E-NOTE FOR INSTRUCTIONAL DELIVERY

AL-HIKMAH UNIVERSITY, ILORIN, NIGERIA

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CENTRE FOR ICT AND DISTANCE LEARNING (IDL)

e-CONTENT DEVELOPMENT (DL) UNIT

A. **Course Lecturer's Detail**

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B. **Faculty, Department and Programme**

Faculty: Education

Department: Science Education

Programme: Chemistry Education

C. **Course Title:** General Chemistry I

D. **Course Code:** CHM 111

E. **Course Credit:** 3

F. **Course Description:** Atoms/structure, molecules and chemical reactions, Chemical equations and Stoichiometry, Periodic table and periodic properties, Properties of gases,liquids and solids; Solution of solid, liquid and gases in liquids; colligative properties of solutions; Equilibrum and thermodynamics.

G. **Learning Objective:** At the completion of this e-note, it is expected that learners will achieve the following:

1. Describe the nature and structure of atoms and molecules

2. Explain the concept of chemical reactions and balancing of chemical equations.

3. Describe the structure of the periodic table and apply the periodic properties.

4. Highlight the properties of the gases, liquids and solids.

5. Describe the solution of gases, liquids and solids in liquid.

6. Substantiate the importance of colligative properties in nature

7. Link equilibrium and thermodynamic concepts and relate same to chemical system.

H. Notes on Course Outline (Topics to be taught)
Atoms and Molecules

Basic Concepts on Particulate Nature and Structure of Atoms

The atom in its structure consists of the denser part nucleus surrounded by orbitals in different shells. Positively charged protons are found in the nucleus as well as neutrons that have no charge. Negatively charged electrons are found in the orbitals at various shells.

Note: Hydrogen atom has no neutron, $_1^1H$.

An atom is electrically neutral because the number of positive charges on the nucleus exactly balanced the equal number of orbital electrons, which are negatively charged. Protons and neutrons particles are of unit mass but electrons are about 1/1836 the mass of protons. Proton, neutron and electron are the basic and fundamental constituents of atoms of every element except hydrogen. Although other particles like positron, neutrino, antineutron can be found in the nucleus of certain atoms of elements that undergo radioactive decay.

Fundamentally, the neutrons have the effect of minimizing the electrostatic repulsion between the positively charge protons in the nucleus and also contributed to the increase in mass of the atom. Some atoms exhibit the phenomenon of isotopic since the number of neutrons in the nucleus of such atoms cannot be predicted reliably.

In the planetary theory of atom, orbital electrons move round the nucleus in circular orbits similar to the movement of planets around the sun. The first orbit can take maximum of two electrons, extra electrons move to second orbit (with maximum of eight electrons). Atoms with atomic number 11 to 18 have their electrons occupying the third orbit. The potential energy of an electron is indirectly depends on its distance from the nucleus. The electrons are electrostatically attracted to the positive nucleus. The electrons closer to the nucleus are

strongly attracted and has a low potential energy but electrons farther from the nucleus are less firmly held and has a high potential energy.

Atomic number is the number of positive charged protons in the nucleus of an atom. Lawrencium for example has atomic number 103, scandium, 21 and zinc 30.

Atom/ion	Atomic number	proton	neutron	electron	Mass number
He					
Al^{3+}					
F^-					
Cl					

Quantum Numbers and Distribution of Electrons in Orbitals

The area within an atom where there is probability of finding an electron is the orbital, to define an orbital; three quantum numbers, n, l and m are needed. n is the principal quantum number for the energy level corresponding to the shells of electrons, (n=1, 2, 3..). l, is the subsidiary quantum no, l = 0,1,2….. while m is magnetic quantum number. To define an electron, the fourth quantum number is required and known as the spin quantum number. Each orbital can hold maximum of two electrons, for the two electrons to stabilize in the orbital and to minimize repulsion between them, they must have opposite spin, and this is describe by the spin quantum number, m_s.

By permutating the quantum numbers, the maximum number of electrons in each main energy level, n can be calculated as $2n^2$.

For   n = 1, maximum number of electrons $= 2(1)^2 = 2$

n = 2 , maximum number of electrons $= 2(2)^2 = 8$

n = 3 , maximum number of electrons $= 2(3)^2 = 18$

n = 4 , maximum number of electrons $= 2(4)^2 = 32$

For value of n = 1 ;   l = 0   ;   m = 0   ; $m_s = -1/2, +1/2$.

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The values of m_s indicate that two electrons are in the shell with n =1, with opposite spin.

For value of n = 2 ;

n		2			
l	0		1		
m	0		-1	0	+1
m_s	-½, + ½		-½, + ½	-½, + ½	-½, + ½

The values of m_s indicate that eight electrons are in the shell with n =2, with opposite spin in four different orbitals.

For value of n = 3 ;

n		3			
l	0		1		2
m	0		-1 0 +1		-2, -1, 0, +1, +2
m_s	-½, + ½	-½, + ½	-½, + ½	-½, + ½	-½, + ½ -½, + ½
	-½, + ½	-½, + ½	-½, + ½		

The values of m_s indicate that eighteen electrons are in the shell with n =3, with opposite spin in nine different orbitals.

There are set of rules that guide the distribution of electrons to the various orbitals.

Electrons are filled into the various orbitals in the following order according to Aufbau principle: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s …….

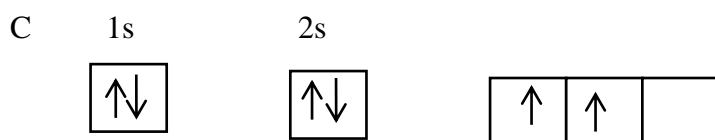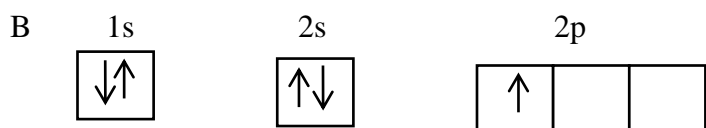s-orbital sub shell: A group of one set of orbitals with the same energy, maximum of 2 electrons

p- orbital sub shell: A group of three set of orbitals with the same energy, maximum of 6 electrons

d – orbital sub shell : A group of five set of orbitals with the same energy, maximum of 10 electrons.

f- orbital sub shell : A group of seven set of orbitals with the same energy, maximum of 14 electrons

- The simplest element, hydrogen has one electron to occupy the 1st level, with n = 1, l = 0, and m_s not important. Helium still occupy 1s level but with n = 1, l = 0, m = 0 and m_s = - ½, + ½ . The trend continues to Boron with, $1s^2 2s^2 2p^1$.
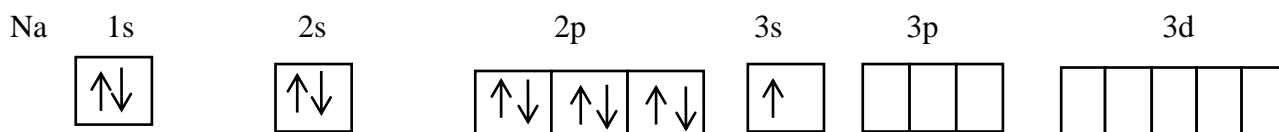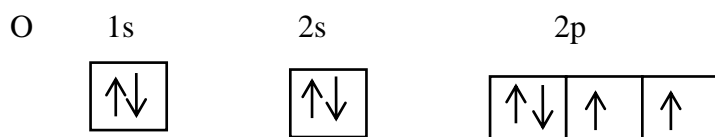
At carbon with atomic number 6, Hund's rule set in. It states that the number of unpaired electrons in a given energy level is a maximum, therefore the sixth electron in carbon occupy a separate orbital in the 2p level but with parallel spin to maximize unpaired principle by Hund's rule.

B   1s   2s   2p

$\boxed{\downarrow\uparrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\,|\,\,|\,\,}$

C   1s   2s

$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\,|\,\uparrow\,|\,\,}$

In carbon, the first orbital in 2p level is not immediately paired, rather unpaired principle is favoured.

N   1s   2s   2p

$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\,|\,\uparrow\,|\,\uparrow}$
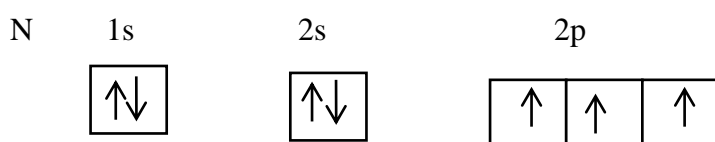
Pairing occurs at 2p level for oxygen

O   1s   2s   2p

$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow\,|\,\uparrow\,|\,\uparrow}$

Na   1s   2s   2p   3s   3p   3d

$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow\,|\,\uparrow\downarrow\,|\,\uparrow\downarrow}$ $\boxed{\uparrow}$ $\boxed{\,\,|\,\,|\,\,}$ $\boxed{\,\,|\,\,|\,\,|\,\,|\,\,}$

- Give the electronic structure of phosphorus and calcium atom in the ground state.

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Note: The sequence in which energy level is filled given as; 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s 4d, 5p, 6s, 4f, 5d, 6p, 7s etc.

This is supported by Aufbau principle, after 3p level has been completely filled for argon, the next electron goes into the 4s level for potassium and calcium.

After 4s level is the 3d level which starts to fill at scandium, scandium to copper, the elements have two electron in 4s level and an incomplete 3d level, with this structure, the elements behave in a similar manner chemically, (Sc – Cu, first transition series).

At strontium, the 5s orbital has been filled. At yttrium, the 4d level begins to fill up. (second transition series).

Third transition series starts at lanthanum where electrons start to fill up 5d level.

Note: Immediately after lanthanum, a complication arises as the 4f level starts to fill. Lanthanum has only one electron in the 5d' level but from cerium to Lutetium, 4f level starts to fill from 1 to 14, (f- electrons). These elements are referred to sometimes as inner transition elements. (Lanthanides or rare earth metals).

Nuclides of Isotopes

Any combination of protons and neutrons forming the nucleus of an atom is called a nuclide, but the number of proton identifies an element. The number of neutrons in a nucleus of a particular element may vary.

Nuclides with the same number of protons but different number of neutrons are called isotopes. Since isotopes have the same proton number, they behave alike chemically although they may have slightly different masses and radioactive properties. The three isotopes of carbon $^{12}_{6}C$, $^{13}_{6}C$ & $^{14}_{6}C$ all have 6 – protons but with 6, 7 & 8 neutrons respectively. ^{12}C & ^{13}C are stable but ^{14}C is radioactive.

The relative atomic mass of an element is the average atomic mass of all its isotopes with reference to the percentage abundance of each isotope.

- Mass spectrometer: it is essentially used for accurate measurement of relative atomic and molecular masses and structure determination.

- The basic principle of operation of a mass spectrometer include:

(i)   Sample is injected directly if it is a gas or volatile liquid. If is a solid or non-volatile liquid, it is vaporized in an oven.

(ii)   Beam of electrons from "electron gun" knocks out electrons from molecules of the sample to form positive ions. The positive ions are accelerated towards plates that are held at a negative potential.

(iii)   Some ions pass through a pair of slits which form them into a beam, the speed with which they reach depends on their mass. The less massive ions are moving faster.

(iv)   The Beam move into a magnetic field at right angle to its direction of travelling. This deflects the ions into an arc of circle. The level of deflection depends on

(a) Mass (b) Magnetic field strength.

(v)   The magnetic field is gradually increased and molecular ions enter the detector, which produces a signal proportional to the number of ions reaching it.

-       *Vapourization, Ionization, Acceleration, Deflection & Detection.*

The advantage of the instrument is its ability to detect individual ion so that isotopes of different masses are detected separately. The output of the detector is presented as a graph of % relative abundance of ions against mass/charge ratio of ions. For the isotopes ^{20}Ne & ^{22}Ne in ratio 9: 1 respectively, the average RAM of neon = (9x20) + (1 x 22)/10 = 20.2

Molecule

A molecule is the smallest part of an element or a compound which can exist alone under ordinary condition e.g. chlorine consists of particles of Cl_2 under ordinary condition but at a very high temperature these split up to form particles of Cl atoms. So molecule of chlorine is Cl_2 & atom of chlorine is Cl. Other diatomic molecules include: Br_2, I_2, F_2 O_2 etc.

Neon, Ne, Argon, Ar, Xenon Xe are monatomic molecule Ozone, O_3 is triatomic; Phosphorus, P_4 and Sulphur S_8 are Polyatomic molecules.

Nature of Intermolecular forces

Generally, there are two types of forces that a substance may possess

(a) Forces of attraction (cohesive forces)

(b) Forces of thermal agitation (thermal forces).

Cohesive forces tend to order molecules while thermal forces tend to disorder molecules. Thermal forces determine the tendency of molecules to move.

In gas molecules, the thermal forces are very much stronger therefore molecules in gas are always in a state of constant motion. Solids are characterized by the cohesive forces which held the molecules together in a regular, ordered structure; therefore do not possess translational motion. Liquids are intermediate between the two extremes. Increase in temperature makes thermal forces stronger and vice-versa. Decrease in temperature favors cohesive forces.

Either cohesive or thermal forces, forces between molecules can sub-divided as

  i.   Hydrogen bonding
  ii.   Permanent dipole- permanent dipole
  iii.   *vander-Waal* force of attraction

  -    Some molecules and the predominant molecular forces: NH_3 – hydrogen bonding, CH_3Cl - Permanent dipole- permanent dipole, Ne - *vander-Waal* force of attraction

-    **Dipole moments of molecule**.

For a neutral molecule in a uniform electric field, there is no net force tending to move the molecule as positive charges in the molecule move in opposite direction to the negative charges and the two forces cancel each other.

-    A difference in electronegativity of the atoms in a molecule causes electrical dipole moment in the molecules.

-    In heteronuclear molecule, HCl. H and Cl atoms contribute an electron each to form the bonding pair, however Cl is more electronegative compare to H, the valance electrons therefore resides more within the influence of chlorine rather than hydrogen nucleus; $H^{\delta+}$ - $Cl^{\delta-}$ such bond constitute a permanent electrical dipole.

The dipole mement of a molecule AB is the distance r ,between the centers of the + & - charge, multiply by the charge Q i.e. N = Qr

Q is the Charge while r is the distance between the centres of the charges.

N = 0 for neutral molecules e.g. H_2, CO_2; O =C=O

For water molecule, H_2O, the dipole moment value, μ = 1.84 D Debye unit

CH_3CL - μ =   1.86 Debye unit, CH_3NH_2 μ = 1.24 Debye unit CS_2 μ =0.0 Debye unit.

Chemical Equation, Reactions and Stoichiometry

During chemical changes, chemical bonds are broken, atoms are rearranged to form new substances as bonds are formed. The substances starting the reaction are reactants and those formed are products.

-      Magnesium + Oxygen $\rightarrow$ Magnesium oxide

-      Aluminium + Oxygen $\rightarrow$ Aluminium oxide

-      Iron + Sulphur $\rightarrow$ Iron II sulphide

-      Some ionic radicals and their valencies.

	Formula	Valency
Nitrate	NO_3^-	-1
Sulphate	SO_4^{2-}	-2
Ammonium	NH_4^+	+1
Nitrite	NO_2^-	-1
Carbonate	CO_3^{2-}	-2
Phosphate	PO_4^{3-}	-3
Hydroxide	OH-	-1
Perchlorate	ClO_4^-	-1
Permaganate	MnO_4-	-1
Heptaoxodichromate VI	$Cr_2O_3^{2-}$	-2

Elements in Group I & II have valences of 1 & 2 respectively. Group 13 valency of 3, e.g N^{3+}, Ga^{3+}. Elements in Group 15, 16 and 17 have valency of 3, 2 and 1 respectively.

Some elements exist in molecular form and are written as such when written chemical equations, e.g oxygen, O_2.

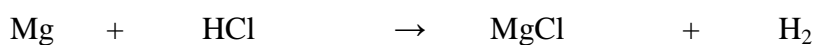Write the chemical formula of the following compounds

      (i)   Aluminium hydroxide - $Al(OH)_3$

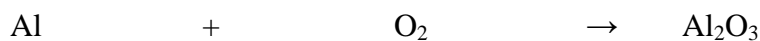   (ii)   Magnesium carbonate - $MgCO_3$

      (iii)   Potassium Oxide - K_2O

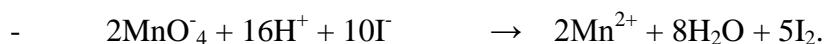**Balancing chemical equations Stoichiometrically**

-    Magnesium + Hydrochloric acid $\rightarrow$ Magnesium chloride +   Hydrogen

    Mg +   HCl $\rightarrow$ MgCl   + H_2

-    Aluminium + Oxygen $\rightarrow$ Aluminium Oxide

    Al   + O_2 $\rightarrow$ Al_2O_3

-    Redox reaction of Permanganate ion + iodide ion in acidic solution.

-    $2MnO_4^- + 16H^+ + 10I^-$ $\rightarrow$ $2Mn^{2+} + 8H_2O + 5I_2$.

Types of Chemical   Reactions

(1)   Synthesis

(2)   Decomposition

(3)   Single replacement
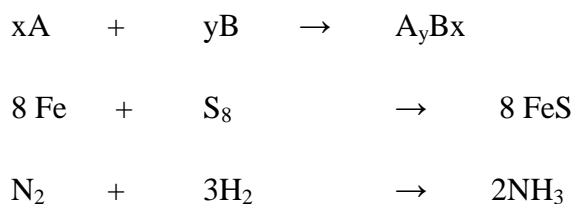
(4)   Double replacement

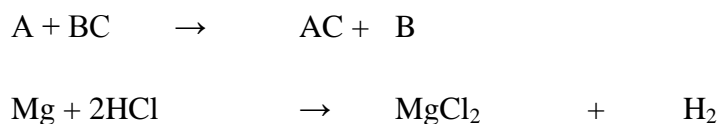**(5)**   Redox

(6)   Complexation

(7)   Precipitation

In synthesis, two or more simple substances chemically combine to give complex substance. One product is always form. Hypothetically

$$xA \quad + \quad yB \quad \rightarrow \quad A_yB_x$$

$$8\,Fe \quad + \quad S_8 \quad \rightarrow \quad 8\,FeS$$

$$N_2 \quad + \quad 3H_2 \quad \rightarrow \quad 2NH_3$$

For decomposition reaction, more complex substance breaks down into its smaller & simpler parts or components that are chemically different from the complex molecule or compound

$$AB \quad \rightarrow \quad A + B$$

$$CaCO_3 \quad \rightarrow \quad CaO \quad + CO_2$$
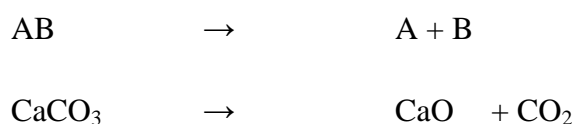
In single replacement reaction, single uncombined element replaces another in a reacting compound

$$A + BC \quad \rightarrow \quad AC + B$$

$$Mg + 2HCl \quad \rightarrow \quad MgCl_2 \quad + \quad H_2$$

For double replacement reaction, anions and cations of two reacting compounds replace the respective anion and cation from one another to give two new compounds.

$$AB \quad + \quad CD \quad \rightarrow \quad AD \quad + \quad CB$$

$$Pb(NO_3)_2 + 2KI \quad \rightarrow \quad PbI_2 \quad + \quad 2KNO_3$$

Redox reactions involve transfer of electrons from one reactant, reducing agent to another reactant, oxidizing agent simultaneously.

$$2MnO_4^- + 16H^+ + 10I^- \quad \rightarrow \quad 2Mn^{2+} + 8H_2O + 5I_2.$$

Complexation reaction is the ligand reaction with metals to form a coordination complex. Lone pair of electrons are shared from ligand to the empty orbital of metals serving as Lewis acid forming dipolar bond.

$$Ni^{2+} \quad + \quad Bipyridine \quad \rightarrow \quad Ni(byp)$$

Precipitation reaction, two soluble substances in their respective solution react to give an insoluble precipitate

$$AgNO_3 \quad + \quad NaCl \quad \rightarrow \quad AgCl(White\ Ppt) \quad + \quad NaNO_3$$
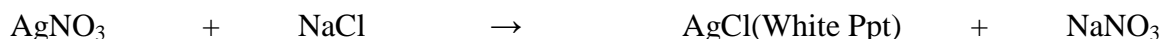
Periodic Table and Periodic Properties

In the periodic table the elements are arranged in order of increasing atomic number. This is also in order of increased nuclear charge or increased number of orbital electrons. Each element contains one more orbital electron than the preceding element.

The periodic table can be divided into four main regions according to whether the s,p,d or f levels are being filled.

- S- block elements: Group 1 and 2 elements.

- p- block elements: Group 13-18 elements

- d- block element: Group 3 -12 elements

- f- block element: The lanthanides and actinides.

Elements in periodic table are arranged in group and period.

Periodic Properties of Elements

- **Atomic Size**

- The size of atoms decreases from left to right across a period in the periodic table.

- Across the period one extra positive charge is added to the nucleus and an extra orbital electron is also added. This brings about increasing the nuclear charge as the orbital electrons being pulled closer to the nucleus (decreasing atomic size)

- Descending the group in the periodic table atomic size increases as more extra shells of electron are being added, this outweighs the effect of increase nuclear charge.

- **Ionic Radii**

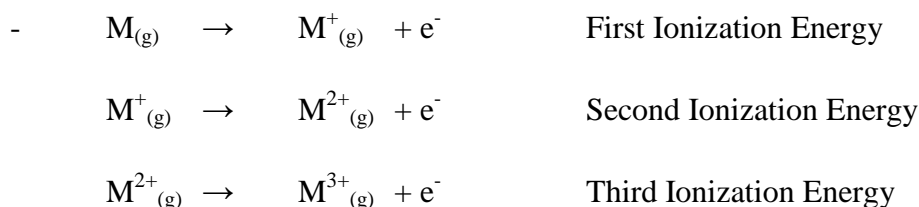- Positive ions are always smaller than the corresponding atom.

- When positive ions are formed, the whole of the outer shell of electrons is usually ionized i.e. removed as outer electron(s) are loss.

- Effective nuclear charge is another factor that affect the positive ionic radii.

- When a positive ion is formed, the number of positive charges on the nucleus exceeds the number of orbital electron and the effective nuclear charge is increased.

* E.N.C = no of charges on the nucleus/ no of electrons.

- The remaining electrons being more strongly attracted by the nucleus and the electrons are pulled in further thereby reducing the size.

- When a negative ion is formed, one or more electrons are added to the atom and the effective nuclear charge is reduced, hence the electrons cloud expands causing negative ions becoming bigger than the corresponding atom.

- Generally, ionic radii increases on descending the group since extra shells of electrons are added.

- Ionic radii decrease on moving from left to right across the period in the periodic table.

- This trend is partly due to the increase number of charge on the nucleus and also to the increasing charge on the ions.

- Ionic radius decreases as more electrons are ionized off for a particular atom, i.e $Yr^{2+} > Yr^{3+} > Yr^{4+}$....

- **Ionization Energies**.

- It is the energy required to remove the most loosely bound electron from an isolated gaseous atom.

- $M_{(g)} \rightarrow M^+_{(g)} + e^-$ First Ionization Energy

$M^+_{(g)} \rightarrow M^{2+}_{(g)} + e^-$ Second Ionization Energy

$M^{2+}_{(g)} \rightarrow M^{3+}_{(g)} + e^-$ Third Ionization Energy

- Factors that influence ionization energy

1. The size of the atom

2. The charge on the nucleus

3. Screening of nuclear charge by inner electron.

4. The type of electron involved (s, p, d or f).

* Other factors being equal, the ionization energies are in the order: s > p > d > f , since all the orbital have different shapes.

- In general, the ionization energy decreases on descending a group and increases across the period, though there are deviations from the general trends. For example, the ionization energy values for Beryllium and Magnesium are higher relatively, this is attributed to the stability of the filled 's' level orbital. The values for Nitrogen and Phosphorus are also higher, this is attributed to a half-filled 'p' level sub-shell which is also particularly stable.

- The ionization value for Boron and Aluminium are lower compare to Beryllium and Magnesium respectively because removal of one electron leaves a stable filled s-shell.

- Discuss the trend of electronegativity and electron affinity on the periodic table.

Properties of Gases, Liquids & Solids

- The four main properties of gases are :

(i) Pressure (ii) Volume (iii) Temperature (iv) Number of mole of gases.

- The four properties are related by the ideal gas equation: $PV = nRT$

Where R is the gas molar constant

- Other gas laws that relate the properties are:

- Charles law, Boyle's law, Gay-Lusaac's law and the general gas equations etc

- Ideal gases obey the ideal gas equation perfectly with respect to the four properties.

- Real gases show deviation from the ideal gas equation with respect to the four properties: pressure, volume, temperature and number of moles.

-      Ideal gas equation, $PV = nRT$

-      1.5mol of an ideal gas occupies 11 litres vol @ 27^0C. What is the pressure of the gas?

-      $PV = \dfrac{nRT}{V}$ $(R = 8.314JK^{-1} mol)$, $T = 273 + 27 = 300K$ 11 litres $= {}^{11}/_{1000}m^3$

$P = \dfrac{nRT}{V}$ $= \dfrac{1.5^1 \times 8.314 \times 300}{0.0l1}$ $= J/m^3.$ $= Pa$

R $=$ 0.082 lit. atm 1 deg 1mol

    $=$ 8.314×10^7 ergs1deg 1mol

    $=$ 8.314 J 1 deg 1mol

    $=$ 1.987 cal 1 deg 1 mol.

-      A 2- litre Dumas Bulb contain n moles of N^2 at 0.5atm pressure at temp T (k). On addition of 0.01 moles of Oxygen, it is necessary to cool the bulb to a temp of 10^0C in order to maintain the same pressure, Calculate the number of mole, n and temperature T.

-      $PV = nRT$, $(n + 0.01) = \dfrac{PV}{RT} = \dfrac{0.5 \times 2}{0.082 \times 283}$

-      $n = 0.0332$ mole

-      But $T = \dfrac{PV}{nT} = \dfrac{0.5 \times 2}{0.0332 \times 0.082}$ $= 367K$

Causes Of Deviation From Ideal Behaviour
-      Remarkable deviation are observed at low temperature and high pressure.
-      Volume occupy by gas molecule is negligible compare to the total volume of the gas.
-      Molecules do not exert any force of attraction on each other.
*   In reality, the two assumptions above according to kinetic theory of gases are wrong.
-      Molecules of gas do occupy some volume,
-      Molecules have collision diameter which can be possible only if the molecules have a finite volume.

-      On decreasing temperature and increase pressure, a stage will be reached when liquidification and finally solidification of gas take place. Gases occupy some volume & liquidification is only possible if there are forces of attraction between molecules.

The *vander Waals* Equation

The equation gives modification of the ideal gas equation by considering finite volume of gases and attractive forces between gas molecules. Molecules with the ideal gas equation.

-        $\left(P + \dfrac{n^2 a}{V^2}\right)(V - nb) = nRT$ for n moles of gas

-        For 1 mole of gas: $\left(P + \dfrac{a}{V^2}\right)(V - b) = RT$

     Note: the constants a and b are known as *vander waals* constant.

-        Calculate the pressure exerted by 1 mole of water vapour in 20 litres volume at 27^0C using the ideal gas law and the *vander waals* equation.

[The constants a and b for water vapour are : 5. 464 litre^2 atm mole^{-2} and 0.03049 litre mol^{-1} respectively, R = 0.08205 litre atm k^{-1} mol^{-1}]

-        $P = \dfrac{nRT}{V} = \dfrac{1 \times 0.08205 \times 300}{20}$ = 1.23 atm

-        $P = \dfrac{RT}{V-b} - \dfrac{a}{V^2} = \dfrac{0.08205 \times 300}{(20 - 0.03049)} =$ 1.218 atm

Properties of Liquids

-Vapour Pressure

- Boiling Point

-Surface tension

 -Viscosity of liquids

-        When the process of evaporation and condensation are in equilibrum with each other, pressure exerted will be termed saturated vapour pressure or vapour pressure of the liquid.

-        According to kinetic theory, molecules of liquid similar to gas molecules are in a state of motion, some of the molecules possess sufficient kinetic energy to overcome the forces of attraction of other molecules in the liquid state, therefore would leave the surface of liquid and accumulate in the space above the liquid and exert a vapour pressure.

-        Vapourization which leads to evaporation is an endothermic process, it is the heat absorbed by the liquid molecule that increase the kinetic energy of the liquid molecules which when sufficiently high, it is used to overcome the cohesive forces between the liquid molecules.

- Boiling point: The Boiling point of a liquid is the temperature at which vapour pressure of the liquid becomes equal to the external pressure.

- Water as liquid at an atmospheric pressure of 760mmHg, on heating the vapour pressure gradually increases. At a temperature of 100^0C, the vapour pressure of water becomes 760mmHg, hence it boils at100^0C.

- The b.pt of a liquid T_b at 1 atmospheric pressure is about two-third of the critical temperature T_C , i.e.

$T_b = {}^2/_3\ T_C.$

T_b & T_C in absolute degree.

- The ratio of molar heat of vaporization in calories of a liquid to its normal Boiling point on the absolute scale is a constant according to Trouton's Rule, i.e.

$$\frac{\triangle Hv}{T_b} = \text{constant (Trouton's Rule)}$$

For most liquids, $\dfrac{\triangle Hv}{T_b} = 21$ cal mol^{-1} deg$_{-1}$

$\dfrac{\triangle Hv}{T_b}$ the ratio is known as entropy of vapourization

- The normal Boiling point of benzene is 353.3K, assuming Trouton's rule is obeyed, estimate the Boiling point of liquid under reduced pressure of 25atm.

$\dfrac{\triangle H_v}{T_b} = 21,\quad \triangle H_v = 353.3 \times 21 = 7419.3$ cal mo^{l-1}

- But $\log\left\{\dfrac{P_2}{P_1}\right\} = \dfrac{\Delta H_v}{2.303R}\left[\dfrac{T_2 - T_1}{T_2.T_1}\right]$

- $P_2 = 760$mm, $T_2 = 353.3$, $R = 1.987$

$P_1 = 25$mm $\quad T_1 =?$

- $\text{Log}\left(\dfrac{760}{25}\right) = \dfrac{7419.3}{2.303\times 1.987}\ \dfrac{\{353.\ 3\text{-}\ T_1\}}{\{T_1 \times 353.3\}}$

$T_1 = 267.1$K

Properties of Solid

- Polymorphism --------
  - Enantiotropy
  - Monotropy
  - Dynamic Allotropy

-      Isomorphism

-   **Polymorphism:** The existence of a substance in more than one modification or form is known as polymorphism.

-      The various modifications are known as polymorphs.

-      Carbon exist in crystallane form as either diamond or graphite, Sulphur as rhombic monoclinic or plastic sulphur etc.

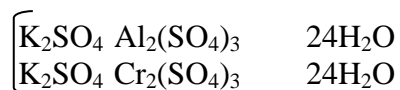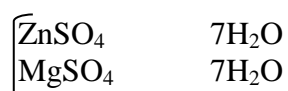**Note:** If polymorphism is with reference to element it is regarded as allotropy.

-      The conversion of one polymorph can be achieved as:

(1)   **Enantiotropy:** Reversible transformation at definite temperature known as transition point.

			Transition temperature (^{o}C)
Sulphur	Rhombic	Monoclinic	95.6
AgI	Rhombic	Regular	146.5
AgNO$_3$	Rhombic	Rhombohedral	160^0
HgI$_2$	Tetragonal	Orthorhombic	126^0

(2)   **Monotropy:** Transformation proceeds at all temperature in one direction and no transition temperature involved.

(3)   **Dynamic Allotropy:** Two forms of the solid exist together in equilibrium, i.e. one form changes to the other form at exactly the same rate and vice- versa.

For example, liquid sulphur consisting of mixture of two forms sulphur in equilibrium with each other.

-      **Isomorphism:** Pair of compounds of similar composition, that crystallize in the same form are said to be isomorphous e.g

$$\begin{cases} Cu_2S \quad\quad KClO_4 \\ Ag_2S \quad\quad KMnO_4 \end{cases}$$

$$\begin{cases} ZnSO_4 \quad\quad 7H_2O \\ MgSO_4 \quad\quad 7H_2O \end{cases}$$

$$\begin{cases} K_2SO_4\ Al_2(SO_4)_3 \quad\quad 24H_2O \\ K_2SO_4\ Cr_2(SO_4)_3 \quad\quad 24H_2O \end{cases}$$

-      For any two substances to be isomorphous, the following conditions must be fulfilled.

(i)   The two substance must be of the same formula type.

(ii)   The relative sizes of the constituent structural units should nearly be the same.

(iii)   The stereochemical form of the radical units, must be similar.

(iv)   The polarising properties of the structural units in the two substances should be almost equal.

Solution of solids in liquids

-       Solid as the solute, liquid as solvent make the solution of solid in liquid.

-       The solution can be saturated, unsaturated or supersaturated.

-       Temperature is a crucial factor to recognize in the classification.

-       The solubility of a solid in a particular solvent at a given temperature is the amount of the solid which dissolves in 100g of the solvent liquid at the given temperature to give a saturated solution.

-       The Solubility depends on the nature of the solid and liquid, the temperature and to lesser extent the pressure of the system.

-       The principle of like dissolves like is also applicable to solution of solids in liquids although there are exception.

-       **Solubility curve**.

-       Graphical relationship between solubility & temperature.

-       The curve can be of two forms:

        (i) Continuous curve

        (ii) Discontinuous curve.

-       Solid substances that do not involve any change in the nature of the saturating solid phase are said to have continuous solubility curve e.g NH_4Br , NH_4NO_3, $NaCl$, $Pb(NO_3)_2$.

-       Solid substances which exhibit a change in the nature of the solid phase, shows a break in the solubility curve and the curve is discontinuous.

-       Transition temperature is the temperature which the solid substance change from one form to another

Discontinuous Curve

-       The change in the nature of the solid phase can be due to any of the following factors.

(1)   Transformation of one crystalline form to another form e.g β -rhombic NH_4NO_3 to δ-rhombic NH_4NO_3 at a temperature of 32^0C.

(2)   Change from hydrated to anhydrous form of salt $Na_2SO_4.10H_2O$ at 32.4^0C to Na_2SO_4 (anhydrous) + solution.

(3)   Change in the degree of hydration of the solid with the saturated solution

$FeSO_4 . 7H_2O$ at 62^0C to $FeSO_4 . 4H_2O$.
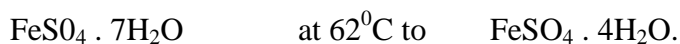
Solution of liquid in liquid (Mixture of two liquid)

-      Two liquids that do not react chemically when mixed can be

(i) Completely Miscible

(ii) Completely Immiscible

(iii) Partially Miscible.

- Water in ethanol, Benzene in toluene constitutes completely miscible system.
- Water in Mercury constitutes completely immiscible system.
- Water in ether, Water in Phenol constitutes partially miscible system.
- Chemical similarity among liquids determine their miscibility, water and alcohol are chemically similar (hydrogen bonding possession), Benzene and toluene both are chemically similar (*vander Waal forces*).
- Calculate the vapour pressure over a solution containing 11.7g benzene and 4.6g methylbenzene at 50^0C, if the vapour pressure of the pure components at the given temperature are $3.6 \times 10^4 \, Nm^{-2}$ and $1.12 \times 10^4 \, Nm^{-2}$ respectively.
- mole of benzene $= \dfrac{11.7}{78} = 0.15$
- Mole of methylbenzene $= \dfrac{4.6}{92} = 0.05$
-      Total mole $= 0.15 + 0.05 = 0.20$

- Mole fraction (benzene) $= \dfrac{0.15}{0.2} = 0.75$,

- Mole fraction (methylbenzene) $= \dfrac{0.05}{0.2} = 0.25$

Partial vapour pressure (benzene) $= 0.75 \times 3.6 \times 10^4 = 2.7 \times 10^4 \, Nm^{-2}$

Partial vapour- pressure of methylbenzene $= 0.25 \times 1.12 \times 10^4$ $= 0.28 \times 10^4 \, Nm^{-2}$

     Total vapour pressure $= 2.98 \times 10^4 \, Nm^{-2}$

Gas in liquid

- Liquid is a medium where most gases dissolve.
- Solubility of a gas in liquid depends on two factors, temperature and pressure.
- Although the nature of the gas and the liquid can also contribute to the solubility.
- Gases that are mostly soluble in liquid usually undergo chemical interaction with such liquid e.g. NH_3 in water, SO_2 in water etc

$NH_3 + H_2O \rightarrow \quad H_2SO_3$

- Gases that are easily liquefied are fairly soluble in common solvents, e.g CO_2.
- Gases that are difficult to liquefied are least soluble in common solvents e.g. O_2, N_2, H_2 etc, they are also referred to as permanent gases.

Effect of temperature on solubility of gases in liquids

- Solubility of a gas in liquid will decrease with increase in temperature. This implies that dissolved gases can simply be removed in liquid by boiling.
- Some gases that show exception to the general trend are H_2, O_2, inert gases in certain organic liquid.

Effect of Pressure on solubility of gases in liquids – Henry's law.

- Henry's law describes the effect of pressure on solubility of gas in liquid.
- Henry's law: At constant temperature, the mass of a gas that dissolve in a unit volume of a liquid is directly proportional to the pressure of the gas above the liquid at equilibrium
- Mathematically, $m \, \alpha \, p$ \qquad at equilibrium

$\qquad m = kp$

m \quad = \quad mass of gas dissolve in unit volume of liquid

p \quad = \quad Pressure of the gas above liquid at equilibrium

k \quad = \quad Henry's law constant.

- Based on Henry's law, solubility = m, plotted against equilibrium pressure gives a straight line with slope k. Passing through origin.
- If 3.5mg of CO_2 dissolves in 7.0ml of a liquid at a pressure of 1.5 atm. Determine the amount of the gas that will dissolve in 30ml of the liquid if pressure in increased to 2.5atm at constant temperature.

- \quad m \quad $= {}^{3.5}/_{7.0}$ \qquad $= {}^{35}/_{70} = ½$

m \quad = \quad kp, \quad ½ = k (1.5),

$1 = k \, (\, 2 \times 1.5),$

$k = {}^1/_3$

- \quad m = \quad kp, \quad $m = {}^1/_3 \, (\, 2.5) = {}^{2.5}/_3$

$$- \quad \frac{x}{30} \quad = \quad \frac{2.5}{3}, \qquad x \quad = \frac{30 \times 2.5}{3} \quad = 25\text{mg}$$

Note: For Henry's law to be perfectly obey the following conditions are required:

    (i)   Temperature should be high

    (ii)   Pressure should be relatively low

    (iii)   No chemical reaction should take place between the dissolved gas and the liquid solvent.

Colligative Properties of Solutions

A colligative property is the property which depends only upon the number of solutes particles present in the solution and by no means depends on the chemical nature of these particles. Solutes involve are usually non-volatile.

The four colligative properties of solutions are:

    i.   Vapour pressure lowering of the solvent

    ii.   Boiling point elevation of the solution

    iii.   Freezing point depression of the solution

    iv.   Osmosis and osmotic pressure of the solution.

Vapour pressure lowering of the solvent

The vapour pressure of a solution is lowered when some non-volatile solute is added. Raoult's law can be used to explain this phenomenon, mathematically

$$P = P^o x_1$$

x_1 = mole fraction of solvent

x_2 = mole fraction of solute

P^o = vapour pressure of pure solvent

P = vapour pressure of solvent above solution.

On adding solute to the solvent, the decrease in vapour pressure, $P^o - P = \Delta P$.

$\Delta P = P^o - P^o x_1 = P^o (1 - x_1)$

But $x_2 = 1 - x_1$

Therefore, $\Delta P = P^o x_2$

The equation above shows that the lowering vapour pressure of the liquid depends on the amount of solute, x_2.

One of the importance of studying colligative properties of solution is the determination of molecular weight of solute. The molecular weight of a solute can be calculated using parameters involving lowering vapour pressure,

$$M_2 = \frac{PW_2M_1}{W_1(P^o - P)}$$

- 18.04g of the sugar alcohol mannitol were dissolved in 100g of water , the vapour of the water at 20^oC was lowered from 17.535mm to 17.226mm of Hg, calculate the molecular weight of the mannitol.

$$M_2 = \frac{PW_2M_1}{W_1(P^o - P)}$$

$$M_2 = \frac{17.226 \times 18.04 \times 18}{100(17.535 - 17.226)}$$

$$M_2 = 181.02$$

Equilibra and Thermodynamics

Reversible processes involve chemical reactions that proceed in both directions, at the instance when the rate of the forward reaction equals the rate of the reverse reaction, the process is said to be at chemical equilibrium. Although the system might be dynamic but no perceptible transformation is observed at equilibrium.

$$H_2 \quad + \quad I_2 \quad \leftrightarrow \quad 2HI$$
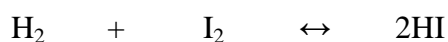
For a reaction of the form, $aA \quad + \quad bB \quad \leftrightarrow \quad cC \quad + \quad dD$
The equilibrium constant

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

At equilibrium, $\Delta G = 0$, $\quad \Delta G^o = -RT\ln K_a$

K_a is the equilibrium constant in terms of activity of each reactant and product in the reactions.

Equilibrum constant in form of partial pressure for reversible system involving gases is related to the equilibrium constant in terms of concentration thus,

$$K_p = K_c (RT)^{\Delta n}$$

Δn is the change in stoichiometric moles of reactants and products.

For the reaction involving dissociation of water molecule at a temperature of $1500^o C$,

$$H_2O \quad \leftrightarrow \quad H_2 \quad + \quad \tfrac{1}{2} O_2$$
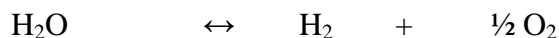
The equilibrium constant in terms of partial pressure K_p in atm is 1.87×10^{-6}. Calculate the value of the corresponding K_c.

$\Delta n = (1 + 1/2) - 1 = \tfrac{1}{2}$, $\quad$ T = 1773K, $\quad$ R = 0.08205litre atm deg^{-1} mol^{-1}.

$$K_c = K_p / (RT)^{\Delta n}$$

$$K_c = \frac{1.87 \times 10^{-6}}{(0.08205 \times 1773)^{1/2}}$$

$$K_c = 1.55 \times 10^{-7} \text{ mol/litre}$$

Questions

1. Give the names of the first thirty elements, state the number of fundamental particles and the nuclear charge value in each case.
2. Give the symbols of the following elements: Manganese, Strontium, Yttrium, Lanthanum, Cerium, Americium, Lutetium, Plutonium, Argon, Zirconium.

3. Draw the shapes of s,p,d & f orbital.

4. State the four quantum numbers required to define an electron.

5. Expalin the predominant intermolecular forces in the following molecules.

   i. H_2O ii. CH_3Cl iii. Ar

6. Write the formula of the following compounds

   i.   Sodium heptaoxodichromate VI ii. Ammonium phosphate   iii Calcium sulphate iv. Sodium Carbonate v. Caesium nitrate vi. Lithium perchlorate vii. Aluminium oxide.

7. Write a balanced equation for the redox reaction between Iron II ion and heptaoxodichromate VI ion in an acidic medium

8. What are the causes of deviation from ideality by real gases?

9. Why is the boiling point elevation regarded as colligative property ?

10. Explain the general trend of the following properties in the periodic table

    a. Electronegativity

    b. First Ionization Energy

    c. Ionic sizes.

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