4 Calculations Used in Analytical Chemisty

4A SOME IMPORTANT UNITS OF MEASUREMENT

4A-1 Sl Units

SI Base Units

Physical Quantity	Name of unit	Abbreviation
Mass	kilogram	**kg**
Length	meter	**m**
Time	second	**s**
Temperature	kelvin	**K**
Amout of substance	mole	**mol**
Electric current	ampere	**A**
Luminous intensity	candela	**cd**

International system of units (SI)

Prefixes for units

Prefix	Abbreviation	Multiplier
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

Prefix	Abbreviation	Multiplier
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}

angstrom (Å) : non-SI unit of length = 0.1 nm = 10^{-10} m.

4A-2 The Distinction Between Mass and Weight

Mass: invariant measure of the amount of matter in an object

Weight: the force of gravitational attraction between that matter and earth

$$W = m \times g$$

W : weight of an object, m : mass,
g : acceleration due to gravity

4A-3 The Mole

Avogadro's number (6.022×10^{23})

the molar mass of formaldehyde CH_2O

$$M_{CH_2O} = \frac{1\,\text{mol C}}{\text{mol } CH_2O} \times \frac{12.0\text{g}}{\text{molC}} + \frac{2\,\text{mol H}}{\text{mol } CH_2O} \times \frac{1.0\text{g}}{\text{molH}} + \frac{1\,\text{mol O}}{\text{mol } CH_2O} \times \frac{16.0\text{g}}{\text{molO}}$$

$= 30.0$ g/mol CH_2O

the molar mass of glucose $C_6H_{12}O_6$

$$M_{C_6H_{12}O_6} = \frac{6\,\text{mol C}}{\text{mol } CH_2O} \times \frac{12.0\text{g}}{\text{molC}} + \frac{12\,\text{mol H}}{\text{mol } CH_2O} \times \frac{1.0\text{g}}{\text{molH}} + \frac{6\,\text{mol O}}{\text{mol } CH_2O} \times \frac{16.0\text{g}}{\text{molO}}$$

$= 180.0$ g/mol $C_6H_{12}O_6$

*** Millimole(mmol) = 10^{-3} mol**
1 mfw = 10^{-3} fw

no. of moles of a species X (no. mol A): $n_X = \frac{m_X}{M_X}$

Ex. 4-1. How many moles and millimoles of benzoic acid (M=122.1 g/mol) are contained in 2.00 g of the pure acid?

amount g HBz = 2.00 g × (1 mol/122.1 g) = 0.0164 mol HBz
amount g HBz = 2.00 g × (1 mmol/0.1221 g) = 16.4 mmol HBz

Ex. 4-2. How many grams of Na^+ (22.99 g/mol) are contained in 25.00 g of Na_2SO_4 (142.0 g/mol)?

amount Na_2SO_4 = 25.00 g × (1 mol/142.0 g) = 0.17606 mol
since 1 mol of Na_2SO_4 contains 2 mol of Na^+,
amount Na^+ = 2 × 0.17606 mol = 0.35211 mol
mass Na^+ = 0.35211 mol × 22.99 g/mol = 8.10 g

4B SOLUTIONS AND THEIR CONCENTRATIONS
4B-1 Concentration of Solutions

Molar Concentration (C)

$$C_X = \frac{n_X}{V}, \quad molarity = M = \frac{\text{no. mol solute}}{\text{no. L solution}} = \frac{\text{no. mmol solute}}{\text{no. mL solution}}$$

Ex 4-3 Calculate the molar conc. of ethanol in an aqueous solution that contains 2.30 g of C_2H_5OH (46.07 g/mol) in 3.50 L of solution.

no. mol = 2.30 g × (1 mol/46.07 g) = 0.04992 mol

$C_{C_2H_5OH}$ = 0.04992 mol/3.50 L = 0.01426 mol/L = 0.0143 M

Analytical Molarity: total number of moles of a solute in 1 L solution

(How a solution has been prepared?)

Ex: 1.0 M H_2SO_4 soln → dissolving 1.0 mol or 98 g H_2SO_4 in water and diluting to exactly 1.0 L.

Equilibrium or Species Molarity: the molar conc. of a particular species in a soln. at equilibrium

Formal Concentration (Formality, F): analytical concentration

Ex: 1.00 F NaOH or H_2SO_4 → equilibrium molar conc. = 0.00 M

Ex 4-4. Calculate the analytical and equilibrium molar conc. of the solute species in an aqueous solution that contains 285 mg of trichloroacetic acid (Cl_3CCOOH, 163.4 g/mol) in 10.0 mL (the acid is 73 % ionized in water).

no. mol HA = 285 mg × (1 g/1000 mg) × (1 mol/163.4 g) = 1.744×10^{-3} mol

$$C_{HA} = \frac{1.744 \times 10^{-3}\ \text{mol HA}}{10.0\ \text{mL}} \times \frac{1000\ \text{mL}}{1\ \text{L}} = 0.174\frac{\text{mol HA}}{\text{L}} = 0.174\text{M}$$

	HA	⇔	H^+	+	A^-
Initial	100%		0%		0%
平衡後	27%		73%		73%

[HA] = 0.174 mol/L × 0.27 = 0.047 mol/L = 0.047 M

$[H_3O^+] = [A^-] = C_{HA} - [HA]$ = 0.174 - 0.047 = 0.127 M

Ex 4-5. Describe the preparation of 2.00 L of 0.108 M $BaCl_2$ from $BaCl_2 \cdot 2H_2O$ (244 g/mol).

2.00 L × 0.108 mol/L = 0.216 mol $BaCl_2 \cdot 2H_2O$

0.216 mol × 244 g/mol = 52.8 g $BaCl_2 \cdot 2H_2O$

Dissolve 52.8 g of $BaCl_2 \cdot 2H_2O$ in water and dilute to 2.00 L.

Ex 4-6. Describe the preparation of 500 mL of 0.074 M Cl^- from solid $BaCl_2 \cdot 2H_2O$ (244 g/mol).

$$\text{mass } BaCl_2 \cdot 2H_2O = \frac{0.0740 \text{ mol Cl}}{\text{L}} \times 0.500\text{ L} \times \frac{1 \text{ mol } BaCl_2 \cdot 2H_2O}{2 \text{ mol Cl}}$$

$$\times \frac{244.3 \text{ g } BaCl_2 \cdot 2H_2O}{\text{mol } BaCl_2 \cdot 2H_2O} = 4.52 \text{ g } BaCl_2 \cdot 2H_2O$$

Dissolve 4.52 g of $BaCl_2 \cdot 2H_2O$ in water and dilute to 500 mL.

Percent Concentration (%, parts per hundred)

$\text{weight \% (w/w)} = \frac{\text{weight solute}}{\text{weight solution}} \times 100\%$	37 % HCl (w/w) soln: 37 g HCl per 100 g soln. 70 % HNO_3 (w/w) soln
$\text{Volume \% (v/v)} = \frac{\text{volume solute}}{\text{volume solution}} \times 100\%$	5 % CH_3OH (v/v) soln: diluting 5.0mL CH_3OH with H_2O to 100mL.
$\text{weight/volume \% (w/v)} = \frac{\text{weight solute, g}}{\text{volume solution, mL}} \times 100\%$	5 %$AgNO_3$(w/v) soln: dissolving 5 g $AgNO_3$ in H_2O to 100 mL.

Parts Per Million and Parts Per Billion (ppm & ppb)

C_{ppm} = (mass of solute/ mass of soln) × 10^6 ppm   1 ppm = 1 mg/L

C_{ppb} = (mass of solute/mass of soln) × 10^9 ppb   1 ppb = 1 μg/L

C_{ppt} = (mass of solute/mass of soln) × 10^3 ppt

Ex 4-7. What is the molarity of K^+ in an aqueous solution that contains 63.3 ppm of $K_3Fe(CN)_6$ (329.2 g/mol).

C_{K^+} = 63.3 g/10^6 g × 10^3 g/L × (1 mol/329.2 g) × 3 = 5.77 × 10^{-4} M

Solution-Diluent Volume Ratios

1:4 : dilute one volume with three volumes.

p-Function or p-value

For chemical species X: $pX = -\log [X]$ $pH = -\log [H^+]$

Ex: 4-8. **2.00 × 10^{-3} M NaCl and 5.4 × 10^{-4} M HCl solution**

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

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

$pCl = -\log (2.00 \times 10^{-3} + 5.4 \times 10^{-4}) = -\log (2.54 \times 10^{-3}) = 2.595$

Ex: 4-9. Calculate the molar conc. of Ag^+ in a solution that has a pAg of 6.372.

$[Ag^+] = \text{antilog}(-6.372) = 4.25 \times 10^{-7}$

4B-2 Density and Specific Gravity of Solutions

***Density: mass per unit volume, kg/m^3, or g/mm^3. (kg/L or g/mL)**

***Specific Gravity:** the ratio of the mass of a substances to the mass of an equal volume of water (4 ℃).

Ex. 4-10. Calculate the molar conc. of HNO_3 (63.0 g/mol) in a soln that has a specific gravity of 1.42 and is 70 % HNO_3 (w/w).

$1.42\ Kg/L \times 10^3\ g/Kg \times 70 g/100 g = 994\ g/L$

$C_{HNO_3} = 994\ g/L \times (1\ mol/63.0\ g) = 15.8\ mol/L = 16\ M$

Ex. 4-11. Describe the preparation of 100 mL of 6.0 M HCl from a conc. reagent that has a specific gravity of 1.18 and is 37 % (w/w) HCl (36.5 g/mol).

$C_{HCl} = 1.18 \times 10^3\ g/L \times 37\ g/100\ g \times (1\ mol/36.5\ g) = 12.0\ M$

amount HCl = 100 mL × (1 L/1000 mL) × 6.0 mol/L = 0.600 mol

vol conc. reagent = 0.600 mol × (1 L/12.0 mol) = 0.0500 L

Dilute 50 mL of the conc. reagent to 100 mL.

Specific Gravities of Commercial Concentrated Acids and Bases

Reagent	Concentration % (w/w)	Specific Gravity
Acetic acid, CH_3COOH	**99.7**	**1.05**
Ammonia, NH_4OH	**29.0**	**0.90**
Hydrochloric acid, HCl	**37.2**	**1.19**
Hydrofluoric acid, HF	**49.5**	1.15
Nitric acid, HNO_3	**70.5**	**1.42**
Perchloric acid, $HClO_4$	**71.0**	**1.67**
Phosphoric acid, H_3PO_4	**86.0**	**1.71**
Sulfuric acid, H_2SO_4	**96.5**	**1.84**

4C CHEMICAL STOICHIOMETRY

Stoichiometry: the mass relationships among reacting chemical species.

4C-1 Empirical Formulas and Molecular Formulas

Empirical formula: the simplest whole-number ratio of atoms in a chemical compound.

Molecular formula: the number of atoms in a molecule.

Structural formula:

	Empirical formula	*Molecular formula*	*Structural formula*
formalaldehyde	CH_2O	CH_2O	HCHO
acetic acid	CH_2O	$C_2H_4O_2$	CH_3COOH
glyceraldehyde	CH_2O	$C_3H_6O_3$	
glucose	CH_2O	$C_6H_{12}O_6$	
ethanol		C_2H_6O	C_2H_5OH
Dimethyl ether		C_2H_6O	CH_3OCH_3

4C-2 Stoichiometric Calculations

Mass → **Moles** → **Moles** → **Mass**

(1) Formula weight; (2) Stoichiometric ratio; (3) Formula weight

Ex. 4-12. What Mass of $AgNO_3$ (169.9 g/mol) is needed to convert 2.33 g of Na_2CO_3 (106.0 g/mol) to Ag_2CO_3? (b) What mass of Ag_2CO_3 (275.7 g/mol) will be formed?

(a) $Na_2CO_3\ (aq) + 2\ AgNO_3\ (aq) \rightarrow Ag_2CO_3\ (s) + 2\ NaNO_3\ (aq)$

Step 1: $n_{Na_2CO_3} = 2.33\ g \times (1\ mol/106.0\ g) = 0.02198\ mol$

Step 2: $n_{AgNO_3} = 0.02198\ mol \times (2/1) = 0.04396\ mol\ AgNO_3$

Step 3: $m_{AgNO_3} = 0.04396\ mol \times 169.9\ g/mol =$ **7.47 g $AgNO_3$**

(b) $n_{Ag_2CO_3} = n_{Na_2CO_3} = 0.02198\ mol$

$m_{Ag_2CO_3} = 0.02198\ mol \times 275.7\ g/mol =$ **6.06 g Ag_2CO_3**

Ex. 4-13. **What mass of Ag_2CO_3 (275.7 g/mol) is formed when 25.0 mL of 0.200M $AgNO_3$ are mixed with 50.0 mL of 0.0800M Na_2CO_3 ?**

n_{AgNO_3} = 25.0 mL × 0.200 M $AgNO_3$ = 5.00 mmol $AgNO_3$

$n_{Na_2CO_3}$ = 50.0 mL × 0.0800 M Na_2CO_3 = 4.00 mmol Na_2CO_3

Na_2CO_3 (aq) + 2 $AgNO_3$ (aq) → Ag_2CO_3 (s) + 2 $NaNO_3$ (aq)

$m_{Ag_2CO_3}$ = 5.00 mmol × 1/2 × 0.2757 g /mmol = 0.689 g Ag_2CO_3

Ex. 4-14. **What will be the molar analytical Na_2CO_3 conc. in the soln produced when 25.0 mL of 0.200 M $AgNO_3$ is mixed with 50.0 mL of 0.0800 M Na_2CO_3?**

$n_{Na_2CO_3}$ = 4.00 mmol - (5.00 mmol × 1/2) = 1.50 mmol Na_2CO_3

$C_{Na_2CO_3}$ = 1.50 mmol/(50.0 + 25.0)mL = 0.0200 M Na_2CO_3