University of Al-mustansiryah

College of Science

Department of Chemistry
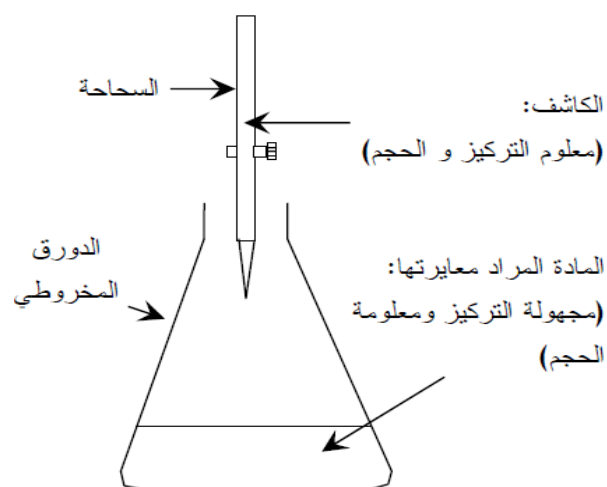
First Grade - First Term

Analytical Chemistry

Dr. Amer Saleh Mahdi   *Dr. Khitam Jaber Nabhan*

السحاحة

الكاشف:
(معلوم التركيز و الحجم)

الدورق
المخروطي

المادة المراد معايرتها:
(مجهولة التركيز ومعلومة الحجم)

Analytical Chemistry
First Grade-First Term (2018-2019)

References:-

(1) "Analytical Chemistry" by Gary D. Christian, 6th Edition, 2004, John Wiley and Sons, Inc.

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

(3)-"An Introduction to Analytical Chemistry" by Doglas 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 constituents 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. **(1st grade)**

(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). **(2nd grade)**

(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). **(4th grade)**

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).

$$\text{Solute (lesser amount)} + \text{Solvent (larger amount)} \rightarrow \text{Solution}$$
$$\mathbf{NaCl_{(s)} + H_2O_{(l)} \rightarrow Salt\ Solution}$$
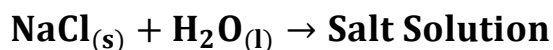
Concentrated Solution has a large amount of solute.
Dilute Solution has a small amount of solute.

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

Classification of solutions according to amount of solute:

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

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

(3) Super saturated solutions: solution that contains a dissolved amount of solute that exceeds the normal solubility limit (saturated solution). Or a solution contains a larger amount of solute than capacity of solvent at high temperature.

**Classification of solution based on solute particle size*:*

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

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

(3) Colloidal solution: homogeneous mixture which does not settle 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.

Gram formula weight (gFw some time F.wt): The sum of the atomic weight of the atoms that make up an ionic formula.

(is the more accurate description for substances that do not exist as molecules but exist as ionic compounds e.q strong electrolytes-acids, bases, salts). Sometimes use the term molar mass (Molecular weight, M.wt) in place of gram formula weight, gFw).

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

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

$$CaSO_4. 7H_2O = 40.08 + 32.06 + (16.0 \times 4) + 7[(2 \times 1.01) + 16.00]$$
$$= 262.25 \text{ g/mol}$$

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.

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

$$\text{mMole} = \frac{\text{weight (mg)}}{\text{formula weight} \left(\frac{mg}{\text{mmole}}\right)}$$

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

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

Solution:

$$\text{mMole} = \frac{\text{wt (mg)}}{\text{M. wt} \left(\frac{mg}{\text{mmole}}\right)} = \frac{500 \text{ (mg)}}{293.8 \left(\frac{mg}{\text{mmole}}\right)} = 1.706 \text{ mmole}$$

$$\text{Mole} = \frac{\text{mmole}}{1000} = \frac{1.706}{1000} = 0.00170 \text{ mol}$$

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

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

No. Molecules = No. moles × Avogadro number

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

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

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

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

Problems

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

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

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

(a) 8.75 g of $\underline{B}_2O_3$. (b) 167.2 mg of $Na_2B_4\underline{O}_7$. $10H_2O$.

(c) 4.96 g of $\underline{Mn}_3O_4$. (d) 333 mg of $Ca\underline{C}_2O_4$.

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

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

(c) 12.92 g of $NaHC\underline{O}_3$. (d) 57 mg of $\underline{Mg}NH_4PO_4$

How do we express concentrations of solutions:-

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

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

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

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

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

Example (5):-A solution is prepared by dissolving 1.26 gm $AgNO_3$ in a 250 mL volumetric flask and diluting to volume. Calculate the molarity of the silver nitrate solution. How many millimoles $AgNO_3$ were dissolved.

Solution:

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

$$= \frac{1.26 \text{ (g)}}{169.9 \, (\frac{g}{\text{mol}})} \times \frac{1000}{250 \text{ (mL)}} = 0.0297 \text{ mol/L}$$

$$\text{Millimoles} = M \left(\frac{\text{mmol}}{\text{mL}}\right) \times V \text{ (mL)}$$

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

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

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

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

Example (7):-How many grams Na_2SO_4 should be weight out to prepare 500 mL of a 0.100 M solution.

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

$$0.10\,mol/L = \frac{wt\,(g)}{142\,(\frac{g}{mol})} \times \frac{1000\,(\frac{mL}{L})}{500\,(mL)}$$

$$wt\,(g) = \frac{0.10\,(\frac{mol}{L}) \times 142\,(\frac{g}{mol})}{2\,(\frac{1}{L})} = 7.1\,g$$

Example (8):- Calculate the concentration of potassium ion in grams per litter after mixing 100 mL of 0.250 M KCl and 200 mL of 0.100 M K_2SO_4.

$$\text{mmol (K}^+\text{)} = \text{mmol (KCl)} + 2 \times \text{mmol (K}_2\text{SO}_4\text{)}$$

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

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

$$= 25 \text{ mmol} + 2 \text{ [20 mmol]}$$

$$= 25 \text{ mmol} + 40 \text{ mmol} = 65 \text{ mmol in 300 mL}$$

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

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

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

$$= 2.541 \text{ gm} \times \frac{1000 \left(\frac{\text{mL}}{\text{L}}\right)}{300 \text{ (mL)}} = 8.47 \left(\frac{\text{gm}}{\text{L}}\right)$$

Homework-(a) How many grams of K_2SO_4 are contained in 50 ml of 0.200 M,
   (b) How many millimoles of K_2SO_4 are present?

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

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

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

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

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

Example (9):-Calculate the molarity of 28.0% NH_3, specific gravity 0.898.

Solution:

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

$$M = \frac{\% \times sp.gr.\ or\ (density) \times 1000}{M.wt}$$

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

Example (10) *:-*How many millilitres of concentrated sulphuric acid, 94.0% (g/100g solution), density 1.831 g/cm^3, are required to prepare 1 liter of a 0.100 M solution.

Solution:

$$M = \frac{\frac{94}{100} \times 1.831 \times 1000}{98.1} = 17.5\ (\frac{mmol}{mL})$$

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

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

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

$$V_1 = 5.71\ mL$$

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

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

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

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

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

$$V_1 = 5.71\ mL$$

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.

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

Example (11):-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: 1.0×10^{-3} **M**

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

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

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

Example (12):-A solution contains 3.30 gm of $Na_2CO_3.10H_2O$ in each 15 ml.What is its molarity? What is its normality? With how many millilitres of 3.1N acetic acid,CH_3COOH,will 25 ml of the carbonate react according to the equation

$$2CH_3COOH \longrightarrow 2CH_3COO + 2H^+$$

$$Na_2CO_3 \longrightarrow 2Na^+ + CO_3^=$$

$$2H^+ + CO_2^= \longrightarrow H_2O + CO_2 ?$$
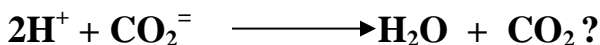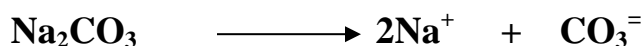
With how many millilitres of 3.1 N H_2SO_4 will 25 ml of the carbonate react?

Solution:

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

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

$M = 0.77M \qquad N = a \ M = 2 \times 0.77 = 1.53N$

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

$\qquad\qquad\qquad V_1 = 12.4 \ ml \ acetic \ acid.$

$\qquad\qquad\qquad V_1 = 12.4 \ ml \ H_2SO_4.$

Example (13):-You wish to prepare 500 mL of 0.1 M $K_2Cr_2O_7$ solution from a 0.250 M solution. What volume of the 0.250 M solution must be diluted to 500 mL.

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

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

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

$$V_1 = 200 \text{ mL}$$

Example (14):-What is the molarity and normality of a 13.0% solution of H_2SO_4? To what volume should 100 ml of acid be diluted in order to prepare a 1.50 *N* solution?

Solution:

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

M=%×SP.gr×1000/M.wt =0.13×1.090×1000/98=1.45M.

N=a M = 2×1.45=2.9 N.

$N_1 V_1$ =N_2 V2   2.9×100 = 1.50×V_2

V_2 = 193 ml .

Example (15):-Prepare 500mL of 0.010M solution of Na^+ from Na_2CO_3.

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

$$\frac{0.01}{2} \qquad 0.01$$

$$M_{Na_2CO_3} = \frac{\text{wt}}{\text{M. wt}} \times \frac{1000}{V(\text{mL})}$$

$$0.005 = \frac{\text{wt}}{106} \times \frac{1000}{500}$$

$$2 \times \text{wt} = 0.005 \times 106$$

$$\text{wt} = \frac{0.005 \times 106}{2} = 0.265 \text{ g Na}_2CO_3$$

Example (16):- 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:

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

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

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

Example (17):- 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.

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

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

$$V_1 = 200 \text{ mL}$$

Example (18):- 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.

$$\text{Let } x = \text{mL Ba(OH)}_2 \text{ and the final volume is } (50+x) \text{ mL}$$

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

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

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

Example (19):- Prepare 500mL of 0.010M solution of Na^+ from solid Na_2CO_3.

$$Na_2CO_3 \rightarrow 2Na^+ + CO_3^{2-}$$
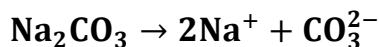
$$\frac{0.01}{2} \qquad 0.01$$

$$M_{Na_2CO_3} = \frac{wt}{M.wt} \times \frac{1000}{V(mL)} \qquad , \qquad 0.005 = \frac{wt}{106} \times \frac{1000}{500}$$

$$2 \times wt = 0.005 \times 106 \quad , \qquad wt = \frac{0.01 \times 106}{2} = 0.265 \text{ g Na}_2CO_3$$

Problems

Q1:Calculate the formula weights of the following substance :(a) $BaCl_2.2H_2O$, (b)$Ag_2Cr_2O_7$,(c)$Ca(PO_4)_2$.

Q2:Asolution containing 10 mmol $CaCl_2$ is diluted to 1 L. Calculate the number of grams of $CaCl_2.2H_2O$ per milliliter of the final solution?

Q3:Calculate the molarity of each of the following solutions:

(a) 10 gm H_2SO_4 in 250 ml of solution,(b)6 gm NaOH in 500 ml of solution,(c)25 gm $AgNO_3$ in 1L of solution.

Q4:Calculate the number of grams in 500 ml of each of the following solutions:(a) 0.1 M Na_2SO_4 ,(b) 0.250 M $Fe(NH_4)_2(SO_4)_2.6H_2O$,(c) 0.667 M $Ca(C_9H_6ON)_2$.

Q5:Calculate the grams of each substance requied to prepare the following solutions:(a)250 ml of 0.1 M KOH ,

(b) 1L of 0.0275 M $K_2Cr_2O_7$,(c)500 ml of 0.05 M $CuSO_4$.

Q6: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?

Q7:Calculate the molarity of each of the following commercial acid or base solutions:(a) 70% $HClO_4$, sp. grv. 1.668 , (b)69% HNO_3 , sp. grv. 1.409 , (c) 85% H_3PO_4 , sp. grv. 1.689 ,(d)99.5% $HC_2H_3O_2$(acetic acid) , sp. grv. 1.051 , (e)28% NH_3 , sp. grv. 0.898 .

Dilution calculation

Q8/A 12.5-mL portion of a solution is diluted to 500 mL, and its molarity is determined to be 0.125. What is the molarity of the original solution?

Q9/ What volume of 0.50 M H2SO4 must be added to 65mL of 0.20 M H2SO4 to give a final solution of 0.35 M? Assume volumes are additive.

Q10/You are required to prepare working standard solutions of 1.00×10^{-5}, 2.00×10^{-5}, 5.00×10^{-5}, and 1.00×10^{-4} M glucose from a 0.100 M stock solution. You have available 100-Ml volumetric flasks and pipets of 1.00-, 2.00-, 5.00-, and 10.00-mL volume. Outline a procedure for preparing the working standards.

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

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

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

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

Solution

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

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

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

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

$$N = \frac{No.\ of\ equivalent}{Solution\ Volumn\ (L)} = \frac{Equivalent\ Weight\ (\frac{gm}{eq})}{\frac{V\ (mL)}{1000\ (\frac{mL}{L})}}$$

$$N = \frac{wt}{Eq.\ wt} \times \frac{1000}{V\ (mL)}$$

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

Equivalent weight (Eq.wt):- is the formula weight divided by the number of reacting units (H^+ for acid-base and electron for oxidation-reduction reaction).

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

$$(Eq.\ wt)\ for\ oxidation - reduction\ reaction = \frac{formula\ weight\ (F.wt)}{No.\ of\ electron}$$

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

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

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

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

Example (21):- Calculate the equivalent weight of the following substances: (a) NH_3, (b) $H_2C_2O_4$ (in reaction with NaOH), and (c) $KMnO_4$ [Mn^{7+} is reduced to Mn^{2+}].

(a)

$$Eq\ wt = \frac{Mwt}{No.\ of\ H^+\ or\ OH^-} = \frac{17.03}{1} = 17.03\ gm/Eq$$

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(b)
$$Eq\ wt = \frac{90.04}{2} = 45.02\ gm/Eq$$

(c)
$$MnO_4^- + 8H^+ + 5e = Mn^{+2} + 4H_2O$$
$$Eq\ wt = \frac{M.wt}{No.of\ electron} = \frac{158.04}{5} = 31.608\ gm/Eq$$

Example (22) :-Calculate the normality of the solutions containing the following:
(a) 5.300gm/L Na_2CO_3 (when the CO_3^{-2} reacts with two protons), (b) 5.267 gm/L
$K_2Cr_2O_7$ (the Cr^{6+} is reduced to Cr^{3+}).
Solution:(a)
$$N = \frac{wt}{Eq.wt} \times \frac{1000}{V\ (mL)} = \frac{5.3}{\frac{105.99}{2}} \times \frac{1000}{1000} = 0.10\ Eq/L$$

(b)
$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
$$= \frac{5.267}{\frac{294.19}{6}} \times \frac{1000}{1000} = 0.1074\ Eq/L$$

Example (23) :-How many millilitres of a 0.25M solution of H_2SO_4 will react
with 10mL of a 0.25M solution of NaOH.

Solution: $\quad$ $N = nM$ $\quad$ (n = No.of equivalent, $H^+, OH^-,$ or electron)
$$N_{H_2SO_4} = 2 \times 0.25$$
$$= 0.5\ \left(\frac{Eq}{L}\right)\ or\ \left(\frac{meq}{mL}\right)\ or\ N$$
$$N_{NaOH} = 1 \times 0.25 = 0.25\ N$$
$$(N \times V)_{H_2SO_4} = (N \times V)_{NaOH}$$
$$(0.5 \times V)H_2SO_4 = (0.25 \times 10)NaOH$$
$$V_{H_2SO_4} = 5.0\ mL$$

Example (24):-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, and (b) if it is used as a diacidic base.
Solution:(a)
$$N = \frac{wt}{Eq.wt} \times \frac{1000}{V\ (mL)} = \frac{0.212}{\frac{106.0}{1}} \times \frac{1000}{100} = 0.020\ meq/mL$$

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(b)

$$N = \frac{0.212}{\frac{106.0}{2}} \times \frac{1000}{100} = 0.040 \text{ meq/mL}$$

Example (25):-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:
$$I_2 + 2e \rightarrow 2I^-$$

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

$$wt = 1.27g$$

Example (26):-Calculate the normality of a solution of 0.25 g/L $H_2C_2O_4$, both as an acid and as a reducing agent.

Solution:
$$H_2C_2O_4 \rightarrow 2CO_2 + H_2O$$

$$N = \frac{wt}{Eq.\,wt} \times \frac{1000}{V\,(mL)} = \frac{0.259}{\frac{90.04}{2}} \times \frac{1000}{1000}$$

$$= 0.00555 \text{ meq/mL}$$

Example(27):-How many milliequivalents are involved in 43.50mL of 0.1379 N $K_2Cr_2O_7$?

Solution: $\quad$ **no. of milliequivalents** $= N \times V$

$$= 0.1379 \frac{meq}{mL} \times 43.50 \text{ mL}$$

$$= 5.9987 \text{ meq}$$

Problems

Q1:To what volume must 750 ml of 2.4 N solution be diluted in order to make it 1.7N?

Q2:How much 0.6 N base must be added to 750 ml of a 0.2 N base in order the solution to be 0.3 N ?

Q3: How many volume of 0.1421 N KOH solution are required to neutralize 13.72 ml of 0.0686 M H_2SO_4 ?

Concentration by percent:-

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

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

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

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

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

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

Example(28):-Calculate the weight percentage of solution prepare by mixing 5.0g $AgNO_3$ with 100mL water (density $1g/cm^3$).

Solution:

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

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

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

Example(29):-Calculate number of grams in 500mL silane solution (wt/v % = 0.859%).

Solution:

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

$$0.859\% = \frac{\text{wt NaCl (g)}}{500} \times 100 \quad , \quad \text{wt NaCl} = \frac{0.859 \times 500}{100} = 4.25 \text{ g NaCl}$$

Example (30):-Calculate the weight of glucose in litter solution(wt/v % = 5 %).
Solution:

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

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

Example(31):-Calculate the volume percentage of solution preparing by mixing 50mL methyl alcohol with 200mL water.

Solution:

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

$$= \frac{V \text{ methyl alcohol (mL)}}{V \text{ methyl alcohol} + V \text{ water (mL)}} \times 100 = \frac{50 \text{ mL}}{(50 + 200)\text{mL}} \times 100 = 20\%$$

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

Example(32): -Calculate the molal concentration for solution preparing from mixing 4 g NaOH with 500 g water.

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

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).

Example(33):-One litter of acetic acid solution contain 80.8 g of acetic acid, the solution density 1.00978 **g/cm^3** or **g/mL**. (**cm^3 = mL**)

Solution:

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

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

$$= \frac{\frac{80.8(g)}{60(\frac{g}{mol})}}{\frac{80.8(g)}{60(\frac{g}{mol})} + \left(\frac{1.009791 \left(\frac{g}{mL}\right) \times 1000mL - 80.8\,g}{18 \left(\frac{g}{mol}\right)} \right)} = 0.025$$

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

$$= \frac{\left(\frac{1.009791 \left(\frac{g}{mL}\right) \times 1000mL - 80.8\,g}{18 \left(\frac{g}{mol}\right)} \right)}{\frac{80.8(g)}{60(\frac{g}{mol})} + \left(\frac{1.009791 \left(\frac{g}{mL}\right) \times 1000mL - 80.8\,g}{18 \left(\frac{g}{mol}\right)} \right)} = 0.975$$

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

Analytical Molarity:

The analytical molarity of a solution gives the total number of moles of a solute in 1 L of the solution (or the total number of millimoles in I mL). That is, the analytical molarity specifies a recipe by which the solution can be prepared. For example, a sulfuric acid solution that has an analytical concentration of 1.0 M can be prepared by dissolving 1.0 mol, or 98 g, of H_2SO_4 in water and diluting to exactly 1.0 L.

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

Solution: (a)

$$F_{BaCl_2} = \frac{wt}{Fwt} \times \frac{1000}{V\ mL} = \frac{1.80}{46.1} \times \frac{1000}{750} = 0.0521\ F\ C_2H_5OH$$

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

(b)

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

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

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

Example (35):- Calculate the analytical and equilibrium molar concentration of the solute species in an aqueous solution that contains 285 mg of trichloroacetic acid, Cl_3CCOOH (Fwt=163.4) in 10.0mL (the acid is 73% ionized in water). Employing HA as the symbol for Cl_3CCOOH, we substitute into equation (law) to obtain the analytical or total concentration of the acid.

Solution

$$C_{HA} = \frac{wt}{M.wt} \times \frac{1000}{V\ mL} = \frac{\frac{285}{1000}}{163.4} \times \frac{1000}{10} = 0.174\ mmol\ HA/mL = 0.174\ M\ HA$$

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

$$[HA] = C_{HA} \times \frac{27.0}{100} = 0.047mmol/mL = 0.047M$$

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

$$[H_3O^+] = [A^-] = 0.174 - 0.047 = 0.127\ mmol/mL = 0.127M$$

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

The relationship between molarity or normality with percentage concentration:-

Example (36):-Calculate the molar concentration for 0.85% (w/v%) sodium chloride solution.

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

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

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

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

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

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

Common Units for Expressing Trace Concentrations

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

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

Example (37):-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?

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

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

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

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

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

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

Example (38):- 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

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

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

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

The relationship between molarity, normality and part per million:-

$$\textbf{M} = \frac{\textbf{ppm}}{\textbf{M.wt} \times \textbf{1000}} \qquad\qquad \textbf{N} = \frac{\textbf{ppm}}{\textbf{Eq.wt} \times \textbf{1000}}$$

Example (39):-(a) Calculate the molar conc. of 1.0 ppm solutions each of Li^+ and Pb^{+2}.(b) What weight of $Pb(NO_3)_2$ will have to be dissolved in 1 liter of water to prepare a 100 ppm Pb^{+2} solution.

Solution:

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

(a)

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

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

(b)

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

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

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

Example (40) :-The concentration of Zinc ion in blood serum is about (1ppm). Express this as meq/L.

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

$$= 3.06 \times 10^{-5} \times 1000 = 3.06 \times 10^{-2}\ meq/L$$

Problems

Q1:Asolution contains 6 μ mole Na_2SO_4 in 250 ml . How many ppm sodium does it contain ? of sulfate ?

Q2:Calculate the molar concentration of 1 ppm solutions of each of the following ?

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

Q3: 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

Q4: You want to prepare 1L of a solution containing 1ppm Fe^{+2} . How many grams ferrous ammonium sulfate, Fe $SO_4(NH_4)_2\ SO_4.6H_2O$, must be dissolved and diluted in 1L ? What would be the molarity of this solution ?

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Q5: How many grams NaCl should be weighed out to prepare 1L of a 100 ppm solution of (a) Na^+ and (b) Cl^-

Q6: One liter of a 500 ppm solution of $KClO_3$ contains how many grams of K^+ ?

Exercises

1- How many moles and millimoles of benzoic acid (Mw = 122.1 g/mol) are contained in 2.00 g of the pure acid?

2- How many grams of Na^+ (22.99 g/mol) are contained in 25.0 g of Na_2S0_4 (142.0 g/mol).

3- Describe the preparation of 500 mL of 0.0740 M Cl^- solution from solid $BaCl_2.2H_2O$ (244.3 g/mol).

4- Find the number of millimoles of the indicated species in (a) 57 mg of P_2O_5 (b) 12.92 g of CO_2 (c) 40.0 g of $NaHCO_3$ (d) 850 mg of $MgNH_4PO_4$

5- What is the mass in grams of

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

6- Calculate the p-value for each of the indicated ions in the following:

a- Ba^{2+}, Mn^{2+}, and Cl^- in a solution that is 7.65×10^{-3} M in $BaC1_2$ and 1.54 M in $MnC1_2$.

b- Cu^{2+}, Zn^{2+}, and NO_3^- in a solution that is 4.78×10^{-2} M in $Cu(NO_3)2$ and 0.104 M in $Zn(NO_3)_2$

c- H^+, Ba^{2+}, and CIO_4 in a solution that is 3.35×10^{-4} M in $Ba(ClO_4)_2$ and 6.75×10^{-4} M in $HC1O_4$.

7- Sea water contains an average of 1.08×103 ppm of Na^+ and 270 ppm of SO_4^-. Calculate(a) the molar concentrations of Na^+ and SO_4^- given that the average density of sea water is*1.02 g/mL.* (b) the pNa and pSO_4 for sea water.

8- A solution was prepared by dissolving 1210 mg of $K_3Fe(CN)_6$ (329.2 g/mol) in sufficient water to give 775 mL. Calculate

(a) the molar analytical concentration of $K_3Fe(CN)_6$.   (b) the molar concentration of K^+. (c) the molar concentration of $Fe(CN)_6^{3-}$. (d) the weight/volume percentage

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of $K_3Fe(CN)_6$. (e) the number of millimoles of K^+ in 50.0 mL of this solution.   (f) ppm $Fe(CN)_6^{3-}$.   (g) pK^+ for the solution.   (h) $pFe(CN)_6^{3-}$ for the solution.

9- A 12.5% (w/w) $NiCl_2$ (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 molar Cl^- concentration of the solution. (c) the mass in grams of $NiCl_2$ contained in each liter of this solution.

 10- Describe the preparation of (a) 2.50 L of 21.0% (w/v) aqueous glycerol ($C_3H_8O_3$ (92.1 g/mol). (b) 2.50 kg of 21.0% (w/w) aqueous glycerol. (c) 2.50 L of 21.0% (v/v) aqueous glycerol.

11- Describe the preparation of 900 mL of 3.00 M HNO_3 from the commercial reagent that is 70.5% HNO_3 (w/w) and has a specific gravity of 1.42.

12- A solution containing 10.0 mmol $CaCl_2$ is diluted to 1 L. Calculate the number of grams of $CaCl_2$. $2H_2O$ per milliliter of the final solution.

13- Calculate the grams of each substance required to prepare the following solutions: (a) 250mL of 0.100 M KOH, (b) 1.00 L of 0.0275 M $K_2Cr_2O_7$, (c) 500mL of 0.0500 M $CuSO_4$.

14- How many milliliters of concentrated hydrochloric acid, 38.0% (wt/wt), specific gravity 1.19, are required to prepare 1 L of a 0.100 M solution?

15- Calculate the molar concentrations of 1.00-mg/L solutions of each of the following. (a) $AgNO_3$, (b) $Al_2(SO_4)_3$, (c) CO_2, (d) $(NH_4)_4Ce(SO_4)_4$. $2H_2O$, (e) HCl, (f) $HClO_4$.

16- How many grams NaCl should be weighed out to prepare 1 L of a 100-mg/L solution of (a) Na^+ and (b) Cl^-?

17- What volume of 0.50 M H_2SO_4 must be added to 65mL of 0.20 M H_2SO_4 to give a final solution of 0.35 M?

18- What is the molar concentration of NO_3^- in a solution prepared by mixing 50.0 mL of 0.050 M KNO_3 with 40.0 mL of 0.075 M $NaNO_3$? What is pNO_3 for the mixture?

19- For each of the following, explain how you would prepare 1.0 L of a solution that is 0.10 M in K^+. Repeat for concentrations of 1.0×10^2 ppm K^+ and 1.0% w/v K^+. a. KCl   b. K_2SO_4 c. $K_3Fe(CN)_6$

20- A solution was prepared by dissolving 5.76 g of $KCl \cdot MgCl_2 \cdot 6H20$ (277.85 g/mol) in sufficient water to give 2.000 L. Calculate: (a) the molar analytical concentration of $KCl.MgCl_2$ in this solution. (b) The molar concentration of Mg_2^+.   (c) The molar concentration of Cl^-. (d) The weight/volume percentage of $KCl.MgCl_2$ .6H20. (e) The number of millimoles of Cl^- in 25.0 mL of this solution. (f) ppm K^+.   (g) pMg for the solution.

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,

$$pX = -\log [X]$$

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

Example (**41**) : 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 $pH = -\log [H^+] = -\log (5.4 \times 10^{-4}) = 3.27$

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

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

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

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

Example (42): Calculate the molar concentration of Ag^+ in a solution that has a pAg of 6.372.

Solution**:**

$pAg = -\log [Ag^+] = 6.372, \log [Ag^+] = -6.372, [Ag^+] = 4.246 \times 10^{-7} = 4.25 \times 10^{-7}$

Volumetric analysis (titration analysis):-

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

The requirements of a titration are as follows:-

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

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$
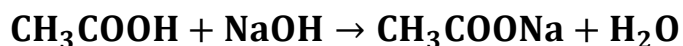
(2) The reaction should be rapid. Most ionic reactions.

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

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

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

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

the titration where the number of moles of titrant = number of moles of analyte. The end point is the observed end of the titration.

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

A primary standard should fulfil these requirements:-

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

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

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

(4) Althogh 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.

Example (43):-A 0.471 g sample containing sodium bicarbonate was dissolved and titrated with standard 0.1067 M hydrochloric acid solution, requiring 40.72 mL. The reaction is: $HCO_3^- + H^+ \rightarrow H_2O + CO_2$

Calculate the percent sodium bicarbonate in the sample.

Solution:

$$\textbf{millimoles NaHCO}_3 = \textbf{ millimoles HCl}$$

$$(\frac{\textbf{wt (g)}}{\textbf{M. wt }(\frac{\textbf{g}}{\textbf{mol}})})_{\textbf{NaHCO}_3}\textbf{X1000} = (\textbf{M} \times \textbf{V})_{\textbf{HCl}}$$

$$(\frac{\textbf{wt (g)}}{\textbf{84. 01 }(\frac{\textbf{g}}{\textbf{mol}})})\textbf{X1000} = \textbf{0. 1067} \times \textbf{40. 72}$$

$$\textbf{wt} = \textbf{0. 365 g}$$

$$\textbf{\%NaHCO}_3 = \frac{\textbf{wt NaHCO}_3}{\textbf{wt sample}} \times \textbf{100} = \frac{\textbf{0. 365 g}}{\textbf{0. 4671 g}} \times \textbf{100} = \textbf{78. 14 \%}$$

Example (44) *:-*A 0.2638 g soda ash sample is analyzed by titrating the sodium carbonate with the standard 0.1288 M hydrochloric solution, requiring 38.27 mL.

The reaction is: $CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2$

Calculate the percent sodium carbonate in the sample.

Solution:

$$\textbf{millimoles Na}_2\textbf{CO}_3 = \frac{\textbf{1}}{\textbf{2}} \textbf{ millimoles HCl}$$

$$(\frac{\textbf{wt}}{\textbf{M. wt}})_{\textbf{Na}_2\textbf{CO}_3}\textbf{X1000} = \frac{\textbf{1}}{\textbf{2}} (\textbf{M} \times \textbf{V})_{\textbf{HCl}}$$

$$\left(\frac{wt}{105.99}\right)X1000 = \frac{1}{2}(0.1288 \times 38.27), \qquad wt = 0.2612\ g$$

$$\%\ Na_2CO_3 = \frac{wt\ Na_2CO_3}{wt\ sample} \times 100 = \frac{0.2612}{0.2638} \times 100 = 99.02\%\ Na_2CO_3$$

Example (45):-How many millilitres of 0.25 M solution of H_2SO_4 will react with 10 mL of a 0.25 M solution of NaOH.

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$
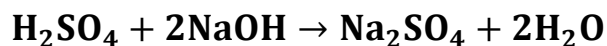
One half as many millimoles of H_2SO_4 will react one millimole NaOH

Back titration:-

Sometimes a reaction is slow to go to completion, and 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.

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^+):

$$HA + H_2O \leftrightarrow H_3O^+ + A^-$$
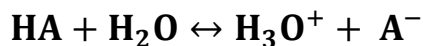
Base:-any substance that ionizes in water to give hydroxyl ions. Weak (partially ionized) to generally ionize as follows:-

$$B + H_2O \leftrightarrow BH^+ - OH^-$$
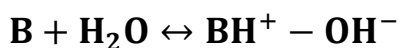
While strong bases such as metal hydroxides (e.g. NaOH) dissociate as

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

This theory is obviously restricted to water as the solvent.

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

Acid:-any substance that can donate a proton.

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

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

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

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

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

$$H_2O + H^+ \leftrightarrow H_2O{:}H^+ (H_3O^+) \qquad HO{:}^- + H^+ \leftrightarrow H{:}OH$$
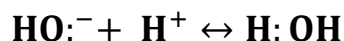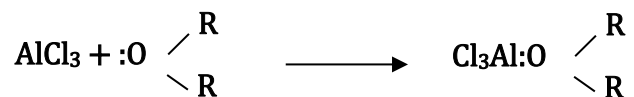
Acid-Base Equilibria in water:-when an acid or base is dissolved in water, it will dissociate, or ionize, the amount of ionization being dependent on the strength of the acid or base. A strong electrolyte is completely dissociated, while a weak electrolyte is partially dissociated.

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

$$HOAc + H_2O \longleftrightarrow H_3O^+ + OAc^-$$
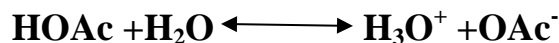
$$(\textbf{weak acid, partially ionized, a few percent})$$

Thermodynamic acidity constant K°

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

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

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

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

$$2H_2O \leftrightarrow H_3O^+ + OH^-$$
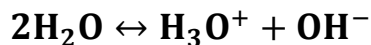
The equilibrium constant for this is:

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

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

$$K_w^\circ = aH_3O^+ \times aOH^-$$

$$K_w^\circ, \textbf{thermodynamicoutoprotolysisorself} - \textbf{ionization, constant})$$

We will use H$^+$ in place of H$_3$O$^+$ for simplification, also, molar concentration will generally be used instead of activities and represented by square brackets [ ] around the species).

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

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

$$H_2O \leftrightarrow H^+ + OH^-, K_w = [H^+][OH^-]$$
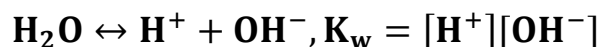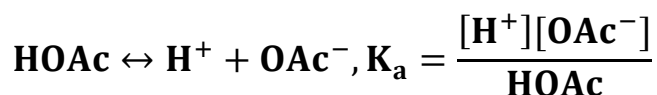
$$1.0 \times 10^{-14} = [H^+][OH^-] \text{ at } 25°C$$

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

Example (46):-A 1.0×10^{-3} M solution of HCl prepared. What is the hydroxyl ion concentration [OH$^-$] ?

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

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

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

The pH scale: $$pH = -\log[H^+] \, , \quad pH = 1 - 14$$

Example (47):- Calculate the pH of a 2×10^{-3}M HCl ?

$$[H^+] = 2 \times 10^{-3} \qquad pH = -\log[H^+]$$

$$= -\log(2.0 \times 10^{-3}) = 3 - \log 2.0 = 2.70$$

$$pOH = -\log[OH^-] \quad pK_w = pH + pOH = 14$$

Example (47):-Calculate the pOH and pH of a 5×10^{-2} M NaOH ?

$$[OH^-] = 5 \times 10^{-2} M \qquad pOH = -\log[OH^-]$$

$$= -\log(5 \times 10^{-2}) = 2 - \log 5 = 2 - 0.70 = 1.30$$

$$pH + pOH = 14 \qquad pH = 14 - pOH \qquad = 14 - 1.30 = 12.70$$

Example (48):-Calculate the pH of a solution prepared by mixing 2.0 mL of a strong acid solution (keep track of millimoles) of Ph=3.0 and 3.0 mL of a strong base of pH= 10.0 ?

$$[H^+] = 1.0 \times 10^{-3} M \quad , \qquad mmol\ H^+ = M \times V$$

$$= 1.0 \times 10^{-3} \times 2.0 = 2 \times 10^{-3}\ mmol$$

$$pOH = 14 - pH = 14 - 10 = 4.0 [OH^-] = 1.0 \times 10^{-4} M$$

$$mmol\ OH^- = M \times V = 1.0 \times 10^{-4} \times 3.0\ mL = 3.0 \times 10^{-4} mmol$$

There is an excess of acid:-

$$mmol\ H^+ = 2.0 \times 10^{-3} - 3.0 \times 10^{-4} = 1.7 \times 10^{-3}\ mmol$$

$$[H^+] = \frac{1.7 \times 10^{-3} mmol}{5mL\ (2+3)} = 3.4 \times 10^{-4} M$$

$$pH = -\log 3.4 \times 10^{-4} = 4 - 0.53 = 3.47$$

Example (49):-The pH of a solution is 9.67. Calculate the hydrogen ion concentration in the solution ?

$$pH = -\log[H^+], \qquad [H^+] = 10^{-pH}, \qquad [H^+] = 10^{-9.67}$$

$$[H^+] = 10^{-10} \times 10^{0.33} = 2.1 \times 10^{-10}\ M$$

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.

Example (50):-Calculate the pH of a buffer prepared by adding 10mL of 0.1M acetic acid to 20mL of 0.1M sodium acetate ?

Henderson-Hasselbalch equation:-

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

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

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

Example (51):-Calculate the pH of a solution prepared by adding 25mL of 0.1M sodium hydroxide to 30mL of 0.2M acetic acid (this would actually be a step in a typical titration ?

$$mmol\ HOAc = 0.2M \times 30mL = 6.0mmol$$

$$mmol\ NaOH = 0.1M \times 25mL = 2.5mmol$$

these react as follows:-

$$HOAc + NaOH \leftrightarrow NaOAc + H_2O$$
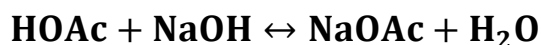
$$\left. \begin{array}{l} mmol\ NaOAc = 2.5mmol \\ mmol\ HOAc = 6.0 - 2.5 = 3.5mmol \end{array} \right] \textbf{after reaction}$$

$$pH = pK_a + \log \frac{[salt]}{[acid]} = 4.76 + \log \frac{2.5}{3.5} = 4.61$$

Example (52):-Calculate the volume of concentrated ammonia and the weight of ammonium chloride you would have taken to prepare 100mL of a buffer at pH 10.0 if the final concentration of salt is to be 0.2M ?

$$pOH = pK_b + \log \frac{[salt]}{[base]} \qquad pH + POH = 14, \qquad 10 + POH = 14$$

$$POH = 14-10 = 4 \qquad 4 = 4.76 + \log\frac{0.2}{[NH_3]}$$

$$-0.76 = \log\frac{0.2}{[NH_3]} \qquad 10^{-0.76} = \frac{0.2}{[NH_3]}$$

$$[NH_3] = \frac{0.2}{10^{-0.76}} = \frac{0.2}{0.173} = 1.15M$$

$$M_1V_1 = M_2V_2 \qquad (\frac{0.28 \times 0.9 \times 1000}{17}) \times V_1 = 1.15 \times 100$$

$$14.8 \times V_1 = 1.15 \times 100 \qquad , \qquad V_1 = 7.8\ mL$$

$$M_{NH_4Cl} = \frac{wt}{M.wt} \times \frac{1000}{V\ mL}$$

$$0.2 = \frac{wt}{53.5} \times \frac{1000}{100} \qquad wt = 1.07\ gm\ NH_4Cl$$

Example (53):-How many grams ammonium chloride and how many millimilters 3.0M sodium hydroxide should be added to 200mL water and diluted to 500mL to prepare a buffer of pH9.50 with salt concentrated of 0.10M ?

$$pOH = pK_b + \log\frac{[salt]}{[base]} \qquad 4.5 = 4.76 + \log\frac{[NH_4^+]}{[NH_3]}$$

$$-0.26 = \log\frac{[NH_4^+]}{[NH_3]} \qquad = 10^{-0.26} = \frac{[NH_4^+]}{[NH_3]}$$

$$0.549 = \frac{0.1}{[NH_3]} \quad \Rightarrow [NH_3] = 0.18M$$

$$mmol\ NH_4^+\ in\ final\ solution = 0.1M \times 500mL = 50\ mmol$$

$$mmol\ NH_3\ in\ final\ solution = 0.18M \times 500mL = 90\ mmol$$

The NH_3 formed from an equal number of millimoles of NH_4Cl. Therefore, a total of $50 + 90 = 140$ mmol NH_4Cl must be taken.

$$mmol\ NH_4Cl = \frac{wt\ (mg)}{M.wt\ (mg/mL)}$$

$$140 = \frac{wt\ (mg)}{53.5} \quad \Rightarrow wt = 7.49\ gm$$

The millimoles of NaOH needed are equal to the millimoles of NH_3:

$$mmol\ NH_3 = M \times V$$

$$90\ mmol = 3.0M \times V \implies V = 30mL\ NaOH$$

External questions

Q1: Calculate the number of mole of ammonia, NH_3, required to produce 2.5 mol of $Cu(NH_3)_4SO_4$ according to the equation :

$$CuSO_4 + 4NH_3 \longrightarrow Cu(NH_3)_4SO_4$$
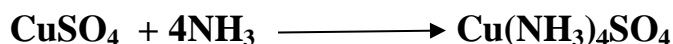
Solve :

$$No.\ of\ mol\ of\ NH_3 = No.\ of\ mol\ of\ Cu(NH_3)_4SO_4 \times 4$$

$$= 2.5 \times 4 = 10\ mol\ of\ NH_3$$

Q2: Calculate the number of mole of $Ca(HCO_3)_2$ required to prepare 1.5 mol of CO_2 according to the equation :

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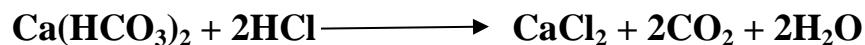
Solve :

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

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

Q3: Calculate the mass of $BaCO_3$ produced when excess CO_2 is bubbled through a solution containing 0.205 mol of $Ba(OH)_2$.

$$Ba(OH)_2 + CO_2 \longrightarrow BaCO_3 + H_2O$$
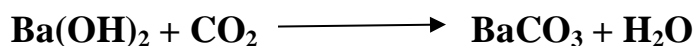
Solve :

$$No.\ of\ mol\ of\ BaCO_3 = No.\ of\ mol\ of\ Ba(OH)_2 = 0.205\ mol$$

$$Mol = \frac{wt}{M.wt} \quad \longrightarrow \quad wt.\ of\ BaCO_3 = mol \times M.wt$$

$$Wt.\ of\ BaCO_3 = 0.205 \times 197.4 = 40.5\ gm$$

Q4: Caustic soda, NaOH, can be prepared commercially by the reaction of Na_2CO_3 with slaked lime, $Ca(OH)_2$. How many gram of NaOH can be obtained by treating 1.000 kg of Na_2CO_3 with $Ca(OH)_2$?

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow 2NaOH + CaCO_3$$
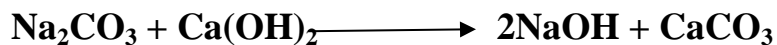
Solve :

$$mol = \frac{wt}{M.wt} \longrightarrow \text{mol of } Na_2CO_3 = 1000 \text{ gm } / 106 \text{ gm . mol}^{-1}$$

mol of Na_2CO_3 = 9.433 mol of Na_2CO_3

No. of mol of NaOH = 2 × No. of mol of Na_2CO_3 = 2× 9.433=18.87 mol

wt of NaOH = mol × M.wt = 18.87 × 40 = 755 gm NaOH

Q5: What mass of KI is needed to produce 69.6 gm of K_2SO_4 by the reaction :

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

Solve :

No. of mol of K_2SO_4= wt / M.wt $\longrightarrow$ 69.6 gm / 174 gm . mol^{-1}= 0.4 mol

No. of mol of KI = 2× 0.4= 0.8 mol

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

Q6: What volume of 1.71 M NaCl solution contains 0.2 mol of NaCl ?

Solve :

Molarity = mol / volume $\longrightarrow$ volume=mol / molarity

V = 0.2 / 1.71 = 0.117 L = 117 ml

Q7: What volume of 0.3 M NaOH (M.wt= 40 g mol^{-1}) can be prepared with 84 gm NaOH ?

Solve :

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

$$3.0 = \frac{84\,(g)}{40\,(\frac{g}{mol})} \times \frac{1000}{V\,(mL)} = 700 \text{ ml}$$

Q8: How many of water must be added to 200 ml of 0.65 M HCl to dilute the solution to 0.2 M ?

Solve :

$M_1 \, V_1 = M_2 \, V_2$ ➤ $200 \times 0.65 = V_2 \times 0.2$

$V_2 = 650 \, ml$ ➤ **approximately $650 - 200 = 450$ ml must be added**

Q9: How much 1.00 M HCl should be mixed with what volume of 0.25 M HCl in order to prepare 1.00 L of 0.500 M HCl ?

Solve :

Let x= volume of 0.25 M HCl ; then 1.00- x = volume of 1.00 M HCl

No. of mol of S1 + No. of S2 = No. of S3

$$(1.00 - x) \, 1.00 + x \, (0.25) = 1.00(0.500)$$

Thus x= 0.667 L = 667 ml of 0.25 M HCl and 1.00 – x=

1.00 – 0.667=0.333 L = 333 ml

Q10: What is the molar concentration of a solution containing 16 gm CH_3OH in 200 ml solution ?

Solve :

$$M = \frac{wt \, (g)}{M.wt \, (\frac{g}{mol})} \times \frac{1000}{V \, (mL)} = \frac{16 \, (g)}{32 \, (\frac{g}{mol})} \times \frac{1000}{200 \, (mL)} = 2.5 \, M$$

Normality

Q11: What is the difference between the definition of an equivalent in an acid- base reaction and an equivalent in an oxidation – reduction reaction?

Solve :

An equivalent in an acid – base reaction is that amount of a substance which reacts with or liberates 1 mol of hydrogen ions ; an equivalent in a redox reaction is that amount of substance which reacts with or liberates 1 mol of electrons .

Q12: What volume of a 0.232 N solution contains **(a)** 3.17 meq of solute **(b)** 6.5 eq of solute ?

Solve:

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

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

(b) Solution Volumn (L) $= \dfrac{\text{No. of equivalent}}{N} = \dfrac{6.5}{0.232} = 28.0 \text{ L}$

Q13: How many **(a)** equivalent and **(b)** milliequivalent of solute are present in 60 ml of 4.0 N solution ?

Solve:

(a) No. of equivalent = No. of liters × normality = 0.060 × 4.0 = 0.24 eq .

(b) 0.24 eq × 1000 = 240 meq .

Q14: How many equivalent of solute are contained in **(a)** 1 L of 2 N solution , **(b)** 1L of 0.5 N solution , **(c)** 0.5 L of 0.2 N solution ?

(a) No. of eq = 2 eq , **(b)** No. of eq = 0.5 eq , **(c)** No. of eq = 0.1 eq

Q15: What is normality of 0.3 M H_3PO_3 when it undergoes the following reaction ? $H_3PO_3 + 2OH^- \longrightarrow HPO_3^{-2} + 2H_2O$

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

Q16: How many cm^3 of concentrated sulfuric acid , of density 1.84

g/ cm^3 and containing 98.0 % H_2SO_4 by weight , should be taken to make **(a)** 1 L of 1 N solution **(b)** 1 L of 3 N solution **(c)** 200 cm^3 of 0.5 N solution ?

(a) 27.2 cm^3 ,**(b)** 81.7 cm^3 , **(c)** 2.72 cm^3.

Mole fraction and Molality

Q17: Calculate the mole fraction(x) of water in a mixture consisting of 9.0 gm water , 120 gm acetic acid , and 115 gm ethyl alcohol ?

Solve:

The molecular weight of water , acetic acid , and ethyl alcohol are 18 , 60 and 46 gm/mol , respectively .

Mol_{water} =wt / M.wt ⟶ 9.0 / 18 = 0.5 mol

$Mol_{acetic\ acid}$ =wt / M.wt ⟶ 120 / 60 = 2.0 mol

$Mol_{ethyl\ alcohol}$ =wt / M.wt ⟶ 115 / 46 = 2.5 mol

Sum of mole = 0.5 + 2.0 + 2.5 = 5.0 mole

$$\text{Mole fraction for water} X = \frac{\text{no. mole water } (n_1)}{\text{sum of mole}}$$

$$\text{Mole fraction for water} X = \frac{0.5 \text{ mole}}{5.0 \text{ mole}} = 0.10$$

Q18: What is the mole fraction of H_2 in a gaseous mixture containing 1.0 gm H_2 , 8.0 gm O_2 , and 16 gm CH_4 ?

Solve:

Mol H_2 =wt / M.wt ⟶ 1.0 / 2.0 = 0.5 mol

Mol O_2 =wt / M.wt ⟶ 8.0 / 32.0 = 0.25mol

Mol CH_4 =wt / M.wt ⟶ 16 / 16 = 1.0 mol

Sum of mole = 0.5 + 0.25 + 1.0 = 1.75 mole

$$\text{Mole fraction for } H_2 (X) = \frac{\text{no. mole H2 } (n_1)}{\text{sum of mole}}$$

$$\text{Mole fraction for } H_2 (X) = \frac{0.5 \text{ mole}}{1.75 \text{ mole}} = 0.29$$

Q19: A solution contains 116 gm acetone (CH_3COCH_3) , 138 gm ethyl alcohol (C_2H_5OH) , and 126 gm water . Determine the mole fraction of each ?

Solve:

Mol $_{acetone}$ =wt / M.wt ⟶ 116 / 58.0 = 2.0 mol

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Mol $_{C2H5OH}$ =wt / M.wt ➤ 138 / 46.0 = 3.0mol

Mol $_{water}$ =wt / M.wt ➤ 126 / 18 = 7.0 mol

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

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

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

$$\text{Mole fraction for C2H5OH(X)} = \frac{3.0 \text{ mole}}{12.0 \text{ mole}} = 0.250$$

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

Q20: Determine the mole fraction of both substances in a solution containing 36.0 gm water and 46.0 gm glycerin , $C_3H_5(OH)_3$?

Solve:

The molecular weight of $C_3H_5(OH)_3$ is 92.0 ; of water , 18.0

Mol $_{glycerin}$ =wt / M.wt ➤ 46.0 / 92.0 = 0.5 mol

Mol $_{water}$ =wt / M.wt ➤ 36.0 / 18.0 = 2.0 mol

Sum of mole = 0.5+ 2.0 = 2.5 mole

$$\text{Mole fraction for glycerin(X)} = \frac{0.5 \text{ mole}}{2.5 \text{ mole}} = 0.20$$

$$\text{Mole fraction for water(X)} = \frac{2.0 \text{ mole}}{2.5 \text{ mole}} = 0.80$$

Check : Sum of mole fractions = 0.20 + 0.80 = 1.0

Q21: The density of a 2.0 M solution of acetic acid (M.wt = 60) in water is 1.02 kg/L . Calculate the mole fraction of acetic acid ?

Solve:

Per liter of solution :

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

$$0.2 = \frac{wt\ (g)}{60\ (\frac{g}{mol})} \times \frac{1000}{1000\ (mL)} = 120\ gm\ acetic$$

Weight = volume × density = 1.000L × 1.02 kg/ L = 1.02kg = 1020 gm of solution .

Weight og water = 1020 – 120 = 900 gm water .

Mol $_{water}$ =wt / M.wt ➠ 900 / 18.0 = 50.0 mol

Sum of mole = 50.0+ 2.0 = 52.0 mole

$$\textbf{Mole fraction for acetic acid (X)} = \frac{2.0\ mole}{52.0\ mole} = 0.038$$

Q22: Asolution contains 10.0 gm acetic acid , CH_3COOH , in 125 gm water . What is the concentration of solution expressed as **(a)** mole fractions of CH_3COOH and water **(b)** molality ?

Solve:

(a) Mol $_{CH3COOH}$ =wt / M.wt ➠ 10.0 / 60.0 = 0.167 mol

Mol $_{water}$ =wt / M.wt ➠ 125 / 18.0 = 6.94 mol

Sum of mole = 0.167+ 6.94 = 7.107 mole

$$\textbf{Mole fraction for } CH_3COOH(X) = \frac{0.167\ mole}{7.107\ mole} = 0.0235$$

$$\textbf{Mole fraction for water}(X) = \frac{6.94\ mole}{7.107\ mole} = 0.965$$

(b) molality = 0.167 mol CH_3COOH / 0.125 kg water = 1.34 m

Q23: Calculate the molalities and mole fractions of acetic acid in two solutions prepared by dissolving 120 gm acetic acid **(a)** in 100 gm water **(b)** in 100 gm ethanol ?

Solve:

(a) in water

$$m = \frac{wt\ (g)}{M.wt\ (\frac{g}{mol})} \times \frac{1000}{wt(gm)}$$

$$m = \frac{120\ (g)}{60\ (\frac{g}{mol})} \times \frac{1000}{100\ gm} = 2.00\ m\ \text{acetic acid}$$

$$\text{Mole fraction for CH3COOH}(X) = \frac{2.00\ mole}{2.00 + 5.55\ mole} = 0.265$$

(b) in ethanol

$$m = \frac{wt\ (g)}{M.wt\ (\frac{g}{mol})} \times \frac{1000}{wt(gm)}$$

$$m = \frac{120\ (g)}{60\ (\frac{g}{mol})} \times \frac{1000}{100\ gm} = 2.00\ \text{acetic acid}$$

$$\text{Mole fraction for CH}_3\text{COOH}(X) = \frac{2.00\ mole}{2.00 + 2.17\ mole} = 0.480$$

Q24: What is the molality of a solution which contains 20.0 gm cane suger , $C_{12}H_{22}O_{11}$, dissolved in 125 gm water ?

Solve: The molecular weight of $C_{12}H_{22}O_{11}$ is 342 .

$$m = \frac{wt\ (g)}{M.wt\ (\frac{g}{mol})} \times \frac{1000}{wt(gm)}$$

$$m = \frac{20.0\ (g)}{342\ (\frac{g}{mol})} \times \frac{1000}{125\ gm} = 0.468\ m$$

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Q25: The molality of a solution of ethanol , C_2H_5OH , in water is 1.54 m. How many gm of ethanol is dissolved in 2.50 kg water ?

Solve:

Molality= mole / wt(kg) ➤ **mole = 2.50 × 1.54 = 3.85 mol**

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

Q26: Calculate the molality of a solution containing **(a)** 0.65 mol glucose , $C_6H_{12}O_6$, in 250 gm water **(b)** 45 gm glucose in 1.00 kg water **(c)** 18 gm glucose in 200 gm water ?

Solve:

(a) Molality= mole / wt(kg) ➤ **molality = 0.65/ 0.250 = 2.6 m**

(b)

$$m = \frac{wt\ (g)}{M.wt\ (\frac{g}{mol})} \times \frac{1000}{wt(gm)}$$

$$m = \frac{45\ (g)}{180\ (\frac{g}{mol})} \times \frac{1000}{1000\ gm} = 0.25\ m$$

(c)
$$m = \frac{wt\ (g)}{M.wt\ (\frac{g}{mol})} \times \frac{1000}{wt(gm)}$$

$$m = \frac{18\ (g)}{180\ (\frac{g}{mol})} \times \frac{1000}{200\ gm} = 0.50\ m$$

Q27: How many gram $CaCl_2$ should be added to 300 ml water to make up a 2.46 m solution ?

Solve:

Assuming that water has a density of 1.00 gm/ ml .

Weight = density × volume ➤ **wt = 300 × 1.00 = 300 gm**

$$m = \frac{wt\ (g)}{M.wt\ (\frac{g}{mol})} \times \frac{1000}{wt(gm)}$$

$$2.46 = \frac{wt\ (g)}{111\ (\frac{g}{mol})} \times \frac{1000}{300\ gm} = 81.9\ gm$$

Acids and bases

Q28: Distinguish between acid strength and acid concentration ?

Solve: The concentration of acid in a solution is determined by how many mol of acid is dissolved per L of solution ; its strength is determined by how completely it ionizes . Both of these factors affect the hydronium ion concentration .

Q29: Explain why a solution containing a strong base and its salts does not act as a buffer solution ?

Solve: Addition of OH^- does not shift an equilibrium toward un-ionized base , as it would with a weak base and its conjugate .

Q30: Explain the difference between a strong electrolyte and a weak electrolyte. Is an "insoluble" salt a weak or a strong electrolyte?

Solve: A strong electrolyte is completely ionized in solution , while a weak electrolyte is only partially ionized in solution .

Q31: What is the Brønsted acid–base theory? What is the Lewis acid–base theory?

Solve: The bronsted acid- base theory assumes that an acid is a proton donor , and a base is a proton accepter . In the lewis theory , an acid is an electron accepter , while a base is an electron donor .

Q32: Calculate the pH of a solution which has a hydronium ion concentration

of 6×10^{-8} M ?

Solve:

$PH = -log[H^+]$ ➡ $PH = -\log 6 - \log 10^{-8} = -0.78 + 8 = 7.22$

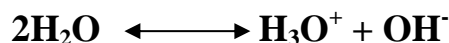Q33: Calculate the hydronium ion concentration of a solution which

 has a pH of 11.73 ?

Solve:

$[H^+] = 10^{-PH}$ ⟶ $[H^+] = 10^{-11.73} = 10^{0.27} \times 10^{-12}$

From the logarithm table , $10^{0.27} = 1.9$ ⟶ $[H^+] = 1.9 \times 10^{-12}$

Q34: Calculate the hydrogen ion concentration and the hydroxide ion concentration in pure water at 25 ^{0}C ?
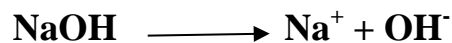
Solve:

$$2H_2O \longleftrightarrow H_3O^+ + OH^-$$

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

Let $x = [H^+] = [OH^-]$, hence $x^2 = 1.0 \times 10^{-14}$ and $x = 1.0 \times 10^{-7}M = [H^+] = [OH^-]$

Q35: Calculate the hydronium ion concentration of a 0.100 M NaOH solution ?

Solve: **NaOH ⟶ Na$^+$ + OH$^-$**

0.100M   0.100M

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

In this solution , $1.0 \times 10^{-14} = [H^+](0.100)$, thus $[H^+] = 1.0 \times 10^{-13}$ M.

Q36: Calculate the PH values , assuming complete ionization , of **(a)** 4.9×10^{-4} M monoprotic acid **(b)** 0.0016 M monoprotic base ?

Solve:

(a) $[H^+] = 4.9 \times 10^{-4}$ ⟶ **PH = -log $[H^+]$ = -log(4.9×10^{-4}) =**

-log 4.9 + 4 = 3.31

(b) $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ ⟶ **$[H^+] = 10^{-14} / [OH^-]$**

$[H^+] = 10^{-14} / 1.6 \times 10^{-3}$

PH = -log $10^{-14} / 1.6 \times 10^{-3}$ = -(- 14 - log 1.6 + 3) = 14 + 0.20 − 3 = 11.20

Q37: Calculate the PH of 1.0×10^{-3} M solutions of each the following: **(a)** HCl **(b)** NaOH   **(c)** Ba(OH)$_2$ **(d)** NaCl   ?

(a) PH $= 3.00$ **(b)** PH $= 11.00$ **(c)** PH $= 11.30$ **(d)** PH $= 7$

Q38: Calculate the pH and pOH of the following strong acid solutions: **(a)** 0.020 M HClO$_4$, **(b)** 1.3×10^{-4} M HNO$_3$, **(c)** 1.2 M HCl?

Solve:

(a) PH = - log [H$^+$] = - log 2× 10^{-2} = 2 – 0.3 = 1.7

   POH = 14 – 1.7 = 12.3

(b) PH = - log [H$^+$] = - log 1.3× 10^{-4} = 4 – 0.11 = 3.89

   POH = 14 – 3.89 = 10.11

(c) PH = - log [H$^+$] = - log 1.2 = - 0.08

   POH = 14 – (-0.08) = 14.08

Q39: Calculate the pH and pOH of the following strong base solutions: **(a)** 0.050 M NaOH, **(b)** 2.4 M NaOH,**(c)** 3.7×10^{-3} M KOH.?

Solve:
(a) POH = - log [OH$^-$] = -log 5× 10^{-2} = 2- 0.7 = 1.3

   PH = 14 – 1.3 = 12.7

(b) POH = - log [OH$^-$] = -log 2.4 = - 0.38

   PH = 14 – (-0.38) = 14.38

(c) POH = - log [OH$^-$] = -log 3.7×10^{-3} = 3 – 0.57 = 2.43

   PH = 14 – 2.43 = 11.57

Q40: Calculate the hydrogen ion concentration of the solutions with the following pH values: **(a)** 3.47, **(b)** 0.20, **(c)** 8.60 ?

Solve: (a) [H$^+$] = 10^{-PH} = $10^{-3.47}$ = $10^{-4} \times 10^{0.53}$ = 3.4 × 10^{-4} M .

(b) $[H^+] = 10^{-PH} = 10^{-0.02} = 10^{-1} \times 10^{0.80} = 6.3 \times 10^{-1}$ M .

(c) $[H^+] = 10^{-PH} = 10^{-8.6} = 10^{-9} \times 10^{0.40} = 2.5 \times 10^{-9}$ M .

Q41: Calculate the pH and pOH of a solution obtained by mixing equal volumes of 0.10 M H_2SO_4 and 0.30 M NaOH ?

Solve:

Assume the volume = 1 ml

Excess of NaOH = mmole of NaOH – mmole of H_2SO_4

$$= 0.3 \times 1 \text{ ml} - 0.1 \times 1 \text{ ml} \times 2 = 0.1 \text{ mmole of NaOH}$$

M = mmole / V(ml) = 0.1 / 2 ml = 0.5 M .

POH = -log [OH⁻] = -log 5×10^{-2} = 2 – 0.7 = 1.3

PH = 14 – 1.3 = 12.70

42: Calculate the pH of a solution obtained by mixing equal volumes of a strong acid solution of pH 3.00 and a strong base solution of pH 12.00 ?

Solve:

Assume the volume = 1 ml

$[H^+] = 10^{-PH}$

$[H^+]$ of acid solution = 1.0×10^{-3} M .

$[H^+]$ of base solution = 1.0×10^{-12} M .

$[H^+][OH⁻] = 1.0 \times 10^{-14}$

$1.0 \times 10^{-12} [OH⁻] = 1.0 \times 10^{-14}$; $[OH⁻] = 1.0 \times 10^{-14} / 1.0 \times 10^{-12} = 1.0 \times 10^{-2}$ M .

Excess of base = mmole of NaOH – mmole of acid

$$= 1.0 \times 10^{-2} * 1 \text{ ml} - 1.0 \times 10^{-3} * 1 \text{ ml} = 9 / 2 \times 10^{-3} = 4.5 \times 10^{-3} \text{ M} .$$

POH = -log [OH⁻] = -log 4.5×10^{-3} = 3 – 0.65 = 2.35

PH = 14 – 2.35 = 11.65