RMIT
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Student Services

Student Learning Centre

Chemistry 'Know-How' Program

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Course Notes & Question Sheets

Adjunct Professor Colin Rix

Chemistry Bridging Program (2017)   Major Topics for Discussion

Adjunct Prof. Colin Rix

Topic 1 :   Atoms & Atomic Structure; the Periodic Table

(Use of P.T. to summarise and systematise chemical & physical properties, eg electronegativity, size & charge, Group and Periodic trends)

Topic 2 :   Electron configurations of atoms / ions

(Relationship to P.T. ; formation of cations & anions)

Topic 3 :   Chemical Bonding, Lewis electron-dot model, Bond types, Polarity, oxidation states, solubility rule

(Molecular structure, intra- and inter- molecular bonding)

Topic 4 :   The Mole and chemical stoichiometry

(Molar amounts of solids and liquids, the molar volume of a gas)

Topic 5 :   Aqueous Solutions, solvents/solutes

(%w/v, %w/w, molarity, dilution , ppm, ppb, molality, p-notation)

Topic 6 :   Chemical reactions-balancing chemical reactions/ stoichiometry
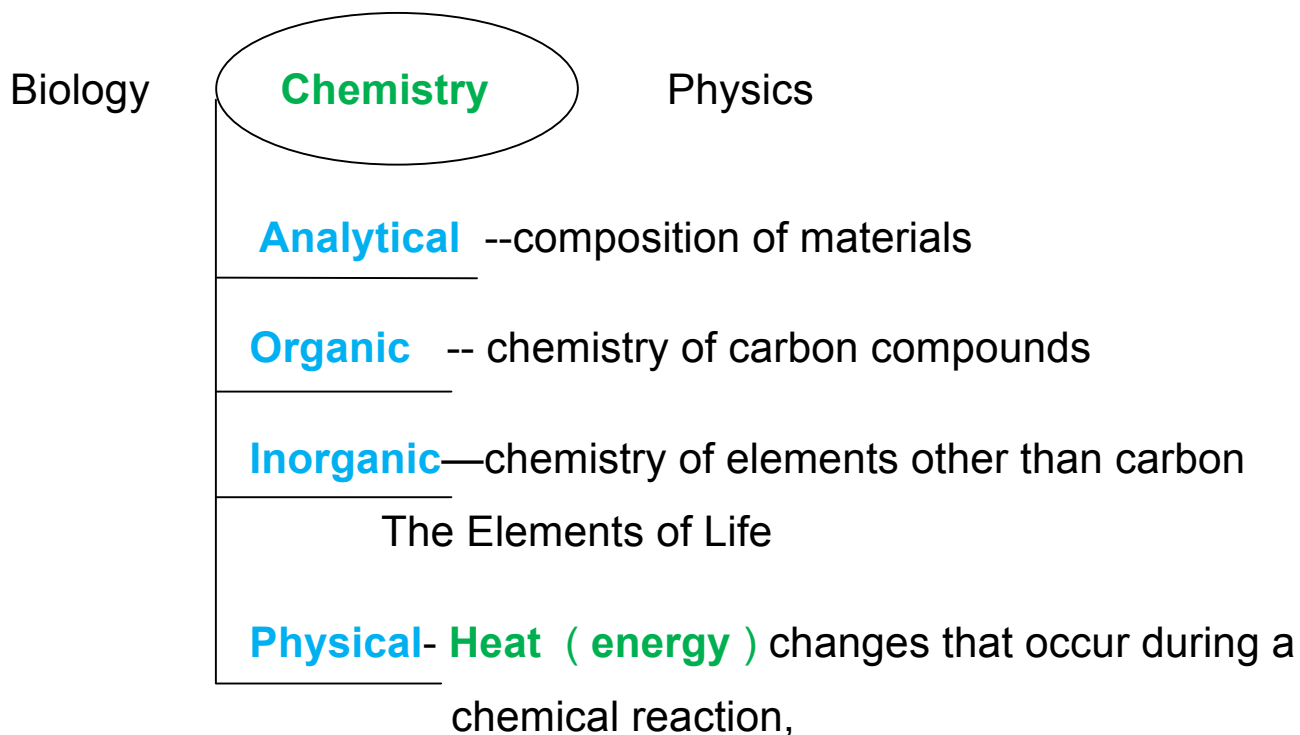
(Simple strategies, acid/base, redox processes)

Topic 7 :   Titrations & reaction stoichiometry, Back titrations

(Practical aspects)

- **Some extension problems**

- **Selected Chemistry & Physics Web sites**

- **Revision Question Sheets**

- **Periodic Table**

WHAT IS CHEMISTRY ABOUT ?

A study of **ATOMS** of **ELEMENTS** (C, Na) or **MOLECULES** of **ELEMENTS** (O_2 , Cl_2, H_2) when they combine to form **COMPOUNDS** containing **MOLECULES** (H_2O, CH_4) or **IONS** (Na^+Cl^-); and, examining the behaviour of such **MATERIALS** so their **CHEMICAL STRUCTURES** can be related to their properties and **FUNCTION**.

Biology   **Chemistry**   Physics

   Analytical --composition of materials

   Organic -- chemistry of carbon compounds

   Inorganic—chemistry of elements other than carbon

     The Elements of Life

   Physical- **Heat** (**energy**) changes that occur during a chemical reaction,

     Reaction "completeness" – **Chemical Equilibrium**

     Kinetics, speeding up or slowing down a chemical reaction (catalysts and inhibitors)

     Mechanism, **structural chemistry** — molecularly engineered reaction sites in enzymes.

Topic 1 : Atoms & Atomic Structure; the Periodic Table

(Use of P.T. to summarise and systematise chemical & physical properties, eg electronegativity, size and charge; Group and Periodic trends)

Chemical symbols, the Periodic table

Matter = Elements, Compounds or mixtures may exist as Solids, Liquids or Gases.

Atoms, Molecules, are uncharged species, eg., He H_2 O_2 CO_2 C_8H_{18}, CH_3COOH, C_2H_5OH

Ions are charged particles, eg., Na^+ Ca^{2+} NH_4^+ Cl^- NO_3^- SO_4^{2-}

Structure of atom

Bohr planetary model (electron treated as a particle) nucleus contains <u>protons (+ve) p</u> and <u>neutrons (neutral) n</u> surrounded by <u>orbiting electrons (-ve) e</u>.
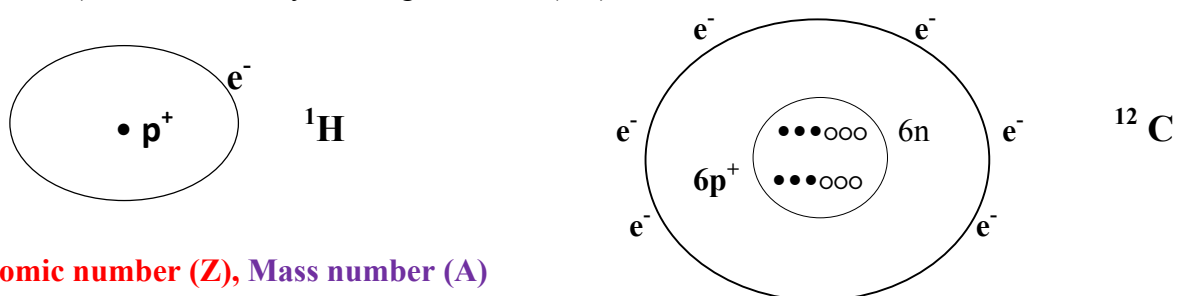
Atomic number (Z), Mass number (A)

Isotopes eg., hydrogen $_1H$ deuterium (D) $_1H$ tritium (T) $_1H$

^{12}C (99%) ^{13}C (1%) ^{14}C

Electronegativity (EN), *the power of an atom to attract electrons.* Atoms at top right of Periodic Table have **largest EN** and so attract electrons strongly to **form anions**, whilst those at bottom left have *smallest EN* and readily give up electrons to *form cations*.

| Group | 1 2 | Transition metals | 3 4 5 6 7 8 |

LOW EN

Lose $e^{-'s}$
Form **cations**

M^{n+}

Usually +1, +2 or +3 **Cations** M^{n+}

Also **oxo-anions** eg MnO_4^-

HIGH EN

Gain $e^{-'s}$
Form **anions**

X^{a-}

SIZE of atoms and ions :
INCREASES *down a Group* (vertical column) due to electrons entering a new shell,
but *DECREASES across a Period* (horizontal row) due to increasing nuclear charge.

Common Ions

Cations	Transition metals	Anions

H^+ Li^+ Cr^{2+} Cr^{3+} Mn^{2+} F^- Cl^- Br^- I^- (halide) OH^- (hydroxide)

Fe^{2+} Fe^{3+} O^{2-} (oxide) S^{2-} (sulphide)

Co^{2+} Co^{3+} CO_3^{2-} (carbonate) HCO_3^- (bicarbonate)

Na^+ K^+ Ni^{2+} SiO_4^{4-} (silicate) PO_4^{3-} (phosphate)

Cs^+ Cu^+ Cu^{2+} NO_2^- (nitrite) NO_3^- (nitrate)

Mg^{2+} Ca^{2+} Zn^{2+} Ag^+ SO_3^{2-} (sulphite) SO_4^{2-} (sulphate)

Ba^{2+} MnO_4^{1-}(permanganate, purple)

NH_4^+ (ammonium) CrO_4^{2-} (chromate, yellow) $Cr_2O_7^{2-}$ (dichromate, orange)

OCl^- (hypochlorite) ClO_2^- (chlorite) ClO_3^- (chlorate)

ClO_4^- (perchlorate) IO_3^- (iodate)

COMMON COMPOUNDS

|		
Sodium hydroxide	Na^+OH^-	**caustic soda (a strong base)**
Potassium hydroxide	K^+OH^-	**caustic potash (a strong base)**
Sodium chloride	Na^+Cl^-	**table salt**
Magnesium sulphate	$Mg^{2+}SO_4^{2-}$	**Epsom salts**
Calcium sulphate	$Ca^{2+}SO_4^{2-}$	**gypsum, plaster of Paris**
Calcium phosphate	$Ca^{2+}_3 (PO_4^{3-})_2$	**bones/teeth**
Ammonium nitrate	$NH_4^+NO_3^-$	**fertilizer**
Ammonium sulphate	$(NH_4^+)_2 SO_4^{2-}$	**fertilizer**
Sodium carbonate	$(Na^+)_2CO_3^{2-}$	**washing soda**
Sodium bicarbonate	$Na^+HCO_3^-$	**cooking soda, bicarb soda**
Potassium iodate	$K^+IO_3^-$	**an oxidant**
Potassium permanganate	$K^+MnO_4^-$	**'condy's crystals' an oxidant**
Potassium dichromate	$(K^+)_2Cr_2O_7^{2-}$	**an oxidant**
Sodium hypochlorite	Na^+OCl^-	**'pool chlorine'**
Iron(III)oxide	$(Fe^{3+})_2(O^{2-})_3$	**'rust'**
Hydrochloric acid	HCl	**pool acid**
Nitric acid	HNO_3	**powerful oxidizing acid**
Sulphuric acid	H_2SO_4	**battery acid**
Phosphoric acid	H_3PO_4	**rust protector**
Methane	CH_4	natural gas
Methanol	CH_3OH	'wood alcohol'
Ethanol	C_2H_5OH	'alcohol' ethyl alcohol
Acetic acid	CH_3COOH	vinegar
Ammonia	NH_3	**cleaning products, refrigerant**
Hydrogen sulphide	H_2S	**''Rotten egg gas''**

Topic 2 : Electron configurations of atoms / ions

(Relationship to position in P.T.; formation of cations & anions)

Bohr planetary (particle) model $E_n = -R / n^2$ n = principal quantum number

(max number of electrons per shell = $2.n^2$, so for n=1, 2e⁻   n=2, 8e⁻   n=3, 18 e⁻ etc)

Schrodinger's wave mechanical model (electron behaving as a wave) (wave functions, Ψ)
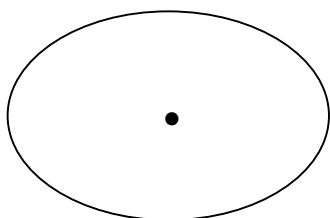
The **four quantum numbers** :

n = principal quantum number, n = 1, 2,3 …..;
Gives the ENERGY of the electron shell via, $E_n = -R/n^2$

ℓ = orbital quantum number, ℓ = 0, 1, 2… (n-1);
Gives the SHAPE of the sub-shell electron cloud (orbital shape)
 ℓ = 0 = s-orbital, spherical; ℓ = 1= p-orbital, dumbbell shape , ℓ = 2 =d-orbital

$m_ℓ$ = magnetic quantum number, $m_ℓ$ = 0, ±1, ±2….± ℓ ;
Gives the NUMBER OF ORBITALS in the sub-shell and their orientation in space
$m_ℓ$ = 0, ONE s-orbital, $m_ℓ$ = 0, ±1, THREE p-orbitals $m_ℓ$ = 0, ±1, ±2, FIVE d-orbitals

m_s = SPIN quantum number, m_s = +½ or -½.

Eg. If **n = 2**, then **ℓ = 0** or 1, and for **ℓ = 0**, **$m_ℓ$ = 0** ; and for **ℓ = 1**, **$m_ℓ$ = 0 +1 -1**,

For **ℓ = 0**, **$m_ℓ$ = 0** only : this defines **one** orbital – in this case the *2s-orbital*.
For **ℓ = 1**, **$m_ℓ$ = 0, +1 or -1** only; this defines **3 separate** orbitals – in this case the three *2p-orbitals*.
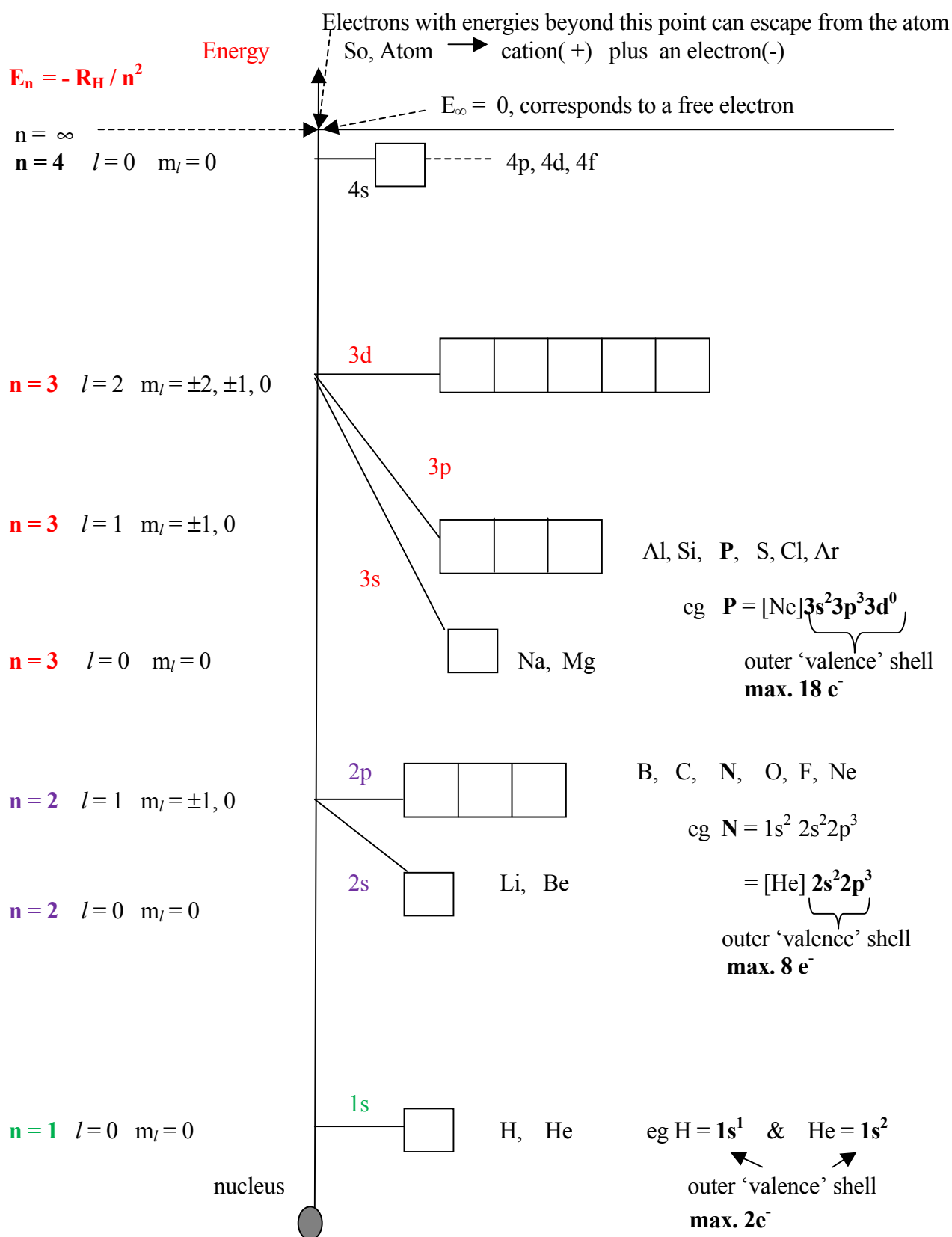
See next page (7) for the shapes of s- p- and d-atomic orbitals.

The arrangement of electron shells and sub-shells are shown on page 8 along with the electron configurations of atoms.

SHAPES OF ATOMIC ORBITALS

1s   2S

$2P_x$ $2P_y$ $2P_z$

$3d_{xy}$ $3d_{xz}$ $3d_{yz}$

$3d_{z^2}$ $3d_{x^2-y^2}$

FOR A **MULTI-ELECTRON ATOM**, we can plot this as shown below :

Electrons with energies beyond this point can escape from the atom

Energy

So, Atom ⟶ cation(+) plus an electron(-)

$E_n = -R_H / n^2$

$E_\infty = 0$, corresponds to a free electron

n = ∞

n = 4 $l = 0$ $m_l = 0$

4s ----- 4p, 4d, 4f

3d

n = 3 $l = 2$ $m_l = \pm 2, \pm 1, 0$

3p

n = 3 $l = 1$ $m_l = \pm 1, 0$

3s

Al, Si, **P**, S, Cl, Ar

eg **P** = [Ne]$\mathbf{3s^2 3p^3 3d^0}$

n = 3 $l = 0$ $m_l = 0$ Na, Mg

outer 'valence' shell
max. 18 e⁻

2p

B, C, **N**, O, F, Ne

n = 2 $l = 1$ $m_l = \pm 1, 0$

eg **N** = $1s^2\ 2s^2 2p^3$

2s   Li, Be

= [He] $\mathbf{2s^2 2p^3}$

n = 2 $l = 0$ $m_l = 0$

outer 'valence' shell
max. 8 e⁻

1s

n = 1 $l = 0$ $m_l = 0$ H, He

eg H = $\mathbf{1s^1}$ & He = $\mathbf{1s^2}$

nucleus

outer 'valence' shell
max. 2e⁻

Note how the filling of the orbitals gives rise to the layout of the Periodic Table shown on the next page.

The Modern Periodic Table of the Elements

GROUP NUMBER = Number of outer shell electrons

Legend:
- Element name → Mercury
- Atomic # → 80
- Symbol → **Hg**
- 200.59 ← Avg. Mass
- Electronegativity → 1.9 (The power to attract electrons)

 # VIII / 18 → INERT GASES — Very Stable electron configuration in outer shell ($8e^-$) ($2e^-$ for He)

I (1)	II (2)	III (3)	4	5	6	7	8	9	10	11	12	III (13)	IV (14)	V (15)	VI (16)	VII (17)	VIII (18)
Hydrogen 1 **H** 1.01 2.1																	Helium 2 **He** 4.00 --
Lithium 3 **Li** 6.94 1.0	Beryllium 4 **Be** 9.01 1.5											Boron 5 **B** 10.81 2.0	Carbon 6 **C** 12.01 2.5	Nitrogen 7 **N** 14.01 3.0	Oxygen 8 **O** 16.00 3.5	Fluorine 9 **F** 19.00 4.0	Neon 10 **Ne** 20.18 --
Sodium 11 **Na** 22.99 0.9	Magnesium 12 **Mg** 24.31 1.2											Aluminum 13 **Al** 26.98 1.5	Silicon 14 **Si** 28.09 1.8	Phosphorus 15 **P** 30.97 2.1	Sulfur 16 **S** 32.07 2.5	Chlorine 17 **Cl** 35.45 3.0	Argon 18 **Ar** 39.95 --
Potassium 19 **K** 39.10 0.8	Calcium 20 **Ca** 40.08 1.0	Scandium 21 **Sc** 44.96 1.3	Titanium 22 **Ti** 47.88 1.5	Vanadium 23 **V** 50.94 1.6	Chromium 24 **Cr** 52.00 1.6	Manganese 25 **Mn** 54.94 1.5	Iron 26 **Fe** 55.85 1.8	Cobalt 27 **Co** 58.93 1.8	Nickel 28 **Ni** 58.69 1.8	Copper 29 **Cu** 63.55 1.9	Zinc 30 **Zn** 65.39 1.6	Gallium 31 **Ga** 69.72 1.6	Germanium 32 **Ge** 72.61 1.8	Arsenic 33 **As** 74.92 2.0	Selenium 34 **Se** 78.96 2.4	Bromine 35 **Br** 79.90 2.8	Krypton 36 **Kr** 83.80 3.0
Rubidium 37 **Rb** 85.47 0.8	Strontium 38 **Sr** 87.62 1.0	Yttrium 39 **Y** 88.91 1.2	Zirconium 40 **Zr** 91.22 1.4	Niobium 41 **Nb** 92.91 1.6	Molybdenum 42 **Mo** 95.94 1.8	Technetium 43 **Tc** (98) 1.9	Ruthenium 44 **Ru** 101.07 2.2	Rhodium 45 **Rh** 102.91 2.2	Palladium 46 **Pd** 106.42 2.2	Silver 47 **Ag** 107.87 1.9	Cadmium 48 **Cd** 112.41 1.7	Indium 49 **In** 114.82 1.7	Tin 50 **Sn** 118.71 1.8	Antimony 51 **Sb** 121.76 1.9	Tellurium 52 **Te** 127.60 2.1	Iodine 53 **I** 126.90 2.5	Xenon 54 **Xe** 131.29 2.6
Cesium 55 **Cs** 132.91 0.7	Barium 56 **Ba** 137.33 0.9	57-70 *	Hafnium 72 **Hf** 178.49 1.3	Tantalum 73 **Ta** 180.95 1.5	Tungsten 74 **W** 183.84 1.7	Rhenium 75 **Re** 186.21 1.9	Osmium 76 **Os** 190.23 2.2	Iridium 77 **Ir** 192.22 2.2	Platinum 78 **Pt** 195.08 2.2	Gold 79 **Au** 196.97 2.4	Mercury 80 **Hg** 200.59 1.9	Thallium 81 **Tl** 204.38 1.8	Lead 82 **Pb** 207.20 1.8	Bismuth 83 **Bi** 208.98 1.9	Polonium 84 **Po** (209) 2.0	Astatine 85 **At** (210) 2.2	Radon 86 **Rn** (222) 2.4
Francium 87 **Fr** (223) 0.7	Radium 88 **Ra** (226) 0.9	89-102 **	Rutherfordium 104 **Rf** (261)	Dubnium 105 **Db** (262)	Seaborgium 106 **Sg** (263)	Bohrium 107 **Bh** (262)	Hassium 108 **Hs** (265)	Meitnerium 109 **Mt** (266)	Darmstadtium 110 **Ds** (271)	Roentgenium 111 **Rg** (272)	Ununbium 112 **Uub** (285)	Ununtrium 113 **Uut** (284)	Ununquadium 114 **Uuq** (289)	Ununpentium 115 **Uup** (288)	Ununhexium 116 **Uuh** (292)		

*lanthanides

Lanthanum 57 **La** 138.91 1.1	Cerium 58 **Ce** 140.12 1.1	Praseodymium 59 **Pr** 140.91 1.1	Neodymium 60 **Nd** 144.24 1.1	Promethium 61 **Pm** (145) 1.1	Samarium 62 **Sm** 150.36 1.2	Europium 63 **Eu** 151.97 1.1	Gadolinium 64 **Gd** 157.25 1.2	Terbium 65 **Tb** 158.93 1.1	Dysprosium 66 **Dy** 162.50 1.2	Holmium 67 **Ho** 164.93 1.2	Erbium 68 **Er** 167.26 1.2	Thulium 69 **Tm** 168.93 1.3	Ytterbium 70 **Yb** 173.04 1.1

Lutetium 71 **Lu** 174.97 1.1

**actinides

Actinium 89 **Ac** (227) 1.1	Thorium 90 **Th** 232.04 1.3	Protactinium 91 **Pa** 231.04 1.5	Uranium 92 **U** 238.03 1.4	Neptunium 93 **Np** (237) 1.4	Plutonium 94 **Pu** (244) 1.3	Americium 95 **Am** (243) 1.3	Curium 96 **Cm** (247) 1.3	Berkelium 97 **Bk** (247) 1.3	Californium 98 **Cf** (251) 1.3	Einsteinium 99 **Es** (252) 1.3	Fermium 100 **Fm** (257) 1.3	Mendelevium 101 **Md** (258) 1.3	Nobelium 102 **No** (259) 1.3

Lawrencium 103 **Lr** (262)

Topic 3 : Chemical Bonding, Lewis electron-dot model, Bond types, Polarity, oxidation states, solubility rule

(Molecular structure, **intra-** and **inter-** molecular bonding)

INTER-ATOMIC BONDING also termed **INTRAMOLECULAR bonding** (between atoms joined in a molecule or ion)

Electronegativity, EN = *the power of an atom to attract electrons*

The larger the value, the greater the electron attracting ability.

For two atoms bonded together :

Largest difference between largest EN **F** (3.98) and smallest EN **Cs** (0.79) : **Cs$^+$F$^-$** ΔEN = 3.19

Smallest difference = 0, for two identical atoms.

Inter-atomic Bond types

Ionic Na$^+$ Cℓ$^-$ (*complete electron transfer from one atom to the other*)

When there is a large difference in EN ($> \approx$ 2.0) we have an ionic compound ;

Usually between an s-block element and a p-block element

Na$^+$ Cℓ$^-$ ΔEN = 0.93 – 3.16 = 2.23 : **Cs$^+$F$^-$** ΔEN = 3.19   **Na •   : Cl •**
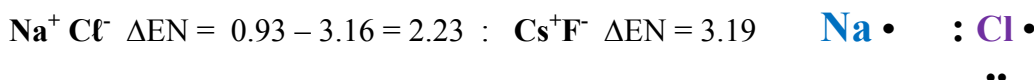
Covalent Br-Br (*sharing of two electrons* creates a single, sigma(σ) covalent bond)

ΔEN(Br/Br) = 2.96 – 2.96 = 0

Smallest difference ΔEN = 0   (termed **non-polar** molecule)   (A ↑) (↓ B)
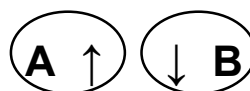
Usually between elements within the p-block

C-H ΔEN(C-H) = 2.55 – 2.20 = 0.35 (This turns out to be small enough that the C-H bond behaves as if it is **non-polar**, with no significant charge separation)

Polar covalent   **H-F** ΔEN = 2.20 – 3.98 = 1.78 (*uneven sharing of two electrons creates a single, sigma(σ) covalent bond, but with a significant 'ionic component' due to difference in electronegativity*)

So, H-F = (δ+)H—F(δ-)   (the **polar molecule** now possesses a dipole moment, designated —|—>, since it contains both a positive electric 'pole' (δ+) and a negative electric 'pole' (δ-), the symbol δ 'delta' means a 'small amount') .

This will be the case, to a greater or lesser extent, for all bonds consisting of different atoms.

Water   **H-O-H** ΔEN(O-H) = 3.44 – 2.20 = 1.24

H δ+   H δ+

O 2δ-
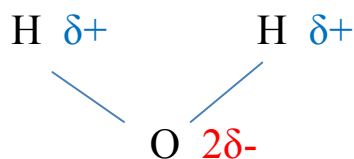
So, **water** is described as a **polar molecule**.

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Donor Covalent   When one atom donates both electrons to the bond :

A   ↑↓   B   ⟶

H₂Ö :   H⁺

H₃N :   H⁺

CH₃N :   Cu²⁺
    H₂

Chemical Bonding   Lewis electron-dot structures as models of chemical bonding (and their use to assign oxidation numbers)

The model is based on the fact that all atoms combine to give compounds in which each atom (or ion) achieves the inert gas valence electron configuration of 's²p⁶'(or s² for H) as this is the most stable configuration.

Eg
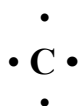
H x • Ö • x H   :Ḟ• x H

• Ċ •   • Ṅ •   • Ö •   :Ḟ •

4 bonds   3 bonds   2 bonds   1 bond
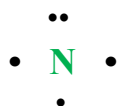
No unshared pairs   1 unshared pair   2 unshared pairs   3 unshared pairs

CARBON DIOXIDE   CO$_2$ SULPHUR DIOXIDE   SO$_2$

O   C   O   O   S   O

Single & Double bonds

When 2 electrons are shared between 2 atoms we describe the bond as a single, SIGMA-bond, when a further 2 electrons are shared between the same 2 atoms we describe the additional bond as a PI-bond, and the combination of the sigma & pi-bonds as a double bond.

SHAPE from Valence Shell Electron Pair Repulsion Theory = VSEPR theory

How many electron domains (groups of electrons) surround the central atom ?

2 electron clouds = linear

3 electron clouds = trigonal planar = triangular
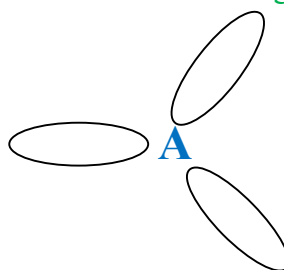
4 electron clouds = tetrahedral
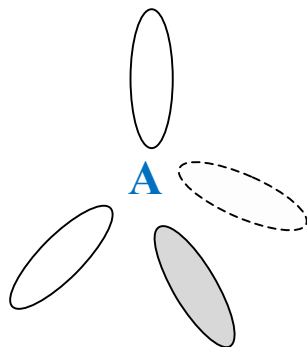
6 electron clouds = octahedral
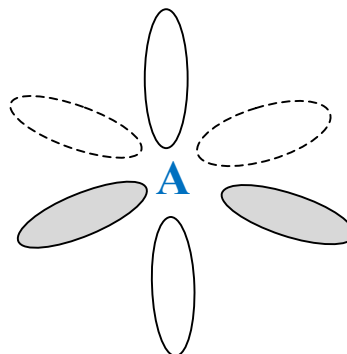
Shapes of CO$_2$ and SO$_2$ molecules

Polarity of molecules   Electro-Negativities : C = 2.5, O = 3.5, S = 2.5

INTERMOLECULAR bonding forces (between separate molecules)

IONIC
(A Strong inter-particle electrostatic attraction between oppositely charged ions which usually gives hard, solid materials due to their regular giant 'lattice' structure)

Eg. Na^+Cl^- $K^+ H_2PO_4^-$ $Mg^{2+}/Ca^{2+} CO_3^{2-}$

Can also get <u>isolated</u> ionic interactions such as an ionic "salt bridge" in a protein structure :

  /\/\/\/-NH$_2$ HOOC-/\/\/\ $\longrightarrow$ /\/\/\/-NH$_3^+$ $^-$OOC-/\/\/\

COVALENT   (or DONOR-COVALENT)
(A Strong bond arising from electron sharing)

C-C, C-O   C-N   C-H   N-H

DIPOLE / DIPOLE (Polar covalent)
(An Intermediate strength bond in solids & liquids arising from attractions between partially charged atoms)

$\delta+$ $\delta-$ $\delta+$ $\delta-$ Cl
>C== O   >C== O $\delta+$ H - C $\diagup$ Cl $\delta-$ Cl
                                               $\diagdown$ Cl $\delta+$ H - C $\diagup$ Cl $\delta-$
        $\delta-$ O== C< $\delta+$ $\diagdown$ Cl

or **ION/DIPOLE**

                H $\delta+$ H $\delta+$
             $\diagup$ $\diagup$
Al^{3+} O 2$\delta-$ = $Al^{3+}$$_{(aq)}$ O 2$\delta-$ Cl^{1-} = $Cl^-$$_{(aq)}$
             $\diagdown$ $\diagdown$
                H $\delta+$ H $\delta+$
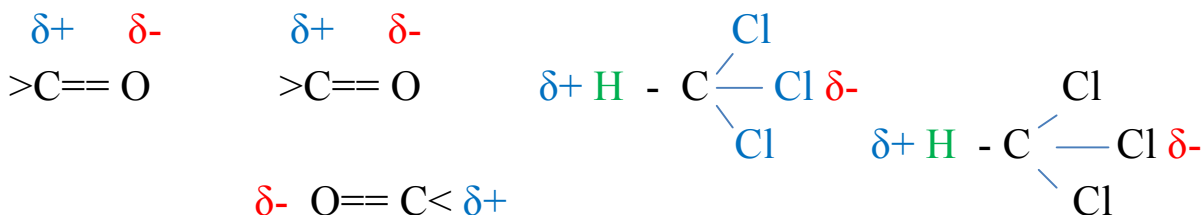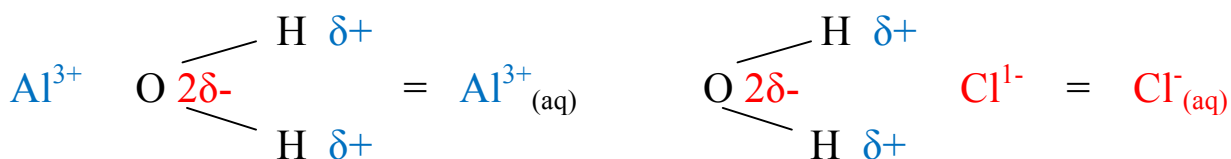
HYDROGEN-BONDING

(An Intermediate strength bond arising from a partially charged hydrogen atom ($H^{\delta+}$) bridging between partially charged negative atoms)

In water   In a protein

$\delta+$ $\delta-$ $\delta+$

H— O $\delta+$ H

       H   O $\delta-$

                   |

             H $\delta+$

O $\delta-$

‖

- C   R

        N

           H $\delta+$

$\delta+$ H — O $\delta-$

           H $\delta+$

O $\delta-$

‖

- C   R

        N

           H $\delta+$
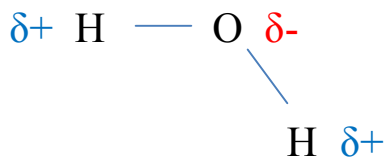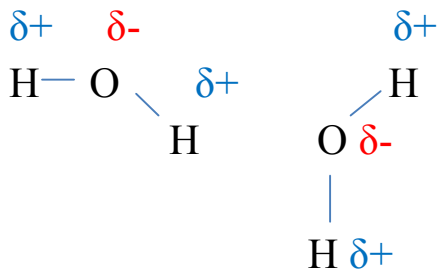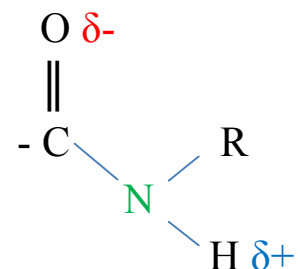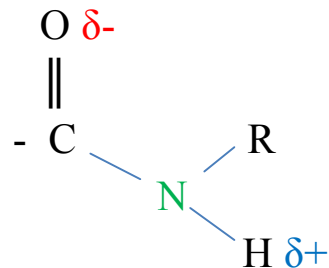
Van Der WAALS (DISPERSION) (also called Hydrophobic Bonding)

(Arises when there are no permanent dipoles in a molecule, then we get a very weak inter-particle bonding interaction arising from transient distortions in the electron distribution in an atom or molecule). In this case the compounds are usually liquids or gases.

Eg. Consider two **long hydrocarbon chains**, as in a fat/oil

The only bonds present are C-C and C-H, which are both non-polar due to the similarity in electronegativities of C & H.
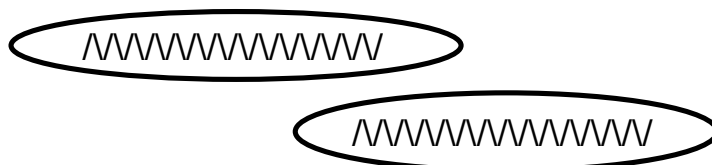
Note the **effect of molecular symmetry** in the following examples :

Chloroform = CHCl₃   Carbon Tetrachloride   CCl₄

$$Cl\ \delta-$$
$$\diagdown$$
$$\delta+\ H - C - Cl\ \delta-$$
$$\diagdown$$
$$Cl\ \delta-$$

$$Cl\ \delta-$$
$$\diagdown$$
$$\delta-\ Cl - C - Cl\ \delta-$$
$$\diagdown$$
$$Cl\ \delta-$$
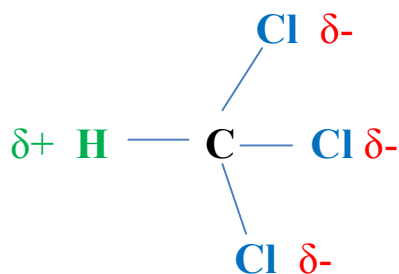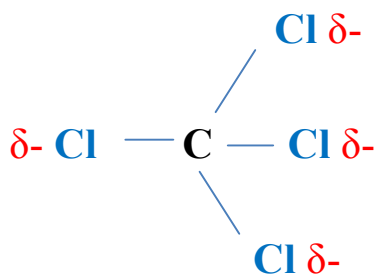
A POLAR molecule   **A NON - POLAR molecule**

Oxidation Numbers (ON) also called Oxidation States (OS)

Definition :

Oxidation **I**s the **L**oss of electrons, **R**eduction **I**s the **G**ain of electrons by a species, "**OILRIG**"

Eg, in Na⁺ Cℓ⁻   Naᵒ [Ne]3s¹ loses one electron to form Na⁺ [Ne]3sᵒ, so it has been oxidised , whilst Clᵒ [1s²2s²2p⁵] gains one electron to form Cℓ⁻ [1s²2s²2p⁶]=[Ne], so it has been reduced, and the two ions have the stable 's²p⁶' electron configuration.

Na⁺ is said to have an OS (ON) of +1, while Cℓ⁻ has an OS (ON) of -1.

Eg

$$H\ x \bullet \overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} \bullet\ x\ H$$

$$: \overset{\bullet\bullet}{\underset{\bullet\bullet}{F}} \bullet\ x\ H$$
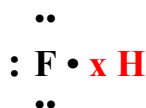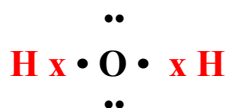
EN(O) = 3.44 > EN(H) = 2.2   EN(F) = 3.98 > EN(H) = 2.2

So O takes share of electrons   So F takes share of electrons

So ON(O) = -2 & ON(H) = +1   So ON(F) = -1 & ON(H) = +1

To calculate oxidation numbers(ON)

Rule for $A_aB_b{}^n$; $a.ON(A)$ + $b.ON(B)$ =   n

Usually take **ON(O) as -2**   **ON(H) = +1**

OCl⁻ hypochlorite anion   Electronegativities :   O, 3.44 ;   Cl, 3.16, so take ON(O) as -2
ON(O) + ON(Cl) = -1   so,   -2 + ON(Cl) = -1,   Hence, ON(Cl) = +1

SO₂ sulphur dioxide   Electronegativities :   O, 3.44 ;   S, 2.58, so take ON(O) as -2
2.ON(O) + ON(S) = 0   so, 2.(-2) + ON(S) = 0 ,   Hence, ON(S) = +4

Elec. Config. $S = [Ne]3s^2 3p^4 3d^0$ so $S^{4+} = [Ne]$

SO₃ sulphur trioxide   Electronegativities :   O, 3.44 ;   S, 2.58, so take ON(O) as -2
3.ON(O) + ON(S) = 0   so, 3.(-2) + ON(S) = 0 ,   Hence, ON(S) = +6

Elec. Config. $S = [Ne]3s^2 3p^4 3d^0$ so $S^{6+} = [Ne]$

Oxidation Numbers:
Iron(III) chloride, **FeCl₃**   Electronegativities :   Cl, 3.16 ;   Fe, 1.83, so take ON(Cl) as -1

   2.Fe + 3.Cl₂ $\longrightarrow$ 2**FeCl₃** (2.Fe³⁺ 6.Cl⁻)

Iron(III) oxide, **Fe₂O₃** Electronegativities :   O, 3.44 ;   Fe, 1.83, so take ON(O) as -2

   4.Fe +   3.O₂ $\longrightarrow$ 2. **Fe₂O₃** (4.Fe³⁺ . 6.O²⁻)
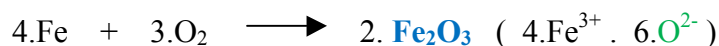
Magnesium(II) oxide, **MgO**   Electronegativities :   O, 3.44 ;   Mg, 1.31, so take ON(O) as -2

   2.Mg + O₂ $\longrightarrow$ 2.**MgO** (Mg²⁺ O²⁻)

SOLUBILITY is an important topic in chemistry because many chemical reactions occur in aqueous fluids. In general, solubility depends on whether the **solute** (usually a *solid*) is ionic or molecular, and whether the **solvent** *liquid* contains polar or non-polar molecules.

Ionic Solutes in polar solvents

Solute e.g. Na^+Cl^- mixture   Solvent   e.g. H_2O

Forces between ions :
Ionic (electrostatic)

Forces between solvent molecules :
dipole – dipole   (electrostatic)
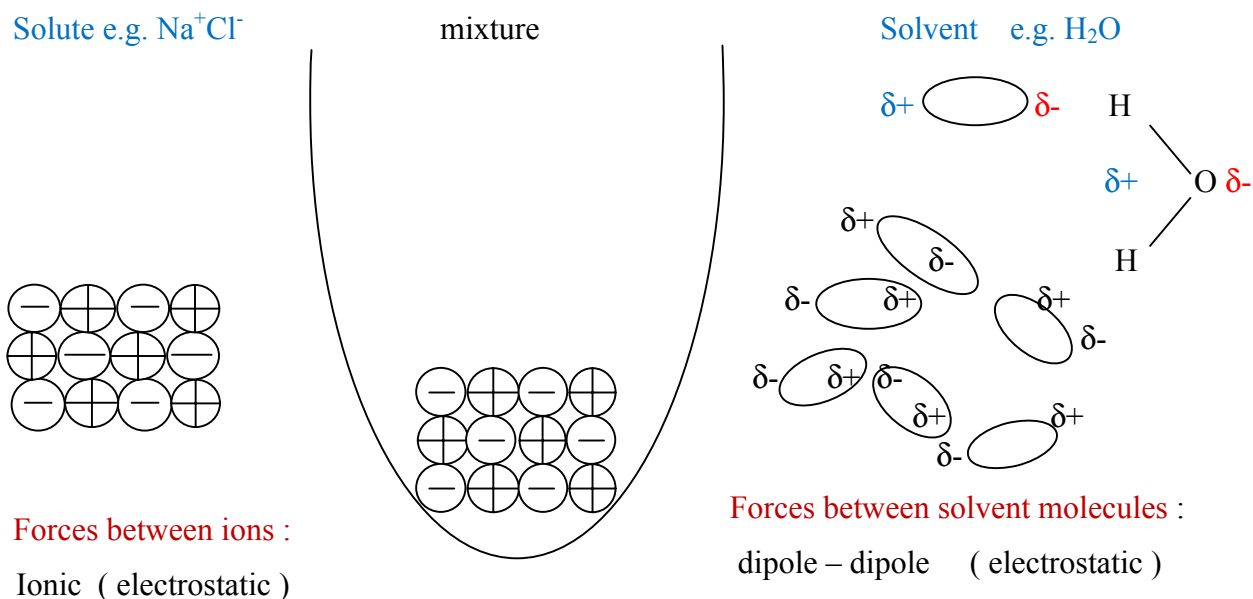
So, the nature of the forces between solute and solvent are comparable .

Hence, the strong electrostatic forces between ions in the crystal lattice can be matched by the ion-dipole electrostatic interaction between ions and the polar solvent molecules. Thus, we can expect *ionic (polar) solutes* to be *soluble* in *polar solvents*.

Molecular solutes in non-polar solvents

mixture

Solute, eg. I_2 Solvent, eg. C_6H_6 (benzene)

Forces between solute molecules:
van der Waals

Forces between solvent molecules :
van der Waals
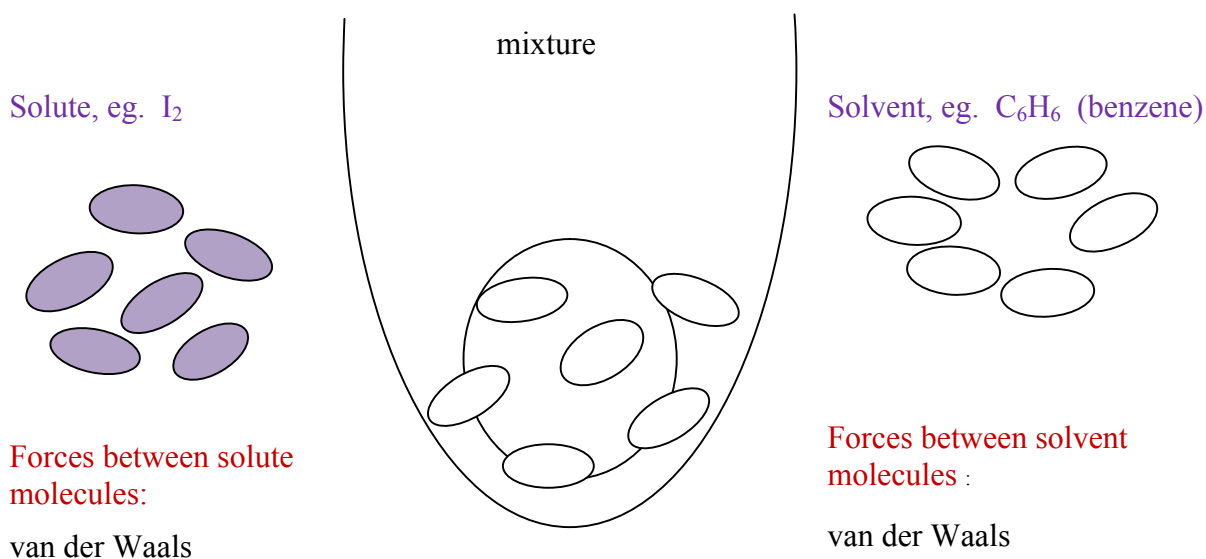
The forces between the solute and solvent molecules are comparable, hence we can expect solubility. In this case both the solute and the solvent are molecular, so when solute contacts solvent the molecules freely intermingle. *Molecular compounds* eg. iodine are therefore generally *soluble* in *non-polar liquids*, eg. benzene.

Solubility Rule   "Like Dissolves Like"

Polar solutes dissolve in polar solvents   Non-Polar solutes dissolve in non-polar solvents

Compare the WATER SOLUBILITY of **HEXANE & GLUCOSE**

Hexane $H_3C\text{-}(CH_2)_4\text{-}CH_3$ Glucose $HO\text{-}H_2C\text{-}(CH\text{-}OH)_4\text{-}CHO$

What about the following PHOSPHO-GLYCERIDE molecule containing both hydro-philic (water-loving) and hydro-phobic (water-hating) regions (termed an amphi-philic molecule) ?

CH₂ –OOCR

CH –OOCR'   O

CH₂ —— O—P—O— R"
                          ****
                          O(-)

≡   -/\\/\\/\\/\\/\\
      -/\\/\\/\\/\\/\\/\\   ≡   **(-)P**-/\\/\\/\\/\\
      -P(-)
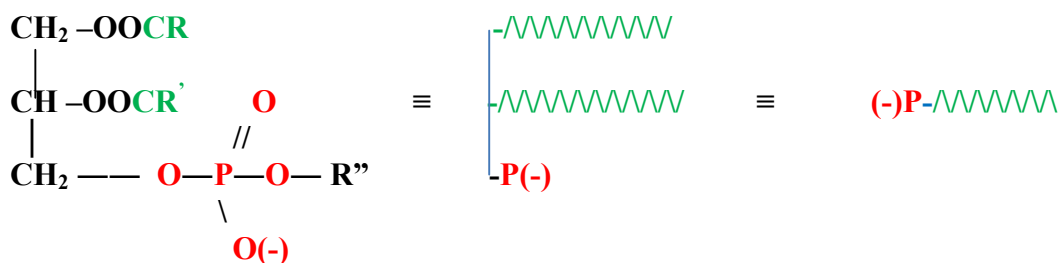
Phospho-glyceride ; when R" = —O-CH$_2$CH$_2$-N(CH$_3$)$_3$$^+$ (= choline)
the **phospholipid** is <u>**lecithin**</u> (composes about 10-15% of egg yolk).
Being amphiphilic it is used as an **emulsifying agent** in foodstuffs such as mayonnaise.

Phospho-lipids (P/L), amphiphiles, in aqueous media

Polar 'head'   **(-)P**-/\/\/\/\/\/\   Non-polar 'Tail'
hydrophilic   Na$^+$ hydrophobic
"Water loving"   "Water hating"

Schematic representation of EMULSION formation

Non-polar oil/fat globule floats on surface of polar water.

Non-polar tails of P/L dissolve in non-polar oil/fat globule, polar heads dissolve in polar aqueous phase.

Emulsion of oil/fat droplets in water is stabilised by like-charge repulsion--so droplets do not coalesce upon colliding.

Topic 4 : The Mole and chemical stoichiometry

(Molar amounts of solids and liquids, the molar volume of a gas)

The mole concept gives us a means of managing fixed numbers of atoms / ions / molecules in weighable amounts.

The Public speak of ;   1 dozen = 12 objects   1 score = 20 objects   1 ream = 500 sheets paper,   and for scientists **1 mole = 6.022 x 10^{23} particles**, called the Avogadro Number (N_A).

Thus, if we had 3.011 x 10^{24} atoms of Gold (Au) the number of mole of gold would be :
   Mole of Au = 3.011 x 10^{24} atoms of Gold / **6.022 x 10^{23} atoms mole^{-1}** = 5.0 mole Au

So **Avogadro's number, N_A** , is the link between the number of atoms (or molecules) of a material and the number of mole of material.

Since the mass of one C-12 atom is 1.992648 x 10^{-23} g, then the mass of a mole of C-12 atoms will be :
= 1.992648 x 10^{-23} g atom^{-1} x 6.02214 x 10^{23} atoms mole^{-1} = 12.0000 g mole^{-1}, which is written as the Relative Atomic Mass (A_r) in the Periodic Table.

So, N_A (particles mole^{-1}) x mass of atom or molecule (g) = atomic or molar mass (g mole^{-1})

The **Molar mass = M_r** = sum of masses of atoms in a mole of the chemical species = **Σ A_r**

Where **A_r is the relative atomic mass of an atom**, obtained directly **from the Periodic Table** in **units of gram.** Eg   O = 16.0 g/mole,   C = 12.0 g/mole   and   Na = 23.0 g/mole.
So for a compound such as sodium carbonate,
 Na_2CO_3 ; **M_r** = 2.Na + 1.C + 3.O = **2** x 23.0 + **1** x 12.0 + **3** x16.0 = 106 g mole^{-1}

For any pure material (solid or liquid) ;
amount (n mole) = mass material (m gram) / (molar mass = M_r g mole^{-1})   so, **n = m/M_r**

So **molar mass**, **M_r** , is the link between number of mole of material (**n**) and mass (**g**) since ;
n (mole) x **M_r** (gram mole^{-1}) = mass **m** (g)

So in 50.0 g of silver (Ag), the number of mole would be given by :
   Mole Ag =   m / A_r = 50.0 **g** / 107.9 **g mole^{-1}** = 0.463 **mole**, which would contain :
Number of atoms of Ag = 6.022 x 10^{23} **atoms mole^{-1}** x 0.463 **mole** = 2.79 x 10^{23} **atoms Ag**

For liquids, **density** (d or ρ) = mass m / volume V,   ie   **d = m / V**

Eg, water, density @ 25 ^{o}C = 0.997 g mL^{-1} = 997 g / 1000 mL $\approx$ 1 kg L^{-1}
And the mole of water per litre = mol H_2O in 0.997 kg of water = 997 g / 18 g mol^{-1} = 55.4 mol

For a gas PV = nRT

(P = pressure, kPa ; V = volume, L ; n = number of mol of gas ;
T = absolute temperature in units of Kelvin K, which is defined as $K = {}^{o}C + 273$;
R = gas constant = 8.314 J $K^{-1}mol^{-1}$ = 8.314 kPa.L $K^{-1}mol^{-1}$ = 8.314 Pa.m^3 $K^{-1}mol^{-1}$ =
= 0.0821 L.atm $K^{-1}mol^{-1}$ and 1 atmosphere = 101.3 kPa)

So for **one mol of gas** at Room Temperature, 25 ${}^{o}C$, and one atmosphere pressure (101.3 kPa);

$$PV = nRT , \quad V = \frac{nRT}{P} = \frac{1 \text{ mol } x \ 298 \text{ K } x \ 8.314 \text{ kPa.L } K^{-1}mol^{-1}}{101.3 \text{ kPa}} = 24.46 \text{ L } (\text{ per mole })$$

or

$$PV = nRT , \quad V = \frac{nRT}{P} = \frac{1 \text{ mol } x \ 298 \text{ K } x \ 0.0821 \text{ L.atm } K^{-1}mol^{-1}}{1 \text{ atm}} = 24.47 \text{ L } (\text{per mole})$$

So **molar volume of a gas** at 25 ${}^{o}C$, and one atmosphere pressure = **24.47 Litre**

ie. One mol of any (ideal) gas occupies 24.7 L = 24,700 cm^3
And $\sqrt[3]{(24,700)}$ = 29.04 cm ie., about a 30 cm cube.

For a **fixed number of mole** (or a fixed mass) **of gas**, $nR = \text{constant} = P_1V_1 / T_1$

Which can be generalised to : $P_1V_1 / T_1 = P_2V_2 / T_2$ for a fixed amount of gas.

Chemical Stoichiometry is based on reacting molar amounts according to the balanced chemical equation, but to perform a reaction in the laboratory, we need to convert to gram in order to weigh out the reacting materials on a balance.

Consider the balanced chemical equation :

1 N_2	**+**	**3 H_2**	**→**	**2 NH_3**
1 mol N_2	reacts with **3** mol H_2		to give	**2** mol NH_3

So the number of mol of H_2 = **3** x number of mol N_2

So, $\frac{\text{mol of } H_2}{} = \text{number of mol } N_2$

and the number of mol of NH_3 = **2** x number of mol N_2

So, $\frac{\text{mol of } NH_3}{} = \text{number of mol } N_2$

So, in general we can say :

$\underline{\text{number of mol of } N_2} = \text{number of mol } H_2 = \text{number of mol of } NH_3$

Consider performing the following chemical reaction described by the balanced equation :

2. Ca₃(PO₄)₂ (s) + 6.SiO₂ (s) + 10.C (s) --heat→   P₄ (s) + 6.CaSiO₃ (s) +   10.CO(gas)

So, $\dfrac{\text{mol Ca}_3(\text{PO}_4)_2}{2}$ = $\dfrac{\text{mol SiO}_2}{6}$ = $\dfrac{\text{mol C}}{10}$ = $\dfrac{\text{mol P}_4}{1}$ = $\dfrac{\text{mol CaSiO}_3}{6}$ = $\dfrac{\text{mol CO}}{10}$

Obtain Molar Masses from the Periodic Table,

$M_r(\text{Ca}_3(\text{PO}_4)_2)$ = 310.2 g/mol, $M_r(\text{SiO}_2)$ = 60.1 g/mol, $A_r(\text{C})$ = 12.0 g/mol, $M_r(\text{P}_4)$ = 124.0 g/mol,
$M_r(\text{CaSiO}_3)$ = 116.2 g/mol, $M_r(\text{CO})$ = 28.0 g/mol

Problem : **(a)** On the basis of the chemical equation given above, calculate the mass of phosphorus that can be obtained from a kilogram of calcium phosphate, and,
        (b) determine what volume of carbon monoxide would be liberated at one atmosphere pressure and 24°C during the reaction .

Answer :

(a)   Since : $\dfrac{\text{mol Ca}_3(\text{PO}_4)_2}{2}$ = $\dfrac{\text{mol P}_4}{1}$ = $\dfrac{\text{mol CO}}{10}$

Now,   mol Ca₃(PO₄)₂ = mass / molar mass = 1000 g / 310.2 g mol⁻¹ = 3.224 mol

Since,   mol P₄ / **1** =   mol Ca₃(PO₄)₂ / **2** =   3.224 mol / **2** = 1.612 mol

So, **mass P₄** = mol P₄ x M_r (P₄) = 1.612 mol x 124 g mol⁻¹ = **199.9 g**

(b) Since   mol CO /**10** = mol Ca₃(PO₄)₂ / **2** , then mol CO = **10** x mol Ca₃(PO₄)₂ / **2**
                 = 5 x 3.224 mol = 16.12 mol

And, temperature = 24 °C   so, T (absolute) K = °C + 273 = 24 + 273 = 297 K

Then , using PV = nRT,   V = nRT/P = $\dfrac{16.12 \text{ mol } x \text{ 0.0821 L.atm K}^{-1}\text{mol}^{-1}\ x \text{ 297 K}}{1.00 \text{ atmosphere}}$

So,   **volume CO**   = 393.1 L = **0.393 m³**   (because 1 m³ = 1000 L)

Topic 5 : Aqueous Solutions, solvents/solutes

(%w/v, %w/w, molarity, dilution, ppm, ppb, molality , p-notation)
[w = weight   m = mass,   but in Chemistry we use :   % w/v = % m/v, and   % w/w = % m/m   ]

Preparation of a solution –a <u>known mass</u> (m gram) of the <u>solute</u> (eg 5.85 g NaCl, M_r = 58.5 g/mol)
is dissolved in a solvent such as water to give a <u>known volume</u> (V mL or Litre) of the <u>solution</u> (eg 250
mL aqueous solution).

Concentration = c = mass (gram) / volume (mL or Litre)
               = 5.85 g / 250 mL = 0.0234 g/mL = 5.85 g / 0.25 L = 23.4 g/L
Then, **%w/v = gram solute in 100 mL of solution** = 2.34 g / 100 mL =   **2.34 %w/v NaCl,**
(This concentration is Temperature Dependent)   =   **2.34 %m/v NaCl.**

Or, we can prepare a solution by dissolving a <u>known mass</u> of the <u>solute</u> in a solvent to give a <u>known mass</u>
<u>of solution</u>;

Then, **% w/w   = gram solute in 100 g solution**
So, if 2.34 g of NaCl is dissolved in 97.66 g of water to give 100 g of solution
Then % w/w   = 2.34 g / 100 g solution
          = **2.34 % w/w NaCl (This concentration is Independent of Temperature)**
          (= 2.34 g in about 98 mL = 2.39 g / 100 mL)

Molarity = <u>M</u> = amount (mole) / solution volume (Litre)
          = { mass (gram)/molar mass (M_r) gram/mol }/volume(L)
          = (5.85 g / 58.5 g mol^{-1}) / 0.25 L = 0.1 mol / 0.25 L = 0.4 mol/L

To calculate the <u>number of mol of material in a given volume of a solution</u> having a
<u>known concentration</u> :

Number of mol = n = concentration (mol L^{-1}) *x* volume (L)

ie, n = C *x* V   or   M(mol L^{-1}) *x* V(L)

TASK : To prepare 500 mL of an approximately 0.05 M Na_2CO_3 solution with an exactly known concentration, from a solid sample of pure Na_2CO_3 (M_r = 106.0 g/mol).

A.   Calculate approximate mass of solid Na_2CO_3 required:

 n= C x V   n = 0.05 x 500/1000 = 0.025 mol

n = m/ M_rm = n x M_r = 0.025 x 106.0 = 2.65 g

B.   Weigh out approximate mass of Na_2CO_3 :   Add solid Na_2CO_3 until ≈2.7 g has been added to weighing bottle (approximate mass)

Na_2CO_3

2.74

Weighing bottle   top loading balance

Using "weighing by difference" transfer solid Na_2CO_3 sample to standard (volumetric) flask

2.7403

0.2171

Exact mass of solid Na_2CO_3 in flask = 2.7403 – 0.2171 g = 2.5232 g

Analytical balance   500.0 mL standard flask   Analytical balance
(weigh accurately)   (weigh accurately)

C. Dissolve exact mass in water to give an exact volume (500.0 mL) of solution :

Rinse funnel and 2/3 rds fill flask with water. Swirl until all solid dissolves

Dilute exactly to volume

Stopper flask and shake to give uniform mixing.

D. Calculate exact concentration of Na_2CO_3solution :

C_{Na2CO3} = n/V   = (m / M_r) / V = (2.5232 / 106.0) / 0.500 = 0.04761 mol/L

Dilution –adding further pure solvent to a solution

Original solution   vol = V_o , conc = C_o *Final solution* vol = V_f , conc = C_f

$n_o = C_o \times V_o$ $n_f = C_f \times V_f$

Only pure solvent is added, so no extra moles of solute are added , so $n_f = n_o$

thus, $C_f \times V_f = C_o \times V_o$

eg, if 10 mL of a 0.4 mol/L solution is diluted to 50 mL, the final concentration can be calculated :

50 mL $\times$ C_f = 10 mL $\times$ 0.4 mol/L   so, $C_f = \dfrac{10 \text{ mL} \times 0.4 \text{ mol/L}}{50 \text{ mL}} = 0.08$ mol/L

Parts per million

ppm = **g solute in 1 million g solution**
       = **g solute in 10^6 g solution   ie., g per tonne (1 000 kg)**   [used in mining industry]
       = **milligram in 10^3 g solution**   [The prefix "milli" means one-thousandth of = 1/1000 = 10^{-3}]
       = **mg per Litre   (1 mg = 0.001 g = 10^{-3} g ;   so 1 gram = 1000 mg)**

Parts per Billion

ppb = **g solute in 1 billion g solution**
       = **g solute in 10^9 g solution = milligram in 10^6 g solution = mg in 10^3 Litre**
       = **microgram in one Litre** [The prefix "micro" means one-millionth of = 1/1 000 000 = 10^{-6}]
       = **μg per Litre   (1 μg = 0.000 001 g = 10^{-6} g ; so 1 gram = 1 000 000 μg)**

Molality

m = mol solute per kilogram of solvent (a temperature independent concentration)
eg, if a solution contains 4.38 g of KCl solute (M_r = 74.6 g mol^{-1}) in 100 g of solvent water.
Molality = $\dfrac{4.38 \text{ g}/74.6 \text{ g mol}^{-1}}{100\text{g} / 1000\text{g kg}^{-1}}$ = $\dfrac{0.0587 \text{ mol}}{0.1 \text{ kg}}$ = 0.587 molal (**m**)

Topic 6 : Chemical reactions-balancing chemical reactions/ stoichiometry

(Simple strategies, acid/base, redox processes)

Reactants $\longrightarrow$ Products (**must have atom & charge conservation for balance**)

eg. $2.C + O_2 \longrightarrow 2 CO$ $\qquad Al^{3+}P^{3-}{}_{(s)} + 3.H_2O_{(l)} \longrightarrow Al(OH)_{3(s)} + PH_{3(g)}$

$Cu^{2+} + Zn \longrightarrow Cu + Zn^{2+}$ $\qquad Cl_2 + 2.I^- \longrightarrow 2.Cl^- + I_2$

Combustion (burning in air (20 %v/v oxygen), or in pure oxygen)

Eg. $2. C_2H_6 + 7. O_2 \longrightarrow 4.CO_2 + 6.H_2O$

Acid/Base Water forms hydrogen ions (**H$^+$**), which are the abbreviated form of the hydronium ion H_3O^+), and hydroxide ions (**OH$^-$**) when it self-ionizes :

```
 H          H
  \          \
  : O :      : O :        ⇌
   |          |
   H          H
```

What is meant by the term, "**CHEMICAL EQUILIBRIUM**" as represented by ⇌ ?

Physical equilibrium is when we have a balanced static system. In contrast, a chemical equilibrium is dynamic, with reactants continually changing into products, and vice-versa, until no overall change in the concentrations of either reactants/products occurs, although they never stop interchanging.

Since at equilibrium there is no change in the overall concentrations of reactants/products, the ratio, [products]/[reactants] is constant, at constant temperature, so we can write the equilibrium constant, K, for the following reaction as :

$$H_2O + H_2O \overset{K}{\rightleftharpoons} H_3O^+ + OH^- \qquad K = [H_3O^+].[OH^-] / [H_2O]^2$$

Because this is in water, and the $[H_2O]$ is essentially constant, the product, $K. [H_2O]^2$ is constant, and given the special symbol, $K_{water} = K_w$ and has the value 10^{-14} @ $25^{o}C$.

$$H_2O + H_2O \overset{K_w}{\rightleftharpoons} H_3O^+ + OH^- \qquad K_w = [H_3O^+].[OH^-] = 10^{-14} @ 25^{o}C$$

WHAT IS AN **ACID** ? Brφnsted concept: **an ACID is an entity which produces H_3O^+ ions (aquated protons) in aqueous solution.**

Why is the proton released ?   Because H is bound to a very electronegative element, eg O, Cl.
(Electronegativity is the ability of an atom/ion to attract electrons).

$$\text{element} - \text{H} \quad + \quad H_2O \quad \rightleftharpoons \quad \text{element} \quad +$$

δ = lower case delta (a small amount of charge)   eg., $H^{\delta+}$
Δ = capital delta (a larger amount of charge)   eg., $H^{\Delta+}$ } so magnitude of charge follows
$\pm$ = integral value of charge   eg., H^+ } the sequence $H^+ > H^{\Delta+} > H^{\delta+}$

Electronegativity values of some common Elements **(See SI Data Book, Table 12)**

H		B	C	N	O	F
2.20		2.04	2.55	3.04	3.44	3.98
Li	**Be**	**Al**	**Si**	**P**	**S**	**Cl**
0.98	1.57	1.61	1.90	2.19	2.58	3.16
Na	**Mg**	**Ga**	**Ge**	**As**	**Se**	**Br**
0.93	1.31	1.81	2.01	2.18	2.55	2.96
K	**Ca**	**In**	**Sn**	**Sb**	**Te**	**I**
0.82	1.00	1.78	1.96	2.05	2.1	2.66

ACETIC ACID

CH_3COOH + H_2O ← (1 % dissociation) K_a → CH_3COO^- + H_3O^+

AMMONIA

NH_3 + H_2O ← (1 % dissociation) K_b → NH_4^+ + OH^-

As an example, **compare Δ(EN) (polarity) of hydrogen (H) bound to C, N, O, F** :

⎯⎯$\diagdown$C(2.6)⎯⎯ H(2.2)   **Δ(EN) = 0.4**   ie., <u>C has **similar EN** to H</u>, so **C-H bond is**

non-polar / polar , so H (in hydrocarbon) is **not acidic** when bound only to C.

$\diagdown$N(3.0) ⎯⎯ H(2.2)   **Δ(EN) =0.8**   ie., <u>N is **slightly more EN** than H</u>, so **N-H bond is**

non-polar / slightly polar , but H (in amine) is **not acidic in water** when bound only to N.

⎯⎯⎯ O(3.4) ⎯⎯ H(2.2)   **Δ(EN) = 1.2**   ie., <u>O is **more EN** than H</u>,   so **O-H bond is**

non-polar / polar, but H (in alcohol) is **not acidic** in water when bound only to O.

H$_3$C - C$\diagup\!\!\diagup$O
$\diagdown$O ⎯ H

                    Δ(EN) > 1.2   (due to proximity of another O in C=O), so **O-H bond in carboxyl group is even more polar than –O-H**, and so H (in carboxylic acid) is **slightly acidic**.

   F(4.0) ⎯⎯ **H(2.2)**   **Δ(EN) = 1.8**   ie., <u>F is **much more EN** than H</u>,   so **F-H bond is**

non-polar / polar, so H (in HF) is **quite acidic**.

Other examples :

Sulphurous acid, dissolved SO$_2$ gas

H   O
 \\   \\\\
 : O :   S :   ↔
  | ‖
  H   O

$H_2SO_3 \leftrightharpoons H^+ + HSO_3^- \leftrightharpoons H^+ + SO_3^{2-}$

Sulphuric acid, dissolved SO₃ gas

```
H        O    O
 \        \\  //
  :O:          S          ↔
   |          ‖
   H          O
```

$$H_2SO_4 \;\rightleftharpoons\; H^+ + HSO_4^- \;\rightleftharpoons\; H^+ + SO_4^{2-}$$

Carbonic acid, dissolved CO₂ gas

$$H_2CO_3 \;\rightleftharpoons\; H^+ + HCO_3^- \;\rightleftharpoons\; H^+ + CO_3^{2-}$$

```
H        O
 \        ‖
  : O :    C    ↔
   |      ‖
   H      O
```

(Note that H^+ and H^+(aq) are abbreviations for the hydronium ion, H_3O^+ - in fact all ions in aqueous solution are always hydrated/solvated)

A scale for reporting acidity / basicity(alkalinity) – the pH scale

_____

For Revision of Logarithms and Exponents see SLC handouts in Appendices at end of these notes.

_____

p notation: is a convenient means of expressing concentrations.
p means '$-\log_{10}$', and we use 'log' to signify '$\log_{10}$' (ie log to the base 10)

So, $\mathbf{pX = -log(X)}$ and $\mathbf{pK_a = -log(\,K_a\,)}$

Hence, $\mathbf{X = 10^{-pX}}$ and $\mathbf{Ka = 10^{-pKa}}$

What do we use this "p" notation for?

To express very low concentrations, especially for acid (H^+) / base (OH^-) solutions :
eg
$$pH = -\log_{10}[H^+] \qquad [H^+] = 10^{-pH}\ \mathbf{M}$$

If $[H^+] = 0.000\,000\,01\ \mathbf{M} = 10^{-8}\ \mathbf{M} = \mathbf{10^{-pH}}$ then pH = 8 ;
If the pH = 3 then $[H^+] = 10^{-3}\ \mathbf{M}$ (because $\mathbf{[H^+] = 10^{-pH}\ M}$) so $[H^+] = 0.001\ \mathbf{M}$

_____

Since :

$$H_2O \ + \ H_2O \ \overset{K_w}{\leftrightarrows} \ H_3O^+ + \ OH^- \quad and \quad K_w = [H_3O^+].[OH^-] = 10^{-14} @ 25^oC$$

then, in **pure water**, $[H_3O^+] \ = \ [OH^-] \ = \ 10^{-7}$ M @ 25^oC.

Now, the pH Scale is defined by : pH = -log₁₀[H⁺]   so,   [H⁺] = 10⁻ᵖᴴ

so in *pure water* where $[H^+] = 10^{-7}$ M $= 10^{-pH}$ **M,** the **pH = 7** *(neutral)*
and   pH + pOH = 14

So the pH scale is a measure from 1 to 14 of the acidity (pH = 1-6), or alkalinity (pH =8-14), of an aqueous solution.

	pH = 2	pH = 7	pH = 12
[H⁺] = 10⁻ᵖᴴ	**[H⁺] = 10⁻²**	**[H⁺] = 10⁻⁷**	**[H⁺] =10⁻¹² mol/L**

pH =   0—1—2—3—4—5—6—7—8—9—10—11—12—13—14
   very acidic   **neutral**   **very basic(alkaline)**
$[OH^-] = 10^{-pOH} = 10^{-(14-pH)}$

	[OH⁻] = 10⁻¹²	[OH⁻] = 10⁻⁷	[OH⁻] =10⁻² mol/L

	pOH = 12	pOH = 7	pOH = 2

stomach pH = 1– 3   **intestines pH =7.6-8.2**   **dishwasher detergent pH =12**

STRONG ACIDS completely dissociate (ionize) in water. e.g., HCl, HNO_3, H_2SO_4.

 HNO_3 + H_2O —100 % dissociation →   +

i.e., a strong acid dissociates / ionizes completely in solution (about 95 – 100 %).   In the stomach HCl forms the strong acid $H^+ Cl^-$ which kills bacteria and activates digestive enzymes .

For a **Strong ACID** dissolved in water : eg. $HCl \ + \ H_2O \ \rightarrow \ H_3O^+ \ + \ Cl^-$
 If $[HCl] \ = \ 0.1$ **M** $= 10^{-1}$ **M,** then $[H_3O^+] = \ [H^+] = 10^{-1}$ **M, so since** $[H^+] = 10^{-pH}$, **pH = 1**

 WEAK ACIDS only **partly** dissociate (partially ionize, about 1-10 %) in water. e.g. carboxylic acids (RCOOH), H_3PO_4, carbonic acid (H_2CO_3), H_2S, HF, boric acid (H_3BO_3).

Eg., Acetic acid – found in vinegar :

CH_3COOH + H_2O ← (1 % dissociation) → CH_3COO^- + H_3O^+

BASES & ALKALIS :   An alkali (or base) is an entity which produces hydroxide (OH^-) ions in solution.
e.g.
     $NaOH$ (Na^+OH^-) + H_2O →   (aq) +   (aq)

Strong bases completely dissociate in water(about 95 – 100 %) i.e. tend to completely ionize in solution to produce OH^- ions, eg NaOH, KOH, $Ba(OH)_2$

$$KOH(K^+OH^-) \ + water \quad -100\ \%\ dissociation \rightarrow \quad K^+(aq) \quad + \quad OH^-(aq)$$

For a **Strong BASE** dissolved in water : eg. $KOH(K^+OH^-)$ + H_2O → $K^+(aq)$ + $OH^-(aq)$

If $[KOH] = 0.1\ M = 10^{-1}\ M$, then $[OH^-] = 10^{-1}\ M$, **so since** $[OH^-] = 10^{-pOH}$, **pOH = 1, and,**
Since, pH + pOH = 14, so pH + 1 = 14, so pH = 13.

Weak bases only partially ionize in water (about 1-10 %); indeed, they tend to remain as molecules e.g., ammonia and amines (RNH_2, $R'R''NH$ etc.) react with water to produce OH^- ions.

$$eg \quad NH_3 \quad + \quad H_2O \quad \leftarrow (1\ \%\ dissociation) \rightarrow \quad NH_4^+ \quad + \quad OH^-$$

```
    H              H
     \              \
      N :          : O:        ↔
     / \            |
    H   H           H
```

NEUTRALISATION is usually the formation of water from an *acid* (H^+) and a *base* (eg. OH^- or :NH₃), and this is always accompanied by the **formation of an ionic salt :**

$$HBr(aq) \quad + \quad KOH(aq) \rightarrow Br^- + H^+ + OH^- + K^+ \rightarrow \qquad \text{soluble salt}$$

"spectator ions"

$$H_2SO_4 = SO_4^{2-} + 2.H^+ + 2.OH^- + 2.Na^+ \longrightarrow 2.H_2O + 2.Na^+ + SO_4^{2-}$$

Acetic acid (in vinegar) $CH_3COOH + OH^- + K^+ \longrightarrow H_2O + CH_3COO^- + K^+$

Neutralisation can also occur when an acid and a base react to give just a salt :

$$Eg., \quad HCl(aq) \quad + :NH_3(aq) \rightarrow Cl^- + H^+ + :NH_3(aq) \rightarrow \qquad \text{soluble salt}$$

(ammon**ia** molecule) \qquad (ammon**ium** ion)

With $Na_2CO_3 = 2.Na^+ + CO_3^{2-} + H^+ + Cl^- \rightarrow Na^+ + HCO_3^- + Na^+ + Cl^-$

Then $Na^+ + HCO_3^- + H^+ + Cl^- \rightarrow Na^+ + Cl^- + H_2CO_3 \rightarrow H_2O + CO_2$
overall
$$2.Na^+ + CO_3^{2-} + 2.H^+ + 2.Cl^- \rightarrow 2.Na^+ + 2.Cl^- + H_2O + CO_2$$

Questions remain after huge HF leak

CHEMICAL SAFETY
Korean residents still afraid to return home

More than two months after eight tonnes of hydrofluoric acid were accidentally released at a chemical plant in South Korea, many of the thousands of local residents who fled the area at the time have reportedly not yet returned to their homes despite assurances from authorities that the area is now safe.

The highly toxic hydrofluoric acid was released on 27 September at the Hube Global chemical plant in Gumi, about 200km from Seoul. The leak killed five workers at the plant and severely injured at least 18 others, including workers and emergency personnel. The plant is reportedly still idle after the accident with no date yet set for resuming operations.

Hydrofluoric acid is used to produce chemical precursors for the pharmaceutical industry and has other industrial applications. Highly corrosive and an acute poison, exposure can cause death and serious damage to the skin, lungs, heart, bones and nervous system.

Initial press reports at the time of the accident said more than 3000 people in villages and farms downwind of the accident inhaled fumes and required emergency treatment for health complaints, including nausea, chest pain, rashes and sore eyes. The accident also contaminated crops and sickened livestock. Around 80 other firms in the area were affected, with damages estimated at more than $20 million (£12.5 million).

The initial government response to the accident, including possible mistakes by firefighters, and a sluggish evacuation of nearby residents, was sharply criticised in the Korean media. The government later acknowledged the severity of the incident on 8 October by designating the area around the

Eight tonnes of hydrofluoric acid were released at Gumi, sickening people and livestock

plant a 'special disaster zone'. Since then, additional information about the aftermath of the accident has slowed to a trickle.

Afraid to return home
A recent local news report says that government officials have declared that hydrofluoric acid concentrations in the air, water and soil in the affected area have dropped to levels that are no longer harmful. But the report adds that most residents are still afraid to return to their homes.

Vladimir Sakharov, director of the environmental emergencies preparedness programme at Geneva-based Green Cross International, tells *Chemistry World* that it is possible that hydrofluoric acid concentrations are now below dangerous levels. 'If the spill was treated with neutralising substances, normally the situation should be under control after more than a month,' he says.

Sakharov adds: 'Depending on the specifics of the response operations and local conditions, soil may become polluted by fluorides, which are strongly retained by soil components. Then, fluorides may accumulate in plants. To what extent soil is polluted by fluorides and whether it is safe to resume agricultural activities, could be determined by chemical and ecotoxicological analyses and tests.'

The commercial area in Gumi where the accident occurred was originally developed with the goal of attracting high-tech firms. But when high-tech demand failed to materialise, zoning regulations were eased to allow other industries in. In 2008, Hube Global, a South Korean–Chinese joint venture headquartered in Seoul, opened the ill-fated plant to supply raw materials to the electronics, chemicals, cosmetics, pharmaceuticals and biotech sectors.

Human error
Police investigating the accident said that the hydrofluoric acid spill may have been caused by human error as two workers were unloading the chemical from a delivery tanker. A closed circuit security video camera recorded the two workers on top of the tanker, both without protective gear. They were connecting an air hose to a valve in the tanker in order to force the chemical out under high pressure. The video shows white vapour erupting at high pressure from the tanker, engulfing the workers.

Police have said the workers were trying to save time and did not follow proper safety procedures. Prosecutors plan to indict three Hube Global executives.

Firefighters who initially responded to the Hube Global accident were not apparently fully briefed on the risks of hydrofluoric acid, according to some reports. The first to arrive on the scene wore typical firefighting garments and masks - inadequate protection against hydrofluoric acid fumes. Firefighters also spread the hydrofluoric acid further by spraying water on it. At the time of the accident, neither the Gumi city government nor the Hube Global plant had supplies of slaked lime, an agent used to neutralise the acid. Slaked lime was not deployed at the accident scene until the day after the leak.

'I am sure that RoK (Republic of Korea) specialists and scientists know what and how to respond from now on in,' Sakharov says. 'I would urge openness and transparency from RoK authorities, so this could benefit the entire international community. Lessons from this environmental emergency would be extremely valuable for all countries: what exactly happened, what was done, what went well and what did not work, positive and negative results, achievements and shortcomings, how to prevent such accidents and be better prepared in the future.' *Ned Stafford*

Biological Examples

METABOLISM : Average Human requires about 8,700 kJ/day $\approx$ 100 J/sec = 100 Watt)

Overall, the metabolism in a Human can be described by the oxidation of glucose as follows :

$$C_6H_{12}O_6 \quad + \quad 6\ O_2 \quad \rightarrow \quad 6\ CO_2 \quad + \quad 6\ H_2O \quad + \quad \text{energy (Life)}$$

And this **generates about 13 mol of carbon dioxide a day.** Subsequently, **this produces 13 mol of protons per day** according to the reaction **:**

$$H_2CO_3 \quad \leftrightarrows \quad H^+ \quad + HCO_3^- \qquad \text{(equivalent to pouring 1.3 litres of conc. HCl into our body !)}$$

The major BASES in biological systems available to react with this huge amount of acid are amines (RNH_2), phosphates (HPO_4^{2-}) and bicarbonate (HCO_3^-) which can react with acids thus:

$$RNH_2 \quad + \quad H^+ \quad \leftrightarrows \quad RNH_3^+$$

$$HPO_4^{2-} \quad + \quad H^+ \quad \leftrightarrows \quad H_2PO_4^-$$

$$HCO_3^- \quad + \quad H^+ \quad \leftrightarrows \quad H_2CO_3$$

And so neutralize the effect of the acid influx.

DIGESTION :   **stomach pH = 2**   **duodenum pH = 5**   **intestines pH = 8**

Bile Na^+ HCO_3^-

Food   + H^+ Cl^- $\rightarrow$ acidic blend $\xrightarrow{\hspace{3cm}}$

Problem **A1** :   Why is it a culinary custom to sprinkle vinegar (acetic acid) or lemon juice (citric acid) on fish?

Answer :   When salt-water fish decay they produce the weak base trimethylamine, $(CH_3)_3N$, a molecule which is readily volatile and strong smelling.

Adding an acid converts the weak base to its salt: $(CH_3)_3NH^+$ plus acetate⁻ / citrate⁻.
The salt is not volatile and hence we do not notice the typical "fishy" odour of the food.

Problem **A2** : Why do mammalian Teeth containing apatite (chemical composition = 3 $Ca_3(PO_4)_2Ca(OH)_2$) decay ?

Answer :   We have a Solubility equilibrium:

$$Ca_5(PO_4)_3(OH) \quad \overset{Ksp}{\leftrightarrows} \quad 5Ca^{2+} \quad + \quad 3PO_4^{3-} \quad + \quad OH^-$$

Sugars in the mouth are decomposed by oral bacteria producing lactic acid. The H^+ from the lactic acid then 'removes' the OH^- and PO_4^{3-} from the system (by converting them to H_2O and HPO_4^{2-}) and the apatite slowly dissolves as the equilibrium moves to the right.

BUFFER SOLUTIONS

A **BUFFER** is an aqueous solution which resists changes in pH when acids or bases are added to it. (To do this, they must contain both an acidic component (to react with added base) and a basic (alkaline) component (to react with added acid).

Eg., $\qquad$ HPO_4^{2-} $\quad + \quad H^+$ $\qquad \rightleftharpoons$ $\qquad H_2PO_4^-$

comprises the major **buffer inside cells** where pH = 7.4

and, $\qquad$ HCO_3^- $\quad + \quad H^+$ $\qquad \rightleftharpoons$ $\qquad H_2CO_3$ (dissolved CO_2)

comprises the major **buffer in blood** where pH = 7.4

A mixture of acetic acid (CH_3COOH) and sodium acetate ($Na^+ CH_3COO^-$) provides a buffer having a pH of 5, whilst a mixture of ammonium chloride ($NH_4^+ Cl^-$) and ammonia (NH_3) provides a buffer of pH 9.

Reduction / Oxidation

Redox reactions – **the key chemical event is the net movement of electron(s) from one reactant to the other,** so REDOX REACTIONS are concerned with chemical changes in which species are **oxidized** (i.e **lose electrons**) or **reduced** (i.e. **gain electrons**).

We can use the mnemonic 'OILRIG' to remember that :

OIL = oxidation is loss of electrons $\qquad$ **RIG = reduction is gain of electrons**

thus $\qquad Cu^{2+} \quad + \quad 2e^- \quad \rightleftharpoons \quad Cu_{(metal)}$ $\qquad$ is a **reduction**

and $\qquad\qquad H_2 \qquad \rightleftharpoons \quad 2H^+ \quad + 2e- \qquad$ is an **oxidation**

Overall $\quad Cu^{2+} \qquad + \qquad H_2 \quad \rightleftharpoons \quad Cu \quad + \quad 2H^+$

Eg. $\qquad CuO\,(s) \quad + \quad H_2(g) \quad ---- \text{ heat } 200\,^oC \rightarrow \qquad Cu(s) \; + \quad H_2O(g)$

The following *chemical* **redox** reaction :

$2.Ag^+ \; + \; Zn \quad \longrightarrow \quad 2.Ag \quad + \quad Zn^{2+} \quad$ "OILRIG"

Can be described by the two so-called *electrochemical* **'half reactions'** :

$\qquad\qquad 2.Ag^+ \; + \; 2e^- \longrightarrow \; 2.Ag \qquad Ag^+$ is reduced

and $\qquad\qquad Zn \quad \longrightarrow \quad Zn^{2+} \; + 2e^- \qquad$ Zn is oxidised

(Note how the charge on LHS of each equation must equal charge on RHS)

OXIDATION NUMBERS

In any discussion of redox reactions it is useful to be able to assign an **oxidation number (ON)** to any element in a given compound in order to keep track of the electrons during a reaction: **ON** is defined as the *apparent* electrical charge on the atom according to a set of rules like those following :

We need to recognize that :

Oxidation leads to a loss of electrons and an increase in oxidation number
Reduction is a gain of electrons, and so leads to a decrease in oxidation number

Oxidation Number Rules

1. **The oxidation number of an atom as an element is zero** (eg., O_2, P_4, S_8, Fe, Mg, Br_2 are the elemental forms at room temperature, and they *all have ON's of zero*).

2. **The oxidation number of oxygen is usually (-II)** (except when bonded to F). Remember that in the element, oxygen **(O_2, O=O)** has an oxidation number of zero, whilst in peroxides **(O_2^{2-}, ^-O-O^-)** each oxygen atom has an oxidation number of (-I).

3. **The oxidation number of a monatomic ion is equal to the ion's charge**, eg .Na^+ = Na(I), Cl^- = Cl(-I), S^{2-} = S(-II).

4. **The algebraic sum of the oxidation numbers in a neutral polyatomic compound is zero; in a polyatomic ion the sum of the oxidation numbers is equal to the ion's overall charge.**

5. In combinations of elements, the more electronegative element has its characteristic negative oxidation number (for example, (-III) for nitrogen,(-II) for oxygen, (-I) for chlorine), and the more electropositive element has a positive oxidation number (for example, (+I) for hydrogen, (+II) for calcium, (+III) for aluminium).

6. **The oxidation number of hydrogen (H) is usually (+I)** - due to its electronegativity being lower than that of the Main-group elements to which it is normally bonded. With more electropositive elements, Hydrogen has an oxidation number of (-I), eg. Na^+H^- .

Example 1. Find the oxidation number of sulfur, **S,** in sulfuric acid, **$H_2SO_{4(aq)}$.**

Using ON for oxidation number, we use rule 4 to write:

$2[ON(H)] + [ON(S)] + 4[ON(O)] = 0$

and rule 2 : [ON(O) = -2], and rule 6 [ON(H) = +1] to write :

$2(+1) + [ON(S)] + 4(-2) = 0$ → ON(S) = +6

Example 2. Find the oxidation number of iodine, **I**, in **ICl_4^-**.

We use rule 4 to write $[ON(I)] + 4[ON(Cl)] = -1$

Chlorine is more electronegative than iodine, so chlorine has the conventional

oxidation number of -1 (rule 3).

Thus $[ON(I)] + 4(-1) = -1 \rightarrow ON(I) = +3$

Predicting the Products of an Oxidation / Reduction reaction :

We can **predict** the outcome of the **reaction** between two redox couples such as **MnO_4^-/Mn^{2+}** and **H_2SO_3/SO_4^{2-}** in the following way:

Each redox reaction has associated with it a voltage, called the standard **reduction potential** (E^0)
defined according to :

$$Ox^{n+} + ne^- \rightarrow Red \qquad E^0 = +/- \quad "A" \quad volt \quad$$ (See SI Data Book Section 21 for a list)

where **Ox^{n+}** = oxidized form of element,

Red = reduced form of element,

n = number of electrons (e^-) transferred in the redox half-reaction

E^0 range $\quad [+3 \, volt \, ------- \, 0 \, ------- \, -3 \, volt]$

Electron acceptors $\qquad$ Electron donors

oxidisers $\qquad\qquad$ **reducers**

E^0 = **standard reduction potential** - which is the e.m.f. for the reaction (ie., the electron driving force for the reaction as it proceeds from left to right) when both 'Ox^{n+}, and 'Red' are present at 1 $\underline{M}$ concentration (or one atmosphere partial pressure for gases), and at 25^0C.

NOTE: The **greater** (more positive) the **value of E^0**, the **greater is the tendency** for:

$$Ox^{n+} + ne^- \rightarrow \quad Red$$

So, from the data in the Table below we can decide on the spontaneous (favourable) reaction :

Ox $^{n+}$ / Red couple/	E^0 / volt	e- donor or e-acceptor ?
MnO_4^- / Mn^{2+}	+1.51	e- donor / e-acceptor
SO_4^{2-} / $H_2SO_3 (SO_2)$	+0.17	e- donor / e-acceptor

It is crucial to note that the redox couple with the more positive E^0 value will REMOVE electrons from a redox couple with a less positive E^0.

In the example above, MnO_4^- has the more positive E^0 and hence the greater affinity (liking) for electrons: therefore **MnO_4^- will behave as the electron acceptor (ie. Oxidant)** . Thus, the sulphur system must donate electrons: hence **H_2SO_3 will be the electron donor (ie Reductant)** .

So we predict : $MnO_4^- \longrightarrow Mn^{2+}$ and $H_2SO_3 \longrightarrow SO_4^{2-}$

REDUCTION & OXIDATION **HALF-REACTIONS &**
THE **BALANCING** OF **REDOX EQUATIONS**

Redox equations are usually written as balanced **net ionic equations**, with spectator ions (ions that do not take part in the overall redox process) being omitted.

The determination of the stoichiometry of a redox reaction can be difficult to deduce even when the products of such a reaction are known. For this reason it is much more convenient and methodical to concentrate upon the stoichiometry of each redox "half-reaction" or "redox couple" individually.

A list of the more important redox half-reactions is presented in Section 21 of the SI data book, although you should be able to write some from memory.

Strategy for balancing redox equations:

A five step method for balancing redox equations, called the "half reaction" method, is used, and after mastering these operations, any chemical redox equation can be balanced by combining the five steps.

1. Step One is to divide the equation into the appropriate 'half-reactions' which can be balanced separately, for example :

Overall reaction $H_2SO_3 + MnO_4^- \rightarrow SO_4^{2-} + Mn^{2+}$

Assign an ON to each element in the ions or molecules of reactants and products :

MnO_4^- ON of Mn =   , and   in Mn^{2+} ON of Mn =

Thus, Mn(VII) is being **reduced** to Mn(II).

So, Reduction half-reaction $MnO_4^- \rightarrow Mn^{2+}$ and ;

H_2SO_3 ON of S =   , and   in SO_4^{2-} ON of S =

So S(IV) is being **oxidised** to S(VI).

So, Oxidation half-reaction $H_2SO_3 \rightarrow SO_4^{2-}$

2. **Step Two** is to write a separate balanced **chemical equation** for each redox-active species – this is the **MASS BALANCE** step :

MnO_4^- $\leftrightarrows$ Mn^{2+}

Note that we 'remove' oxygen(O^{2-}) as water (still O(-II)) by combination with H^+.

And :

H_2SO_3 $\leftrightarrows$ SO_4^{2-}

Note that we 'add 'oxygen(O^{2-}) as water (still O(-II)) to the appropriate side of the equation, and then add H^+ ions to balance hydrogen.

3. **Step Three** : Although we have now achieved **MASS** balance, we also need to balance **CHARGE,** by adding electrons (e^-, negative charge) as needed—this generates the balanced **electrochemical half-reaction**. The total charge on each side of a balanced reaction must be the same.

MnO_4^- + **8H**$^+$ $\leftrightarrows$ Mn^{2+} +   **4** H_2O
(LHS total charge =   )   (RHS total charge =   )

and H_2SO_3 + H_2O $\leftrightarrows$ SO_4^{2-} +   **4H**$^+$
    (LHS total charge =   )   (RHS total charge =   )

If all three steps have been done correctly, <u>one half-reaction will have electrons on the left</u> hand side of the equation (the reduction half-reaction), while <u>the other half-reaction will have electrons on the right hand side of the equation </u>(the oxidation half-reaction).

4. **Step Four** : The balanced half-reactions can be termed **electro**chemical equations, since they involve the electron.   To obtain a **chemical** equation for the reaction, we need to eliminate the electron from the overall equation .
Hence, the fourth step is the addition of the two half-reactions in such a way that the electrons cancel out – this may require multiplying one equation, or both, by an appropriate integer.
For the two half-reactions above:

$5e^-$ + $8H^+$ + MnO_4^- $\leftrightarrows$ Mn^{2+} +   4 H_2O
H_2SO_3 + H_2O $\leftrightarrows$ SO_4^{2-} + $4H^+$ + $2e^-$

The **first** reaction is multiplied by **two** and the **second** reaction is multiplied by **five** and both are added to give:

$$5 \, H_2SO_3 \; + \; 2MnO_4^- + \; 16 \, H^+ + \; 5 \, H_2O + \; 10e^- \leftrightarrows 2Mn^{2+} + \; 5 \, SO_4^{2-} + \; 20 \, H^+ + \; 8 \, H_2O + 10e^-$$

Note the equal number of electrons on each side of the equation.

5. The **final step** is to cancel the electrons and simplify the ***chemical equation*** by eliminating any chemical species common to each side of the equation :

$$H_2SO_3 \; + \; MnO_4^- \quad \leftrightarrows \quad Mn^{2+} + \; SO_4^{2-} \; + \; H_2O \; + \; H^+$$

The **Reaction Stoichiometry** for the balanced chemical equation, above, is then :

$$\underline{mol \, H_2SO_3(\, SO_2\,)} \; = \; \underline{mol \; MnO_4^-} \; = \; \underline{mol \, Mn^{2+}} \; = \; \underline{mol \, SO_4^{2-}} \; = \; \underline{mol \, H_2O} \; = \; \underline{mol \, H^+}$$

So we can use these stoichiometric relationships to solve for mol or mass as required.

Example :   Calculate the volume of a 0.0200 mol/L solution of $K^+ MnO_4^-$ required to react completely with 5 litres of sulphur dioxide produced at 25 ^oC and one atmosphere.

T = absolute temperature (Kelvin K, defined as $K = {}^oC + 273 = 25 + 273 = 298$ K)
R = gas constant, 8.314 J $K^{-1}mol^{-1}$ = 8.314 kPa.L $K^{-1}mol^{-1}$ = 8.314 Pa.m^3 $K^{-1}mol^{-1}$
  = 0.0821 L.atm $K^{-1}mol^{-1}$ and, 1 atmosphere = 101.3 kPa

Stoichiometric equations :

Since ; $H_2O \; + \; SO_2 \; = \; H_2SO_3$ then the   **mol SO_2 = mol H_2SO_3**,
so we can use the balanced equation from above,

$$5 \, H_2SO_3 \, (\, = 5.SO_2 \,) \; + \; 2 \, MnO_4^- \; \leftrightarrows \; 2 \, Mn^{2+} \; + \; 5 \, SO_4^{2-} + \; 4 \, H^+ + \; 3 \, H_2O$$

Mol SO_2 $PV = nRT$, So, $n = PV/RT$ = $\dfrac{1 \text{ atmosphere } x \; 5 \text{ L}}{0.0821 \text{ L.atm } K^{-1}mol^{-1} \; x \; 298 \text{ K}}$ = **0.2044 mol SO_2**

Stoichiometric mole ratio   mol SO_2 (H_2SO_3) / 5   =   mol MnO_4^- / 2

Now,   **mol MnO_4^- = 2 x mol SO_2 / 5** = 2 x 0.2044 / 5 = 0.08175 mol
              = concentration of MnO_4^- x volume MnO_4^- (using **n = C x V**)

So,   0.08175 mol = 0.0200 mol L^{-1} x V L

Hence,   **V($K^+ MnO_4^-$) = 4.087 L**

Topic 7 : Titrations & reaction stoichiometry, Back titrations (Practical aspects)

Volumetric Analysis - when the analysis is performed by *measuring volumes of solutions* –using a **burette** and **pipette.**

The material in solution is called the **analyte**; the volume of analyte taken is called the **aliquot,** it is delivered by a *pipette* of fixed volume into a conical flask**.**

A *burette* is a graduated tube with a tap that is used to deliver a controlled volume of **titrant** to the solution being analysed in the conical flask – the titrant is added to the solution until the reaction is complete, called the 'end-point' (stoichiometric point) and the volume measured is called the **titre.** The completion of the reaction (when it reaches the stoichiometric point) is determined by an **indicator,** which is usually a coloured dye that changes colour –when this occurs, it is called the **'end point'** of the titration.

The overall process, as one liquid is added to the other, is called a **titration.**

Eg. Consider the **Acid / Base** titration (A neutralisation reaction)

$$\textbf{1}\ Na_2CO_3\ +\ \textbf{2}\ HCl\ \rightarrow\ 2\ NaCl\ +\ H_2CO_3$$

Stoichiometry :

$$\frac{mol\ Na_2CO_3}{1} = \frac{mol\ HCl}{2}$$

So, mol Na_2CO_3 = 2 x mol HCl

TASK : To determine the exact concentration of a HCl solution by titration of an aliquot of a standard Na₂CO₃ solution ([Na₂CO₃] = 0.04761 mol/L).

A. Place an exact volume of standard Na₂CO₃ solution (25.00 mL) in a conical titration flask :

Pipette filler

Pipette volume

(aliquot) = 25.00 mL

C_{Na2CO3} = 0.04761 M

B. Using a burette, add an exact volume of HCl(21.32 mL) to neutralise the Na₂CO₃ using an appropriate indicator for the following overall chemical reaction :

Na_2CO_3 + 2HCl → 2 NaCl   + H_2CO_3

Start   1.57 mL

Finish (at end point)

22.89 mL

Titre = 22.89 -1.57 = 21.32 mL

C. Calculate the exact concentration of the HCl solution:

From balanced equation

　　　　mol HCl = 2 x mol Na₂CO₃

C_{HCl} x V_{HCl} = 2 x C_{Na2CO3} x V_{Na2CO3}

C_{HCl} x 21.32 / 1000 = 2 x 0.04761 x 25.00/1000   so C_{HCl} = 0.1117 mol/L

As another example, consider the **Acid / Base** titration (A neutralisation reaction)

$$(H_2SO_4)\ 2.H^+ + SO_4^{2-} + \textbf{2.}\ Na^+OH^- \longrightarrow 2.Na^+ + SO_4^{2-} + 2.H_2O$$

When a 25.00 mL aliquot of a solution of sodium hydroxide (NaOH) was titrated with a 0.0987 molar solution of sulphuric acid (H_2SO_4), an average titre of 15.48 mL was obtained to the stoichiometric point.   What is the molar concentration of the NaOH solution, and what mass of NaOH ($M_r = 40.0$ g mol^{-1}) does it contain per litre ?

From the stoichiometric equation;

$$\frac{\text{mol H}_2\text{SO}_4}{\textbf{1}} = \frac{\text{mol   NaOH}}{\textbf{2}}$$

Now, number of mol = concentration x volume   ie. n = C x V

$$\frac{\text{mol H}_2\text{SO}_4}{\textbf{1}} = \frac{0.0987 \text{ mol L}^{-1} x\ 15.48 \text{ mL}}{1000\ \text{ mL L}^{-1}} = \frac{\text{mol   NaOH}}{\textbf{2}} = \frac{[\text{NaOH}] \text{ mol L}^{-1}\ x\ 25.00 \text{ mL}}{\textbf{2}\quad x\quad 1000\ \text{ mL L}^{-1}}$$

So,   [NaOH] $=$ $\dfrac{\textbf{2}\ x\ 0.0987 \text{ mol L}^{-1} x\ 15.48 \text{ mL}}{25.00 \text{ mL}}$ $=$ 0.1222   mol L^{-1}

Now mass NaOH per L $=$ Conc mol L^{-1} x M$_r$ g mol^{-1}

$$= 0.1222 \text{ mol L}^{-1} x\ 40.0 \text{ g mol}^{-1} = 4.888 \text{ g L}^{-1}$$

Back Titrations   are performed when it is not practical to titrate by direct reaction.   In this case an amount of reagent is added in excess, then after reaction with the analyte is complete, the excess reagent remaining is determined by direct titration.

Eg : **CaCO$_3$** (limestone, coral, sea shells)

       Halides (Cl^{-1}, Br^{-1}, I^{-1}) by Volhard method (in seawater or waste water)

eg CaCO₃ (limestone, coral, sea shells)

Total mol HCl added

$= C_{HCl} \times V_{HCl}$ (added)

Mol HCl reacted with CaCO₃

mol HCl reacted / **2** = Mol CaCO₃

2.HCl + CaCO₃

↓

Ca^{2+} + H_2O + CO_2 + $2Cl^-$

Mol HCl in excess (titrated with NaOH)

$= C_{NaOH} \times V_{NaOH}$

HCl + NaOH

↓

H_2O + Na^+ + Cl^-

Now,   Total mol HCl added = mol HCl in excess + mol HCl reacted with CaCO₃

So, $C_{HCl} \times V_{HCl}$ (added) $= C_{NaOH} \times V_{NaOH}$ (back titration of excess) + mol HCl reacted with CaCO₃

mol HCl reacted with CaCO₃ $= C_{HCl} \times V_{HCl}$ (added) $- C_{NaOH} \times V_{NaOH}$ (back titration of excess)

Mol CaCO₃ $= ½ [C_{HCl} \times V_{HCl}$ (added) $- C_{NaOH} \times V_{NaOH}$ (back titration of excess) **]**

Halides (Cl^{-1}, Br^{-1}, I^{-1})

Total mol AgNO₃ added

$= C_{AgNO3} \times V_{AgNO3}$ (added)

Mol AgNO₃ reacted with chloride

Mol Cl^- = mol AgNO₃

Ag^+ + Cl^-

↓

AgCl

Mol AgNO₃ in excess (titrated with CNS^-)

$= C_{CNS^-} \times V_{CNS^-}$

Ag^+ + CNS^-

↓

AgCNS

Now,   Total mol AgNO₃ added = mol AgNO₃ in excess + mol AgNO₃ reacted with Cl^-

So, $C_{AgNO3} \times V_{AgNO3}$ $= C_{CNS^-} \times V_{CNS^-}$ (back titration of excess) + mol AgNO₃ reacted with Cl^-

mol AgNO₃ reacted with Cl^- $= C_{AgNO3} \times V_{AgNO3} - C_{CNS^-} \times V_{CNS^-}$ (back titration of excess)

Some Extension Problems

1. What mass, and volume, of fuel (petrol) can be injected into a motor car engine cylinder for complete combustion ?

Assume the fuel is pure octane (C_8H_{18} M_r = 114.2 g/mol; density of liquid = 0.698 g/mL), that the cylinder has a volume of one litre and fills with air at one atmosphere at room temperature (25 ^{o}C), that air contains 20%v/v oxygen, and that the molar volume of a gas at room temperature, 25 ^{o}C = 24.47 L mol^{-1} at 1 atmosphere pressure.

How much energy would be evolved by your calculated amount of octane if the combustion of octane releases 5470 kJ mol^{-1} of octane ? *(Ans : 0.0747 g, 0.107 mL,   3.58 kJ)*

2.   Calculate the amounts of Fe and S required to prepare 5 g of FeS.   Hence, calculate the volume of H_2S liberated at room temperature (25 ^{o}C) and one atmosphere pressure when 2 g of FeS is reacted with excess sulphuric acid. *(Ans :   3.18 g Fe, 1.82 g S, 556 mL H_2S)*

3. (a)   What mass of sodium carbonate (Na_2CO_3 , M_r = 106.0 g mol^{-1}) is required to prepare 500 mL of a 0.1500 mol L^{-1} solution ? *(Ans : 7.95 g)*

     (b)   Ten litres of an approximately 0.1 mol L^{-1} solution of hydrochloric acid (HCl) needs to be standardised. If 25.00 mL aliquots of the HCl are to be titrated against a standard sodium carbonate solution, what mass of sodium carbonate is required to prepare 250 mL of a solution that would give Na_2CO_3 titres of 20 .00 mL ? *(Mass Na_2CO_3 = 1.66 g)*

4.   The amount of the principal component of sea shells, calcium carbonate ($CaCO_3$, M_r = 100.1 g mol^{-1}) is to be determined in a sample of ground shell. The reaction cannot be performed by direct titration as the shell material reacts too slowly in the cold, so an excess of HCl is to be added, and the mixture boiled for several minutes until all the shell dissolves.   When cool, the excess acid will be determined by titrating the solution with standard NaOH (0.0875 mol L^{-1}).

If a 0.3765 g sample of ground shell was reacted with 40.00 mL of 0.2035 mol L^{-1} HCl and the back titre of NaOH was 21.93 mL, what percentage $CaCO_3$ was in the sea shell ? *(Ans : 82.7 % $CaCO_3$)*

5.   A sample of estuarine water is to be analysed for its chloride content using the Volhard, back titration, method.

A 25.00 mL sample of the water was first diluted to 250.0 mL with distilled water in a volumetric (or standard) flask. Then, 25.00 mL aliquots of the diluted sample were pipetted into 300 mL conical flasks and 50.00 mL of 0.0513 mol/L $AgNO_3$ solution added to precipitate all the chloride.

 The solid AgCl precipitate was then filtered off, and the entire filtrate titrated with 0.1036 mol/L KSCN [where the key reaction was : Ag^+(excess)   +   SCN$^-$ → AgSCN(s)] to give a titre of 21.56 mL, using Fe^{3+} as indicator to the stoichiometric point.

Calculate the molar concentration of Cl$^-$ in the original estuarine water sample, and convert your result to gram NaCl /L and ppm Cl$^-$. (Take M_r NaCl = 58.4 g/mol) *(Ans: [Cl$^-$] =0.1326 M, 7.74 g NaCl/L, 4701 ppm Cl$^-$)*

6.   a) Use the Lewis electron-dot model to rationalise the bonding in the following molecules or ions:
     H$_2$**O** N**H**$_3$ H**C**N **Si**F$_4$ **S**O$_2$ **S**O$_3$ HO**Cl**   **S**O$_4^{2-}$ **N**O$_2^-$ **C**O$_3^{2-}$ **Cl**O$_3^-$ **I**Cl$_4^-$
     (The central atom is bold and underlined)

     b) Hence, determine the oxidation number for each atom in the molecule/ion. Use the following electronegativities, taken from Table 12, page 122 in the 5th Edition of the SI Data Book :
     H = 2.20   C = 2.55   N = 3.04   O = 3.44   F = 3.98   Si = 1.90   S = 2.58   Cl = 3.16   I = 2.66

     c) Use the **V**alence **S**hell **E**lectron-**P**air **R**epulsion **T**heory (VSEPRT) approach to determine the stereochemistry (shape) of each of the molecules or ions, clearly showing if any un-shared pairs of electrons are present.   Where necessary, clearly distinguish between the symmetry of the electron-clouds, and the atomic symmetry, about the central atom.

Some CHEMISTRY & PHYSICS web sites that you may find useful :

Khan Academy-on Google- provides a comprehensive discussion of most chemistry topics

<**www.periodicvideos.com** > this site provides a clip for every element in the Periodic Table, explaining something of their properties, history and roles.

<**www.chemistryworld.org/elements**> provides facts about more than 75 elements—as you visit the *Chemistry in its element,* interactive periodic table.

<**www.sixtysymbols.com**> this takes more than 60 symbols used by Chemists and Physicists, and has scientists discuss what they mean.

<**www.test-tube.org.uk**>   this site offers a series of short videos that take you 'behind the scenes in the world of science'.   Here there are scientists looking and talking like everyone else as they describe their work.

ChemTube3D <**www.chemtube3d.com** > there are a large number of clips on You tube illustrating scientific principles and chemical processes – simply search for your area of interest.

VirtualChembook by Charles E Ophardt of Elmhurst college at:
http://www.elmhurst.edu/~chm/vchembook/index.html

Chem$_1$ General Chemistry Virtual Textbook by Stephen Lower of Simon Fraser University at:

http://www.chem1.com/acad/webtext/virtualtextbook.html

and Purdue University General Chemistry topics at:

http://chemed.chem.purdue.edu/genchem/topicreview/index.php

Useful free-ware for ***CHEMICAL STRUCTURE DRAWING*** can be found at **isisdraw** and **marvinsketch.**

The A thru E **Approach to Problem Solving** in Chemistry by Dave Woodcock is devoted to looking at problems in General Chemistry.

Intro is at : **http://www.molecularmodels.ca/probsol/ps_intro.html**

For students - The A thru E approach to Problem Solving starts at:
 http: //www.molecularmodels.ca/probsol/ps_A-E.html

Woodcock has some Beginning **Organic Chemistry** at :
http://www.molecularmodels.ca/boc/boc_index.html

And a Section on Nomenclature at :
http://www.molecularmodels.ca/index.html

A good General Chemistry site, www.bestchoice.net.nz that has a good explanation of scientific notation and arithmetic operations involving numbers in scientific notation. You do have to register to gain access to the site, and can do so by choosing "other" for institution.

Another useful site, developed by the University of Maryland, called MathBench Biology modules, can be accessed at the home page (http://mathbench.umd.edu/index.html) where there are numerous interactive activities based on a wide range of biological topics that have a Maths component.

1. Concentrated Hydrochloric acid contains 44.6 %w/v HCl, while concentrated "880" ammonia solution contains 25.8 %w/v NH_3.
    i)   What is the molarity of each reagent? *(Ans: HCl = 12.23 M ;   NH$_3$ = 15.18 M)*
    ii)   What volume of each would be required to prepare 2 litres of 2M reagent ?
             (Ans : HCl = 327 mL,   NH$_3$ = 250 mL)
    iii)   Calculate the volume of each of the concentrated reagents necessary
             to prepare 1 kg of NH_4Cl. *(Ans : HCl = 1.528 L,   NH$_3$ = 1.20 L)*

2. You are required to prepare a standard reference solution containing 0.02 M Ca^{2+}.
    i) What mass of A.R. $CaCO_3$ will be required to prepare one litre of solution ?
    ii) $CaCO_3$ is not soluble in water, hence calculate the volume of 0.1 M HCl
        that will just dissolve the necessary amount of $CaCO_3$ before dilution.
    (Ans : (i) mass = 2.0 g ; (ii) volume = 400 mL   )

3. The concentration of zinc in the blood is about 1 ppm: what molar (M) concentration does this correspond to?   *(Ans : 1.53 x 10^{-5} M)*

4. A urine specimen has a chloride concentration of 150 millimol per litre.
    If it is assumed that all the chloride is present as sodium chloride, what mass of this salt is dissolved per 200 mL of urine?   *(Ans : 1.76 g NaCl)*

5. Calculate the pH of the following:
    i)   "coke", $[H^+]$ = 1.77 x 10^{-3} M   *(pH = 2.75)*
    ii)   Saturated solution of Aspirin, $[H^+]$ = 1.26 x 10^{-3} M   *(pH = 2.90)*
    iii)   An oven cleaner, $[OH^-]$ = 5.03 x 10^{-1} M   *(pH =13.70)*

    What is the $[H^+]$ in each of the following:
    i)   Stomach pH = 1.6 ?   *([H$^+$] = 2.51 x 10^{-2} M)*
    ii) Soil sample pH = 5.56 ? *([H$^+$] = 2.75 x 10^{-6} M)*

6. Write a balanced chemical equation for each of the following reactions:

i) the <u>decomposition</u> to elements of nitrogen trichloride.
ii) the <u>combustion</u> of ammonia in oxygen to form nitrogen and water.
iii) the <u>decomposition</u> of solid ammonium nitrate at 400^{0}C to form
nitrous oxide (dinitrogen oxide= N_2O - laughing gas) and water vapour.

7. A solution of potassium permanganate is standardized with pure
iron metal as primary standard. The iron is dissolved in acid,
reduced to Fe^{2+}, and titrated with permanganate according to the reaction :

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

 If 33.00 mL of permanganate is needed to titrate a 0.2793g sample
of iron, what is the concentration of the permanganate ?
(Take the atomic mass Fe = 55.85 g/mol).

 (Ans : Conc KMnO$_4$ = 0.03031 M)

8.   A weighed sample of pure copper wire (0.1178g) is dissolved in hot nitric acid and after necessary pre-treatment an excess of KI is added. The liberated iodine is titrated with 38.42 mL of sodium thiosulfate solution, to the starch end-point. A sample of a copper ore concentrate (0.2750g) is treated in the same way, 28.38 mL of the same thiosulfate solution being required for the titration. Calculate:

        i)   the concentration of the sodium thiosulfate solution
        ii)   the percentage of copper in the ore concentrate.
   [Take the atomic mass Cu =63.54 g/mol]

$$Cu + 4H^+ + 2NO_3^- \rightarrow Cu^{2+} + 2NO_2 + 2H_2O$$
$$2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$$
$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^- \quad (\text{To starch end-point})$$

(Ans : (i) [Na₂S₂O₃] = 0.04825 M, (ii) % Cu = 31.64)

9.   Non-safety matches contain P_4S_3 in the match head which is ignited by friction.

(i)   Write a balanced chemical equation for the complete combustion of P_4S_3 with excess air to give P_4O_{10} and SO_2.

(ii)   What volume of air (20% v/v oxygen), at 1 atmosphere pressure and 20^0C, would be required for the complete combustion of 10 milligrams of P_4S_3?

(Use R = 8.314 JK^{-1} mol^{-1} = 8.314 kPa L K^{-1} mol^{-1} = 82.06 cm^3 atm K^{-1} mol^{-1})
(1 atmosphere = 101,325 Pa)   *(Ans : vol air = 43.7 mL)*

10.   A well aerated river water sample contains 10.0 ppm (part per million) dissolved dioxygen (O_2) at ambient temperature. Calculate the molar concentration of dioxygen in this sample.

(Ans : [O₂] = 3.125 x 10⁻⁴ M   )

REVISION QUESTION SHEET 2 (Redox)

1.   (a) In neutral solution the cyanide ion can be oxidized by permanganate to the cyanate ion (^-OCN). Write a redox half-reaction for the conversion of cyanide to cyanate, and the reduction of MnO_4^- to MnO_2.   Hence, combine the two half-reactions to deduce a balanced chemical equation for the overall redox reaction.

(b) The reaction in (a) has been used to determine the cyanide content of an effluent from a metal plating factory. In that instance an 80.0 mL aliquot of effluent gave a mean titre of 16.8 mL when titrated with a 0.0125 M solution of $KMnO_4$.

On the basis of your balanced chemical equation from part (a), calculate the molarity of cyanide in the effluent from the above analysis results.   Convert the calculated cyanide molarity to an equivalent concentration of cyanide in parts per million (ppm).
(Ans : [CN⁻] = 3.94 x 10⁻³ M =   102 ppm)

2.   Write redox equations to illustrate:-
      (i)   the oxidation of Hydrogen peroxide by permanganate, in alkali, to produce MnO_2,
      (ii)   the oxidation of toluene to benzoic acid using MnO_4^-.

3. The modern car battery (the so-called lead-acid accumulator) is based on the $PbSO_4/Pb$ and $PbO_2/PbSO_4$ redox couples (consult the SI Data Book, Section 21, for E^0 values).
Write the two redox half-reactions and add them together to obtain the overall reaction occurring when the battery is discharging, i.e. doing external work.

4. The following incomplete equations present the reactants and products of some aqueous redox reactions. Write the separate partial equations for reduction and oxidation and use them to obtain the overall redox equation:
(i) $Cr_2O_7{}^{2-}$ + CH_3CH_2OH $\xrightarrow{acid}$ CH_3CHO + Cr^{3+}
(ii) $AsO_4{}^{3-}$ + Zn $\xrightarrow{acid}$ Zn^{2+} + AsH_3

5. Use the E^0 values listed in Section 21 of the SI Data Book to determine the expected reaction between each of the following redox couples:
(i) H_2SO_3/S and S/H_2S
(ii) $CO_2/H_2C_2O_4$ and $MnO_4{}^-/Mn^{2+}$
(iii) $NO_3{}^-/N_2O_4$ and Cu^{2+}/Cu
In each case write the overall balanced redox equation.

6.   Write partial ionic equations and overall ionic equations for each of the following:

(a) zinc metal decolourises copper (II) sulfate solution.
(b) chlorine turns an NaBr solution brown as Br_2 forms.
(c) magnesium dissolves in hydrochloric acid and liberates $H_2(g)$.
(d) MnO_2 reacts with concentrated HCl, producing a greenish gas (Cl_2) and a solution of $MnCl_2$.
(e) Na_2SO_3 decolourises a purple solution of acidified $KMnO_4$.
(f) An $SnCl_2$ solution turns orange $K_2Cr_2O_7$ solution green (due to $Cr^{3+}(aq)$) in acid solution.

7.   State <u>which of the following reactions are redox reactions</u> (for the redox reactions, provide the partial equations to show both reduction and oxidation components):
(a) $2Hg^{2+}$ + Sn^{2+} → $Hg_2{}^{2+}$ + Sn^{4+}
(b) $CaCO_3$ + $2H^+$ → Ca^{2+} + CO_2 + H_2O
(c) $2H_2O_2$ → $2H_2O$ + O_2
(d) $Hg_2{}^{2+}$ + H_2S → HgS + Hg + $2H^+$
(e) $2CrO_4{}^{2-}$ + $2H^+$ → $Cr_2O_7{}^{2-}$ + H_2O
(f) $4XeO_3 + 12OH^-$ → Xe + $3XeO_6{}^{4-}$ + $6H_2O$

8. <u>Balance the following redox reactions</u> (the best way to achieve this is to establish the separate partial equations and then combine these, making allowance for the electron balance):
(a) $ClO_3{}^-$ + $MnO_4{}^-$ + H^+ → MnO_2 + $ClO_4{}^-$ + H_2O
(b) $Cr_2O_7{}^{2-}$ + H^+ + I_2 → $IO_3{}^-$ + Cr^{3+} + H_2O
(c) H_2SO_3 + $MnO_4{}^-$ → Mn^{2+} + H_2O + $SO_4{}^{2-}$ + H^+
(d) $NO_3{}^-$ + H^+ + S + H_2O → NO + H_2SO_3
(e) $MnO_4{}^{2-}$ + H^+ → $MnO_4{}^-$ + MnO_2 + H_2O
(f) PbO_2 + H^+ + Mn^{2+} → $MnO_4{}^-$ + Pb^{2+} + H_2O
(g) CuS + H^+ + $NO_3{}^-$ → Cu^{2+} + S + NO + H_2O
(h) $CrO_2{}^-$ + Na_2O_2 + H_2O → $CrO_4{}^{2-}$ + Na^+ + OH^-

9. Develop ionic partial equations to show-

(a) the reduction of hypobromous acid (HBrO) to give bromine
(b) the reduction of nitrous acid (HNO_2) to give nitrogen(I) oxide (N_2O)
(c) the reduction of the vanadyl ion (VO^{2+}) to give the vanadium(III) ion, in acid medium
(d) the reduction of manganese dioxide, in acid solution, to give the manganese(II) ion
(e) the oxidation of iodine, in acid medium, to give the iodate ion (IO_3^-)
(f) the oxidation of the hydroxide ion to give oxygen
(g) the oxidation of the ammonium ion to nitric acid (HNO_3)
(h) the oxidation of sulfur dioxide, in acid solution, to give sulfuric acid (H_2SO_4).

10. Using the information below, which one or more of the following reactions would be expected to proceed substantially to the right:
(a) $AuCl_4^- + 3Ag \rightleftharpoons 3AgCl + Au + Cl^-$?
(b) $2Co^{2+} + MnO_2 + 4H^+ \rightleftharpoons 2Co^{3+} + Mn^{2+} + 2H_2O$?
(c) $2Ag^+ + Mn^{2+} + 2H_2O \rightleftharpoons MnO_2 + 4H^+ + 2Ag$?
(d) $Co^{3+} + Ag \rightleftharpoons Co^{2+} + Ag^+$?

Data:	E^0 / V
$Co^{3+} + e^- \rightarrow Co^{2+}$	+ 1.82
$MnO_2 + 4H^+ + 2e^- \rightarrow 2H_2O + Mn^{2+}$	+ 1.23
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	+ 1.00
$Ag^+ + e^- \rightarrow Ag$	+ 0.80
$AgCl + e^- \rightarrow Ag + Cl^-$	+ 0.22

11.   What volume of H_2S (at S.T.P.) is required to reduce 3.16 g of $KMnO_4$ in acidified solution to Mn^{2+} and liberate sulphur (S) ? Note: one mole of gas occupies 22.4 litres at S.T.P. *(Ans : 1.12 litres)*

12. 4.00 g of impure iron wire was dissolved in excess dilute H_2SO_4 and the solution made up to 500   mL. A 25.0 mL aliquot of this solution required 20.0 mL of 0.0300 M potassium permanganate solution for complete oxidation. What percentage of the wire is iron?   *(Ans : 83.8 % Fe)*

13. An impure sample of sodium peroxide, Na_2O_2 , (0.390 g) was dissolved in water and the solution made up to 100 mL in a standard flask. 20.00 mL aliquots were titrated with 0.0150M potassium permanganate, giving an average titre of 21.40 mL. Calculate the percentage purity of the sample. *(Ans : 80.3 %)*

14 .   A sample of chrome ochre contains chromium(III) oxide (Cr_2O_3) and unreactive silica. 1.000 g of the substance was treated with alkali to give a solution of chromite (CrO_2^-) that was separated from the insoluble silica by filtration and oxidised to chromate (CrO_4^{2-}) with hydrogen peroxide. Excess peroxide was destroyed by boiling and the chromate converted to dichromate ($Cr_2O_7^{2-}$) by acidification. To this dichromate solution was added 25.00 mL of iron(II) sulfate solution, the excess of which was back titrated with 0.0147 M standard dichromate solution, 22.74 mL being required. When 10.00 mL of the iron (II) sulfate solution was titrated with the standard dichromate solution, 25.43 mL was required. Calculate the percentage chromium in the original sample.   (This is a very difficult question, beyond examination standard).   *(Ans : 6.24 % Cr in ore)*

15.   Potassium permanganate in acid solution oxidises oxalic acid $(COOH)_2$ to carbon dioxide.
   (a) Develop and identify the separate oxidation and reduction reactions involved.
   (b) If 1.000 g of a moist sample of oxalic acid is titrated with acidified 0.1234 M potassium permanganate, and 32.33 mL is required, what is the percentage water in the sample?
(Ans : 10.2 % water)

16.   A 25.00 mL aliquot of a solution of hydrogen peroxide is titrated with 0.0525 M potassium permanganate solution. The average titre is 31.12 mL**.**
(a)   Calculate the concentration of hydrogen peroxide in g /L**.** *(Ans : 5.55 g/L   )*

(b)   What volume of oxygen, measured at 24 °C and 1.00 x 10^5 Pa pressure, is evolved during the titration? *(Ans : Volume O_2 = 100.9 mL)*

17.   The chemistry that formed the basis of the original 'breathalyser' test is based on the fact that acidified dichromate may be used to quantitatively oxidise ethyl alcohol (ethanol = C_2H_5OH) :
$$C_2H_5OH + H_2O \rightarrow CH_3COOH + 4H^+ + 4e^-.$$
The orange dichromate is reduced to green chromium(III) ions. If ethyl alcohol is the only component involved, how many gram of alcohol are present in a 1 litre sample of beer, 25.00 mL of which required 24.21 mL of 0.685 M potassium dichromate?
(Ans : 45.87 g ethanol)

18 .   2.79 g of pure iron was dissolved in dilute sulfuric acid to give a solution of Fe(II) sulphate, and the solution volume made up to 200.0 mL. If 20.00 mL of this solution required 33.30 mL of a potassium permanganate solution for complete oxidation to Fe(III), what was the molarity of the permanganate solution?
(Ans : [MnO_4] = 0.030 mol/L)

1.   Describe what is meant by a Bronsted acid, and give <u>two</u> examples.

2.   A student titrated a 20.00 mL aliquot of ammonia solution ($NH_3(aq)$) of unknown concentration with a 0.100 <u>M</u> solution of H_2SO_4 and obtained a mean titre of 14.6 mL.

   (i)   Write a chemical equation which indicates the stoichiometry of the reaction occurring.

   (ii)   Calculate the molarity of the ammonia solution. *(Ans : [NH$_3$] = 0.146 M)*

3.   Determine the pH of each of the following solutions after 50 mL of 0.1 molar NaOH has been added to each:

   (i)   500 mL distilled water   *(pH = 11.96)*
   (ii)   500 mL 0.01 <u>M</u> HCl   *(pH = 7.0)*
   (iii)   500 mL 0.02 <u>M</u> HCl   *(pH = 2.04)*

4.   0.513 g of an anhydrous ammonium halide salt (NH_4^+ X^-) was reacted with 50.0 mL of 0.250 <u>M</u> NaOH and the solution boiled until no further ammonia was evolved.

   i)   Write a balanced chemical equation for the reaction occurring.

   ii)   How would you test for the completeness of evolution of ammonia ?

   When cool, the NaOH remaining was titrated with 0.150 <u>M</u> HCl, 20.6 mL being required for neutralization.

   iii)   Which ammonium halide salt was weighed out ?

For NH_4^+ X^- = F^-	molar mass/g = 37.0	*(Ans : M$_r$ = 54.5 g, from data,*
= Cl^-	= 53.5	*so closest to NH$_4^+$Cl$^-$)*
= Br	= 98.0	
= I^-	= 145.0	

    (This type of analysis is called a "back titration" since the titration measures the excess of a reagent added-see pages 42/43 of these notes for an explanation.)

5.   To 0.538 g of a weak diprotic acid of formula $HOOC-(CH_2)_n-COOH$ (H_2A) was added 50.0 mL of 0.200 <u>M</u> KOH and the mixture allowed to stand for 10 minutes.

   a.   Write a balanced chemical equation for the reaction occurring.

   The excess KOH was then titrated with 0.100 <u>M</u> HCl giving a titre of 10.3 mL.

   b.   Write a balanced chemical equation for the reaction occurring.
   c.   What is the molar mass of the diprotic acid ? *(Ans : 120 g/mol)*

d.   What is the value of "n" in the above formula, and what is the name of the
  acid ? (See SI Data Book, Table 6A "Dicarboxylic acids")
(This type of analysis is called a "back titration" since the titration measures the excess of a reagent
added - see pages 42/43 of these notes for an explanation.)
(Closest dicarboxylic acid from data is 118.1 g /mol, giving 'n' = 2, succinic acid)

6. A sample of household cloudy ammonia is found to contain 4.90 % w/v ammonia (NH_3).
   What is the molarity of this solution ?   *(Ans : [NH₃] =2.88 mol/L)*

7. Sulfuric acid is made by the conversion of iron pyrites to sulphur dioxide
   ($4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8\ SO_2$), followed by the oxidation of the sulphur dioxide to sulphur
    trioxide ($2SO_2 + O_2 \rightarrow 2SO_3$), and finally the conversion of sulphur trioxide to sulfuric acid
($SO_3 + H_2O \rightarrow H_2SO_4$). What is the theoretical mass of sulfuric acid that can be expected from
1000 kg of iron pyrites?   *(Ans : 1635 kg)*

8. Aluminium reacts with iron (II, III) oxide ($Fe_3O_4 = FeO.Fe_2O_3$) according to the equation :

$$8Al + 3Fe_3O_4 \rightarrow 4Al_2O_3 + 9Fe$$
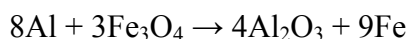
(a)   How many mol of Al are needed for the complete reduction of 4.8 mol of
        Fe_3O_4 ?   *(Ans : 12.8 mol)*
(b)   What mass of iron is produced by the reaction of each gram of aluminium ?
                    (Ans : 2.33 g)

9. In each of the following reactions, state whether the **first substance** is acting as :

(a)   a Bronsted **acid**,
(b)   a Bronsted **base**,
(c)   **neither an acid nor a base** in the Bronsted sense :

(i) $\mathbf{H^+} + OH^- \rightarrow H_2O$
(ii) $\mathbf{H_2SO_4} + Cl^- \rightarrow HCl + HSO_4^-$
(iii) $\mathbf{H_2} + Cl_2 \rightarrow 2HCl$
(iv) $\mathbf{CH_3COOH} + HBr \rightarrow CH_3COOH_2^+ + Br^-$
(v) $\mathbf{HNO_3} + HF \rightarrow H_2NO_3^+ + F^-$
(vi) $\mathbf{CO_2} + H_2O \rightarrow H^+ + HCO_3^-$
(vii) $\mathbf{CH_3OH} + H^- \rightarrow CH_3O^- + H_2$

10.   0.25 mol of KOH is dissolved in water to give 500 mL of solution. Calculate:

(a) the molarity, (b) the $[OH^-]$, (c) the $[H_3O^+]$, (d) the pH of the solution.
 (Ans : 0.5 M, 0.5 M, 2 x 10⁻¹⁴M, pH =13.7)

11.   5.0 mL of 10 M NaOH is made up to 500 mL with water. Calculate:

(a)   the molarity of the solution formed
(b)   the $[OH^-]$
(c)   the $[H_3O^+]$
(d)   the pH.   *(Ans : 0.1 M, 0.1M, 10⁻¹³M, pH =13)*

12.   12.6 g of anhydrous HNO_3 is made up to 200 mL with water. Calculate:

(a) the molarity,   (b) the $[H_3O^+]$,   (c) the pH of the solution.

(Ans : 1.0 M,   1.0 M,   pH=0)

13.   What volume of 0.1 M sulfuric acid (H_2SO_4) would be required to neutralise 100 mL of NaOH
      solution with a pH of 13.30 ?

  Hints : (i) Write out the balanced neutralisation reaction assuming the H_2SO_4 is acting as a diprotic
  acid, and
  (ii) Use the pH of the NaOH solution to determine the initial $[HO^-]$, and the fact that when neutral,
  the final pH = 7, and hence, by difference, determine the number of mol of OH^- to react.
    (Ans : Volume H_2SO_4 = 99.8 mL)

14.   Gastric juice consists essentially of a solution of hydrochloric acid and the enzyme pepsin. It is
       normally at a pH in the range of 0.3 to 1.2 with the lower figure leading to hyperacidity. Relief
       from hyperacidity is provided by commonly available antacids. Aluminium hydroxide is
       sometimes used for this purpose. What mass of aluminium hydroxide must be used in an antacid
       tablet if it is designed to increase the pH of 500 mL of gastric juice from 0.3 to 1.2 ?

       Hints : (i) Write out the balanced neutralisation reaction, and (ii) Use the pH's of the initial and
       final solution to determine the initial and final $[H_3O^+]$, and hence, by difference, the number of
       mol of H_3O^+ to react.

       Aluminium hydroxide = $Al(OH)_3$ = 78.0 g/mol

       (Ans : Mass $Al(OH)_3$ = 5.7 g)

Number of outer shell electrons = Group Number

The Modern Periodic Table of the Elements

Element name → Mercury
Atomic # → 80
Symbol → Hg
200.59 — Avg. Mass
Electronegativity 1.9

The power to attract electrons

INERT GASES
Very Stable
electron
configuration
in outer
shell (8e⁻)
(2e⁻ for He)

Group																	VIII / 18
I / 1																	He 2 4.00 --

Hydrogen 1 H 1.01 2.1

II / 2
Beryllium 4 Be 9.01 1.5
Magnesium 12 Mg 24.31 1.2
Calcium 20 Ca 40.08 1.0
Strontium 38 Sr 87.62 1.0
Barium 56 Ba 137.33 0.9
Radium 88 Ra (226) 0.9

Lithium 3 Li 6.94 1.0
Sodium 11 Na 22.99 0.9
Potassium 19 K 39.10 0.8
Rubidium 37 Rb 85.47 0.8
Cesium 55 Cs 132.91 0.7
Francium 87 Fr (223) 0.7

Group 3
Scandium 21 Sc 44.96 1.3
Yttrium 39 Y 88.91 1.2
Lutetium 71 Lu 174.97 1.1
Lawrencium 103 Lr (262)

Group 4
Titanium 22 Ti 47.88 1.5
Zirconium 40 Zr 91.22 1.4
Hafnium 72 Hf 178.49 1.3
Rutherfordium 104 Rf (261)

Group 5
Vanadium 23 V 50.94 1.6
Niobium 41 Nb 92.91 1.6
Tantalum 73 Ta 180.95 1.5
Dubnium 105 Db (262)

Group 6
Chromium 24 Cr 52.00 1.6
Molybdenum 42 Mo 95.94 1.8
Tungsten 74 W 183.84 1.7
Seaborgium 106 Sg (263)

Group 7
Manganese 25 Mn 54.94 1.5
Technetium 43 Tc (98) 1.9
Rhenium 75 Re 186.21 1.9
Bohrium 107 Bh (262)

Group 8
Iron 26 Fe 55.85 1.8
Ruthenium 44 Ru 101.07 2.2
Osmium 76 Os 190.23 2.2
Hassium 108 Hs (265)

Group 9
Cobalt 27 Co 58.93 1.8
Rhodium 45 Rh 102.91 2.2
Iridium 77 Ir 192.22 2.2
Meitnerium 109 Mt (266)

Group 10
Nickel 28 Ni 58.69 1.8
Palladium 46 Pd 106.42 2.2
Platinum 78 Pt 195.08 2.2
Darmstadtium 110 Ds (271)

Group 11
Copper 29 Cu 63.55 1.9
Silver 47 Ag 107.87 1.9
Gold 79 Au 196.97 2.4
Roentgenium 111 Rg (272)

Group 12
Zinc 30 Zn 65.39 1.6
Cadmium 48 Cd 112.41 1.7
Mercury 80 Hg 200.59 1.9
Ununbium 112 Uub (285)

III / 13
Boron 5 B 10.81 2.0
Aluminum 13 Al 26.98 1.5
Gallium 31 Ga 69.72 1.6
Indium 49 In 114.82 1.7
Thallium 81 Tl 204.38 1.8
Ununtrium 113 Uut (284)

IV / 14
Carbon 6 C 12.01 2.5
Silicon 14 Si 28.09 1.8
Germanium 32 Ge 72.61 1.8
Tin 50 Sn 118.71 1.8
Lead 82 Pb 207.20 1.8
Ununquadium 114 Uuq (289)

V / 15
Nitrogen 7 N 14.01 3.0
Phosphorus 15 P 30.97 2.1
Arsenic 33 As 74.92 2.0
Antimony 51 Sb 121.76 1.9
Bismuth 83 Bi 208.98 1.9
Ununpentium 115 Uup (288)

VI / 16
Oxygen 8 O 16.00 3.5
Sulfur 16 S 32.07 2.5
Selenium 34 Se 78.96 2.4
Tellurium 52 Te 127.60 2.1
Polonium 84 Po (209) 2.0
Ununhexium 116 Uuh (292)

VII / 17
Fluorine 9 F 19.00 4.0
Chlorine 17 Cl 35.45 3.0
Bromine 35 Br 79.90 2.8
Iodine 53 I 126.90 2.5
Astatine 85 At (210) 2.2

VIII / 18
Helium 2 He 4.00 --
Neon 10 Ne 20.18 --
Argon 18 Ar 39.95 --
Krypton 36 Kr 83.80 3.0
Xenon 54 Xe 131.29 2.6
Radon 86 Rn (222) 2.4

57-70 *
89-102 **

*lanthanides
Lanthanum 57 La 138.91 1.1
Cerium 58 Ce 140.12 1.1
Praseodymium 59 Pr 140.91 1.1
Neodymium 60 Nd 144.24 1.1
Promethium 61 Pm (145) 1.1
Samarium 62 Sm 150.36 1.2
Europium 63 Eu 151.97 1.1
Gadolinium 64 Gd 157.25 1.2
Terbium 65 Tb 158.93 1.1
Dysprosium 66 Dy 162.50 1.2
Holmium 67 Ho 164.93 1.2
Erbium 68 Er 167.26 1.2
Thulium 69 Tm 168.93 1.3
Ytterbium 70 Yb 173.04 1.1

**actinides
Actinium 89 Ac (227) 1.1
Thorium 90 Th 232.04 1.3
Protactinium 91 Pa 231.04 1.5
Uranium 92 U 238.03 1.4
Neptunium 93 Np (237) 1.4
Plutonium 94 Pu (244) 1.3
Americium 95 Am (243) 1.3
Curium 96 Cm (247) 1.3
Berkelium 97 Bk (247) 1.3
Californium 98 Cf (251) 1.3
Einsteinium 99 Es (252) 1.3
Fermium 100 Fm (257) 1.3
Mendelevium 101 Md (258) 1.3
Nobelium 102 No (259) 1.3