CHE 1000 – Introduction to Chemistry

Lecture notes on Stoichiometry and Gases

LECTURE 1

Stoichiometry – What is Stoichiometry?

Stoichiometry is a term derived from the Greek term *Stoicheion* meaning *element* and *metron* meaning *measure*.

Its used in chemistry to describe all quantitative aspects of chemical composition and reaction.

Measurements

A quantitative observation, or measurement, always consists of two parts: a number and a scale (called a unit). Both parts must be present for the measurement to be meaningful.

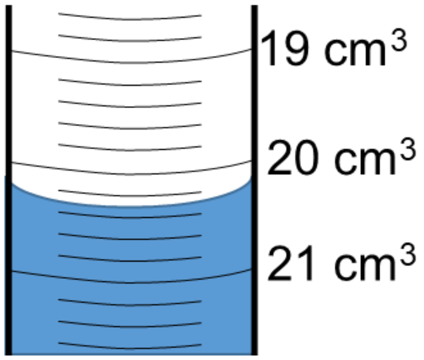
We measure volume, mass, temperature length, time electric current, amount of substance etc.

Elements in measured physical quantity

[Physical quantity] = [measurement] [prefix if necessary] [Unit]

Example volume of water is V= 25.00 mL

1.1 Significant figures in a measurement are a number of digits that are known with some degree of confidence
A burette reading 20.25 cm^3 can be reported as 20.24, 20.25, 20.26 cm^3 by 3 different students.



Student A 20.25 cm^3

Student B 20.24 cm^3

Student C 20.26 cm^3

The first 3 digits remain the same regardless of which student takes the reading. These are called CERTAIN and the last digit UNCERTAIN. We customarily report a measurement by recording all the certain digits plus the first uncertain digit.

Rules of significant figures

Rule 1

1.1 Digits 1-9 are always significant

1.2 Zeroes to the right of the significant digit after a decimal place are significant,.e.g. 25.00

1.3 Zeroes the right of significant digit are not significant e.g.2500

Rule 2

When adding or subtracting numbers, your answer can only have as many decimal places as the measurement having the least number of decimal places,

Example 2.2 + 4.53 = 6.73 and final answer = 6.7

Rule 3

When multiplying or dividing, your answer may only show as many significant figures showing the least number of significant digits.

Example number of mol n = 0.033 mol/L x 0.002500 L
= 0.00082500 mol
= 0.00083 mol to 2 sig fig.

Rule 4

The number in the conversion factors, molar masses, atomic masses, physical constants are considered to be exact, have more significant figures than shown and are not included in establishing the number of significant figures.

Example number of moles n= 0.2512 g/1.01g/ mol
= 0.2487129 mol
= 0.2487 mol

Rule 5
Rounding of Rule
If the digit next to the significant digit is smaller than 5, the significant digits is unchanged.
If the digit next to the significant digit is greater than 5, the significant digit is increased by one

Example 5.042 mol/L = 5.04 mol/L to 3 sig fig or 6. 47 g = 6.5 g to 2 sig fig

1.2 **Fundamental SI Unites (Base quantities and base Units)**

Base quantity	Symbol	Base unit	Symbol
1. length	l	meter	m
2. mass	m	kilogram	kg
3. time	t	second	s
4. Thermodynamic temperature	T	Kelvin	K
5. Electric current	I	ampere	A
6. Amount of substance	n	mole	mol
7. Luminous intensity	I_v	candela	cd

1.3 Non- SI Physical quantities in common use

Physical quantity	Symbol	Unit	Symbol	Conversion
Volume	V	Litre	L	$1L=10^{-3} m^3$
Length	l	angstrom	Å	$1Å=10^{-10}$ m
Pressure	P	atmosphere	atm	1 atm =101325Pa
		bar	bar	1bar= 100000 Pa
		torr	torr	1torr =133.24 Pa
		mmHg	mmHg	1 mmHg =133.25 Pa
Energy	E	Electron volt	eV	1 eV =1.601 $x10^{-19}$J
Temperature	t	Degree centigrade	°C	1°C= T-273.15 K
Concentration	c	Molarity	M	mol/L

1.4. Prefixes

Because the fundamental units are not always convenient (expressing the mass of a pin in kilograms is awkward), prefixes are used to change the size of the unit.

Exponential notation	Name	Symbol	Expanded form and meaning	US name
10^{12}	tera	T	1 000 000 000 000	trillion
10^{9}	giga	G	1 000 000 000	billion
10^{6}	mega	M	1 000 000	million
10^{3}	kilo	k	1 000	thousand
10^{2}	hecto	h	100	hundred
10^{1}	deca	da	10	ten
10^{0}			1	one
10^{-1}	deci	d	0.1	tenth
10^{-2}	centi	c	0.01	hundredth
10^{-3}	milli	m	0.001	thousandth
10^{-6}	micro	µ	0.000 001	millionth
10^{-9}	nano	n	0.000 000 001	billionth
10^{-12}	pico	p	0.000 000 000 001	trillionth
10^{-15}	femto	f	0.000 000 000 000 001	quadrillionth

Example Convert 5.01 mg to g expressing it in scientific notation

= 5.01×10^{-3} g.

Volume is very important in chemistry. Its not an SI unit but is derived from the SI unit, length (v = l x w x h).

Express 1L in dm^3, cm^3 m^3

10 cm = 1 dm, therefore $(10)^3\ cm^3 = (1)^3\ dm^3$

$1L = 1dm^3 = 1000\ cm^3$

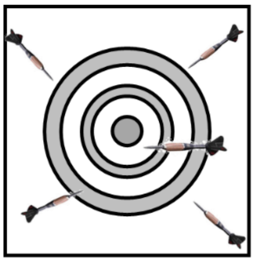
1m = 10 dm, therefore $1m^3 = (10)^3\ dm^3 = 1000\ dm^3$

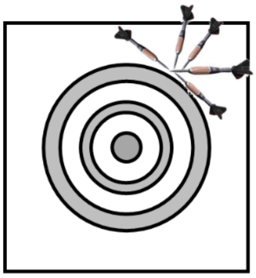
$1dm^3 = 1L = 1 \times 10^{-3}\ m^3$

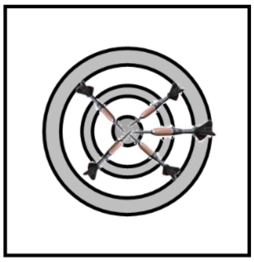
1.5 Precision and Accuracy

Precision indicates how close together or how repeatable the results of the measurement are to each other

Accuracy indicates the closeness of a measurement to a true value







Poor precision Poor Accuracy	Good precision Poor accuracy	Good precision Good accuracy

1.6 Dimensional analysis

Dimensional analysis is used to convert units to other units. We use the equivalence statement

Example

Convert 10 km to miles

Solution

We need to know the equivalence statements

1km = 1000 m, 1 m = 1.094 yards, 1 mi = 1760 yards (usually given)

Convert km to m i.e. $10\text{ km} \times \frac{1000\text{ m}}{\text{km}} = 1 \times 10^4\text{ m}$

Convert m to yards $1 \times 10^4\text{ m} \times \frac{1.094\text{ yard}}{\text{m}} = 1.094 \times 10^4\text{ yards}$

Finally, convert yards to miles $1.094 \times 10^4\text{ yards} \times \frac{1\text{ mi}}{1760\text{ yards}} = 6.22\text{ mi}$

LECTURE 2

2.1 Elementary idea of atoms, molecules and ions

All substances are made of atoms, molecules, and ions

2.2 Atomic structure

Each atom has a nucleus which consists of protons (p) and neutrons (n). Part of the mass of p, and n are used up as binding energy. Surrounding the nucleus are electrons in different shells.

Masses of p, n, e in kg and u(amu)

Particle	Mass in grams	Mass in unified mass unit, u
Electron	9.10956×10^{-28}	0.00054859
Proton (P)	1.67261×10^{-24}	1.007277
Neutron (N)	1.67492×10^{-24}	1.008665

1u = 1/ N_A =1.6605×10^{-24} g by definition

2.3 Isotopes, Atomic and molecular masses

Symbol for isotopes of element X, ${}^{A}_{Z}X$ A= Z +N

A= mass number

Z= number of protons = atomic number

N= number of neutrons

2.4 Isotopic mass, A_i,

Because of loss of mass to binding energy isotopic masses and % abundance are measured using a Mass Spectrometer (MS)

Atomic mass (u)

The units of atomic mass are in u (formerly a.m.u)

Physical scale of atomic masses of elements are based on the ${}^{12}_{6}C$, where the MS is calibrated to read the ${}^{12}_{6}C$ peak at exactly 12.0000 u

2.5 **Atomic mass (or atomic weight or relative atomic mass)**

The atomic mass, A, of an element is calculated as $A = \sum_{i=1}^{n} A_i f_i$ where f_i = % abundance/100 %

The atomic mass is the mass of **one** element

Example

The mass values for ^{63}Cu (69.09 %) and ^{65}Cu (30.91%) are 62.93 amu and 64.93 amu, respectively . Calculate the average atomic mass of copper

Solution

Average atomic mass = $\frac{69.09}{100} \times 62.93u + \frac{30.91}{100} \times 64.93u = 63.55$ u

2.6 Molecular mass (or molecular weight) is sum of the atomic masses of all the atoms in a molecule

2.7 **Definition of Avogadro number and Avogadro constant**

2.8 Avogadro constant

The Avogadro constant, N_A, is defined as the number of atoms or molecules, in one mole, that is the number of carbon in 12.0000 g of carbon-12.

N_A = 6.022 141 79 x10^{23} mol^{-1} to 9 sig. fig.

$N_A = 6.022 \times 10^{23} mol^{-1}$ to 4 sig. fig.

2.9 Formula for calculating mass of one atom of an element

$$m = 1.6605x10^{-24} \tfrac{g}{u} xA(u) = 1.6605x10^{=24} A\ g$$

Example

Calculate the mass of 6 atoms of Americium (Am)

Solution

1 atom of Am weighs 243 u

6 atoms = 6 x 243u/atom = 1.46 x 10^3 u

1 u= 1.6605 x 10^{-24}g

Mass = 1.66 x 10^{-24} g/u x 1.46 x 10^3 u = 2.42 x10^{-21} g

2.10 Formula for calculating mass of one mole of atoms

$$M = 1.6605x10^{-24} \tfrac{g}{u} xA(u)x6.22141x10^{23} mol^{-1} = A\, g\, mol^{-1}$$

M is called the **molar mass** with units of g mol^{-1}.

For molecules the molecular mass, M(u) is used in the above expressions

2.11 Ions

Ionic compounds such as NaCl exist as ion in solution

$NaCl(aq) = Na^+(aq) + Cl^-(aq)$

LECTURE 3

Mole and Mole concept

3.1 The Mole

The mole is defined as the amount of a substance that contains as many entities (such as atoms, molecules, ions, electrons, photons, protons etc) as there are in exactly 12 g of carbon-12 isotope.

One mole of something consists of 6.022×10^{23} units of that substance.

The following formulas can be used to calculate the number of moles, n, of a substance

1. $n = \frac{N}{N_A}$
2. $n = \frac{m}{M}$,   m = mass in grams, M = molar mass in g mol^{-1}.
3. $n = MV$ M = molarity in mol/L, V= volume in L for solutions
4. $n = \frac{PV}{RT}$ for ideal gases
5. $n = \frac{It}{F}$ I = current in ampre (C s^{-1}, t =time in s , F =96485 $Cmol^{-1}$ under Electrolysis

Examples

Calculate the number of moles for 5.00×10^{20} Co atoms

$$n=\frac{N}{N_A}=\frac{5.00\times 10^{20}\text{ atoms}}{6.02\times 10^{23}\text{ atoms/mol}}=8.30\times 10^{-4}\text{ mol Co}$$

How many mole are in 0.2512 g of hydrogen atoms sample

$$n = \frac{m\ (g)}{\text{molar mass g/mol}} = \frac{0.2512\ g}{1.01\ g/mol} = 0.2487\ mol$$

Calculate the number of moles of a gas at 1.5 atm in 8.56 L volume at 273 K.

$$n = \frac{PV}{RT} = \frac{1.5\ atm \times 8.56\ L}{0.08206\ L.\frac{atm}{K.mol} \times 273\ K} = 0.57\ mol$$

Home practice

Calculate the number of moles of 0.033 mol/L acid in 0.025 L solution

3.2 **Mole concept**

Mole concept provides a simple mole-mole relationship in:

1. Species in a molecular formula
2. Species in a balanced chemical reaction

Example

$$aA + bB \rightarrow cC + dD$$

Small letters a, b, c and d are the stoichiometric coefficient on the chemical species A, B, C and D respectively in a balanced chemical reaction (atoms on the LHS =atoms on RHS consequently mass is conserved)

$$\frac{n_A}{a} = \frac{n_B}{b} = \frac{n_C}{c} = \frac{n_D}{d}$$

Example 2

Calculate the number of moles of aluminum in 10 g sample

1 mol Al = 26.98 g

x mol $\longrightarrow$ 10 g

cross multiply and make x the subject of the formula

$$x = \frac{1\,mol\ Al\ \times 10g}{26.98\ g} = 0.371\ mol$$

Calculate the number of atoms in 10 g Al

10 g Al = 0.371 mol

1 mol Al atoms = 6.022×10^{23} atoms

0.371 mol $\longrightarrow$ x atoms

Cross multiply and make x the subject = 2.23×10^{23} atoms

How many Si atoms are present in 10 mg Si

1 mol Si = 6.022×10^{23} atoms = 28.09 g

28.09 g = 6.022×10^{23} atoms

10/1000 g $\longrightarrow$ x atoms

Cross multiply and solve for x = 2.14×10^{20} atoms

LECTURE 4

Chemical formula: Empirical, Molecular and Structural formulae

4.1 Empirical shows the simplest ratios of atoms in a chemical formula

Molecular formula shows the actual number of number of atoms in a given molecule

Structural formula shows spatial or geometric representation of a molecule in which the relative positions of the atoms are shown and the bonds are indicated by lines.

4.2 Determination of empirical, molecular formulae

One of the method of the empirical formula is determine products produced in a chemical reaction by gravimetric method or combustion reaction

The molecular formula is determined by performing an additional experiment on determining the molecular mass of the analyte.

Example

Cumene is a compound containing C and H that is used in the production of acetone and phenol in the chemical industry. Combustion of 47.6 mg of cumene produced some CO_2 and 42.8 mg water. The molar mass cumene is 125 g/mol. Determine the empirical and molecular formulas of cumene.

Solution

$$C_xH_y + O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

Stoichiometric equivalents

x atoms C y atoms H or on a mole ration x mol C and y mol H

molar mass of water 18.02 g/mol

Number of moles of water in 42.8mg = $n = \frac{\frac{42.8}{1000}g}{18.02g/mol} =$ $0.0023575\, mol$

1mol of H_2O yields 2mol H.

So 0.0023575 yields 2 x 0.002375 = 0.00475 mol.

Total number of moles of H = 0.00475 in cumene.

1mol H= 1.01 g so 0.00475mol = 0.00479g.

Mass of Carbon is total mass of cumene used minus mass of hydrogen i.e 0.0476-0.00478=0.04281 g

Moles of carbon = 0.04281/12.01 = 0.00356

	C	H
Mass in g	0.04281 g	0.00479 g
Mol	0.00356	0.00475
Mole ratio	1	1.333
Factor (3)	3	3.99≈4

Therefore, empirical formula is C_3H_4

Molecular formula is $(E.F)_n$=molar mass where n is a small whole number

$(C_3H_4)n=125$ $(40.07)n=125$

n= 125/40.07= 3.11 ≈3 therefore molecular formula is

C_9H_{12}

Molecular formulae from percentage composition

Percent composition

This is the quantitative approach to know the relative masses of elements in a compound.

% by mass of element=$\frac{mass\ of\ element}{mass\ of\ whole\ sample} \times 100\%$

Mass of element X=$\frac{A_X S_X}{M_Y} \times m_Y$

Where A_X= atomic mass of element X

S_X= stoichiometric coefficient of the element X

M_Y= molar mass of compound

m_Y= mass of compound

e.g in the combustion of m_{cpd} of $C_rH_sO_t$:

For product H_2O: m_Y = mass of H_2O produced, X= H, S_X =2 ,M_Y =18.02 u, A_X = 1.01 u

For product CO_2: m_Y = mass of CO_2 produced, X= C, S_X =1 ,M_Y =44.01 u, A_X = 12.01 u

For O: m_O= m_{cpd} - m_H + m_C

$$\%C = \frac{m_C}{m_{cpd}} \times 100\%$$

$$\%H = \frac{m_H}{m_{cpd}} \times 100\%$$

$$\%O = \frac{m_O}{m_{cpd}} \times 100\%$$

Example

A sample of a liquid with mass 8.657 g was decomposed into its elements and gave 5.217 g of carbon, 0.9620 g of hydrogen and 2.478 g of oxygen. What is the percentage composition and empirical formula for the compound?

Solution

$$\%C = \frac{m_C}{m_{cpd}} \times 100\% \Rightarrow \frac{5.217\ g}{8.657\ g} \times 100\% = 60.263\%\ C$$

$$\%H = \frac{m_H}{m_{cpd}} \times 100\% \Rightarrow \frac{0.9620\ g}{8.657\ g} \times 100\% = 11.112\%\ H$$

$$\%O = \frac{m_O}{m_{cpd}} \times 100\% \Rightarrow \frac{2.478\ g}{8.657\ g} \times 100\% = 28.624\%\ O$$

Total is 99.999% which if rounded off to 4 sig fig is 100.00%

Choosing a mass of 100 g, percentages are numerically equal to masses hence

	C	H	O
Mass in g	60.263 g	11.112 g	28.624 g
mol ($n = \frac{m\ (g)}{M\ (\frac{g}{mol})}$)	$\frac{60.263\ g}{12.01\ g/mol} = 5.0177$	$\frac{11.112\ g}{1.01\ g/mol} = 11.0019$	$\frac{28.624\ g}{16.00\ g/mol} = 1.789$
Mole ratio	$\frac{5.0177\ mol}{1.789\ mol} = 2.80$	$\frac{11.0019\ mol}{1.789\ mol} = 6.149$	$\frac{1.789\ mol}{1.789\ mol} = 1$
Factor (round off easily)	3	6	1

E.F = C_3H_6O

Percent yield

$$\% \, yield = \frac{actual \, yield \, from \, experiment}{Theoretical \, yield \, from \, balanced \, equation} \times 100\%$$

When potassium chromate (K_2CrO_4) is added to a solution containing 0.500 g silver nitrate ($AgNO_3$), solid silver chromate (Ag_2CrO_4) is formed.

a) Determine the theoretical yield of the silver chromate precipitate.

b) If 0.455 g of silver chromate is obtained, calculate the percent yield.

Solution

a) First write a balanced chemical equation

$K_2CrO_4(aq)$ + **2**$AgNO_3(aq) \rightarrow Ag_2CrO_4(s)$ + **2**$KNO_3(aq)$

$$n = \frac{0.5 \, g}{169.9 \frac{g}{mol}} = 2.943 \times 10^{-3} mol AgNO_3$$

2 mol $AgNO_3$ $\rightarrow$ 1 mol Ag_2CrO_4

2.943×10^{-3} mol $AgNO_3$ $\rightarrow$ *x* mol Ag_2CrO_4

Cross multiply and make *x* the subject = 1.47×10^{-3} mol Ag_2CrO_4

Theoretical yield = mol Ag_2CrO_4 x molar mass of Ag_2CrO_4

1.47×10^{-3} mol x 331.7 g/mol = **0.488 g**

b)

$$\% \, yield = \frac{0.455}{0.488} \times 100\% = 93.2 \, \%$$

LECTURE 5

Limiting and Excesses reagent

5.1 Limiting reagent and excess reagent

A limiting reagent is a reactant that will be exhausted in a chemical reaction and the reaction will stop.
The limiting reagent determines how much part of the excess reagent will be used up and how much of the products are to be formed.

An excess reagent is a reactant that will remain in excess after the reaction has stopped

5.2 Finding the limiting reagent in a reaction below

$$aA + bB \rightarrow cC + dD$$

1. From data given in the question calculate, n_A and n_B
2. Calculate $R_A = n_A/a$ and $R_B = n_B/b$
3. If $R_A < R_B$ then A is a limiting reagent
4. Perform mole concept based on the limiting reagent

Example

Hydrogen cyanide is produced industrially from the reaction of gaseous ammonia, oxygen and methane:

$$2NH_3(g) + 3O_2(g) + 2CH_4(g) \rightarrow 2HCN(g) + 6H_2O(g)$$

If 5.00 x 10^3 kg each NH_3, O_2 and CH_4 are reacted, what mass of HCN and of H_2O will be produced, assuming 100% yield?

$$n_{NH_3} = \frac{5.00 \times 10^3\ kg \times 10^3 g/kg}{17.04\ g/mol} = 2.934 \times 10^5\ mol$$

$$R_{NH_3} = \frac{n_{NH_3}}{2} = \frac{2.934 \times 10^5}{2} = 1.467 \times 10^5$$

$$n_{O_2} = \frac{5.00 \times 10^3\ kg \times 10^3 g/kg}{32.00\ g/mol} = 1.5625 \times 10^5\, mol$$

$$R_{O_2} = \frac{n_{O_2}}{3} = \frac{1.5625 \times 10^5}{3} = 5.2083 \times 10^4$$

$$n_{CH_4} = \frac{5.00 \times 10^3\ kg \times 10^3 g/kg}{16.05\ g/mol} = 3.115 \times 10^5\, mol$$

$$R_{CH_4} = \frac{n_{CH_4}}{2} = \frac{3.115 \times 10^5}{2} = 1.5575 \times 10^5$$

- $R_{O_2} < R_{NH_3} < R_{CH_4}$

O_2 is the limiting reagent and must be used for calculating other amounts

3 mol O_2 → 2 mol HCN

1.5625×10^5 mol → x

$$x = \frac{2\ mol\ HCN \times 1.5625 \times 10^5\ \cancel{mol\ O_2}}{3\ \cancel{mol\ O_2}} = 1.0416 \times 10^5\, mol\ HCN$$

Mass of HCN = $1.0416 \times 10^5 \times 27.03$ g/mol = 2.815×10^6 g

3 mol O_2 → 6 mol H_2O

1.5625×10^5 mol → y

$$y = \frac{6\ mol\ H_2O \times 1.5625 \times 10^5\ \cancel{mol\ O_2}}{3\ \cancel{mol\ O_2}} = 3.125 \times 10^5\, mol\ H_2O$$

Mass of HCN = $3.125 \times 10^5 \times 18.02$ g/mol = 5.631×10^6 g

LECTURE 6

Solution stoichiometry

Molarity is defined as the number of moles of a substance in 1 liter or solution

$$M = \frac{moles\ (n)}{Volume\ (mol/L)}$$

Units of M is mol L^{-1}.

Dilution= changing concentration from high to low in a given volume

$$n_i = M_i V_i = M_d V_d = n_d$$

Reactions in solutions

1. Acid-base reactions

Bronsted-Lowry definition of acids and bases

An acid is a proton donor

A base is a proton acceptor

Acid-base reaction always occurs together, as in the example below:

HCl(aq) + NaOH(aq) →NaCl(aq)+H_2O(l)

2. Precipitation reactions

Na_2SO_4(aq)+ $BaCl_2$(aq)= $BaCl_2$(s)+2NaCl(aq)   molecular rxn

$2Na^+(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2Cl^-(aq) \rightarrow BaSO_4(s) + 2Na^+(aq) + 2Cl^-(aq)$ ionic rxn

$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$ net ion rxn

3. **Reduction-oxidation (Redox) reaction**

A Reduction-oxidation reaction or Redox reaction is an electron transfer reaction between electrons in one half-reaction to the other half reaction.

Oxidation reaction and reduction reactions always occurs together.
Redox reaction involves change in oxidation number of one of the atoms in each half-reaction.
In a reduction reaction the oxidation number of one of the atoms in the half-reaction decreases. The reactant in the reduction reaction is called an oxidant or oxidizing reagent.

In an oxidation reaction, the oxidation number of one of the atoms in the half-reaction increases. The reactant in the oxidation reaction is called a reductant or reducing reagent.

Rules for Assigning Oxidation numbers

Compound	**Oxidation number = ON**	**Exception**
1, Pure elements	+0	
2. Monoatomic ion	±z, z = charge on the ion	
3. Polyatomic ion	Sum of ON = ±z	
4. F in compounds	-1	
5. H in compounds	+1	H^- = -1
6. O in compounds	-2	H_2O_2 = -1
7. Neutral molecules	Sum of ON= 0	
8. Diatomics, Cl_2,O_2,N_2, etc.	0	
9. Group I element	+1	
10 Group II element	+2	
11. C in compounds	-4 to +4	

Steps for balancing Redox reactions by Ion-electron method

Example

Balance the following redox reaction in an acidic media

$$Cr_2O_7^{2-}(aq) + CH_3CH_2OH(aq) \rightarrow Cr^{3+}(aq) + CO_2(g) + H_2O(l)$$

Step 1: Divide reaction into half reactions, and assign the oxidation numbers

+6 -2 +3

$Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$ Reduction half reaction

-2 +1 -2 +1 -2 +1 +2 -2 +1 -2

$C\ \ H_3\ C\ \ H_2\ O\ \ H(aq) \rightarrow C\ \ O_2(g) + H_2\ O(l)$ Oxidation half reaction

The number in bracket is the ON, and outside the bracket is the coefficient on the element

Step 2: Balance atoms other than H and O

$$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$$

$$CH_3CH_2OH(aq) \rightarrow 2CO_2(g) + H_2O(l)$$

Step 3: Balance O by adding H_2O on the side deficient with O

$$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(\mathrm{l})$$

$$CH_3CH_2OH(aq) + 4H_2O(\mathrm{l}) \rightarrow 2CO_2(g) + H_2O(l)$$

$$CH_3CH_2OH(aq) + 3H_2O(\mathrm{l}) \rightarrow 2CO_2(g)$$

Step 4: Balance H by adding H^+

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O$$

$$CH_3CH_2OH(aq) + 3H_2O(\mathrm{l}) \rightarrow 2CO_2(g) + 12H^+(aq)$$

Step 5: Balance net charge by adding electrons to the side with more positive charges

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

(-2)1 (+1)14 (-1)6 = (+3)2

$$CH_3CH_2OH(aq) + 3H_2O(\text{l}) \rightarrow 2CO_2(g) + 12H^+(aq) + 12e^-$$

0 0 0 (+)12 (-1)12

Step 6: Balance electron gain = electron loss, and add the two half-reactions

$$2 \times [Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O]$$

$$1 \times [CH_3CH_2OH(aq) + 3H_2O(\text{l}) \rightarrow 2CO_2(g) + 12H^+(aq) + 12e^-]$$

$$2Cr_2O_7^{2-}(aq) + 28H^+(aq) + 12e^- \rightarrow 4Cr^{3+}(aq) + 14H_2O$$

$$CH_3CH_2OH(aq) + 3H_2O(\text{l}) \rightarrow 2CO_2(g) + 12H^+(aq) + 12e^-$$

$$\mathbf{2}Cr_2O_7^{2-}(aq) + CH_3CH_2OH(aq) + \mathbf{28}H^+(aq) + \mathbf{3}H_2O(l) \rightarrow \mathbf{4}Cr^{3+}(aq) + \mathbf{2}CO_2(g) + \mathbf{14}H_2O(l) + \mathbf{12}H^+(aq)$$

Step 7: Cancel anything that is common on both sides of the equation

$$2Cr_2O_7^{2-}(aq) + CH_3CH_2OH(aq) + 16H^+(aq) \rightarrow 4Cr^{3+}(aq) + 2CO_2(g) + 11H_2O(l)$$

Steps for balancing Redox reaction in basic media

Follow steps 1- 7 and add the following additional steps:

Step 8: Add on both sides of the equation the same number of OH^- to eliminate H^+ in step 7

$$2Cr_2O_7^{2-}(aq) + CH_3CH_2OH(aq) + 16H^+(aq) + 16OH^-(aq) \rightarrow 4Cr^{3+}(aq) + 2CO_2(g) + 11H_2O(l) + 16OH^-(aq)$$

Step 9: Combine OH^- and H^+ to form water

$$2Cr_2O_7^{2-}(aq) + CH_3CH_2OH(aq) + 16H_2O(l) \rightarrow 4Cr^{3+}(aq) + 2CO_2(g) + 11H_2O(l) + 16OH^-(aq)$$

Step10: Cancel any water that you can.

$$2Cr_2O_7^{2-}(aq) + CH_3CH_2OH(aq) + 5H_2O(l) \rightarrow 4Cr^{3+}(aq) + 2CO_2(g) + 16OH^-(aq)$$

Take home practice questions

Balance the following in acidic media

$$MnO_4^-(aq) + ClO_3^-(aq) \rightarrow ClO_4^-(aq) + Mn^{2+}(aq) + H_2O(l)$$

Solution

$$2MnO_4^-(aq) + 16H^+(aq) + 10e^- \rightarrow 2Mn^{2+}(aq) + 8H_2O(l)$$

$$5ClO_3^-(aq) + 5H_2O(l) \rightarrow 5ClO_4^-(aq) + 10H^+(aq) + 10e^-$$

$$\mathbf{2MnO_4^-(aq) + 5ClO_3^-(aq) + 6H^+(aq) \rightarrow 5ClO_4^-(aq) + 2Mn^{2+}(aq) + 3H_2O(l)}$$

Balance the following in basic media

$$Ag(s) + CN^-(aq) + O_2(g) \rightarrow Ag(CN)_2^-(aq)$$

Solution

$$4Ag(s) + 8CN^-(aq) \rightarrow 4Ag(CN)_2^-(aq) + 4e^-$$

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$$

$4Ag(s) + 8CN^-(aq) + O_2(g) + 4H^+(aq) \rightarrow 4Ag(CN)_2^-(aq) + 2H_2O(l)$ as in acidic media

$$4Ag(s) + 8CN^-(aq) + O_2(g) + 4H^+(aq) + 4OH^-(aq) \rightarrow 4Ag(CN)_2^-(aq) + 2H_2O(l) + 4OH^-(aq)$$

$$4Ag(s) + 8CN^-(aq) + O_2(g) + 4H_2O(l) \rightarrow 4Ag(CN)_2^-(aq) + 2H_2O(l) + 4OH^-(aq)$$

$$\mathbf{4Ag(s) + 8CN^-(aq) + O_2(g) + 4H_2O(l) \rightarrow 4Ag(CN)_2^-(aq) + 4OH^-(aq)}$$

Students should ask tutors if they fail

LECTURE 7

TITRATIONS

7.1 Titration is a chemical analysis method in which the quantity of the sample (analyte) is determined by placing it in the conical flask and after stepwise addition of a standardized solution from the burette, the end-point is reached.

The end point is determined by adding an indicator to the analyte solution. Some redox titration reactions are self-indicating. The molarity of the standardized solution, M_s, is known, and the volume of the titre, V_s, is found at the end-point.

7.1 Forward or Normal Titration

They are of two types:

1. Single reaction

   Here the analyte and the titrant are in a single reaction

$$\underset{\text{standard}}{MnO_4^-(aq)} + \underset{\text{analyte}}{5Fe^{2+}(aq)} + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$$

2. Sequence of reactions

   Here the analyte and the titrant are in separate reaction reactions

$$\underset{\text{analyte}}{Mn_2O_7(s)} + H_2O(l) \rightarrow MnO_4^-(aq) + 2H^+(aq)$$

$$MnO_4^-(aq) + \underset{\text{standard}}{5C_2O_4^-(aq)} + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O + 10CO_2(g)$$

Note that the molarity of the std $M_{C_2O_4^{2-}}$ and the volume of the titre $V_{C_2O_4^{2-}}$ found at the end-point are known

Steps in the calculation are:

1. $n_{C_2O_4^{2-}} = M_{C_2O_4^{2-}} V_{C_2O_4^{2-}}$

2. $\frac{n_{C_2O_4^{2-}}}{5} = \frac{n_{MnO_4^-}}{1}$

3. $\frac{n_{MnO_4^-}}{1} = \frac{n_{Mn_2O_7((s)}}{1}$

7.2 Back Titration

Back titration is carried on the excess moles of the excess reagent left after the completion of the reaction.

Here the analyte is the limiting reagent.

The excess reagent left after the completion of the reaction is titrated using a suitable standard.

Example

A 0.2719 g sample containing $CaCO_3$ reacted with 20.00 mL of 0.2254 M HCl. The excess HCl required exactly 20.00 mL of 0.1041 M NaOH to reach the phenophalene end point. Determine percent $CaCO_3$ in the sample. The reaction involved is

$$\underset{\text{resgent}}{\underset{\text{limiting}}{CaCO_3(s)}} + \underset{\text{reagent}}{\underset{\text{excess}}{2HCl(aq)}} \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

The titration reaction is

$$\underset{\text{left}}{\underset{\text{excess}}{HCl(aq)}} + \underset{\text{standard}}{NaOH(aq)} \rightarrow NaCl(aq) + H_2O(l)$$

1. Start calculation from the titration rxn

$$\frac{n_{HCl,excess}}{1} = \frac{n_{NaOH}}{1}$$

2. Calculate the initial moles of HCl

$n_{HCl,initial}$

3. Calculate moles of HCl that reacted with $CaCO_3$

$$n_{HCl,reacted} = n_{HCl,initial} - n_{HCl,excess}$$

4. $$\frac{n_{HCl,reacted}}{2} = \frac{n_{CaCO_3}}{1}$$

5. From n_{CaCO_3} calculate mass of $CaCO_3$ and percent