times 106 \quad , \quad wt = \frac{0.005 \times 106}{2} = 0.265 \text{ g Na}_2\text{CO}_3$$

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 **HIO₃** in **20.0mL** (the acid is **71.0%** ionized in this solution).

Solution: (a)

$$F_{\text{ethanol}} = \frac{\text{wt}}{\text{Fwt}} \times \frac{1000}{(\text{V}) \text{ mL}} = \frac{1.80}{46.1} \times \frac{1000}{750} = 0.0521 \text{ F C}_2\text{H}_5\text{OH}$$

The only solute species present in significant amount in an aqueous solution of ethanol is **C₂H₅OH**, therefore; **M = F = 0.0521**

(b)

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

Here, only **29.0%** (**100% - 71.0% = 29.0%**) of the solute exists as un dissociated **HIO₃**. Thus, the molar concentration of this species will be:

$$\frac{29.0}{100} \times 0.104\text{F} = 0.0302\text{M HIO}_3$$

Example (23):- Calculate the analytical and equilibrium molar concentration of the solute species in an aqueous solution that contains **285 mg** of trichloroacetic acid, **Cl₃CCOOH** (Fwt=163.4) in **10.0mL** (the acid is **73% ionized** in water). Employing **HA** as the symbol for **Cl₃CCOOH**, we substitute into equation (law) to obtain the analytical or total concentration of the acid.

Solution:

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

Because all but **27%** of the acid is undissociated into **H₃O⁺** and **A⁻**, the species concentration of **HA** is:

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

The molarity of **H₃O⁺** as well as that of **A⁻** equal to the analytical concentration of the acid minus the species concentration of dissociated acid.

$$[\text{H}_3\text{O}^+] = [\text{A}^-] = 0.174 - 0.047 = 0.127 \text{ M}$$

Note: the analytical concentration of HA is the sum of the species concentration of HA and A⁻

$$C_{\text{HA}} = [\text{HA}] + [\text{A}^-] = [\text{HA}] + [\text{H}_3\text{O}^+]$$

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.

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

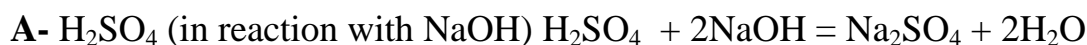
$$\text{(Eq. wt)} \left(\frac{\text{gm}}{\text{Eq}} \right) \text{ for (oxidation - reduction) reaction} = \frac{\text{formula weight (F. wt)}}{\text{No. of electrons}}$$

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

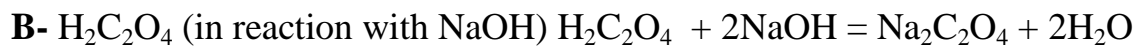
Example (24):- Calculate the equivalent weight of the following substances:

1 - (Bases) $\text{NH}_3 + \text{H}_2\text{O} = \text{NH}_4^+ + \text{OH}^-$, Eq wt = $\frac{\text{Mwt}}{\text{No. of H}^+ \text{ or OH}^-} = \frac{17.03}{1} = 17.03 \left(\frac{\text{gm}}{\text{Eq.}} \right)$

2- (Acids)

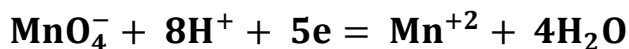


$$\text{Eq wt} = \frac{98.078 \left(\frac{\text{gm}}{\text{mol}} \right)}{2 \left(\frac{\text{eq}}{\text{mol}} \right)} = 49.04 \left(\frac{\text{gm}}{\text{Eq}} \right)$$



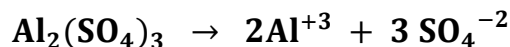
$$\text{Eq wt} = \frac{90.049 \left(\frac{\text{gm}}{\text{mol}} \right)}{2 \left(\frac{\text{eq}}{\text{mol}} \right)} = 45.02 \left(\frac{\text{gm}}{\text{Eq}} \right)$$

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



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

4- (Salts) $\text{Al}_2(\text{SO}_4)_3$.



$$\begin{aligned} \text{Eq wt} &= \frac{\text{M. wt}}{\text{No. of (cations or anions)} \times \text{charge of ion}} \\ &= \frac{342.15}{|2 \times 3|} = \frac{342.15}{6} = 57 \left(\frac{\text{gm}}{\text{Eq}}\right) \end{aligned}$$

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

$$6\text{- CaCl}_2 \text{ - Eq wt} = \frac{\text{M.wt (CaCl}_2\text{)}}{2}$$

$$7\text{-AlCl}_3 \text{ - Eq wt} = \frac{\text{M.wt (AlCl}_3\text{)}}{3}$$

$$8 \text{ - Na}_2\text{CO}_3 \text{ - Eq wt} = \frac{\text{M.wt (Na}_2\text{CO}_3\text{)}}{2}$$

$$9 \text{ - NaHCO}_3 \text{ - Eq wt} = \frac{\text{M.wt (NaHCO}_3\text{)}}{1}$$

Normal concentration

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

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

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

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

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

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

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

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

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

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

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

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

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

(a) 5.300gm/L Na₂CO₃ (when the CO₃⁻² reacts with two protons),

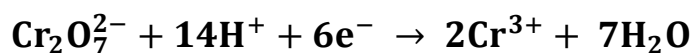
(b) 5.267 gm/L K₂Cr₂O₇ (the Cr⁶⁺ is reduced to Cr³⁺).

Solution : (a)



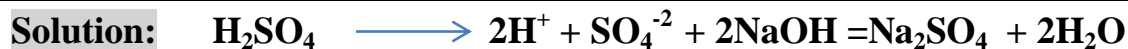
$$N = \frac{\text{wt}}{\text{Eq. wt}} \times \frac{1000}{V (\text{mL})} = \frac{5.3}{\frac{105.99}{2}} \times \frac{1000}{1000} = 0.10 \text{ Eq/L.}$$

(b)



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

Example (26):- How many millilitres of a 0.25M solution of H₂SO₄ will react with 10mL of a 0.25M solution of NaOH.



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

$$N_{\text{H}_2\text{SO}_4} = 2 \left(\frac{\text{eq}}{\text{mol}}\right) \times 0.25 \text{ M} \left(\frac{\text{mol}}{\text{L}}\right) = 0.5 \text{ N} \left(\frac{\text{Eq}}{\text{L}}\right) \text{ or } \left(\frac{\text{meq}}{\text{mL}}\right)$$

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

$$(N \times V)_{\text{H}_2\text{SO}_4} = (N \times V)_{\text{NaOH}}$$

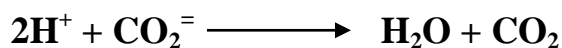
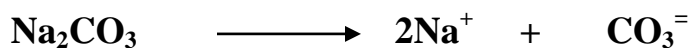
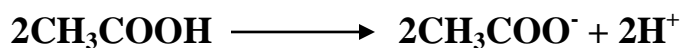
$$(0.5 \times V)_{\text{H}_2\text{SO}_4} = (0.25 \times 10)_{\text{NaOH}}, \quad V_{\text{H}_2\text{SO}_4} = 5.0 \text{ mL}$$

Example (27):- A solution contains 3.30 gm of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ in each 15 ml.

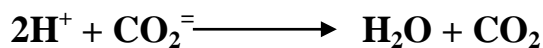
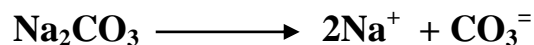
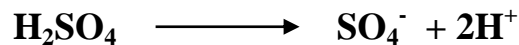
1- What is its molarity?

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



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



Solution:

$$1 - \quad M = \frac{\text{wt (g)}}{\text{M. wt } \left(\frac{\text{g}}{\text{mol}}\right)} \times \frac{1000}{V \text{ (mL)}}$$

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

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

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

$$V_1 = 12.4 \text{ ml acetic acid.}$$

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

$$V_1 = 12.4 \text{ ml H}_2\text{SO}_4.$$

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.

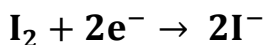
Solution:

$$(a) - \quad N = \frac{\text{wt}}{\text{Eq. wt}} \times \frac{1000}{V (\text{mL})} = \frac{0.212}{\frac{106.0}{1}} \times \frac{1000}{100} = 0.020 \frac{\text{meq}}{\text{mL}}$$

$$(b) - \quad N = \frac{0.212}{\frac{106.0}{2}} \times \frac{1000}{100} = 0.040 \text{ meq/mL}$$

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:



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

Example (30):- Calculate the normality of a solution of 0.25 g/L $\text{H}_2\text{C}_2\text{O}_4$, both as an acid and as a reducing agent.

Solution: as an acid $\text{H}_2\text{C}_2\text{O}_4 + 2\text{NaOH} \rightarrow \text{Na}_2\text{C}_2\text{O}_4 + \text{H}_2\text{O}$

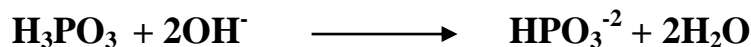
as a reducing agent $\text{C}_2\text{O}_4^{-2} \rightarrow 2\text{CO}_2 + 2\text{e}^-$

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

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

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

Example (32):- What is normality of 0.3 M H_3PO_3 when it undergoes the following reaction ?



Solution: Normality = a × molarity = $2 \times 0.3 = 0.6 \text{ N}$.

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-

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

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

$$0.0147 \text{ gm} \times 1000 (\text{mg/gm}) = 14.7 \text{ mg}$$

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

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

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

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:

$$(a) \quad N = \frac{\text{No. of milliequivalent}}{\text{Solution Volume (ml)}}$$

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

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

Concentration by percent

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

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

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

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

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

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

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

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

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

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

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

Example(35):- Calculate the weight percentage of solution prepared by mixing 5.0g AgNO₃ with 100mL water (density of water 1g/cm³).

Solution:

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

$$\left(\frac{\text{wt}}{\text{wt}}\%\right) = \frac{\text{wt solute (AgNO}_3\text{)(g)}}{\text{wt solute + wt solvent (H}_2\text{O) (g)}} \times 100$$

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

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

Solution:

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

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

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

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

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

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

Solution:

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

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

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

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

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

Solution:

$$\begin{aligned} \left(\frac{\text{V}}{\text{V}}\%\right) &= \frac{\text{V solute (mL)}}{\text{V solution or sample (mL)}} \times 100 \\ &= \frac{50 \text{ mL}}{250\text{mL}} \times 100 = 20 \left(\%\frac{\text{V}}{\text{V}}\right) = 20 \left(\frac{\text{cL}}{\text{L}}\right) \end{aligned}$$

Example (39):- Calculate the volume of ethanol in liter solution consists of ethanol and water $0.9 \left(\%\frac{\text{V}}{\text{V}}\right)$.

Solution:

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

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

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

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

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

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

Solution (b) –

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

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

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

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

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

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).

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.*

$$\text{molality}(m) = \frac{\text{No. of moles solute}(mol)}{\text{mass of solvent by (kg)}} = \frac{\frac{wt(gm)}{M.wt \left(\frac{gm}{mol}\right)}}{\frac{wt(gm)}{1000 \left(\frac{gm}{Kg}\right)}}$$

$$\text{molality}(m) = \frac{wt(gm)}{M.wt \left(\frac{gm}{mol}\right)} \times \frac{1000 \left(\frac{gm}{Kg}\right)}{wt(gm)}$$

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

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

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

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

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

The relationship between Molarity concentration, molality concentration and density :

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

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

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 (67g/mol).

Solution :-

$$\text{molality (m)} = \frac{\text{wt}(\text{gm})}{\text{M.wt} \left(\frac{\text{gm}}{\text{mol}}\right)} \times \frac{1000 \left(\frac{\text{gm}}{\text{kg}}\right)}{\text{wt}(\text{gm})} = 0.5 \times \frac{1000}{200} = 2.5 \left(\frac{\text{mol}}{\text{kg}}\right)$$

$$(\text{Molarity})M = \frac{\text{md}}{1 + \frac{\text{Mwt}}{1000}} = \frac{2.5 \times 1.02}{1 + (67/1000)} = \frac{2.55}{1.067} = 2.39 \left(\frac{\text{mol}}{\text{L}}\right)$$

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 :-

$$\text{molality (m)} = \frac{\text{wt}(\text{gm})}{\text{M.wt} \left(\frac{\text{gm}}{\text{mol}}\right)} \times \frac{1000 \left(\frac{\text{gm}}{\text{kg}}\right)}{\text{wt}(\text{gm})} = \frac{15}{100} \times \frac{1000}{400} = 0.375 \left(\frac{\text{mol}}{\text{kg}}\right)$$

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

Example (44):- The molality of a solution of ethanol , C₂H₅OH , in water is 1.54 m. How many gm of ethanol is dissolved in 2.50 kg water ?

Solution :-

$$\text{Molality} = \left(\frac{\text{mole}}{\text{wt}(\text{kg})}\right) \quad \longrightarrow \quad \text{mole} = 2.50 \times 1.54 = 3.85 \text{ mol}$$

$$\text{and mass of ethanol} = \text{mole} \times \text{M.wt} \quad \longrightarrow \quad 3.85 \times 46.1 = 177 \text{ gm}$$

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.

$$\text{Mole fraction for solute (X}_1\text{)} = \frac{\text{no. mole solute (n}_1\text{)}}{\text{no. mole solute (n}_1\text{)} + \text{no. mole solvent (n}_2\text{)}}$$

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

Example (45):- One liter of acetic acid solution contain 80.8 g of acetic acid, the solution density 1.00978 g/cm³ or g/mL. (cm³ = mL) calculate the mole fraction (X₁) for the solute and mole fraction (X₂) for the solvent in this solution

Solution:

$$\begin{aligned} \text{Mole fraction for solute } (X_1) &= \frac{\text{no. mole solute } (n_1)}{\text{no. mole solute } (n_1) + \text{no. mole solvent } (n_2)} \\ &= \frac{\left(\frac{\text{wt(g)}}{\text{M.wt}\left(\frac{\text{g}}{\text{mol}}\right)}\right)_{\text{CH}_3\text{COOH}}}{\left(\frac{\text{wt(g)}}{\text{M.wt}\left(\frac{\text{g}}{\text{mol}}\right)}\right)_{\text{CH}_3\text{COOH}} + \frac{\left(\text{density of solution}\left(\frac{\text{g}}{\text{mL}}\right) \times \text{volume of solution(mL)} - \text{wt of solute(g)}\right)}{\left(\text{Mwt of Solvent}\left(\frac{\text{g}}{\text{mol}}\right)\right)}} \\ &= \frac{\frac{80.8}{60}}{\frac{80.8}{60} + \left(\frac{(1.009791 \times 1000) - 80.8}{18}\right)} = \frac{\frac{80.8}{60}}{\frac{80.8}{60} + \left(\frac{1009.791 - 80.8}{18}\right)} = \frac{\frac{80.8}{60}}{\frac{80.8}{60} + \left(\frac{929}{18}\right)} \\ &= \frac{1.35}{1.35 + 51.6} = \frac{1.35}{52.95} = 0.025 \end{aligned}$$

$$\begin{aligned} \text{Mole fraction for solvent } (X_2) &= \frac{\text{no. mole solvent}}{\text{no. mole solute } (n_1) + \text{no. mole solvent } (n_2)} \\ &= \frac{\left(\frac{(1.009791 \left(\frac{\text{g}}{\text{mL}}\right) \times 1000\text{mL} - 80.8 \text{ g})}{18 \left(\frac{\text{g}}{\text{mol}}\right)}\right)}{\frac{80.8(\text{g})}{60\left(\frac{\text{g}}{\text{mol}}\right)} + \left(\frac{1.009791 \left(\frac{\text{g}}{\text{mL}}\right) \times 1000\text{mL} - 80.8 \text{ g}}{18 \left(\frac{\text{g}}{\text{mol}}\right)}\right)} = \frac{\left(\frac{(1.009791 \times 1000) - 80.8}{18}\right)}{\frac{80.8}{60} + \left(\frac{(1.009791 \times 1000) - 80.8}{18}\right)} \\ &= \frac{\left(\frac{1009.791 - 80.8}{18}\right)}{\frac{80.8}{60} + \left(\frac{1009.791 - 80.8}{18}\right)} = \frac{\left(\frac{929}{18}\right)}{\frac{80.8}{60} + \left(\frac{929}{18}\right)} = \frac{51.6}{1.35 + 51.6} = \frac{51.6 \text{ mol}}{52.95 \text{ mol}} = 0.975 \end{aligned}$$

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

The mole fraction - for a homogeneous solution consisting of three compounds A, B, and C is (X₁) for compound A and (X₂) for compound B and (X₃) for compound C .

Example (46):-A solution contains 116 gm acetone (CH_3COCH_3), 138 gm ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$), and 126 gm water . Determine the mole fraction of each ?

Solution -

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

$$\text{Mol}_{\text{C}_2\text{H}_5\text{OH}} = \text{wt} / \text{M.wt} \longrightarrow 138 / 46.0 = 3.0 \text{ mol}$$

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

$$\text{Sum of mole} = 2.0 + 3.0 + 7.0 = 12.0 \text{ mole}$$

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

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

$$\text{Mole fraction for C}_2\text{H}_5\text{OH}(X_2) = \frac{3.0 \text{ mole}}{12.0 \text{ mole}} = 0.250$$

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

$$X_1 + X_2 + X_3 = 1, \quad 0.167 + 0.250 + 0.583 = 1$$

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.

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

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

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

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

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

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

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

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	

^apL = 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?

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

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

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

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

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

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

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

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

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

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

Example (49-B):- prove the

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

Solution:

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

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

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

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

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

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

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

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

The relationship between molarity, normality and part per million

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

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

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

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

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

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

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

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

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

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

Example (50):- (a) Calculate the molar conc. of 1.0 ppm solutions each of Li^+ and Pb^{+2} . (b) What weight of $\text{Pb}(\text{NO}_3)_2$ will have to be dissolved in 1 liter of water to prepare a 100 ppm Pb^{+2} solution.

Solution:

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

(a)

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

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

(b)

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

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

$$4.83 \times 10^{-4} = \frac{\text{wt}}{283.2} \times \frac{1000}{1000} \quad \text{wt} = 0.137\text{g Pb}(\text{NO}_3)_2$$

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

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

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

Problems

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

- a) AgNO_3 b) $\text{Al}_2(\text{SO}_4)_3$ 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, $\text{Fe SO}_4(\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$, 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,

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

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 2.00×10^{-3} M in NaCl and 5.4×10^{-4} M in HCl.



Solution

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

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

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

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

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

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

Solution:

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

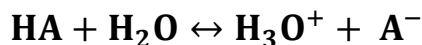
$$[\text{Ag}^+] = \frac{-6.372}{\text{Log}} = \text{Log}^{-1} (-6.372) = 4.246 \times 10^{-7} = 4.25 \times 10^{-7} \text{ M}$$

Acid-Base Equilibria

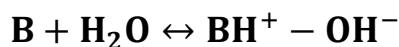
Acid-base theories:-

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^+):



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



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



This theory is obviously restricted to water as the solvent.

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

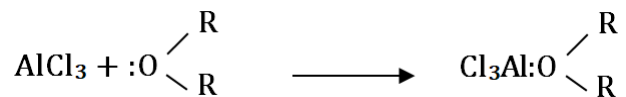
Acid:-any substance that can donate a proton.

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

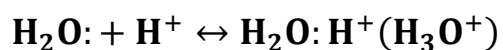


3) Lewis Theory (taking and giving electrons):-

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



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



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

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

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.



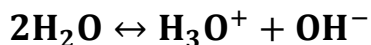
Thermodynamic acidity constant K°

$$K^\circ = \frac{a_{\text{H}_3\text{O}^+} \times a_{\text{OAc}^-}}{a_{\text{H}_2\text{O}} \times a_{\text{HOAc}}}$$

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

$$K_a = \frac{a_{\text{H}_3\text{O}^+} \times a_{\text{OAc}^-}}{a_{\text{HOAc}}}$$

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



The equilibrium constant for this is:

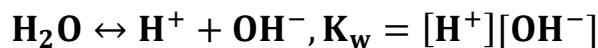
$$K_w^\circ = \frac{a\text{H}_3\text{O}^+ \times a\text{OH}^-}{a\text{H}_2\text{O}^2}$$

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

$$K_w^\circ = a\text{H}_3\text{O}^+ \times a\text{OH}^-$$

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).



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

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

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

Solution:

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

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

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

The pH scale:

$$\text{pH} = 14 - 11 = 3$$

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



$$K_a = \frac{\{A^-\}\{H_3O^+\}}{\{HA\}}, \quad \{H_3O^+\} = \{H^+\}$$

$$\{A^-\}\{H^+\} = K_a \times \{HA\}, \quad \{H^+\} = \frac{K_a \times \{HA\}}{\{A^-\}}$$

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

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

$$pH = pK_a + \log \frac{\{\text{salt}\}}{\{\text{acid}\}} \quad (\text{Henderson - H, Equation for acidic Buffer solutions}).$$

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



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

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

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

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

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

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:-

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

$$\text{pH} = -\log 1.75 \times 10^{-5} + \log \frac{\left(\frac{0.1 \times 20}{30}\right)}{\left(\frac{0.1 \times 10}{30}\right)} = 4.76 + \log 2.0 = 5.06$$

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.

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

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: $dpH = \text{final pH} - \text{initial pH}$

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:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}] - [\text{adding acid}]}{[\text{acid}] + [\text{adding acid}]}$$

$$(\text{pH})_2 = 4.76 + \log \frac{[0.2 \times 10] - [0.1 \times 1]}{[0.2 \times 10] + [0.1 \times 1]} = 4.71$$

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

$$\Delta \text{pH} = (\text{pH})_1 - (\text{pH})_2 = 4.76 - 4.71 = 0.05$$

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.

$$\begin{aligned} \text{Buffer capacity } (\beta) &= \left(\frac{\frac{n(\text{mol})}{V_L(\text{Buffer solutio})}}{dpH}\right) = \left(\frac{\frac{M \times V(L)(\text{acid})}{V_L(\text{Buffer solutio})}}{0.05}\right) \\ &= \left(\frac{\frac{0.1 \times 0.001}{\frac{10}{1000}}}{0.05}\right) = \left(\frac{\frac{0.0001}{0.01}}{0.05}\right) = \left(\frac{0.01}{0.05}\right) = 0.2 \end{aligned}$$

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

Solution:

$$\text{pH} = 4 \text{ (before dilution), } \text{pH} = -\log [\text{H}^+], 4 = -\log [\text{H}^+],$$

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

$$(\text{M}_1 \times \text{V}_1)_{\text{before dilution}} = (\text{M}_2 \times \text{V}_2)_{\text{after dilution}}$$

$$(1 \times 10^{-4} \times \text{V}) = (\text{M}_2 \times 100\text{V}), \text{M}_2 = \left(\frac{1 \times 10^{-4} \times \text{V}}{100\text{V}}\right) = 1 \times 10^{-6} \text{ M}$$

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

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

Solution: The equation of acidic Buffer solution

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

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

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

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

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

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

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

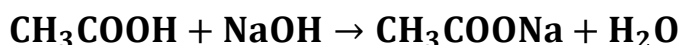
This result means that the pH of this solution did not change due to dilution because it is a buffer solution.

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 flask reacts 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..



(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.

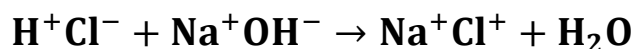
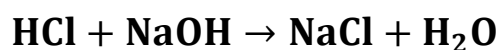
(4) Reduction-Oxidation titrations: These (redox) titrations involve the titration of an oxidizing agent with a reducing agent, or vice versa .An oxidizing agent gains electrons and a reducing agent loses electrons in a reaction between them.

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:



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

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

(2) At 5 mL titration: before equivalence point

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

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

$$\begin{aligned}\text{mmol HCl remaining} &= \text{mmol HCl total} - \text{mmol NaOH added} \\ &= 5.0 - 0.5 = 4.5\end{aligned}$$

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

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

(3) At 45 mL titration: before equivalence point

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

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

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

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

(4) At 50 mL titration: Equivalence Point

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

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



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

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

$$\text{pH} = -\log 10^{-7} = 7 \text{ (neutrization step)}$$

(5) At 55 mL titration: after equivalence point

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

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

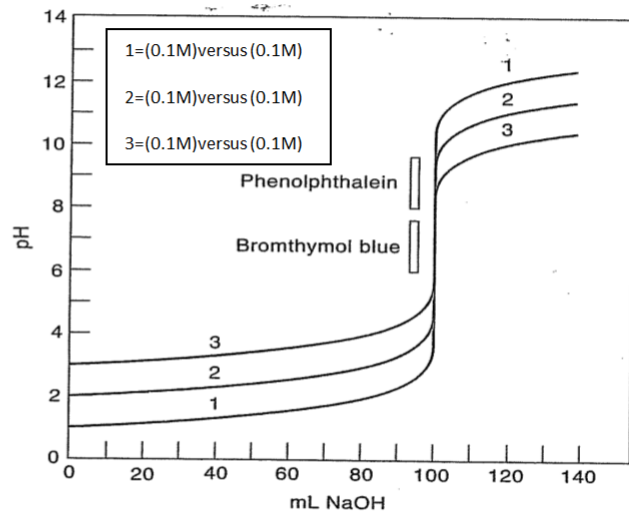
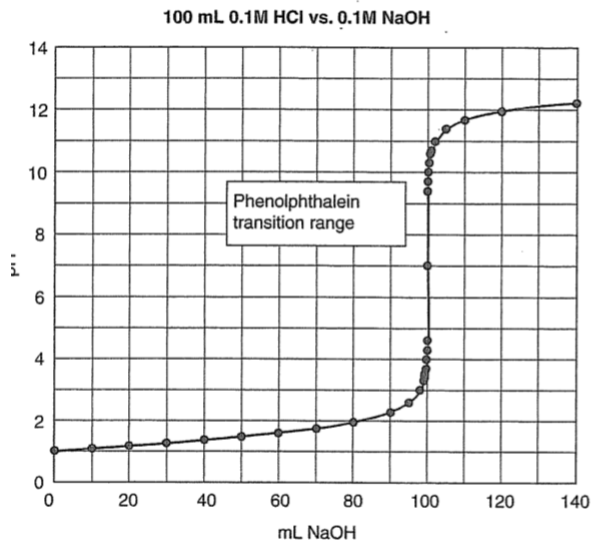
$$M_{\text{NaOH}} = \frac{\text{mmol}}{V} = \frac{0.5}{50 + 55} = 0.00476\text{M}$$

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

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

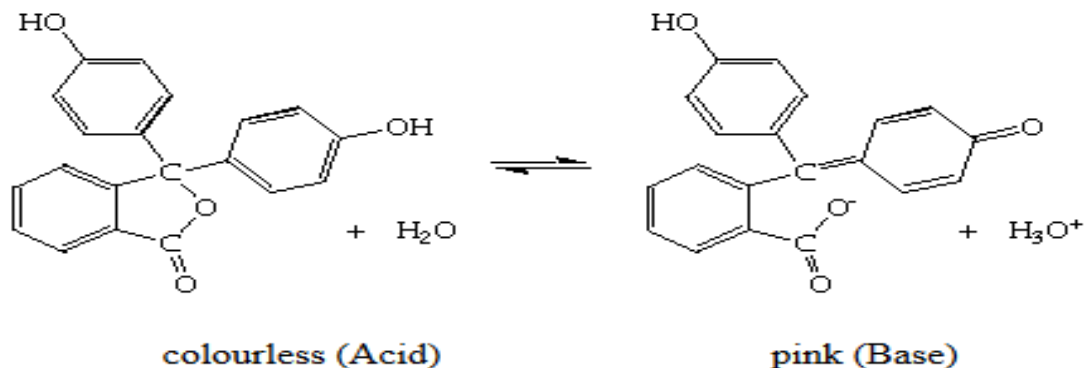
Construction (plot) titration curve of strong acid versus strong base:-

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.

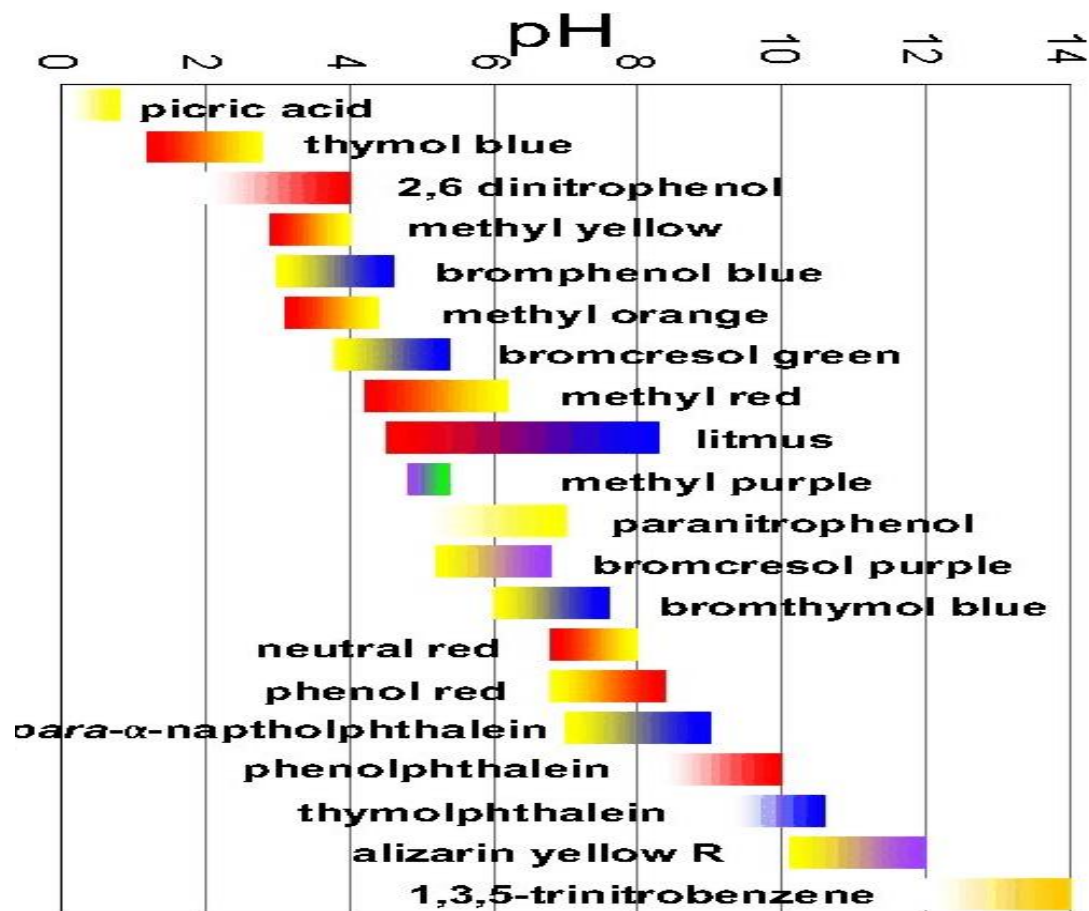
Indicators (Acid-Base):- are substances which change colour with change pH.



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.

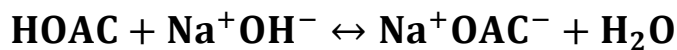
Common Acid – Base Indicators

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



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

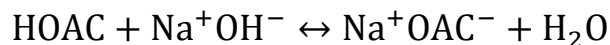
Solution:

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

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

$$\text{pH} = -\log[\text{H}^+] = -\log 1.23 \times 10^{-3} = 2.88$$

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



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

mmol of HOAc (total) = $M \times V = 0.1 \times 50 = 5.0$

mmol of HOAc remaining (unreacted) = $5.0 - 1.0 = 4.0$

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

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

mmol NaOH added = $M \times V = 0.1 \times 25 = 2.5$ mmol.
= mmol of NaOAc (salt) formed

mmol of HOAc remaining (unreacted) = $5.0 - 2.5 = 2.5$ mmol

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

pH = pKa (mid – point)

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

mmol NaOH added = $M \times V = 0.1 \times 50 = 5.0 =$ mmol of NaOAc (salt) formed

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



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

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

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

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

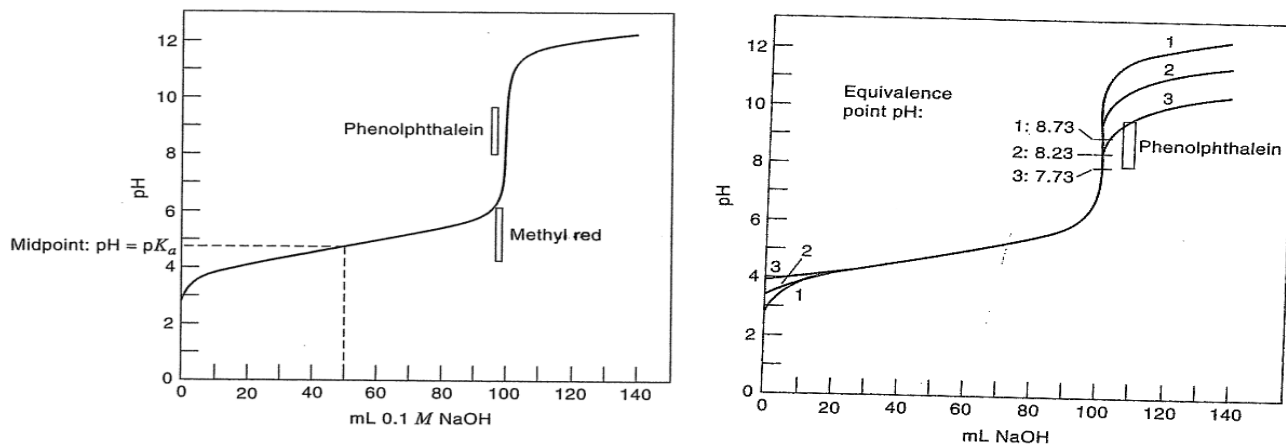
mmol NaOH added = $M \times V = 0.1 \times 60 = 6.0$ mmol

mmol of NaOH remaining (excess) = $6.0 - 5.0 = 1.0$ mmol

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

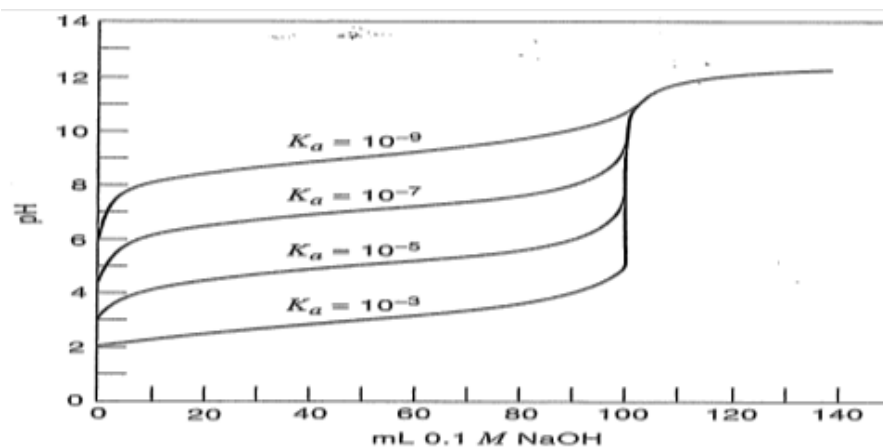
$$pH = 14 - 2.04 = 11.96$$

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 NH₃ (K_b=1.75×10⁻⁵) with 0.1M HCl?

(1) At 0mL titrant (0.1M HCl): NH₃ solution alone

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

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

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

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

$$\text{mmol HCl added} = M \times V = 0.1 \times 10 = 1.0 = \text{mmol of NH}_4\text{Cl (salt) formed}$$

$$\text{mmol NH}_3 \text{ total} = M \times V = 0.1 \times 50 = 5.0$$

$$\text{mmol NH}_3 \text{ remaining (unreacted)} = 5.0 - 1.0 = 4.0$$

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]} = 4.75 + \log \frac{1.0}{4.0} = 4.15$$

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

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

$$\begin{aligned} \text{mmol HCl added} &= M \times V = 0.1 \times 25 = 2.5\text{mmol} \\ &= 2.5\text{mmol of NH}_4\text{Cl (salt) formed} \end{aligned}$$

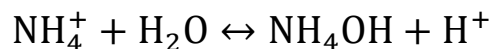
$$\text{mmol NH}_3 \text{ remaining (unreacted)} = 5.0 - 2.5 = 2.5$$

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]} = 4.75 + \log \frac{2.5}{2.5} = 4.75 \quad \text{pOH} = \text{p}K_b \text{ mid - point}$$

(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 NH₃ to its salt NH₄Cl



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

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

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

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

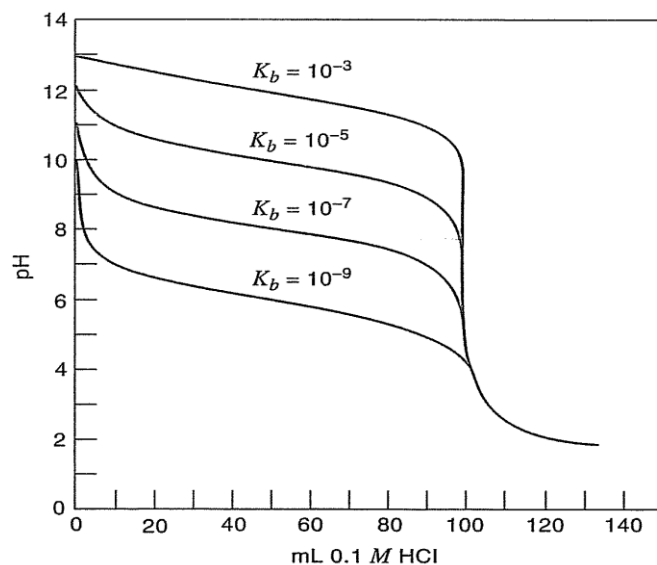
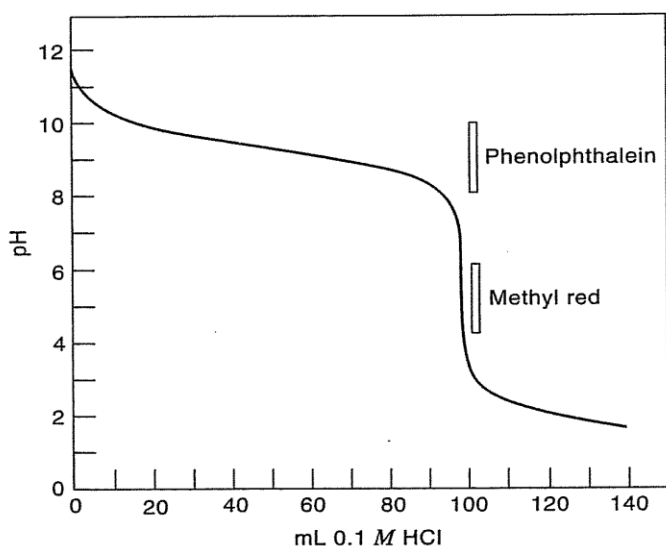
$$\text{mmol HCl remaining (excess)} = 6.0 - 5.0 = 1.0$$

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

$$\text{pH} = -\log 0.00909 = 2.05$$

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.

$$\text{mmol of analyte} = \text{mmol first titrant} - \text{mmol back titrant}$$

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:



$$\text{mmol Na}_2\text{CO}_3 = (\text{mmol HCl} \times \frac{1\text{mmol.Na}_2\text{CO}_3}{2\text{mmol.HCl}}) - \text{mmol NaOH}$$

$$\left(\frac{\text{wt}}{\text{M.wt}} \times 1000\right)_{\text{Na}_2\text{CO}_3} = \left(\text{M} \times \text{V} \times \frac{1}{2}\right)_{\text{HCl}} - (\text{M} \times \text{V})_{\text{NaOH}}$$

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

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

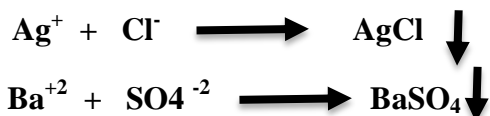
$$wt \times 1000 = (1.94 \times 106) \quad , \quad wt_{\text{Na}_2\text{CO}_3} = \frac{206}{1000}$$

$$wt_{\text{Na}_2\text{CO}_3} = 0.206 \text{ gm} \quad , \quad \% \text{Na}_2\text{CO}_3 = \frac{wt \text{ Na}_2\text{CO}_3}{wt \text{ sample}} \times 100$$

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

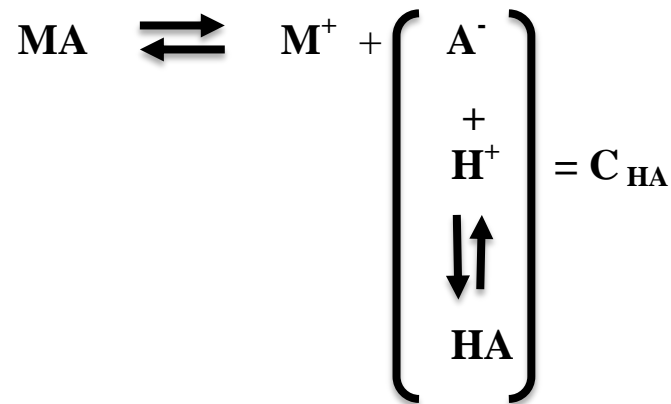
Precipitation Reactions and Titrations

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

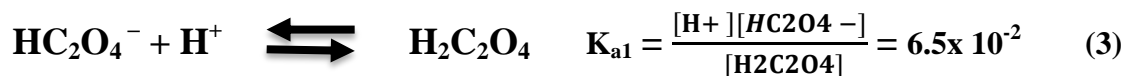


Effect of acidity on solubility of precipitates Conditional solubility product [K_{sp}'].

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).



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

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

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

$$\alpha_1 = \frac{[\text{HC}_2\text{O}_4^-]}{[\text{H}_2\text{C}_2\text{O}_4] + [\text{HC}_2\text{O}_4^-] + [\text{C}_2\text{O}_4^{2-}]} = \frac{[\text{HC}_2\text{O}_4^-]}{C_{\text{H}_2\text{C}_2\text{O}_4}} \longrightarrow [\text{HC}_2\text{O}_4^-] = \alpha_1 \times C_{\text{H}_2\text{C}_2\text{O}_4}$$

$$\alpha_2 = \frac{[\text{C}_2\text{O}_4^{2-}]}{[\text{H}_2\text{C}_2\text{O}_4] + [\text{HC}_2\text{O}_4^-] + [\text{C}_2\text{O}_4^{2-}]} = \frac{[\text{C}_2\text{O}_4^{2-}]}{C_{\text{H}_2\text{C}_2\text{O}_4}} \longrightarrow [\text{C}_2\text{O}_4^{2-}] = \alpha_2 \times C_{\text{H}_2\text{C}_2\text{O}_4}$$

$$\mathbf{K_{sp} = [\text{Ca}^{+2}][\text{C}_2\text{O}_4^{-2}] = [\text{Ca}^{+2}] \times C_{\text{H}_2\text{C}_2\text{O}_4} \times \alpha_2}$$

We can write then

$$\frac{K_{sp}}{\alpha_2} = K_{sp}' = [\text{Ca}^{+2}] \times C_{\text{H}_2\text{C}_2\text{O}_4} = S^2$$

$$\alpha_2 = \frac{K_{a1} K_{a2}}{[\text{H}^+]^2 + [\text{H}^+]K_{a1} + K_{a1}K_{a2}}$$

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?



$$K_{sp}(\text{CaC}_2\text{O}_4) = 2.6 \times 10^{-9}, K_{a1} = 6.5 \times 10^{-2}, K_{a2} = 6.1 \times 10^{-5}$$

$$\text{Solubility of CaC}_2\text{O}_4 \text{ in water } K_{sp}(\text{CaC}_2\text{O}_4) = [\text{Ca}^{+2}][\text{C}_2\text{O}_4^{-2}] = S^2$$

$$S^2 = \sqrt{K_{sp}(\text{CaC}_2\text{O}_4)} = \sqrt{2.6 \times 10^{-9}} = 5.09 \times 10^{-5} \text{ M}$$

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

$$\alpha_2 = \frac{K_{a1} K_{a2}}{[\text{H}^+]^2 + [\text{H}^+]K_{a1} + K_{a1}K_{a2}}$$

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

$$\alpha_2 = 5.7 \times 10^{-2} \rightarrow S = \sqrt{\frac{K_{sp}}{\alpha_2}} = \sqrt{\frac{2.6 \times 10^{-9}}{5.7 \times 10^{-2}}} = 2.1 \times 10^{-4} \text{ M}$$

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

$$\begin{aligned} \text{The Comparison} &= \frac{S_{\text{in acid solution}}}{S_{\text{in water}}} \times 100 \\ &= \frac{2.1 \times 10^{-4}}{5.09 \times 10^{-5}} \times 100 = 412.6\% \text{ (increase in solubility)} \end{aligned}$$

Method of driving values of α_0 , α_1 and α_2

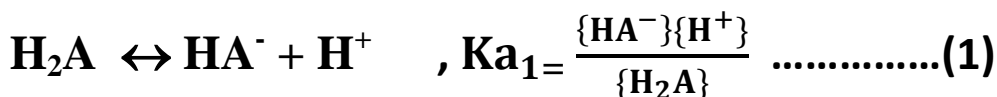


$$\{\text{HA}\}_T = \{\text{HA}\} + \{\text{A}^-\} \quad , \quad \alpha_0 = \frac{\{\text{HA}\}}{\{\text{HA}\} + \{\text{A}^-\}} \quad , \quad \alpha_1 = \frac{\{\text{A}^-\}}{\{\text{HA}\} + \{\text{A}^-\}}$$

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

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

$$\text{In the same way } \alpha_1 = \frac{\{\text{A}^-\}}{\{\text{HA}\} + \{\text{A}^-\}} = \frac{K_a}{\{\text{H}^+\} + K_a}$$



$$\{\text{H}_2\text{A}\}_T = \{\text{H}_2\text{A}\} + \{\text{HA}^-\} + \{\text{A}^{2-}\}$$

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

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

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

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

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

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

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

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

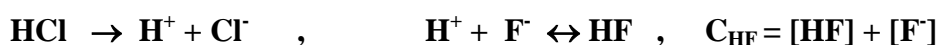
$$\alpha_0 = \frac{\{H^+\}^2}{\{H^+\}^2 + \{H^+\}Ka_1 + Ka_1 Ka_2}$$

In the same way $\alpha_1 = \frac{\{H^+\}Ka_1}{\{H^+\}^2 + \{H^+\}Ka_1 + Ka_1 Ka_2}$

and $\alpha_2 = \frac{Ka_1 Ka_2}{\{H^+\}^2 + \{H^+\}Ka_1 + Ka_1 Ka_2}$

Example 2 :- Calculate the solubility of CaF_2 in 0.1 M HCl. Also calculate equilibrium concentration of F^- and HF. $K_{sp}(CaF_2) = 3.9 \times 10^{-11}$, $K_a(HF) = 6.8 \times 10^{-4}$,

solution



$$K_{sp}(CaF_2) = [Ca^{+2}] [F^-]^2 \quad [F^-] = \alpha_1 C_{HF}$$

$$K_{sp}(CaF_2) = [Ca^{+2}] [\alpha_1 C_{HF}]^2 , \quad K_{sp}(CaF_2) = [Ca^{+2}] [\alpha_1^2 C_{HF}^2] ,$$

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

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

$$\alpha_1 = \frac{Ka}{[H^+] + Ka} = \frac{6.8 \times 10^{-4}}{0.1 + 6.8 \times 10^{-4}} = \frac{6.8 \times 10^{-4}}{0.100068} = 6.75 \times 10^{-3}$$

$$K'_{sp} = \frac{K_{sp}}{\alpha_1^2} = \frac{3.9 \times 10^{-11}}{(6.75 \times 10^{-3})^2} = 8.559 \times 10^{-7} , \quad K'_{sp} = [S] [2S]^2 \rightarrow 4S^3$$

$$S = \sqrt[3]{\frac{K'_{sp}}{4}}, \quad S = \sqrt[3]{\frac{8.559 \times 10^{-7}}{4}} = \sqrt[3]{2.139 \times 10^{-7}} = 5.98 \times 10^{-3} \text{ M}$$

$$C_{\text{HF}} = 2S = 5.98 \times 10^{-3} \times 2 = 0.01196 \text{ M}$$

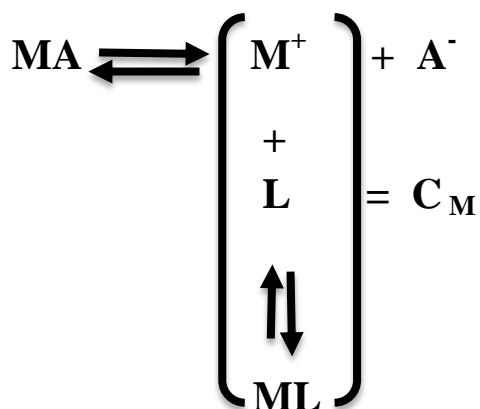
$$[\text{F}^-]_{\text{eq.}} = \alpha_1 C_{\text{HF}} = 6.75 \times 10^{-3} \times 0.01196 = 8.073 \times 10^{-5} \text{ M}$$

$$[\text{HF}]_{\text{eq.}} = C_{\text{HF}} - [\text{F}^-] = 0.01196 - 8.073 \times 10^{-5} = 1.1879 \times 10^{-2} \text{ M}$$

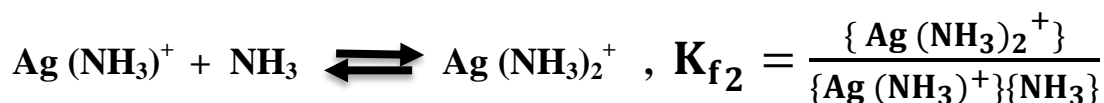
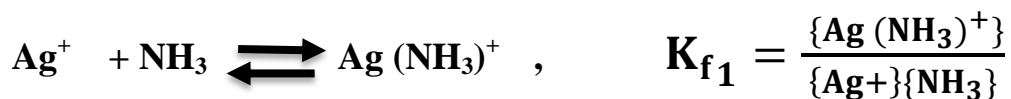
$$\text{OR -- } [\text{HF}]_{\text{eq.}} = \alpha_0 C_{\text{HF}} = (1 - \alpha_1) C_{\text{HF}} = (1 - 6.75 \times 10^{-3}) \times 0.01196 = 1.1879 \times 10^{-2} \text{ M}$$

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 $[\text{MA}]$ that dissociate to give $[\text{M}^+]$ and $[\text{A}^-]$ and whose metal complexes with the ligand L to form $[\text{ML}^+]$ would have the following equilibria:-



The sum of M^+ and $[\text{ML}^+]$ is the analytical concentration C_{M} in equilibrium, which is equal to $[\text{A}^-]$. 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:-



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

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

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 $C_{Ag} \beta_0$ for $[Ag^+]$ in the K_{sp} expression. Where β_0 is the fraction of silver species present as $[Ag^+]$.

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

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

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

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

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

We can write then

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

$$\beta_0 = \frac{1}{1 + K_{f1}\{NH_3\} + K_{f1} K_{f2}\{NH_3\}^2}$$

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? $K_{sp} = 4 \times 10^{-13}$, $K_{f1} = 2.5 \times 10^3$, $K_{f2} = 1.0 \times 10^4$.

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

$$S^2 = \sqrt{K_{sp(AgBr)}} \sqrt{4 \times 10^{-13}} = 6.3 \times 10^{-7} M$$

Solubility of $AgBr$ in a solution containing 0.1M NH_3 .

$$B_0 = \frac{1}{1 + K_{f1}\{NH_3\} + K_{f1} K_{f2}\{NH_3\}^2}$$

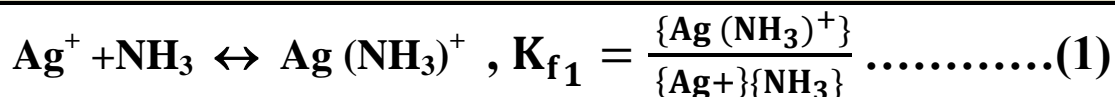
$$B_0 = \frac{1}{1 + (2.5 \times 10^3) \times (0.1) + (2.5 \times 10^3) \times (1 \times 10^4) \times (0.1)^2} = 1 \times 10^{-6}$$

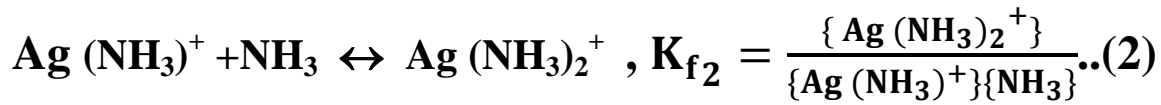
$$S = \sqrt{\frac{K_{sp}}{\beta_0}} = \sqrt{\frac{4 \times 10^{-13}}{4 \times 10^{-6}}} = 3.2 \times 10^{-4} M$$

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

The Comparison = $\frac{S_{\text{in ammonia solution}}}{S_{\text{in water}}} = \frac{3.2 \times 10^{-4}}{6.3 \times 10^{-7}} = (508 \text{ times more soluble})$

Method of deriving values of B_0 , B_1 and B_2





$$\{\text{Ag}^+\}_T = \{\text{Ag}^+\} + \{\text{Ag}(\text{NH}_3)^+\} + \{\text{Ag}(\text{NH}_3)_2^+\}$$

$$B_0 = \frac{\{\text{Ag}^+\}}{\{\text{Ag}^+\} + \{\text{Ag}(\text{NH}_3)^+\} + \{\text{Ag}(\text{NH}_3)_2^+\}},$$

$$B_1 = \frac{\{\text{Ag}(\text{NH}_3)^+\}}{\{\text{Ag}^+\} + \{\text{Ag}(\text{NH}_3)^+\} + \{\text{Ag}(\text{NH}_3)_2^+\}}$$

$$B_2 = \frac{\{\text{Ag}(\text{NH}_3)_2^+\}}{\{\text{Ag}^+\} + \{\text{Ag}(\text{NH}_3)^+\} + \{\text{Ag}(\text{NH}_3)_2^+\}},$$

From equation no 2 $\{\text{Ag}(\text{NH}_3)_2^+\} = K_{f2} \{\text{Ag}(\text{NH}_3)^+\} \{\text{NH}_3\}$

$$B_0 = \frac{\{\text{Ag}^+\}}{\{\text{Ag}^+\} + \{\text{Ag}(\text{NH}_3)^+\} + \{\text{Ag}(\text{NH}_3)_2^+\}}$$

$$B_0 = \frac{\{\text{Ag}^+\}}{\{\text{Ag}^+\} + \{\text{Ag}(\text{NH}_3)^+\} + K_{f2} \{\text{Ag}(\text{NH}_3)^+\} \{\text{NH}_3\}},$$

From equation no 1 $\{\text{Ag}(\text{NH}_3)^+\} = K_{f1} \{\text{Ag}^+\} \{\text{NH}_3\}$

$$B_0 = \frac{\{\text{Ag}^+\}}{\{\text{Ag}^+\} + K_{f1} \{\text{Ag}^+\} \{\text{NH}_3\} + K_{f1} K_{f2} \{\text{Ag}^+\} \{\text{NH}_3\} \{\text{NH}_3\}}$$

$$B_0 = \frac{\{\text{Ag}^+\}}{\{\text{Ag}^+\} (1 + K_{f1} \{\text{NH}_3\} + K_{f1} K_{f2} \{\text{NH}_3\}^2)},$$

$$B_0 = \frac{1}{1 + K_{f1}\{\text{NH}_3\} + K_{f1} K_{f2}\{\text{NH}_3\}^2}$$

In the same way

$$B_1 = \frac{K_{f1}\{\text{NH}_3\}}{1 + K_{f1}\{\text{NH}_3\} + K_{f1} K_{f2}\{\text{NH}_3\}^2}$$

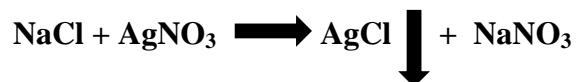
and

$$B_2 = \frac{K_{f1} K_{f2}\{\text{NH}_3\}^2}{1 + K_{f1}\{\text{NH}_3\} + K_{f1} K_{f2}\{\text{NH}_3\}^2}$$

Precipitation Titration (Argentometric Titration)

Example 4:- Calculate pCl for the titration of 100 mL of 0.10 M NaCl with (0.1 M) AgNO₃ after addition of [0.0, 20.0, 99.0, 99.50, 100.0, 100.50 and 110.0 mL] AgNO₃?

$$K_{sp} (\text{AgCl}) = 1.0 \times 10^{-10}$$



At 0.00 mL

$$\text{pCl} = -\log [\text{Cl}^-] \longrightarrow -\log [0.1] \longrightarrow \text{pCl} = 1.00$$

At 20.0 mL

$$\text{mmol Cl}^- = M \times V = 0.1 \text{ mmol/mL} \times 100 \text{ mL} = 10.0 \text{ mmol}$$

$$\text{mmol Ag}^+ = M \times V = 0.1 \text{ mmol/mL} \times 20 \text{ mL} = 2.0 \text{ mmol}$$

$$\text{Cl}^- \text{ left} = 10 - 2 = 8 \text{ mmol} \longrightarrow [\text{Cl}^-] = (\text{mmol}/V_T) = 8/120 = 0.0667\text{M}$$

$$\text{pCl} = -\text{Log} [0.0667] = 1.18$$

At 99.0 mL

$$\text{mmol Ag}^+ = 99 \text{ mL} \times 0.1 \text{ mmol/mL} = 9.9 \text{ mmol}$$

$$\text{Cl}^- \text{ left} = 10 - 9.9 = 0.1 \text{ mmol} \longrightarrow [\text{Cl}^-] = (\text{mmol}/V_T) = 0.1/199 = 5 \times 10^{-4} \text{ M}$$

$$\text{pCl}^- = -\text{Log} [5 \times 10^{-4}] = 3.26$$

At 99.5 mL

$$\text{mmolAg}^+ = 99.5 \text{ mL} \times 0.1 \text{ mmol/mL} = 9.95 \text{ mmol}$$

$$\text{Cl}^- \text{ left} = 10 - 9.95 = 0.05 \text{ mmol} \longrightarrow [\text{Cl}^-] = (\text{mmol}/V_T) = 0.05/199.5 = 2.5 \times 10^{-4} \text{ M}$$

$$\text{pCl}^- = -\text{Log} [2.5 \times 10^{-4}] = 3.6$$

At 100 mL

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

$$[\text{Cl}^-] = \sqrt[2]{K_{sp}(\text{AgCl})} = \sqrt[2]{1.0 \times 10^{-10}} = 1.0 \times 10^{-5} \text{ M}$$

$$\text{pCl}^- = -\text{Log} [1.0 \times 10^{-5}] = 5$$

At 100.5 mL

$$\text{mmolAg}^+ = 100.5 \text{ mL} \times 0.1 \text{ mmol/mL} = 10.05 \text{ mmol}$$

$$\text{Ag}^+ \text{ left} = 10.05 - 10 = 0.05 \text{ mmol} \longrightarrow [\text{Ag}^+] = (\text{mmol}/V_T) = 0.05/200.5 = 2.5 \times 10^{-4} \text{ M}$$

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

$$\text{pCl}^- = -\text{Log} [4 \times 10^{-7}] = 6.4$$

At 110 mL

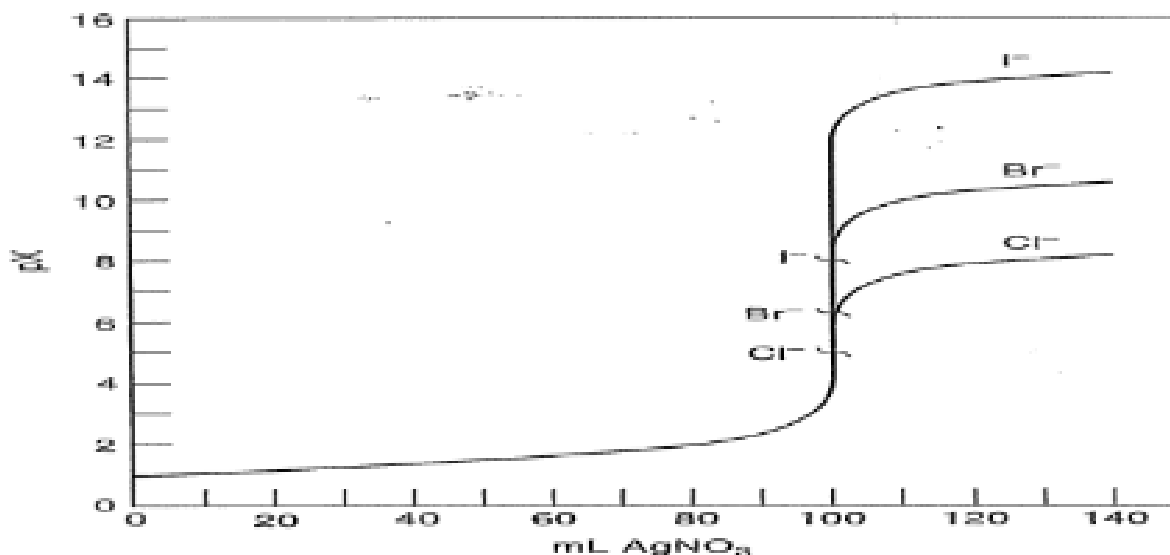
$$\text{mmolAg}^+ = 110 \text{ mL} \times 0.1 \text{ mmol/mL} = 11 \text{ mmol}$$

$$\text{Ag}^+ \text{ left} = 11 - 10 = 1 \text{ mmol} \longrightarrow [\text{Ag}^+] = (\text{mmol}/V_T) = 1/210 = 4.76 \times 10^{-3} \text{ M}$$

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

$$\text{pCl}^- = -\text{Log} [2.1 \times 10^{-8}] = 7.67$$

Titration curves for 100mL 0.1M Cl⁻, Br⁻, and I⁻ solutions versus 0.1M AgNO₃.



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):

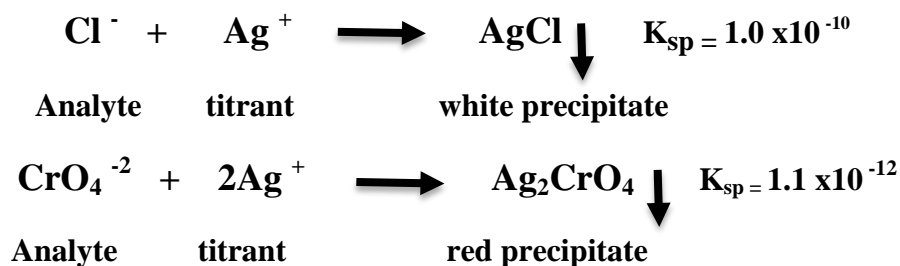
We can detect the endpoint by measuring either pCl or pAg with two types of indicators:

(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 AgNO₃, the excess (after drops) of AgNO₃ than reacting with the indicator (K₂CrO₄) to form red precipitate Ag₂CrO₄.



The concentration of the indicator is important. The Ag_2CrO_4 should just start precipitating at the equivalent point, where we have a saturated solution of AgCl . From K_{sp} , the concentration of Ag^+ at the equivalent point is 10^{-5}M . (It is less than this before the equivalent point). So, Ag_2CrO_4 should precipitate just when $\text{Ag}^+ = 10^{-5}\text{M}$. The solubility product of Ag_2CrO_4 is 1.1×10^{-12} . By inserting the Ag^+ concentration in the K_{sp} equation for Ag_2CrO_4 , we calculate that, for this to occur, $[\text{CrO}_4^{2-}]$ should be 0.011M .

$$[10^{-5}]^2 \times [\text{CrO}_4^{2-}] = 1.1 \times 10^{-12}$$

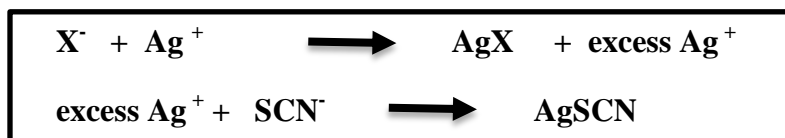
$$[\text{CrO}_4^{2-}] = 1.1 \times 10^{-2} \text{ M}$$

If the concentration is greater than Ag_2CrO_4 will begin to precipitate when $[\text{Ag}^+]$ is less than 10^{-5} M (before the equivalent point). If it is less than 0.011M , then the $[\text{Ag}^+]$ will have exceeded 10^{-5} M (beyond the equivalent point) before precipitation of 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 Ag_2CrO_4 precipitate color, and an excess of 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 $[\text{HCrO}_4^-]$, and more $[\text{Ag}^+]$ will be required to form the $[\text{Ag}_2\text{CrO}_4]$ 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 (Cl^- , Br^- , and SCN^-) and it is performed in acid (HNO_3) solution. In this procedure, we add a measured excess of AgNO_3 to precipitate the anion and then determine the excess Ag^+ by back titration with standard potassium thiocyanate solution:-



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:-



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**:-



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⁺**.



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.



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

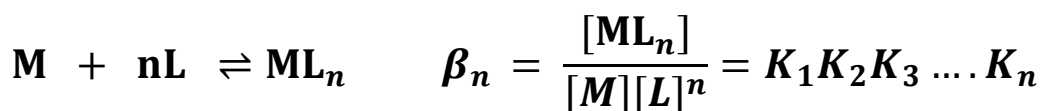
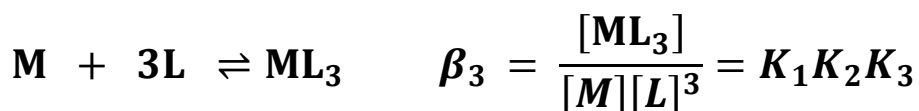
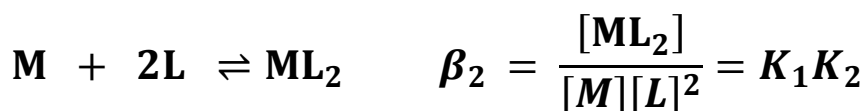
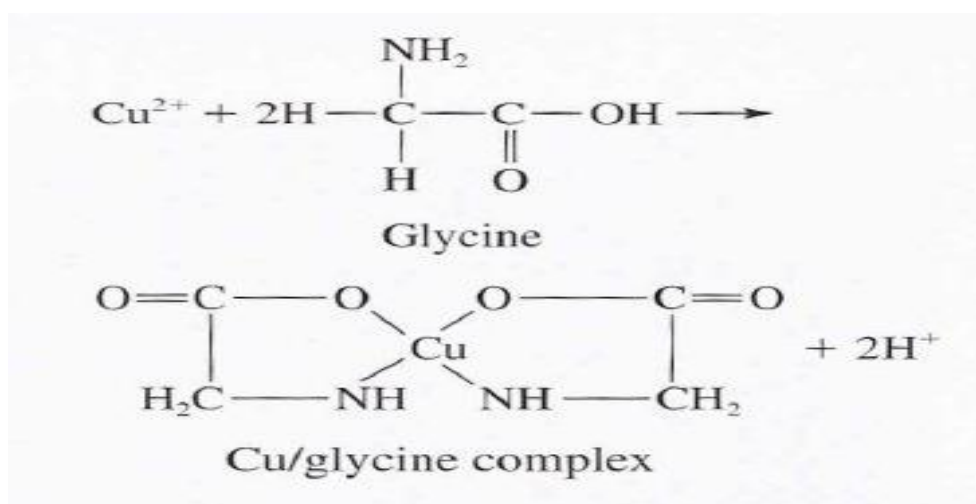
- 1- Explain the Volhard Titration of Chloride, the Fajan's titration which is used for acid solutions. Why?
- 2- Explain the principles of adsorption indicators.
- 3- Calculate the solubility of PbS in (0.01M) HCl? And calculate the equilibrium concentrations of S^{-2} , HS^{-} and H_2S . $K_{sp}(PbS)= 3 \times 10^{-28}$, $K_{a1}=9.6 \times 10^{-8}$, $K_{a2}=1.3 \times 10^{-14}$.

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.



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 $c_M = [M] + [ML] + [ML_2] + \dots + [ML_n]$

From the overall formation constants the concentration of the complexes can be expressed in the terms of the free metal concentration [M], to give

$$c_M = [M] + \beta_1 [M][L] + \beta_2 [M][L]^2 + \dots + \beta_n [M][L]^n$$

$$= [M]\{1 + \beta_1 [L] + \beta_2 [L]^2 + \dots + \beta_n [L]^n\}$$

Now α_M can be found as:

$$\alpha_M = \frac{[M]}{c_M} = \frac{[M]}{[M] + \beta_1 [M][L] + \beta_2 [M][L]^2 + \beta_3 [M][L]^3 \dots \dots \beta_n [M][L]^n}$$

$$\alpha_M = \frac{[M]}{c_M} = \frac{[M]}{[M]\{1 + \beta_1 [L] + \beta_2 [L]^2 + \beta_3 [L]^3 \dots \dots \beta_n [L]^n\}}$$

$$\alpha_M = \frac{[M]}{c_M} = \frac{1}{1 + \beta_1 [L] + \beta_2 [L]^2 + \beta_3 [L]^3 \dots \dots \beta_n [L]^n}$$

From above Equations. We can find α_{ML} from

$$\alpha_{ML} = \frac{[ML]}{c_M} = \frac{\beta_1 [M][L]}{[M] + \beta_1 [M][L] + \beta_2 [M][L]^2 + \beta_3 [M][L]^3 \dots \dots \beta_n [M][L]^n}$$

$$\alpha_{ML} = \frac{[ML]}{c_M} = \frac{\beta_1 [M][L]}{[M]\{1 + \beta_1 [L] + \beta_2 [L]^2 + \beta_3 [L]^3 \dots \dots \beta_n [L]^n\}}$$

$$= \frac{\beta_1[L]}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 \dots \dots \beta_n[L]^n}$$

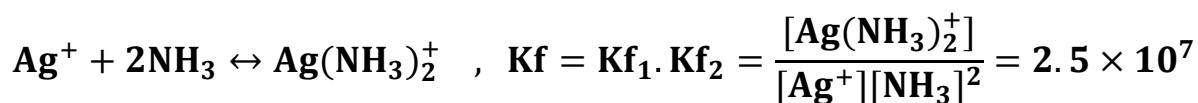
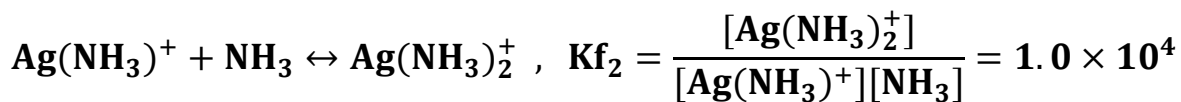
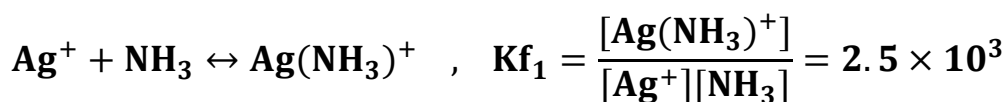
$$\alpha_M = \frac{1}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 \dots \dots \beta_n[L]^n}$$

$$\alpha_{ML} = \frac{\beta_1[L]}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 \dots \dots \beta_n[L]^n}$$

$$\alpha_{ML_2} = \frac{\beta_2[L]^2}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 \dots \dots \beta_n[L]^n}$$

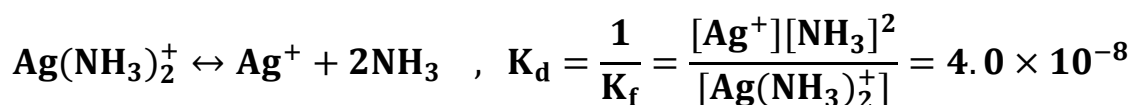
$$\alpha_{ML_n} = \frac{\beta_n[L]^n}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 \dots \dots \beta_n[L]^n}$$

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.

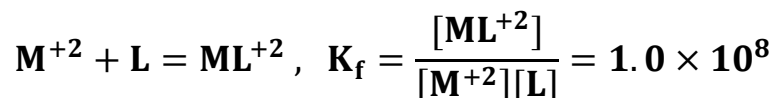


Formation constant (K_f):- the formation constant is also called the stability constant K_s or K_{sp} .

$$K_f = K_s = \frac{1}{K_i} = \frac{1}{K_d}$$



Example (1) :- A divalent metal M^{+2} reacts with a ligand L to form 1:1 complex.



Calculate the conc. of M^{+2} in a solution prepared by mixing equal volume of 0.2M (M^{+2}) and 0.2M (L), $K_f = 1.0 \times 10^8$.

Solution:

The concentration of complex =

$$\frac{M^{+2}}{\text{mmol}(m \times V)} + \frac{L}{\text{mmol}(m \times V)} = \frac{ML^{+2}}{[ML^{+2}]} = \frac{(m \times V)M^{+2}}{(v_T = 2v)_{mix}}$$

$$[ML^{+2}] = \frac{(m \times V)}{2v} = \frac{0.2 v}{2v} = \frac{0.2}{2} = 0.1 M$$

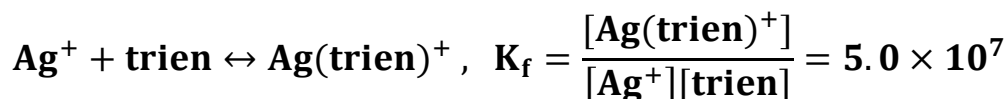
$$K_f = \frac{[ML^{+2}]}{[M^{+2}][L]} = 1.0 \times 10^8 = \frac{0.1 M}{(x)(x)}$$

$$0.1 M = 1.0 \times 10^8 \times x^2, \quad x^2 = \left(\frac{0.1 M}{1.0 \times 10^8} \right) = 1.0 \times 10^{-9}$$

$$x = \sqrt[2]{1.0 \times 10^{-9}}, \quad x = [M^{+2}] = 3.2 \times 10^{-5} M$$

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, $K_f = 5.0 \times 10^7$?

Solution



$[Ag^+]_{\text{unreacted}} = x$

$$\text{mmol } Ag^+ = M \times V = 0.01 \times 25 = 0.25 \text{ mmol}$$

$$\text{mmol trien} = M \times V = 0.015 \times 50 = 0.75 \text{mmol}$$

$$\text{mmol trien unreacted} = 0.75 - 0.25 = 0.5 \text{mmol}$$

$$M_{\text{trien}} = \frac{\text{mmol}}{V} = \frac{0.5}{50+25} = 6.7 \times 10^{-3} \text{M}$$

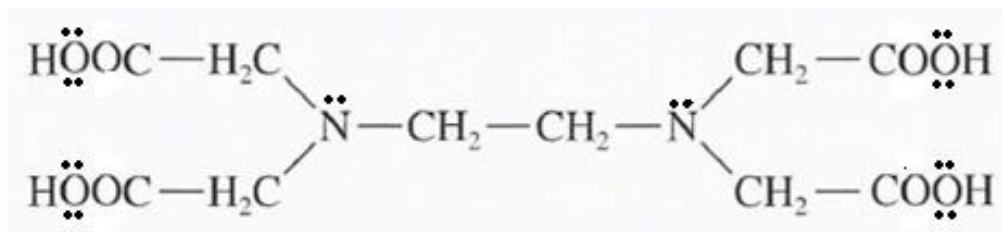
$$K_f = \frac{[\text{Ag}(\text{trien})^+]}{[\text{Ag}^+][\text{trien}]} = 5.0 \times 10^7 = \frac{\frac{0.25 \text{mmol}}{50+25}}{x(6.7 \times 10^{-3})} = \frac{3.3 \times 10^{-3}}{x(6.7 \times 10^{-3})}$$

$$x = \frac{3.3 \times 10^{-3}}{5.0 \times 10^7 \times 6.7 \times 10^{-3}} = [\text{Ag}^+] = 9.8 \times 10^{-9} \text{M}$$

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.

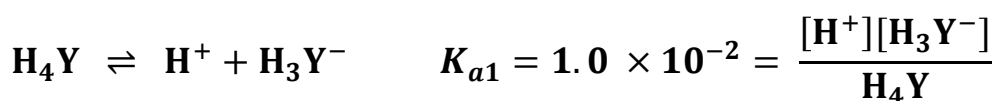
The term chelate is derived from the Greek term meaning (claw like) chelating agents literally wrap themselves around a metal ion.

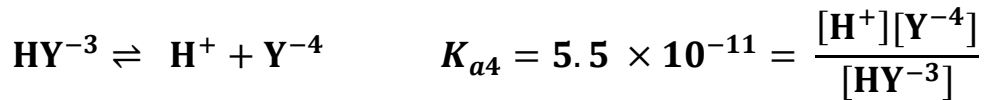
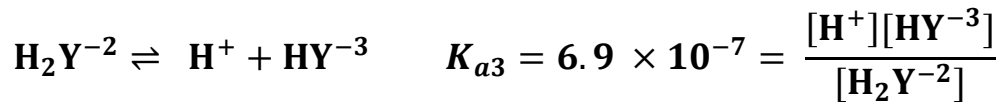
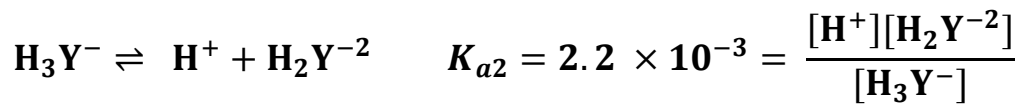
EDTA equilibrium:-The protons in EDTA Ethylene Diamine Tetra Acetic acid are displaced upon complexing with a metal ion. Negatively charged chelate results



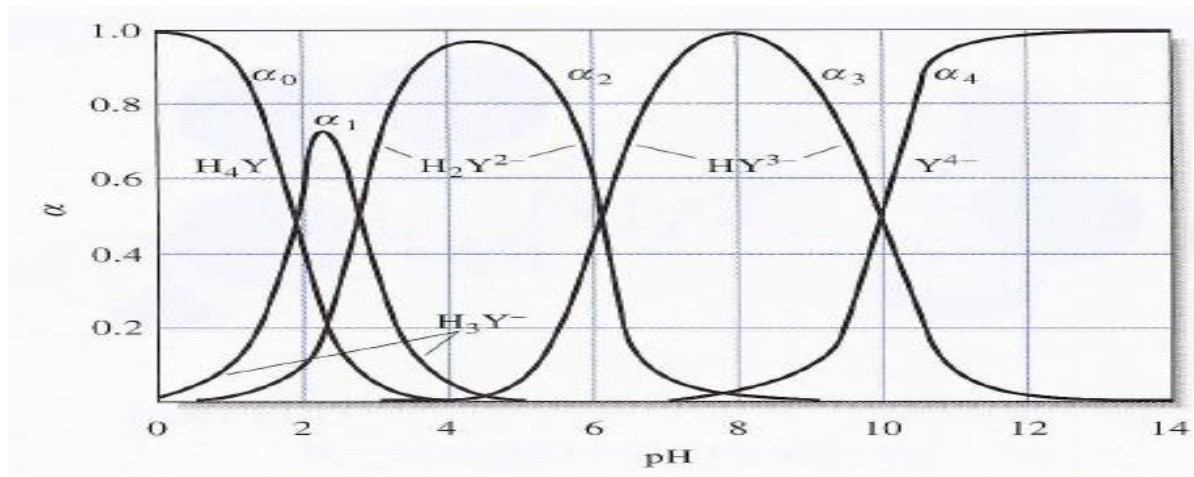
Tetraprotic acid (H_4Y): six complexing groups (**hexadentate**) multidentate

Formation constant:-Lets EDTA =





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-}

$$C_T = [\text{Y}^{4-}] + [\text{HY}^{3-}] + [\text{H}_2\text{Y}^{2-}] + [\text{H}_3\text{Y}^-] + [\text{H}_4\text{Y}]$$

$$\alpha_4 = \frac{[\text{Y}^{4-}]}{C_T}, \quad \alpha_3 = \frac{[\text{HY}^{3-}]}{C_T}, \quad \alpha_2 = \frac{[\text{H}_2\text{Y}^{2-}]}{C_T}, \quad \alpha_1 = \frac{[\text{H}_3\text{Y}^-]}{C_T}, \quad \alpha_0 = \frac{[\text{H}_4\text{Y}]}{C_T}$$

Example 3:- A solution has 0.1 M of EDTA Calculate the approximate concentration of this species $[\text{Y}^{4-}]$, $[\text{HY}^{3-}]$, $[\text{H}_2\text{Y}^{2-}]$, $[\text{H}_3\text{Y}^-]$, $[\text{H}_4\text{Y}]$ at pH 2, 4, 6, 8, 10.

Solution: - the concentration of $[Y^{4-}]$ at pH 2 = $\alpha_4 \times C_T = 0 \times 0.1 = 0 \text{ M}$

the concentration of $[HY^{3-}]$ at pH 2 = $\alpha_3 \times C_T = 0 \times 0.1 = 0 \text{ M}$

the concentration of $[H_2Y^{2-}]$ at pH 2 = $\alpha_2 \times C_T = \sim 0.1 \times 0.1 = \sim 0.01 \text{ M}$

the concentration of $[H_3Y^-]$ at pH 2 = $\alpha_1 \times C_T = \sim 0.6 \times 0.1 = \sim 0.06 \text{ M}$

the concentration of $[H_4Y]$ at pH 2 = $\alpha_0 \times C_T = \sim 0.4 \times 0.1 = \sim 0.04 \text{ M}$

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 ($\alpha_4 = 0.35$) after adding 100mL of 0.1M EDTA. $K_f = 4.943 \times 10^{10}$

The fraction of $[Y^{4-}]$ at pH = 10 , $\alpha_4 = \frac{[Y^{4-}]}{C_T}$, $[Y^{4-}] = \alpha_4 C_T$,

$$[Y^{4-}] = 0.35 \times 0.1 \text{ M} = 0.035 \text{ M}$$

- The pCa mmol $Ca^{2+} = M \times V = 0.1 \times 100 = 10.0 \text{ mmol}$

mmol EDTA = $M \times V = 0.1 \times 100 = 10.0 \text{ mmol}$

We have formed 10.0mmol CaY^{2-} in 200mL, or 0.050M

$$K_f = \frac{[CaY^{2-}]}{[Ca^{+2}]\alpha_4[C_{H_4Y}]} = \frac{0.05}{(x)(0.35)(x)} = \frac{0.05}{(0.35) \times x^2}$$

$$4.943 \times 10^{10} = \frac{0.05}{(0.35) \times x^2} , \quad 0.05 = 4.943 \times 10^{10} \times 0.35 \times x^2$$

$$x^2 = \frac{0.05}{4.943 \times 10^{10} \times 0.35} = 2.9 \times 10^{-12}$$

$$x = \sqrt{2.9 \times 10^{-12}} = 1.7 \times 10^{-6} \text{ M}$$

$$\text{pCa} = -\log 1.7 \times 10^{-6} = 5.77$$

Conditional formation constant (used for a fixed pH):

$$K_f' = \text{conditional formation constant} = K_f \alpha_4 = \frac{[CaY^{2-}]}{[Ca^{+2}][C_{H_4Y}]}$$

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). $K_f = 4.2 \times 10^{18}$



Since the complex is the only source of both Ni^{2+} and the EDTA species,

$$[Ni^{2+}] = [Y^{4-}] + [HY^{3-}] + [H_2Y^{2-}] + [H_3Y^{-}] + [H_4Y] = C_T$$

$$K_{fNiY} = \frac{[NiY^{2-}]}{[Ni^{2+}] \alpha_4 C_T} = \frac{[NiY^{2-}]}{[Ni^{2+}]^2 \alpha_4}$$

a) At pH 3

$$K_{fNiY} = \frac{[NiY^{2-}]}{[Ni^{2+}]^2 \alpha_4} = 4.2 \times 10^{18} = \frac{0.015}{[Ni^{2+}]^2 \times 2.5 \times 10^{-11}}$$

$$2.5 \times 10^{-11} \times 4.2 \times 10^{18} = \frac{0.0150}{[Ni^{2+}]^2} = 1.05 \times 10^8$$

$$[Ni^{2+}]^2 \times 1.05 \times 10^8 = 0.0150,$$

$$[Ni^{2+}]^2 = \frac{0.0150}{1.05 \times 10^8} = 1.43 \times 10^{-10}$$

$$[Ni^{2+}] = \sqrt[2]{1.43 \times 10^{-10}} = 1.2 \times 10^{-5} \text{ M}$$

b) At pH 8

$$K_{f \text{ NiY}} = \frac{[\text{NiY}^{2-}]}{[\text{Ni}^{2+}]^2 \alpha_4} = 4.2 \times 10^{18} = \frac{0.015}{[\text{Ni}^{2+}]^2 \times 5.4 \times 10^{-3}}$$

$$5.4 \times 10^{-3} \times 4.2 \times 10^{18} = \frac{0.0150}{[\text{Ni}^{2+}]^2} = 2.268 \times 10^{16}$$

$$[\text{Ni}^{2+}]^2 \times 2.268 \times 10^{16} = 0.0150,$$

$$[\text{Ni}^{2+}]^2 = \frac{0.0150}{2.268 \times 10^{16}} = 6.6 \times 10^{-19}$$

$$[\text{Ni}^{2+}] = \sqrt[2]{6.6 \times 10^{-19}} = 8.1 \times 10^{-10} \text{ M}$$

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) $\text{pCa} = -\log[\text{Ca}^{2+}] = -\log 0.1 = 1.0$

(2) At 50mL: before equivalence point

$$\text{mmol Ca}^{2+} = M \times V = 0.1 \times 100 = 10.0 \text{ mmol}$$

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

$$\text{mmol Ca}^{2+} \text{ unreacted} = 10.0 - 5.0 = 5.0 \text{ mmol}$$

$$\text{pCa} = -\log[\text{Ca}^{2+}] = -\log \frac{5.0 \text{ mmol}}{100 \text{ mL} + 50 \text{ mL}} = 1.48$$

(3) At 100mL: equivalence point

$$K_f = \frac{[\text{CaY}^{2-}]}{[\text{Ca}^{+2}][\text{C}_{\text{H}_4\text{Y}}]} = 1.8 \times 10^{10} = \frac{10 \text{ mmol}}{(x)(x)}$$

$$1.8 \times 10^{10} = \frac{0.05}{(x)^2}, \quad (x)^2 = \frac{0.05}{1.8 \times 10^{10}} = 2.8 \times 10^{-12},$$

$$x = \sqrt[2]{2.8 \times 10^{-12}} = 1.7 \times 10^{-6} \text{ M}$$

$$pCa = -\log[Ca^{2+}] = -\log 1.7 \times 10^{-6} = 5.77$$

(4) At 150mL: after equivalence point

$$\text{mmol EDTA} = M \times V = 0.1 \times 150 = 15.0 \text{ mmol}$$

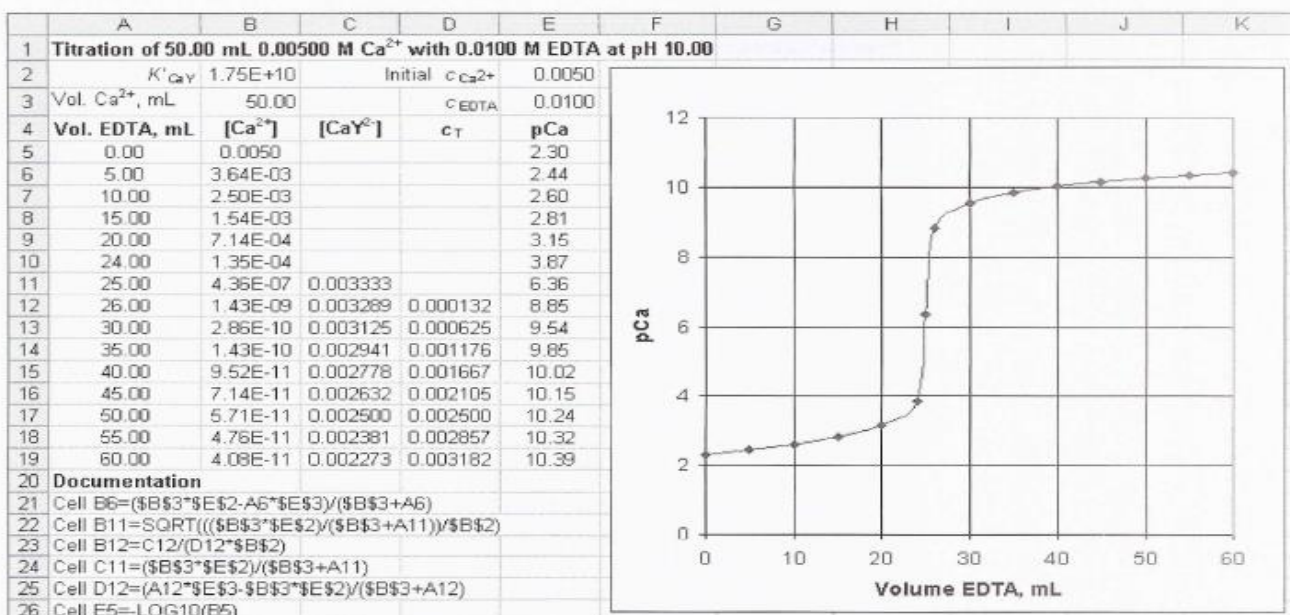
$$\text{mmol EDTA unreacted} = 15.0 - 10.0 = 5.0 \text{ mmol}$$

$$M_{\text{EDTA}} = \frac{5 \text{ mmol}}{100 \text{ mL} + 150 \text{ mL}} = 0.02 \text{ M}, \quad [CaY^{-2}] = \frac{10 \text{ mmol}}{100 \text{ mL} + 150 \text{ mL}} = 0.04 \text{ M}$$

$$K_f = \frac{[CaY^{-2}]}{[Ca^{+2}][C_{H_4Y}]} = \frac{0.04}{[Ca^{+2}](0.02)} = 1.8 \times 10^{10}$$

$$0.04 = [Ca^{+2}] \times 0.02 \times 1.8 \times 10^{10}, \quad [Ca^{+2}] = \frac{0.04}{0.02 \times 1.8 \times 10^{10}} =$$

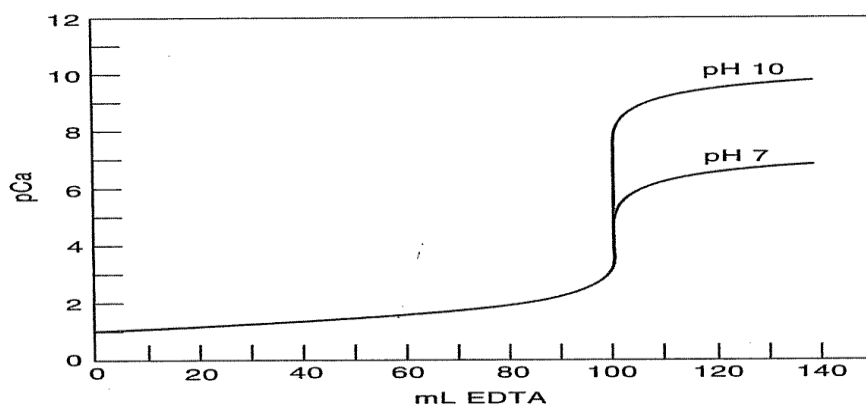
$$[Ca^{+2}] = 1.1 \times 10^{-10} \text{ M}, \quad pCa = -\log 1.1 \times 10^{-10} = 9.95$$



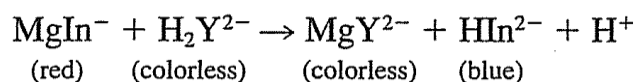
Spreadsheet for the titration of 50.00 mL of 0.00500 M Ca²⁺ with 0.01 M EDTA in a solution buffered at pH 10

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



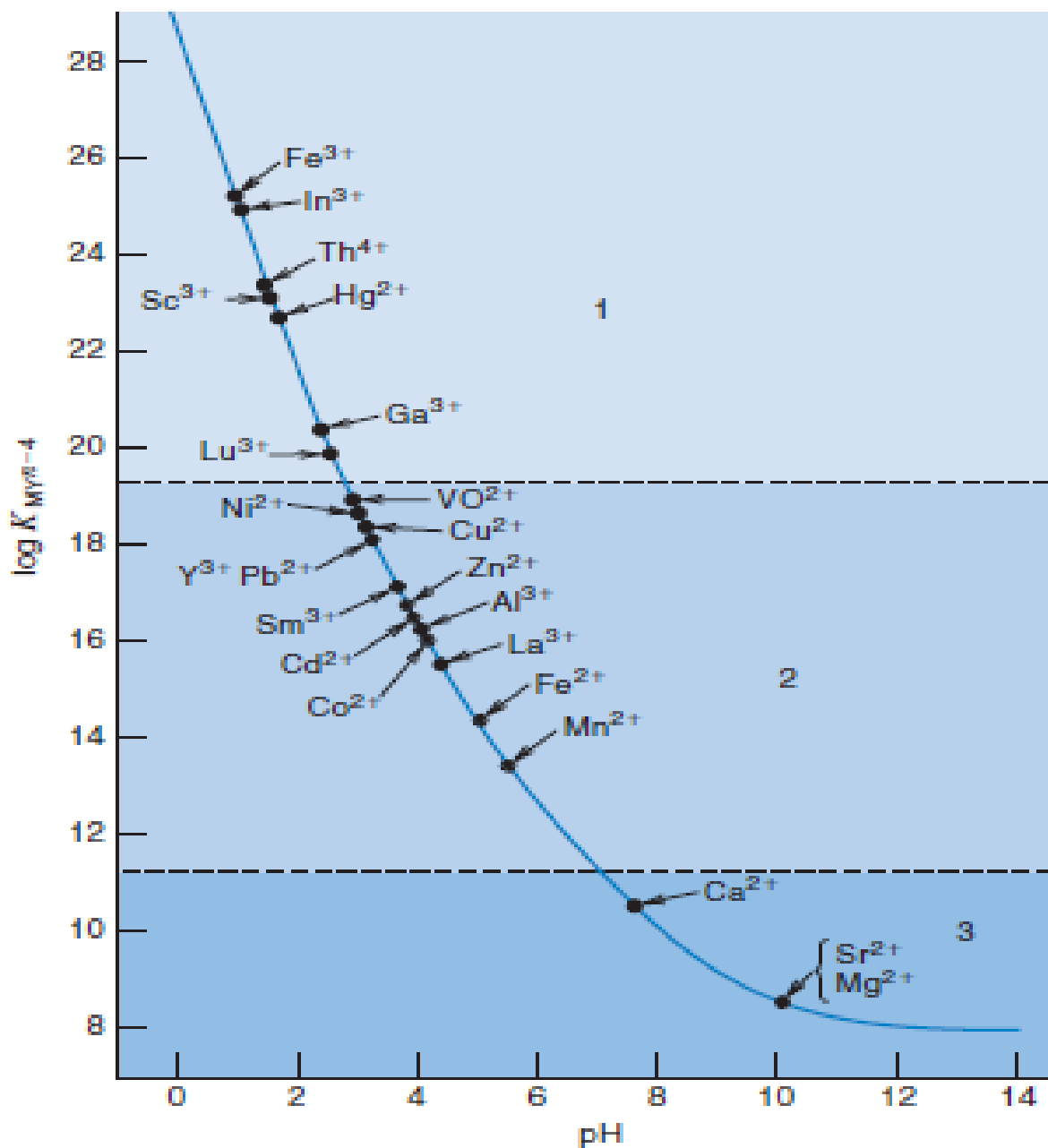
chelometric titrations are themselves chelating agents. They are usually dyes of the o,o'-dihydroxyazo type.: is a typical indicator it contains three ionisable protons, so we will represent it by H_3In . This indicator can be used for the titration of Mg^{+2} with **EDTA**. A small amount of indicator 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.



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 K_f 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 $\sim \geq 8$. 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** $< \sim 3$) 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 (III) and indium(III)**.



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, O₂, H₂ (0 for all of these)

2. For any monatomic ion, the oxidation number is equal to the charge on the ion.

Examples: Fe²⁺, F⁻, O²⁻, 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

MgF₂ = Mg²⁺ + 2 F⁻ = +2 + 2(-1) = 0

K₂Cr₂O₇ = 2 K⁺ + 2 Cr + 7 × O²⁻

= 2(+1) + 2(X) + 7 × (-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 O₂²⁻)

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

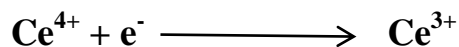
Group 6A
Has $6e^-$ in the outermost shell
Tend to gain $2e^-$
Oxidation state -2
Group number - 8

Chalcogens

Group 7A
Has $7e^-$ in the outermost shell
Tend to gain $1e^-$
Oxidation state -1
Group number - 8

Halogens

Oxidizing agent an oxidizing substance which tend to take on an electron or electrons and be reduced to a lower oxidation state. For example -



- Oxidizing ability depends strongly on pH value.

KMnO₄ in presence of dil. H₂SO₄

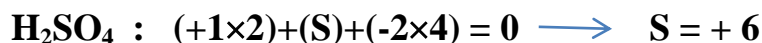


Reducing agent an reducing substance which tend to give up an electron or electrons and be oxidized to a higher oxidation state. For example -



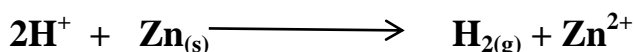
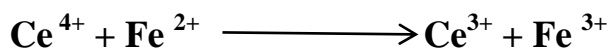
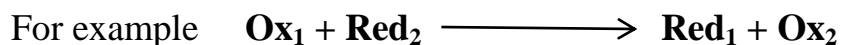
Q – Calculate the oxidation number for the central atom in the following compounds.

KMnO₄, K₂Cr₂O₇, H₂O₂, HNO₃, H₂SO₄, KIO₃, H₂C₂O₄·2H₂O, H₂S, SnCl₂



REDUCTION - OXIDATION REACTION

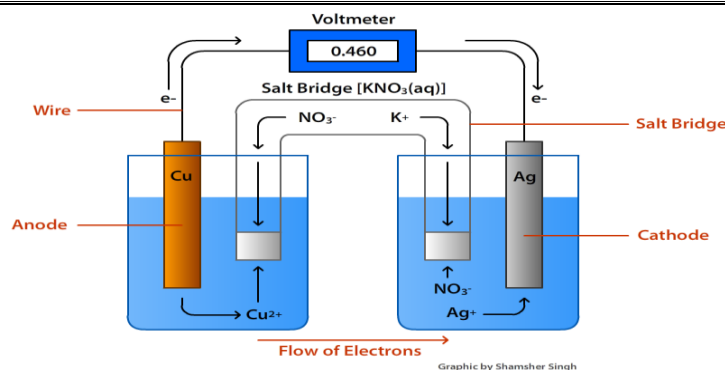
Is one that occurs between a reducing and an oxidizing agent,



Electro chemical cells:

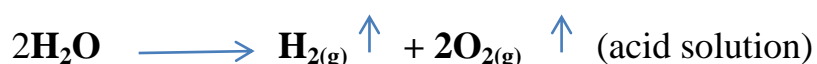
There are two kinds of electrochemical cells, galvanic (voltaic) and electrolytic cell.

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.



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



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.

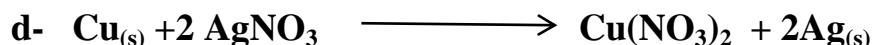
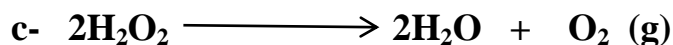
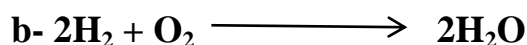
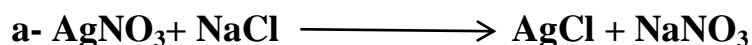
Cathode is the electrode at which reduction occurs.

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.

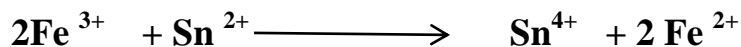
Salt bridge allows charge transfer through the solution but prevent mixing of the solution .

Q- The equation that is not represented as a redox reaction is,

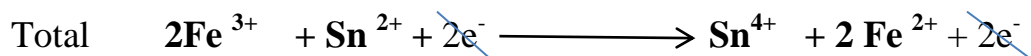
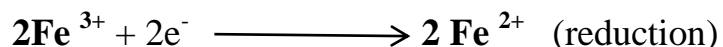


Redox reaction as two half reaction As a redox reaction involves both oxidation and reduction components, it is possible to divide the total reaction , these clearly demonstrate which species gains electrons and which losses them .

This can be suitably illustrated by the reaction between iron (III) and tin (II).



This reaction can be divided into two half reactions show below

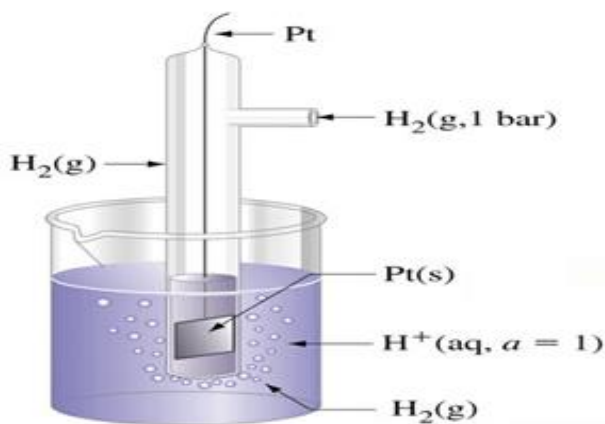


This method of expressing a redox reaction as two half reactions provide a kind of flexibility to the concept of redox reaction.

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



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
$ClO_{4}^{-}_{(aq)} + H_{2}O_{(l)} + 2e^{-} \rightarrow ClO_{2}^{-}_{(aq)} + 2OH^{-}_{(aq)}$	0.17
$AgCl_{(s)} + e^{-} \rightarrow Ag_{(s)} + Cl^{-}_{(aq)}$	0.22
$Cu^{2+}_{(aq)} + 2e^{-} \rightarrow Cu_{(s)}$	0.34
$ClO_{2}^{-}_{(aq)} + H_{2}O_{(l)} + 2e^{-} \rightarrow ClO_{2}^{-}_{(aq)} + 2OH^{-}_{(aq)}$	0.35
$IO_{3}^{-}_{(aq)} + H_{2}O_{(l)} + 2e^{-} \rightarrow I^{-}_{(aq)} + 2OH^{-}_{(aq)}$	0.49
$Cu^{+}_{(aq)} + e^{-} \rightarrow Cu_{(s)}$	0.52
$Ag^{+}_{(aq)} + e^{-} \rightarrow Ag_{(s)}$	0.80
$O_{2(g)} + 4H^{+}_{(aq)} + 4e^{-} \rightarrow 2H_{2}O_{(l)}$	1.23
$Cr_{2}O_{7}^{2-}_{(aq)} + 14H^{+}_{(aq)} + 6e^{-} \rightarrow 2Cr^{3+}_{(aq)} + 7H_{2}O_{(l)}$	1.33
$Ce^{4+}_{(aq)} + e^{-} \rightarrow Ce^{3+}_{(aq)}$	1.44
$MnO_{4}^{-}_{(aq)} + 8H^{+}_{(aq)} + 5e^{-} \rightarrow Mn^{2+}_{(aq)} + 4H_{2}O_{(l)}$	1.49
$H_{2}O_{2(aq)} + 2H^{+}_{(aq)} + 2e^{-} \rightarrow 2H_{2}O_{(l)}$	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 $\text{Ce}^{4+} + \text{Fe}^{2+} \rightleftharpoons \text{Ce}^{3+} + \text{Fe}^{3+}$

Pt/ Fe²⁺(C₁) , Fe³⁺(C₂) // Ce⁴⁺(C₃) , Ce³⁺(C₄) /Pt

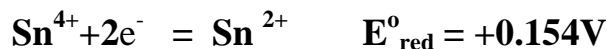
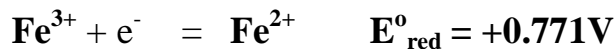
C₁ C₂ C₃ and C₄ represent the concentration of the different species , the double line represents the salt bridge.

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

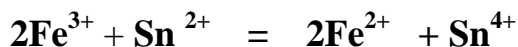
$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

So a positive potential difference provides the necessary negative free energy and the chemical reaction spontaneously. For example Electro chemical cells

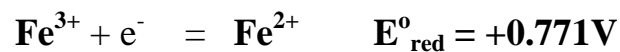


$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} - E^{\circ}_{\text{Sn}^{4+}/\text{Sn}^{2+}}$$

$$= 0.771 - (0.154) = 0.617\text{V}$$



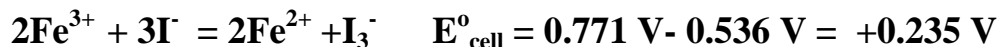
Example (1) - determine the reaction between the following half-reaction and calculate the corresponding cell voltage:



Solution: since the $\text{Fe}^{3+}/\text{Fe}^{2+}$ potential is the more positive, Fe^{3+} is a better oxidizing agent than I_3^{-} . Fe^{3+} will oxidize I^{-} to give I_3^{-} (Triiodide ion) and

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = E^{\circ}_{\text{cell}} = E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} - E^{\circ}_{\text{I}_3^{-}/\text{I}^{-}}$$

In the some fashion, the second half-reaction must be subtracted from the first (multiplied by 2) to give the overall cell reaction,



* 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



1- We write and balance the two half-reaction involved.



To account for the 4 oxygen atoms on the left-hand side of the equation we add $4\text{H}_2\text{O}$ on the right-hand side of the equation, which means that we must provide 8H^+ on the left.



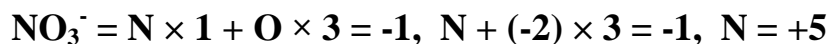
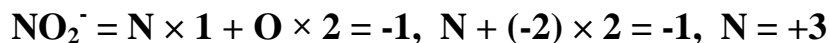
To balance the charge, we need to add 5 electrons to the left side of the equation. Thus



For the other half-reaction



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



Then we add two electrons to the right-hand side to balance the charge



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



Which then rearranges to the balanced equation

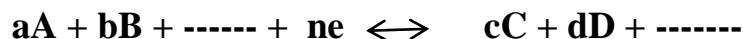


Q - Complete and balance the following equation after adding H⁺, OH⁻, or H₂O as needed



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



The electrode potential for this reaction is given by the equation

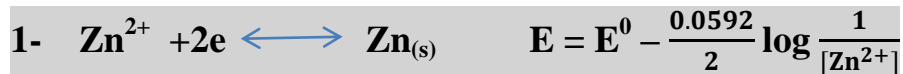
$$E = E^0 - \frac{RT}{nF} \ln \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

Where **E⁰** = 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**, **ln** = natural logarithm = 2.303 log,

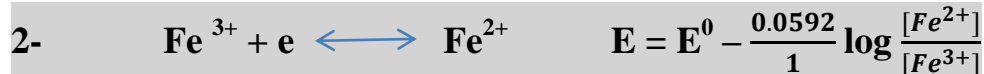
If we substitute numerical values for the constants convert to bas 10 logarithms and specify 25 °C for the temperature, we gat

$$E = E^0 - \frac{0.0592}{n} \log \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

Examples : Typical half-cell reactions and their corresponding nernst expressions follow.

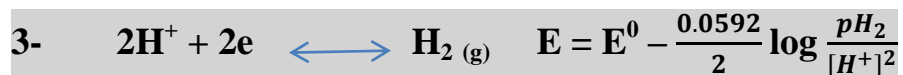


$\text{Zn}_{(s)}$ is not included in the logarithmic because it is a pure solid. Thus, the electrode potential varies linearly with the logarithm of the reciprocal of the zinc ion concentration $[\text{Zn}^{2+}]$.

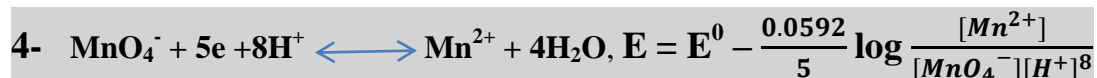


The potential for this couple can be measured with an inert metallic electrode immersed in a solution containing both iron species.

The potential depends on the logarithm of the ratio between the molar concentrations of these ions.



In this example $p\text{H}_2$ is the pressure of hydrogen (in atm) at the surface of the electrode.



Here, the potential depends not only on the concentration of manganese species but also on the pH of the solution.



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 $K_{\text{sp}}(\text{AgCl}) = 1.82 \times 10^{-10}$.



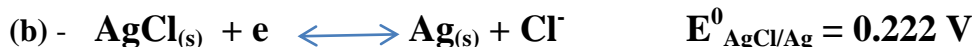
$$E = E^0_{\text{Ag}^+/\text{Ag}} - \frac{0.0592}{1} \log \frac{1}{[\text{Ag}^+]}$$

The $[\text{Ag}^+]$ concentration of this solution is given by

$$[\text{Ag}^+] = \frac{K_{sp}}{[\text{Cl}^-]} = \frac{1.82 \times 10^{-10}}{0.05} = 3.64 \times 10^{-9} \text{M}$$

Substitution into Nernst expression gives:

$$E = 0.776 - 0.0592 \log \frac{1}{3.64 \times 10^{-9}} = 0.299 \text{ V}$$



$$E = E^0_{\text{AgCl}/\text{Ag}} - \frac{0.0592}{1} \log [\text{Cl}^-] \quad \text{Concentration of } [\text{Cl}^-] = 0.05 \text{ M}$$

Here we may write

$$E = 0.222 - 0.0592 \log [\text{Cl}^-] = 0.222 - 0.0592 \log 0.05 = 0.299 \text{ V}$$

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 Fe²⁺** with **0.10 M Ce⁴⁺** in a medium that is **1.0 M in H₂SO₄** at all time.



Solution:

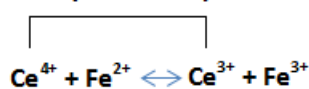
At all times during the titration this reaction is rapid and reversible and in equilibrium hence .

E_{system} is the potential of the titration and is the value plotted on the y-axis.

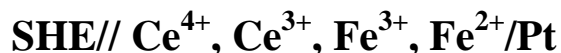
E_{system} represents the potential of the electrochemical cell:



+e⁻ (reduction)



-e⁻ (oxidation)



We can follow either **E_{Ce⁴⁺,Ce³⁺}** or **E_{Fe³⁺,Fe²⁺}**

$$E_{\text{system}} = E_{\text{Ce}^{4+},\text{Ce}^{3+}} = E_{\text{Fe}^{3+},\text{Fe}^{2+}}$$

(a) At Volume [Ce⁴⁺] solution = 0 mL

In the beginning of the titration the solution would contain only **Fe²⁺** ions and may have traces of **Fe³⁺** due the aerial oxidation of the solution.

As the concentration of the **Fe³⁺** ion is too small the calculation of the potential has no meaningful significance.

(b) At Volume [Ce⁴⁺] solution = 5 mL

Excess of **Fe²⁺** concentration of (**Fe²⁺ / Fe³⁺**) are measurable.

$$E_{\text{system}} = E_{\text{Fe}^{3+},\text{Fe}^{2+}} = E^{\circ}_{\text{Fe}^{3+},\text{Fe}^{2+}} - \frac{0.0592}{n} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

$$[\text{Fe}^{2+}] = \frac{50 \times 0.05 - 5 \times 0.1}{50 + 5} + [\text{Ce}^{4+}] \approx \frac{50 \times 0.05 - 5 \times 0.1}{50 + 5} = \frac{2.0}{55} \text{ M}$$

$$[\text{Fe}^{3+}] = \frac{5 \times 0.1}{50 + 5} - [\text{Ce}^{4+}] \approx \frac{0.5}{50 + 5} = \frac{0.5}{55} \text{ M}$$

$$E_{\text{system}} = E_{\text{Fe}^{3+}, \text{Fe}^{2+}} = 0.68 - \frac{0.0592}{1} \log \frac{\left(\frac{2.0}{55}\right)}{\left(\frac{0.5}{55}\right)} = 0.64 \text{ V}$$

(c)- At Volume [Ce⁴⁺] solution = 25 mL at the eq. point : no excess of [Fe²⁺]

$$[\text{Ce}^{4+}] \times V_{\text{total}} = [\text{Fe}^{2+}] \times V_{\text{total}} \text{ and } [\text{Ce}^{3+}] \times V_{\text{total}} = [\text{Fe}^{3+}] \times V_{\text{total}}$$

The reaction takes place in one vessel

$$[\text{Ce}^{4+}] = [\text{Fe}^{2+}] \text{ and } [\text{Ce}^{3+}] = [\text{Fe}^{3+}]$$

$$E_{\text{eq}} = E_{\text{Fe}^{3+}, \text{Fe}^{2+}} = E^{\circ}_{\text{Fe}^{3+}, \text{Fe}^{2+}} - \frac{0.0592}{n} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \text{ -----(1)}$$

$$E_{\text{eq}} = E_{\text{Ce}^{4+}, \text{Ce}^{3+}} = E^{\circ}_{\text{Ce}^{4+}, \text{Ce}^{3+}} - \frac{0.0592}{n} \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} \text{ -----(2)}$$

Summation of eq(1) and eq(2)

$$2E_{\text{eq}} = E^{\circ}_{\text{Fe}^{3+}, \text{Fe}^{2+}} + E^{\circ}_{\text{Ce}^{4+}, \text{Ce}^{3+}} - \frac{0.0592}{n} \log \frac{[\text{Fe}^{2+}][\text{Ce}^{3+}]}{[\text{Fe}^{3+}][\text{Ce}^{4+}]}$$

$$= E^{\circ}_{\text{Fe}^{3+}, \text{Fe}^{2+}} + E^{\circ}_{\text{Ce}^{4+}, \text{Ce}^{3+}}$$

$$E_{\text{eq}} = \frac{E^{\circ}_{\text{Fe}^{3+}, \text{Fe}^{2+}} + E^{\circ}_{\text{Ce}^{4+}, \text{Ce}^{3+}}}{2} = \frac{0.68 + 1.44}{2} = 1.06 \text{ V}$$

(d)- At Volume [Ce⁴⁺] solution = 25.10 mL > V_{eq} = 25 mL

After the eq. point : excess of [Ce⁴⁺] and concentration of [Ce³⁺] / [Ce⁴⁺]

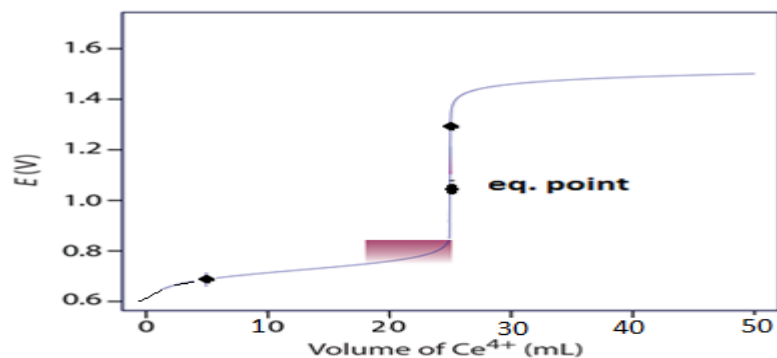
Are measurable. Hence E_{system} post-eq = E_{Ce⁴⁺, Ce³⁺}

$$E_{\text{system}} = E_{\text{Ce}^{4+}, \text{Ce}^{3+}} = E^{\circ}_{\text{Ce}^{4+}, \text{Ce}^{3+}} - \frac{0.0592}{n} \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]}$$

$$[\text{Ce}^{4+}] = \frac{25.1 \times 0.1 - 50 \times 0.05}{50 + 25.1} + [\text{Fe}^{2+}] \approx \frac{25.1 \times 0.1 - 50 \times 0.05}{50 + 25.1} = \frac{0.01}{75.1} \text{ M}$$

$$[\text{Ce}^{3+}] = \frac{25 \times 0.1}{50 + 25.1} - [\text{Fe}^{2+}] \approx \frac{2.5}{75.1} = \frac{2.5}{75.1} \text{ M}$$

$$E_{\text{system}} = 1.44 - \frac{0.0592}{1} \log \frac{2.5}{0.01} = 1.3 \text{ V}$$



Redox titration methods :

- 1- Permanganometry
- 2- Dichromatometry
- 3- Cerimetry
- 4- Iodometry and Iodimetry
- 5- Iodametry
- 6- Bromatometry

Permanganometric Titration :

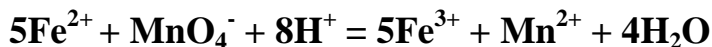
This method is based on reactions of oxidation by permanganate ion.

Oxidation may proceed in acid or in alkaline or neutral solution. When KMnO_4 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;



Or in ionic form



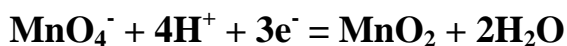
The decrease of the valence of manganese by **5** shows that the KMnO_4 molecule gains 5 electrons this is also very clear from the following equation:



It follows that in this case the gram-equivalent of KMnO_4 is

$$\text{g/eq} = 158.03/5 = 31.61 \text{ g/eq}$$

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



Therefore in this case the gram-equivalent of KMnO_4 has a different value namely

$$\text{g/eq} = 158.03/3 = 52.68 \text{ g/eq}$$

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



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 $\mathbf{R = 8.314 \text{ K}^{-1} \text{ mol}^{-1}}$ and $\mathbf{F = faraday \ constant = 96485 \text{ C}}$

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:



10 - The element that undergoes oxidation is: $\text{H}_2 + \text{O}_2 \longrightarrow \text{H}_2\text{O}$

11- The element that undergoes reduction is: $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$

اسماء وشحنات بعض الجذور الكيميائية

Nitrate	NO ₃	-1
Nitrite	NO ₂	-1
Chloride ,Bromide, & Iodide	(Cl, Br, & I)	-1
Acetate	CH ₃ COO	-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 ₂ O ₃	-2
Oxalate	C ₂ O ₄	-2
Chromate	CrO ₄	-2
Dichromate	Cr ₂ O ₇	-2
Phosphate	PO ₄	-3
Phosphite	PO ₃	-3

Dr: Khitam Jaber Nabhan

& Dr: Amer Saleh Mahdi

The Periodic Table of the Elements

group 1 18

period 1 2

period 2 10

period 3 18

period 4 36

period 5 54

period 6 86

period 7 118

atomic mass
or most stable mass number

1st ionization energy
in kJ/mol

chemical symbol

name

electron configuration

55.845

26

Fe

Iron

[Ar] 3d⁶ 4s²

atomic number

electronegativity

oxidation states
most common are bold

alkali metals

metalloids

nonmetals

alkaline metals

other metals

transition metals

lanthanoids

actinoids

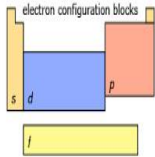
halogens

noble gases

unknown elements

radioactive elements have masses in parentheses

1	2											13	14	15	16	17	18
H Hydrogen 1.00794 1.00811	He Helium 4.002602											B Boron 10.811	C Carbon 12.0107	N Nitrogen 14.0067	O Oxygen 15.9994	F Fluorine 18.998403	Ne Neon 20.1797
Li Lithium 6.941	Be Beryllium 9.012182											Al Aluminum 26.981538	Si Silicon 28.0855	P Phosphorus 30.973762	S Sulfur 32.065	Cl Chlorine 35.453	Ar Argon 39.948
Na Sodium 22.989769	Mg Magnesium 24.3050	Sc Scandium 44.955912	Ti Titanium 47.867	V Vanadium 50.9415	Cr Chromium 51.9962	Mn Manganese 54.938045	Fe Iron 55.845	Co Cobalt 58.933195	Ni Nickel 58.6934	Cu Copper 63.546	Zn Zinc 65.38	Ga Gallium 69.723	Ge Germanium 72.64	As Arsenic 74.92160	Se Selenium 78.96	Br Bromine 79.904	Kr Krypton 83.798
Rb Rubidium 85.4678	Sr Strontium 87.62	Y Yttrium 88.90585	Zr Zirconium 91.224	Nb Niobium 92.90638	Mo Molybdenum 95.96	Tc Technetium (98)	Ru Ruthenium 101.07	Rh Rhodium 101.07	Pd Palladium 106.42	Ag Silver 107.8682	Cd Cadmium 112.411	In Indium 114.818	Sn Tin 118.710	Sb Antimony 121.760	Te Tellurium 127.60	I Iodine 126.9045	Xe Xenon 131.293
Cs Cesium 132.90545	Ba Barium 137.327	Lu Lutetium 174.9668	Hf Hafnium 178.49	Ta Tantalum 180.94788	W Tungsten 183.84	Re Rhenium 186.207	Os Osmium 190.23	Ir Iridium 192.222	Pt Platinum 195.084	Au Gold 196.96657	Hg Mercury 200.59	Tl Thallium 204.3833	Pb Lead 207.2	Bi Bismuth 208.9804	Po Polonium (210)	At Astatine (210)	Rn Radon (222)
Fr Francium (223)	Ra Radium (226)	Lr Lawrencium (262)	Rf Rutherfordium (261)	Db Dubnium (262)	Sg Seaborgium (266)	Bh Bohrium (264)	Hs Hassium (277)	Mt Meitnerium (268)	Ds Darmstadtium (271)	Rg Roentgenium (272)	Cn Copernicium (285)	Uut Ununtrium (284)	Fl Flerovium (289)	Uup Ununpentium (288)	Lv Livermorium (292)	Uus Ununseptium (294)	Uuo Ununoctium (294)



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.

138.90547	140.116	140.9076	144.242	(145)	150.36	151.964	157.25	158.92535	162.500	164.93033	167.259	168.9342	173.054	70									
La Lanthanum (139)	Ce Cerium (140)	Pr Praseodymium (141)	Nd Neodymium (144)	Pm Promethium (145)	Sm Samarium (150)	Eu Europium (152)	Gd Gadolinium (157)	Tb Terbium (159)	Dy Dysprosium (163)	Ho Holmium (165)	Er Erbium (167)	Tm Thulium (169)	Yb Ytterbium (173)										
(227)	89	232.0377	231.0368	238.02891	(237)	237	(244)	244	(243)	247	(247)	97	(251)	98	(252)	99	(257)	100	(258)	101	(259)	102	
Ac Actinium (227)	Th Thorium (232)	Pa Protactinium (231)	U Uranium (238)	Np Neptunium (237)	Pu Plutonium (244)	Am Americium (243)	Cm Curium (247)	Bk Berkelium (247)	Cf Californium (251)	Es Einsteinium (252)	Fm Fermium (257)	Md Mendelevium (258)	No Nobelium (259)										

امنياتنا بالتوفيق