Chapter 1 - Atomic And Nuclear Structure

Q.1. Write the important postulate of Bhor's theory; And also write th equations for radii and energy of n^th orbit of hydrogen atom. (201

Ans. Bohr's Theory Of Atomic Model: -

In 1913 Neils Bohr pointed out that Rutherford's atomic model wa highly unreliable. Earlier Maxwell was established that whenever a charge particle moving at constant velocity with respect to any inertial frame then will lose energy. Since electron being a charge particle and due to continuou change is its direction of motion, so it will lose the energy continuously. S that path will become continuously reduced and finally it will collide with th nucleus. However, this not a case.

Neils Bohr retained the basic concept as Rutherford's-model that in a atom electron revolve around the central nucleus but he has given hi assumption based on Max Planck quantum mechanism.

According to him: -

(i) Electrons revolve around the nucleus in stationary circular orbits.

(ii) Energy of an electron remains constant as long as it revolves in rectangular orbit so that as long as electrons revolve in orbit, it neithe absorbs energy nor radiate energy i.e the energy of the shell is quantize (fixed) and he has given in number n = 1, 2, 3, 4 or in letters K ,L, M As w move away from the nucleus the energy of the orbits increases.

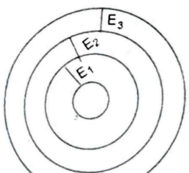
i) Angular momentum of the moving electron governs the energy of th electron in an orbit, since the energy is quantized therefore angula momentum is equal to the integral multiple of $n\frac{h}{2\pi}$ and momentum = mv

$mvr = n\frac{h}{2\pi}$, where $n = 1, 2, 3, 4$

$\frac{h}{2\pi}$ = magnitude of photon.

When electrons move in one orbit to another orbit it will absorb or radiat energy. When it jumps form one orbit to another , the difference in energ s equal to the difference in energies of the two concerned level

$\Delta E = E_2 - E_1$



ination of Radius of an atom/ Hydrogen atom:-

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If an electron of mass m, moving with velocity v, around the nucleus in an orbit of radius r then centrifugal force

$= \frac{mv^2}{r}$ (Which tends to through the e⁻ out of the orbit).....(1)

If the charge of the electron is e and the nuclear charge of au atom is + Ze then coulombic or electrostatic force (EF) is as:



$$E.F = \frac{Ze^2}{4\pi \epsilon_0 r^2} \quad .....(2)$$

to remain an electron is an orbit these two force (centrifugal and centripetal) should be equal

i.e, $$\frac{mv^2}{r} = \frac{Ze^2}{4\pi \epsilon_0 r^2} \quad .....(3)$$

Or $$v^2 = \frac{Ze^2}{4\pi \epsilon_0 r^2} \times \frac{r}{m} = \frac{ze^2}{4\pi \epsilon_0 rm}$$

According to one of the postulate of Bohr's theory, angular momentum of revolving electron is given by the expression

$$mvr = n\frac{h}{2\pi} \quad \text{or} \quad v^2 = \frac{n^2h^2}{4\pi^2m^2r^2} \quad .....(4)$$

Equating equation (3) and (4) we get,

$$\frac{Ze^2}{4\pi \epsilon_0 mr} = \frac{n^2h^2}{4\pi^2m^2r^2}$$

Or, for hydrogen atom Z = 1

$$r_H = \frac{\epsilon_0 h^2}{\pi me^2}\frac{n^2}{Z} \quad .....(5)$$

For hydrogen the charge on the nucleu Z = 1 and if n = 1, this gives a value of

$r = 1 \times 0.529 \overset{0}{A}$

for n = 2 $r = 2^2 \times 0.529 \overset{0}{A}$

It is clear from the above equation that the radius of the orbit in hydrogen atom is directly proportional so $1^2, 2^2, 3^2$..

Calculation of energy: -

If an electrons jumps flow higher energy level to lower energy leve

then it will always radiate energy. i.e $E = -\frac{1}{2}mv^2$

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Substituting the value of V^2 from equation (3) we get

$$= -\frac{ze^2}{8\pi \epsilon_o r}$$

Substituting the value of r from equation (5) we get

$$E = -\frac{e^4 m z^2}{8 \epsilon_o^2 h^2 n^2}$$

Calculating the values for constant we get, $\frac{e^4 m}{8 \epsilon_o^2 h^2} = 13.6$

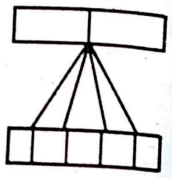
$$E = -13.6\frac{z^2}{n^2} eV/atm \qquad \text{or} \qquad E. = -2.18\times10^{-18}\frac{z^2}{n^2} J/atom.$$

When electron moves from n_2 to n_1 energy level than its energy change will be given as

$$\Delta E = E_2 - E_1$$

Substituting the value of E from equation (6) the energy change will be

$$\Delta E = \frac{Z^2 e^4 m}{8 \epsilon_o^2 h^2}\left[\frac{1}{n_2^2} - \frac{1}{n_1^2}\right]$$



We know $E = h\bar{v}$ (Plank equation)

Or $E = hc\bar{v}$

Substituting the value of E is above equation

$$\bar{v} = \frac{Z^2 e^4 m^2}{8 \epsilon_o^2 h^3 c}\left[\frac{1}{n_2^2} - \frac{1}{n_1^2}\right]$$

Or $$\bar{v} = R\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]$$ (Redberg Equation)

Where $R = \frac{Z^2 e^4 m^2}{8 \epsilon_o^2 h^3 c}$ where R is Rydberg constant

Experimental value of $R = 109679\ cm^{-1}$

Theoretical value of $R = 109677\ cm^{-1}$

The agreement between experimental and theatrical value of R is the success of Bohr's theory.

Drawbacks: -

(i) His theory fails to explain the spectra, other than hydrogen.

(ii) When lines spectrum is observed closely then it is found that a single line is made up of fine lines. Bohr's theory failed to explain the reason for it.

iii) When a light emitting source is kept under the influence of magnetic field a single line splits into number of lines. This effect in known as Zemann effect.

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(iv) Splitting of line occurred under the influence of electrical field.

Bohr's theory failed to explain these effects.

Q.2 Define Sommerfeld's atomic model. **(2006)**

Ans. Sommerfeld's Theory:-

Though **Bohr's** Theory was highly appreciated and he was awarded noble prize. The hydrogen spectrums generally consist of single sharp lines. But on examination by a high resolution spectrometer each single line is found to consist of a group of lines closely spaced together. **Bohr** fails to explain these lines. At this stage **Sommerfeld** came forward with his "concept of elliptical orbits".

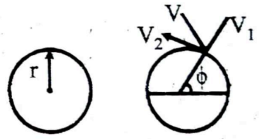
Summerfield explain these lines by considering the concept of elliptical orbits. Elliptical orbits have one major axis and one minor axis. When the major axis becomes equal to the minor axis the orbit will be circular one

We know that in circle having only one coordinate that change is angle of rotation but in elliptical orbit having two co-ordinate i.e. radius vector (r) and azimuthal angle changes.

The tangential motion of electron at any point of the ellipse can be restoring in two components, radial motion (along radial factor and transfers or angular motion along 1 to the radial motion. Radial motion will give angular momentum. These two momentums are also quantized, according to Sommer field these momentum give two new quantum no.

$$mvr = n_r \frac{h}{2\pi}$$

$$mvr = n_\phi \frac{h}{2\pi}$$



Where n_r and n_ϕ radial momentum quantum no. and angular momentum quantum no. These two quantum no. can be related to Bohr's quantum number as $n = n_r + n_\phi$. The ratio of n and n_ϕ i.e the ratio of length of major axis and length of minor axis gives the geometry of the ellipse or the shape of the orbit.

$$\frac{n}{n_\phi} = \frac{n_r + n_\phi}{n_\phi} = \frac{\text{length of major axis}}{\text{length of minor axis}}$$ These may be various conditions possible.

(i) If $n_\phi = n$ It means that the length of minor axis and major axis are equal which resets in a circular orbit. It means that circular orbit is one of the conditional orbit if an ellipse.

(ii) If $n_\phi = 0$ This indicates that linear motion of e$^-$ passing through nucleus which in never possible.

(iii) If $n_\phi > n$: This condition is not possible i.e minor axis never exceed major axis.

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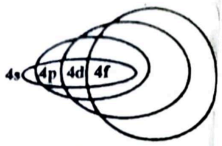
(iv) If $n_\phi < n$: In that case the no. of elliptical orbits or sub shells will be equa to the of n i.e if n = 4 then these will be four sub orbit as

(i) $\frac{n}{n_\phi} = \frac{4}{4} = 1 \rightarrow$ circular orbit

(ii) $\frac{4}{3} \rightarrow$ elliptical orbit .

(iii) $\frac{4}{2} \rightarrow$ more ellipse

(iv) $\frac{4}{1} \rightarrow$ even more ellipse



Sommerfeld orbits for n =

These orbits have little difference in energies which are responsible fo the four structures in high resolution.

Drawback of Summerfield: -

(i) He does not explain electric field effect for Starks effect.
(ii) He has not taken the wave properties of the elements.
(iii) His theory does not reveal the maximum no. of electrons can be held b an orbit.
(iv) It does not gave any explanation about the intensity of spectral line.
(v) He has given a misleading a explanation for momentum.

Q.3 The first, second, third and fourth shells of an atom may contain upt 2, 8, 18 and 32 electrons, respectively. Explain this arrangement in terms quantum numbers. **(2005)**

Ans. Principal quantum number is the most important quantum number sinc it tells the principal energy level or shell which the electron belongs. It alway a integer value except zero i.e. n =1,2,3....and these energy shells als designated by the letters K, L, M, N.....etc. The first principal shell (K), n= which means that this energy shell is of lowest energy and lies closest to th nucleus and similar to second principal shell (L), n=2 and so on .The maximun number of electron present in any principal shell is given by $2n^2$ where n is th number of the principal shell.

Q.4 "It is ψ^2 and not ψ related to the probability of finding an electron i space." Elaborate. **(2007)**

Related Questions

. What is the angular wave function? Discuss the shapes of d-orbitals **(2006)**

Elaborate ψ and ψ^2 related to the probability of finding an electron space. **(2013)**

What is the significance of ψ and ψ^2? **(2017)**

. Significance of Ψ and Ψ^2: -

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In all wave equations, the square of the wave function is the property which has physical significance. For example in case of light wave, square of the amplitude of the wave at a point is proportional to the intensity of the light wave. Similarly in electron wave motion, square of Ψ (Ψ) should represent intensity. According to uncertainty principle, the position of electron cannot be determined with certainty. We can say greater the intensity of a wave function at a particular point greater is the probability of locating the electron at that point. Thus Ψ^2 may be interpreted as being proportional to electron density. In order to avoid imaginary value $\Psi\Psi^*$ is used for Ψ^2. Ψ^* is a complex conjugate of Ψ, we expect that if Ψ extends over a finite volume in space then the electron would be found in that volume. So $\Psi\Psi^* d\tau$ gives the probability of finding the electron is finite, which means $\Psi\Psi^* d\tau$ must give real values. If Ψ has real value then $\Psi = \Psi^*$ and we can use $\Psi^2 d\tau$ in place of $\Psi\Psi^* d\tau$.

Q.5 Describe the Radial and angular wave functions. **(2005, 14)**

Other Related Questions -

Q. Write short note on Radial and angular wave functions. **(2018)**

Ans. The method of describing the shape of an orbital in terms of its projection of its wave function along an axis, as in the p_x orbital case, is a way of describing the orientation dependent part of the wave function. That the wave function of the p_x orbital is orientationally dependent means that its projection is not the same along each of the cartesian axis.

The electronic wave function, as we have seen above, describe the distribution of the electron positions in terms of the distance of the electron from the nucleus, **r**, and the orientation of the electron relative to the nucleus. We can separate the wave function into an orientationally dependent part, known as the **angular wave function**, and an orientationally independent part, which is known as the **radial wave function**.

$$\psi_{n,\ell,ml}(r,\theta,\phi) = R_{n,\ell}(r)\,Y_{\ell,ml}(\theta,\phi)$$

The Radial Wave function, Rnl(r), depends only on the distance of the electron from the nucleus, and is characterized by the values of the principal and orbital angular momentum quantum numbers, whereas the angular wave function, Y, depends on the angles of the electron from the nucleus, and is characterized by the values of the orbital angular momentum and magnetic quantum numbers.

The s orbitals consist only of a radial part to the wave function, and Y = 1. The angular wave functions for other types of orbitals are complicated mathematical expressions, so generally only the shapes of the orbitals, as shown above, are important.

Another important function we need to consider if the **Radial Distribution Function**, $P_{nl}(r)$. This is defined as the probability that an electron in the orbital with quantum numbers n and l will be found at a

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distance r from the nucleus. It is related to the radial wave function by the following relationship:

$P_{n,l}(r) = 4\pi r^2 R_{n,l}(r)$; normalized $\int_0^\infty P_{n,l}(r)dr = 1$

Q.6 What is an orbital? Distinguish between p and d orbital with respect to shape and orientation in space. (2005)

Related Questions -

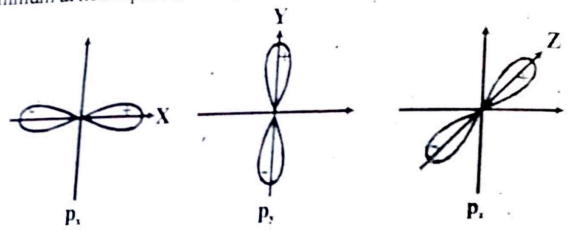
Q. Write short notes on shape of d-orbitals. (2015, 18)

Ans. Atomic orbital: -

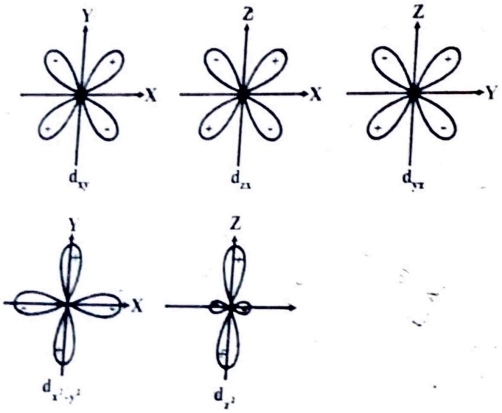
Atomic orbital is defined as the three dimensional region of the space around the nucleus where the probability of finding electron is maximum . it is usually denoted by Ψ^2.

Shape of p-orbitals:-

Shape of p-orbital is Dumb-bell shaped. Since p-subshell have three value of m. i.e. -1, 0, +1, thus they contain three p-orbital p_X, p_Y, p_Z. Each p-orbital is present on the axis. The possibility of finding of electron is maximum at end point and minimum at nodal plane. Each p-orbital contain one nodal plane.



Shape of d-orbitals:-



Shape of d-orbitals is double dumb-bell shape. Since d-subshell have values of 'm' i.e. -2, -1, 0, +1, +2, thus they contain five orbitals , which

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have different orientation. Out of five orbitals three (d_{xy}, d_{yz}, d_{zx}) have orientation in between the axis and rest two have orientation on the axis. Each d-orbital contain two nodal plane.

Q.7. Give the number of nodal points in the radial distribution plots of 3s and 3d orbitals. (2009)

Ans. The radial nodes of any orbital = $(n-\ell-1)$

For 3s the radial node = (3-0-1) =2

For 3d the radial node = (3-2-1) =0

Q.8. Give the number of nodal points in the radial distribution plosts of 3s, 3p and 4d orbitals. (2016)

Ans. Radial distribution curve gives an idea about the electron density at a radial distance from the nucleus. The value of $4\pi r^2\psi^2$ (radial probability density function) becomes zero at a nodal point, also known as radial node.

The number of radial nodes for an orbital = n - l - 1.

Where n = principal quantum number and l = azimuthal quantum number.

For 3s, n = 3, l = 0

According to formula,

number of radial nodes = n - l - 1 = 3 - 0 - 1 = 2

For 3p; n = 3, l = 1

According to formula,

number of radial nodes = n - l - 1 = 3 - 1 - 1 = 1

For 4d; n = 4, l = 2

According to formula,

number of radial nodes = n - l - 1 = 4 - 2 - 1 = 1

Q.9 A moving cricket ball, weighing 200g, is to be located within 0.2 Å. What is the uncertainty in its velocity? Comment on your result : Given : h = 6.6262×10^{-34} Js. (2008, 2010)

Ans. According to Heisenberg uncertainty principle

$$xp = \frac{h}{4\pi} \quad \Rightarrow \quad xmv = \frac{h}{4\pi}$$

$v = h/4\pi m = 6.6 \times 10^{-34}/4 \times 3.14 \times 0.2 \times 0.2 \times 10^{-10}$

$= 6.6 \times 10^{-34}/0.5024 \times 10^{-10} = 13.13 \times 10^{-24}\ ms^{-1}$

Heisenberg uncertainty principle holds good for all object but is it is significance and it is only for microscopic particle. The above result in uncertainty in velocity is so low as compared to electron so that the Heisenberg uncertainty principal not imply this system.

Q.10 Describe Heisenberg uncertainty principle. (2010, 2007, 2006, 14)

Related Question -

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Q. Write short note on Heisenberg uncertainity principle. **(2016, 18)**

Ans. This principle proposed by Werner Heisenberg in 1927. According to this principle , "It is impossible to determine simultaneously the exact position and momentum of a moving particle like electron, proton, neutron, etc."

Mathematically,

$$\Delta x \times \Delta p \geq \frac{h}{4\pi}$$

Q.11 Write short note on the Mass defect and binding energy of the nucleus. **(2009, 14, 18, 19)**

Ans. Mass Defect: -

Careful measurements have shown that the mass of a particular atom is always slightly less than the sum of the masses of the individual neutrons, protons, and electrons of which the atom consists. The difference between the mass of the atom and the sum of the masses of its parts is called the *mass defect* (Δm). In calculating the mass defect it is important to use the full accuracy of mass measurements because the difference in mass is small compared to the mass of the atom. Rounding off the masses of atoms and particles to three or four significant digits prior to the calculation will result in a calculated mass defect of zero. $\Delta m = [Z(mp + me) + (A-Z)mn] - m_{atom}$ (1) where: Δm = mass defect (amu) m_p = mass of a proton (1.007277 amu) m_n = mass of a neutron (1.008665 amu) m_e = mass of an electron (0.000548597 amu) m_{atom} = mass of nuclide ${}_Z X^A$ (amu) Z = atomic number (number of protons) A = mass number (number of nucleons).

Q.12 Write short note on Nuclear binding energy. **(2005)**

Ans The binding energy of a nucleus may be defined as the amount of energy released during the formation of hypothetical nucleus from its proton and neutron. Or in other way we can say the amount of energy will require to separate the proton and neutron.

Q.13 Which of the lanthanide element is radioactive? **(2009)**

Ans. Promethium

Q.14 Describe stability of nucleus and N/P ratio. **(2013, 14, 19)**

Related Questions -

Q. Why is a higher ratio of neutrons to proton to be expected in heavier nuclei? **(2006)**

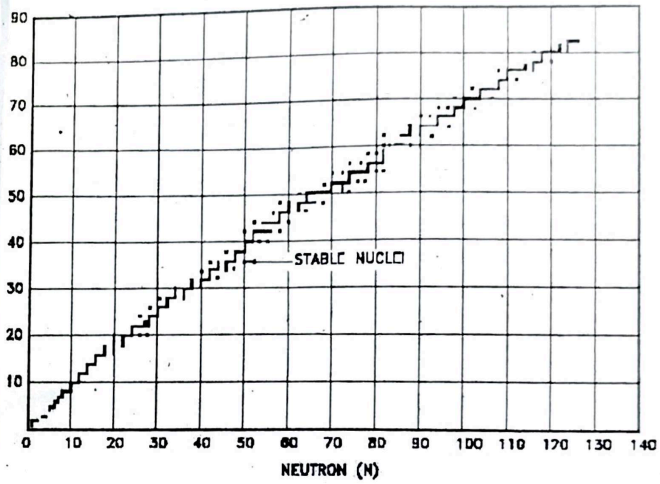
Q. Write short note on Nuclear stability - N/P ratio and nuclear binding energy. **(2015)**

Q. Write short note on Statbility of nucleus and N/P ratio. **(2016, 18)**

Ans. The nuclear stability is found to be related to the neutron/proton ratio, mass defect, packing fraction. For different element the number of neutron is

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otted against the number of protons. it is found that the elements with stable uclei i.e. nonradioactive lie within a region know as zone or belt of stability.



igure shows the distribution of the stable nuclides plotted on the same axes s the chart of the nuclides. As the mass numbers become higher, the ratio of neutrons to protons in the nucleus becomes larger. For helium-4 (2 protons and 2 neutrons) and oxygen-16 (8 protons and 8 neutrons) this ratio s unity. For indium-115 (49 protons and 66 neutrons) the ratio of neutrons to protons has increased to 1.35, and for uranium-238 (92 protons and 146 neutrons) he neutron - to-proton ratio is 1.59. Neutron - Proton Plot of the Stable Nuclides. f a heavy nucleus were to split into two fragments, each fragment would form a nucleus that would have approximately the same neutron-to-proton ratio as the heavy nucleus. This high neutron-to-proton ratio places the fragments below and to the right of the stability curve displayed by Figure 1. The nstability caused by this excess of neutrons is generally rectified by successive beta emissions, each of which converts a neutron to a proton and moves the nucleus toward a more stable neutron-to-proton ratio.

Nuclear Binding Energy: -

Nuclear binding energy is the energy that would be required to disassemble the nucleus of an atom into its component parts. These component parts are neutrons and protons, which are collectively called nucleons. The binding energy of nuclei is due to the attractive forces that hold these nucleons together and this is usually a positive number, since most nuclei would require the expenditure of energy to separate them into individual protons and neutrons. The mass of an atomic nucleus is usually less than the sum of the individual masses of the constituent protons and neutrons (according to

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Einstein's equation $E=mc^2$) and this 'missing mass' is known as the mass defect, and represents the energy that was released when the nucleus was formed.

The term nuclear binding energy may also refer to the energy balance in processes in which the nucleus splits into fragments composed of more than one nucleon. If new binding energy is available when light nuclei fuse, or when heavy nuclei split, either process can result in release of this binding energy. This energy may be made available as nuclear energy and can be used to produce electricity as in (nuclear power) or in a nuclear weapon. When a large nucleus splits into pieces, excess energy is emitted as photons (gamma rays) and as the kinetic energy of a number of different ejected particles (nuclear fission products).

The nuclear binding energies and forces are on the order of a million times greater than the electron binding energies of light atoms like hydrogen.

The mass defect of a nucleus represents the mass of the energy of binding of the nucleus, and is the difference between the mass of a nucleus and the sum of the masses of the nucleons of which it is composed.

Q.15. A particle of mass 3×10^{-4} amu is moving in a circular orbit of diameter $0.9\,\text{Å}^0$ with speed of 3×10^4 cm/sec accurate upto 0.002%. What is the uncertainty in locating its position.
(Given $h = 6.26 \times 10^{-34}$ JS) (2011)

Sol. Given $m = 3 \times 10^{-4}$ amu, $v = 3 \times 10^{-4}$ cm/sec, $h = 6.73 \times 10^{-4}$ cm/sec 10^{-27} Ags

$$\Delta x.\Delta p = \frac{h}{4\pi} \Rightarrow \Delta x \frac{h}{4\pi.\Delta p} = \frac{6.7\times10^{-27}\times7}{3\times10^{-4}\times3\times10^{4}\times22} = 5.8\times10^{-29}\,\text{cm}$$

Q. 16 The nuclide $_{62}Sm^{150}$ under goes positron decay as well as electron capture. What are the products in each case? (2011)

Ans.
$$_{62}Sm^{150} + {}_{+1}e^0 \longrightarrow {}_{63}Eu^{150}$$
Prositron

$$_{63}Eu^{150} + {}_{-1}e^0 \longrightarrow {}_{62}Sm^{150}$$
Electron

Q.17 Write short note on the Schrodinger Wave Equation. (2011)

Related Questions -

Q. Write the Schrodinger Wave equation and explain the terms involved (2012)

Q. Write short notes on Schrodinger wave equation. (2015, 16)

Ans.
$$\frac{\partial^2\psi}{\partial^2 x} + \frac{\partial^2\psi}{\partial^2 y} + \frac{\partial^2\psi}{\partial^2 z} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

where ψ = wave function, E = total energy, V = potential energy, x, y, z = coordinates.

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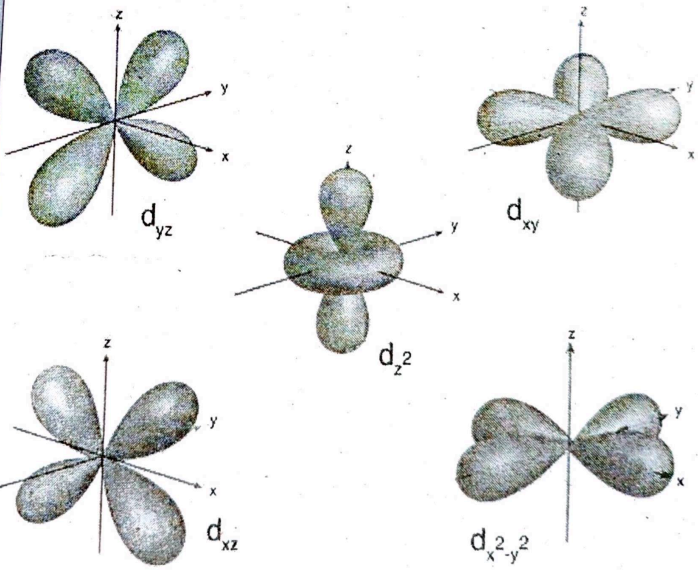
Q. 18. Differentiate between an orbit and an orbital. (2012, 14, 16, 17, 18, 19)

Ans.

Orbit	Orbital
It is well-defined circular path followed by electron around nucleus.	It is a region of space around the nucleus where the probability of finding an electron is maximum.
It represents two dimensional motion of electron around nucleus.	It represents three dimensional motion of electron around nucleus.
The maximum no. of electrons in an orbit is $2n^2$.	The maximum no. of electrons in an orbital is 2.
Orbit is circular in shape and denoted as K, L, M, N.	Orbitals have different shapes and it is denoted as s, p, ... etc and s carry one orbital, p carry three orbital p_x, p_y and p_z

Q.19. Write short note on shape of d-orbitals. (2019)

Ans. d Orbitals: -



In addition to s and p orbitals, there are two other sets of orbitals which become available for electrons to inhabit at higher energy levels. At the

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$$\text{Packing fraction} = \frac{\text{isotopic mass} - \text{mass number}}{\text{mass number}} \times 10^4$$

Packing fraction can be positive or negative. If packing fraction is tive, the isotopic mass is less than the mass number and in that case the get transformed into energy in the formation of that nucleus according to ormula $E = mc^2$. This nuclei is more stable.

A positive packing fraction would mean a tendency towards instabil- his is not essentially correct for atoms will lower atomic mass though. It ıld be noted that the element with mass number more than 230 are radioac- and goes through spontaneous disintegration.

lear Stability: -

The stability of nuclei are classified according to even and odd num- of photons and neutrons

otons	Neutrons	Stable Nuclei
ven	Even	160
ven	Odd	56
dd	Even	52
dd	Odd	4

For stable nuclie, we can see that nature prefers even number of tons and an even number of neutrons. The odd combination of proton and ıtron in the nucleus are very less and are found only in lighter elements. For ments with large number of proton in the neucleus, the coulomb electro- tic force of repulsion becomes significant and the number of neutrons must greater to compensate this repulsion effect.

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Chapter 2 - Properties Of Elements

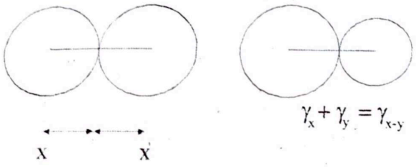
Properties of The Element: -

Atomic Properties: -

1. Atomic and ionic radius/size.
2. Ionization energy.
3. Electron affinity.
4. Electro negativity.

(1) Atomic and Ionic Radius/Size: -

The distance of the outer most electron or orbit from the nucleus of an atom or ion is called atomic or ionic radius /size. No direct method available to determine the size of the atom or ion, however indirectly the size of atom can determine as follows.



Homonuclear

Additive princple

$\gamma_x + \gamma_y = \gamma_{x-y}$

Hetronuclear

Homonuclear or Diatomic molecule like (X_2): -

Equal division of experimentally determined bond length, inter nuclear distance gives the size of the atom for e.g.

(i) C – C bond length in diamond is 154 Pm hence

$\gamma_c = 154/2 = 77$ Pm.

(ii) Cl – Cl bond length in Cl_2 is 198 Pm hence

$\gamma_c = 198/2 = 99$ Pm.

Thus it is evident that the size of the atom increases when in a molecule bon length is increases.

Hetronuclear Diatomic molecules like (X – Y): -

Equal division of experimentally determined bond length does not ga the correct size of the atom, however in such case the additive principle ($\gamma_x + \gamma_y = \gamma_{x-y}$) may be applied to determine the size of atom.

$\gamma_x + \gamma_y = \gamma_{x-y}$

Where γ_x and γ_y = radius of X and Y respectively γ_{x-y} = bond lengt Therefore beside bond length the size of one of the atom must be note determine the size of atom for e.g.

In CCl_4 the C – Cl bond length is 176 Pm and γ_c is 77 Pm.

$\therefore \gamma_C + \gamma_{Cl} = \gamma_{C-Cl} = 176 - 77 = 99$ Pm

Often erroneous result are obtained and the factors which are responsible f the introduction of errors are

(a) Bond Ionicity: -

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This represents the presence of ionic character in the covalent bond as bond ionicity increases the percentage of error in the determination of error also gets increase a suitable correction to minimize this error can be made in the additive principle.

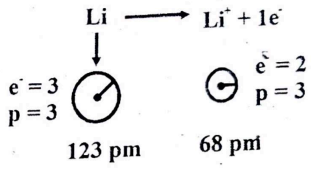
(b) Bond Multiplicity: -

This factor causes error in the radius of atoms. When there occur some multiple bonding in the single covalent bond it causes decrease in the size a suitable correction against this factor can also be reproduce in the additive principle to get correct values.

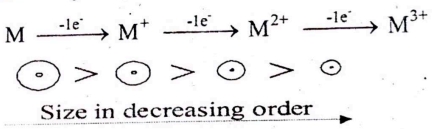
(c) Oxidation state and **(d)** hybridization.

Trend of ionic size: -

(a) Size of cations: -



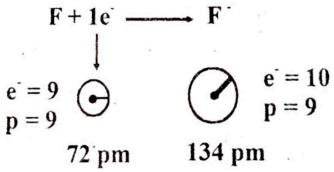
In common way: -



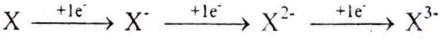
The cation is always smaller than its parent atom because it has less number of electrons and therefore the attraction of the nucleus on its outer most electron increases causes a decrease in the radii. Hence as the number of electron decreases the size of the atom also decreases.

Size of anions: -

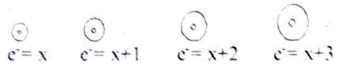
The anion is always bigger than the parent atom because it has more electrons and therefore the attraction of the nucleus on the outer most electrons gets decreases therefore size increases.



As charge on anion increases its size also further increases. This happen because with the increase of the charge there occurs addition of more and more electron the attraction of the nucleus therefore decreases on the outer most electron causing an increase in the size.



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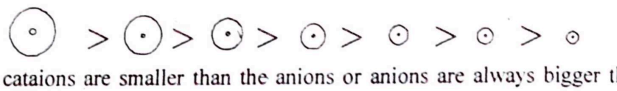
Q.1 Which of the following has least radius? (2005, 16, 18, 19)
O^{2-}, F, Na^{+}, Mg^{2+}

Ans. Na^{+}

Q.2. Arrange the following in the order of decreasing size.
(a) O^{2-}, O, O^{-} **(b)** N^{-}, N^{3-}, N, N^{2-} **(c)** P^{2-}, P^{3-}, P, P^{-}

Ans: (a) $O^{2-} > O^{-} > O$ (b) $N^{3-} > N^{2-} > N^{-} > N$ (c) $P^{3-} > P^{2-} > P^{-} > P$

Arrangement of cataions and anions having identical parent atom.



cataions are smaller than the anions or anions are always bigger than th cataions.

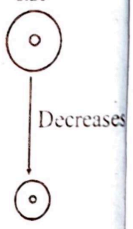
Q.3. Arrange the following in order of increasing size.
(a) N^{2-}, N^{3+}, N, N^{5-} **(b)** Cl^{5+}, Cl, Cl^{3+}, Cl^{-}

Ans: (a) $N^{3+} < N < N^{2-} < N^{5-}$ (b) $Cl^{5+} < Cl^{3+} < Cl < Cl^{-}$

Size of isoelectronic series of ions: -

Different ions having same number of ions called isoelectronic ions. Their size decreases with the increases of nucleus charge / atomic number of proton for e.g.

Ions	no. of electrons	nuclear charge/atomic no./no. of proton
C^{4-}	10	6
N^{3-}	10	7
O^{2-}	10	8
F^{-}	10	9
Na^{+}	10	10
Mg^{2+}	10	11
Al^{3+}	10	12
Si^{4+}	10	13



Trend of size in periodic table: -

In group — atomic size

$_{3}Li$ — 123 Pm
$_{11}Na$
$_{19}K$
$_{37}Rb$
$_{55}Cs$
$_{87}Fr$ — 265 Pm

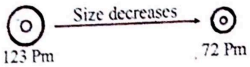
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Following factors operates on going down the group.
(i) Nuclear charge always increases many field effective but the effective nuclear charge remain constant through out the group hence its effect also remain constant through out the group.
(ii) Another factor is that principle quantum number on going down the group new shell is added on every step this should increase the size of atom and ion.

It is quit clear from the above description, when we move from top to bottom the atomic size increases.

In period: -

II^{nd} period $_{3}Li \longrightarrow {}_{9}F$



effective nuclear charge (ENC) $\rightarrow$ 1.7P $\xrightarrow{\text{inreases, ENC} \propto \frac{1}{\text{size}}}$ 5.6 P

on moving left to right there occurs decrease in the size because effective nuclear charge increases, while there occurs no change in principle quantum number. Thus in a group size increases due to increase of the effective nuclear charge.

Q.4. Write a short notes on ionization energy. (Imp.)

Related Questions -

Q. Explain the term ionization potential and the factors on which it depends. (2010)

Ans: Ionization potential or ionization energy: -

The minimum energy required to remove the most loosely bound electron from an isolated gaseous atom from its lowest energy state is known as first ionization potential. For e.g.

$$Al \xrightarrow{I^{st}\ I.P.,\ -e} Al^{+} \xrightarrow{II^{nd}\ I.P.,\ -e} Al^{2+} \xrightarrow{III^{rd}\ I.P.,\ -e} Al^{3+}$$

Similarly II^{nd} and III^{rd} I.P. would arises from the removal of most loosely bound electron from singly positive, doubly positive ions respectively. By algebraic convention all ionization is taken as positive. It is denoted by symbol I. It is determined from spectra and is measured in

(i) Isolated atom = eV/atom (ii) gaseous phase = J/mole
(iii) ground state = cal/mole.

Factor, which affect the numerical value of ionization potential: -

(a) Size: - Smaller the size greater will be ionization potential

$$\text{size} \propto \frac{1}{\text{I.P.}}$$

Q.5 Which of the following element has the least electron affinity?
B, C, N, F

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Ans: B

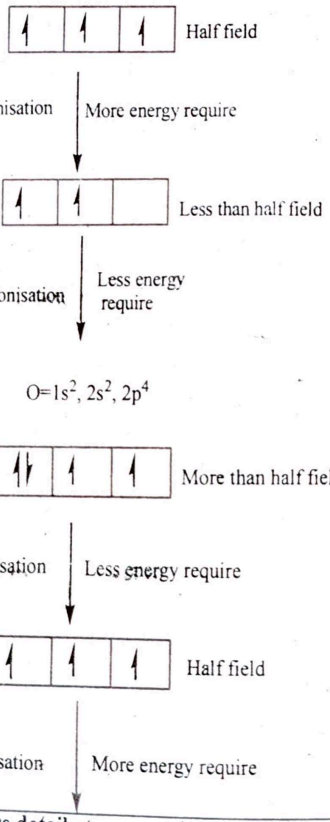
Q.6 The Ist ionization energy of nitrogen is greater than of oxygen wh the reverse is true for second ionization energy. (2005

Related Questions -

Q. First ionisation energy of nitrogen is higher than that of Oxyge Give the reason. (2007

Ans. The electronic configuration of nitrogen is $1s^2$, $2s^2$, $2p^3$. Since nitroge contains half filled p-subshell, thus it become symmetrical and achieve extra stabilit This cause the difficulty in ionisation of nitrogen atom. Due to this reason fir ionisation energy of nitrogen become higher than Oxygen and after one electro the ejection from both species the case is reverse. Now oxygen attain half fie situation and resultant the II ionization energy is higher than nitrogen.

$N=1s^2, 2s2, 2p^3$



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Q.7. Which of the following has least radius? (2014)

O^{2-}, F, Na^+, Mg^{2+}

Ans. Na+

Q.8. Distinguish between electron affinity and electronegativity. What are the units in which these values are reported? (2017)

Ans. Electron Affinity: -

Electron affinity is a property of an isolated atom in the gaseous state. It is an energy term and is measured in units of joules per mole.

Electronegativity is a property of an atom in a molecule. It can be expressed only in arbitrary dimensionless units with respect to a reference atom.

Electron affinity, *EA*, measures the energy released when an electron adds to a gaseous atom.

It is usually reported as the energy per mole of atoms. For example,

$$Cl(g) + e^- \rightarrow Cl^-(g); \quad EA = -349KJ/mol$$

Electronegativity: -

Electronegativity, (χ,) is a measure of the tendency of an atom to attract a bonding pair of electrons. The Pauling scale is the most commonly used.

Electronegativity cannot be directly measured. It must be calculated from other properties such as bond energies, ionization energies, and electron affinities of the bonded atoms.

This gives a dimensionless quantity on a relative "Pauling scale" that runs from around 0.7 to 3.98. Hydrogen is assigned an arbitrary value of 2.20 "Pauling units".

Unit: - Like ionization energy, electron affinity is measured either in electron volt (eV) per atoms or kJ per mole. And Electronegativity has no unit (dimensionless).

Q.9. Explain why the species Be^+ does not exit though the first ionization energy (899 $kJmol^{-1}$) of be is much lower than the second ionization energy (1757 $kJmol^{-1}$). (2006)

Related Questions -

Q. Explain why the II nd ionization energy is greater than the first ionization energy. (2000)

Ans: Magnitude of nuclear charge: -

In general as the nuclear charge increases among atoms with similar outer electronic configuration ionization potential will increase because of the increase of nuclear attraction for electron. Hence II nd ionization potential (IP) is greater than the I st ionization potential.

Oxidation state: -

(i) Positive oxidation state: -

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$M_{(g)} \xrightarrow{-e} M^{+}_{(g)} \xrightarrow{-e} M^{2+}_{(g)} \xrightarrow{-e} M^{3+}_{(g)}$

Oxidation state 0 +I +II +III

Size

Positive oxidation state α I.P.

For e.g. I.P. of $Fe^{3+} > Fe^{2+}$

(ii) Negative Oxidation sate: -

$X \xrightarrow{+e} X^{-} \xrightarrow{+e} X^{2-} \xrightarrow{+e} X^{3-}$

Oxidation state 0 -I -II -III

Size

Negative oxidation state $\propto \frac{1}{\text{I.P.}}$, e.g. I.P. of $O^{-} > O^{2-}$

Electronic Configuration: -

Element showing extra stable electronic configuration has extra stabili also therefore they also have ionization potential.

For e.g. Ist I.P. of N > O Because N has extra stable half filled 2p orbital.

Similarly inert gases also have very higher ionization potential a they have either duplet or extra stable electronic configuration.

Trend of I.P. in periodic table: -

In group,

I.A. Ionization Potential Effective nuclear charge size

$_{3}Li$ 5.4 ev/atom

D e c r e a s e s

C o n s t a n t

Size α $\frac{1}{\text{I.P.}}$

$_{87}Fr$ 3.9 ev/atom

A small decrease in ionization potential occurs on moving top to botto of a group. This happens because of increase of nuclear charge, has no effe on ionization potential as the effective nuclear charge remains constant th group.

In period: -

On moving from the left to right there occurs significant increase in th onization potential because size decreases and effective nuclear charg ncreases both factor are trying to increase ionization potential hence th ncrease in ionization potential becomes significant.

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Q.10. Explain the Ist ionization potential of Be > B and similarly Ist I.P. of N > O.

Related Questions -

Q. Which amongst the following pairs has the higher first ionization potential and why? (i) N or O (ii) Be or B **(2010)**

Ans: On moving from Li to Be the increase in effective nuclear charge is of high magnitude, which greater increase in I.P. However, on moving from Be to B the magnitude of increase in effective nuclear charge is comparatively lesser and therefore the increase in I.P. from Li to B is also lesser hence I.P. of Be is greater than I.P. of B.

$_{7}N = [He]\ 2s^2 2p^3$ $\uparrow\downarrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ Stable

$\downarrow -1e^-$

$\uparrow\downarrow$ | $\uparrow$ | $\uparrow$ Unstable

$_{8}O = [He]\ 2s^2 2p^4$ $\uparrow\downarrow$ | $\uparrow\downarrow$ | $\uparrow$ | $\uparrow$ Unstable

$\downarrow -1e^-$

$\uparrow\downarrow$ | $\uparrow$ | $\uparrow$ | $\uparrow$ Stable

Form the above diagram it is quit clear that N has extra stability, because half filled p-orbital. While oxygen has less stable, incomplete filled p-orbital, hence Ist I.P. of N > O.

(3) Electron affinity: -

Let us consider

$_{9}F + e^- \longrightarrow {}_{10}F^- + E\uparrow$

2,7 2,8

It is the energy realized when an isolated gaseous atom gain extra electron into its valency in the ground state.

If first electron gain termed as E^1 [first electron affinity] and second electron gain termed as E^2 then in general

$E_1 > E_2 > E_3 > \ldots\ldots\ldots$

Above trend follow because as each successive electron enters, it experience increase in repletion by the electron already present.

$_{26}O \xrightarrow{+e,(E_1)} {}_{27}O^- \xrightarrow{+e,(E_2)} {}_{28}O^{--}$

+ve EA -ve EA

energy released energy supplied

Electron affinity is termed as positive when energy is released on going an electron; such as the highly electronegative element like F. The electron affinity is termed as negative when energy has to be supplied in going extra electron; such as from highly electro positive atom. For e.g.

From the above description O^- is more stable than O^{--} because the net energy ($E_1 + E_2$) is released and stable gas configuration is formed.

Factor Influence EA.: -

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In general electron affinity increases with increase in nuclear charg and decreases in atomic radius and decreasing in screening factor. In a sho way

(i) Nuclear charge $Z \uparrow - E \uparrow$ (ii) radius or ionic size $r \uparrow - E \downarrow$

(iii) screaning factor $\sigma \uparrow - E \downarrow$

(iv) For sub shell – electron affinity decreases as follows $s > p > d > f$

Variation in periodic table: -

(a) On going from left to right along a period

Li Be B C N O F →

Z = increases, r = decreases, σ = unchanged

hence EA increases from left to right in a period.

Exceptions: -

As a common trend in a period electron affinity increases from left right but Li has higher EA than Be. Li = [He] $2s^1$, Be = [He] $2s^2$, element havin extra stable electronic configuration have no electron affinity for extra electro and therefore the I^s EA of such element is either zero or it becomes endothermic As same explanation for carbon has higher EA than nitrogen.

On going down the group: -

In general EA decreases from top to bottom in a group.

Q.11. Arrange the following ions in order of decreasing electronegativity $M_0(II), M_0(III), M_0(IV), M_0(V)$, and $M_0(VI)$. **(2009)**

Ans.: $M_0(II) < M_0(III) < M_0(IV) < M_0(V), < M_0(VI)$.

Q.12. Electron affinity of nitrogen is almost zero while that of fluorine i very high. **(2008)**

Ans: The energy released when an extra electron is added to a neutral gaseou isolated atom is termed the electron affinity. This depends on atomic size an effective nuclear charge. Since on moving from N to F the effective nuclear charg increases and the atomic size decreases hence the Ability to get added wit electron also increases. Therefore on going from N to F, electron affinity increases

Q.13. Discuss the basis of pauling scale of electronegativity. How does i help in determining the nature of ionic bond? **(2005)**

Related Questions -

Q. Write short note on Pauling's electronegativity. **(2015**

Ans. It is the power or tendency of an electron to attract electron towards itself in the bonding state. Electro negativity is not a directly measurable parameter unlike electron affinity. The value of electronegativity is ordinari chosen and assigned to the different element on the basis of thermo chemica

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energy. For e.g. according to Mullkien the mean of ionization potential and electron affinity may be taken to represent electro negativity.

$$\chi_{(mullkien)} = \frac{I.P. + EA.}{2}$$

$$\chi_{(Albred\&Rochow)} = 0.744 + \frac{0.359 \times Z_{effective} \times e^2}{r^2}$$

Where (χ = chi), $Z_{effective}$ = effective nuclear charge, e = charge on electron, r = covalent radius of atom.

The most satisfactory set of values of electro negativity is given by Pauling's electro negativity scale.

The values of Pauling's are based on energy data and can be arrived as in the following manner. Let E_A represent bond energy of A-A, E_B represent bond energy of B-B, and E_{AB} represent bond energy of A-B compound.

Then $\Delta = E_{AB} - \sqrt{E_{A\text{-}A} . E_{B\text{-}B}}$ where Δ = extra bond energy in Kcal/mole.

Pauling states that the electroegativity difference between two atoms is equal to $0.208\sqrt{\Delta}$

Hence $\chi_{(pauling)} = 0.208\sqrt{\Delta}$

Sometimes Δ is known as ionic covalent resonance energy. in this way the electronegative values for some of the values are

H Li Be B C N O F
2.1 1.0 1.5 2.0 2.5 3.0 3.5 4.0

Cl →3
Br→2.8
I →2.5
At→2.2

According the values of electro negativity increases from left to right along a period and decrease on going down the group.

Importance of electro negativity: -

(i) In general higher electro negativity greater will be the oxidizing power, non-metallic character and tendency fro anion formation. Thus F having the highest electro negativity among all elements and most strong oxidizing and greater tendency for anion formation.

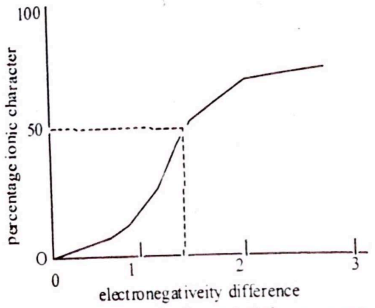
(ii) Relationship the nature and chemical bonds whether a bond between the elements A and B will be ionic or covalent or partially both shall dependent upon the difference in electro negativity between the A and B.

(a) When $\Delta x = 0$ this means that the two bonding atoms shall equally share the bonding electron. Such a bond is termed as pure or 100% covalent bond such bonds are homo nuclear bond e.g. H-H, O-O etc.

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(b) When Δx exceed from zero the covalent bond develops partially ioni character $\left(\overset{+\delta}{A}:\overset{-\delta}{B} \text{ if } x_B > x_A\right)$, which increases as Δx increases.

When a graph is plotted between Δx and %ionic characters the grap somewhat as shown in the fig.



According to graph when Δx is about 1.8 the percentage ionic charact is 50. One of the eq. used for calculating %ionic character is Henry-Smith equation.

% Ionic character = $16(\Delta x) + 3.5(\Delta x)^2$

Thus when Δx is less than or equal to 1.8 the bond is termed predominantly covalent on the other hand when Δx is greater than 1.8 t bond is predominantly ionic.

It may be noted that the values of electro negativity are not rigoro (accurate) enough to be of quantitative important.

(c) Thus when x is nearly similar for the bonding atoms the bond is expect to be covalent and when Δx is larger it is expected to be ionic.

Q.14. Given the electronegativity of hydrogen as 2.1, calculate th electronegativity of atom X from the given data : (200

Bond energy of H X molecule = 430.0 KJ mole^{-1}

H-H bond energy = 458.0 KJ mole^{-1}

X-X bond energy = 242.7 KJ mole^{-1}

Ans: A-B compound.

Then, $\Delta = E_{AB} - \sqrt{E_{AA}E_{BB}}$ where Δ = extra bond energy in KJ mol

Using above formula we get extra bond energy = 93.0 KJ mole-1

Pauling states that the electroegativity difference between two atoms is eq to

Hence, $\chi_{(Pauling)} = 0.208\sqrt{\Delta}$

Putting above value in this formula we get the electronegativity atom X = 2.0058

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Q.15. Transuranium elements **(2006)**

Ans: Before five decade, a number of elements beyond uranium, i.e., beyond atomic number 92, have been prepared in the laboratory through nuclear reactions. These elements are known as transuranic elements. They are all of f block elements.

Q.16. What is lattice energy and how does the solubility of an ionic solid depends upon the lattice energy? (2007, 2011)

Other Related Questions -

Q. Write short note on Lattice energy. (2017)

Ans. Lattice energy: -

The lattice energy (U) of a crystal is the energy evolved when one-gram molecule of the crystal is formed from gaseous state.

$$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow NaCl_{(crystal)} \qquad U = -782 \text{ KJMol}^{-1}.$$

Lattice energy cannot be measured directly; they are either determined indirectly by using Born Haber Cycle or calculated theoretically by the formula.

$$U_o = -\frac{N_o A Z^+ Z^- .e^2}{r}\left(1 - \frac{1}{n}\right)$$

Where A = Madelung constant, e = charge on an electron, N = Avogadro number, r = inter ionic distance, Z^+ = cationic charge, n = Born exponent, Z^- = anionic charge.

Above equation is called Born-Lande equation. It allows the lattice energy to be calculated from knowledge of the geometry of the crystal. According the lattice, energy is expected to increase ionic charge and decrease ionic radius (since inter ionic distance = $r^+ + r^-$).

Thus between NaCl and $MgCl_2$, the lattice energy will be expected to be higher $MgCl_2$ since Mg^{++} is more highly charged and smaller size than Na^+.

Importance: -

(i) Stability of ionic solid: - In general higher the lattice energy greater will be the stability of ionic solid.

(ii) Melting point and hardness of ionic solids: - In general higher the lattice energy greater will be melting point and hardness.

(ii) Solubility of the ionic solids in water: - In general higher the lattice energy lower the solubility.

Remark: - For solubility of particular compound it must be posses greater hydration energy as compared to lattice energy.

Q.17. The ionic radii of Ca^{2+} and Hg^{2+} ions are almost similar size (115 pm) but the melting point of CaC_2 (782°C) is higher than that of $HgCl_2$ (276°C) Explain. (2009)

Ans: The lattice of CaC_2 is distorted cubic in nature and the packing is very strong on the other hand the H.

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Q.18. The electronic configuration of an element is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10}$. Give the symbol, atomic number and the block in which it belong

Ans. Symbol = Pb, atomic number = 46, block = d

Q.19. NO_2 has a greater tendency for dimerisation than NO.

Ans: The NO_2 electronic structure is as O=N→O and obviously it has unpaired electron. On the other hand the N=O containing one odd electro So that NO_2 has a greater tendency for dimerisation than NO.

Q.20. Calculate the percentage ionic character of Li-F bond in LiF, known the values of electronegativity of Li and F are respectively 1 and 4.

Ans: % Ionic character $= 16(\Delta x) + 3.5(\Delta x)^2 = 16(1) + 3.5(4)^2 = 72\%$

Hence LiF is ionic species.

Q.21. Why and in what ways does Li resemble with Mg?

Ans. Diagonal relationship: The effect in nonmetal can be explained on t basis of similarly in electro negativities of diagonal elements. The elec negativity on moving from top to bottom decreases, while it increases fr left to right in a period. Therefore the element situated at the diagonal has similar value of electro negativity. For e.g.

$X_C = 2.5$ $X_N = 3.0$ $X_O = 3.5$

$X_P = 2.1$ $X_S = 2.5$ $X_F = 3.1$

Where X = chi for EN



The change in property on moving from top to bottom in a gro which is cancelled by moving from left to right in a period is the cause diagonal relationship.

Q.22. What would be the name of the element having atomic number 106 the basic of IUPAC recommendations?

Ans. un-nil-hexium

Q.23. Given the electronegativity of hydrogen as 2.1, calculate t electronegativity of atom X from the given data :

Bond energy of H X molecule = 430.0 KJ mole^{-1}

H-H bond energy = 458.0 KJ mole^{-1}

X-X bond energy = 242.7 KJ mole^{-1}

Ans. A-B compound.

Then, $\Delta = E_{AB} - \sqrt{E_{A\text{-}A} \cdot E_{B\text{-}B}}$ where Δ = extra bond energy in Kcal mole

Using above formula we get extra bond energy = 93.0 KJ mole-1

Pauling states that the electroegativity difference between two atoms is equal to

Hence, $\chi_{(Pauling)} = 0.208\sqrt{\Delta}$

Putting above value in this formula we get the electronegativity of atom

$\chi = 2.0058$

Q.24. Write the IUPAC name of the element having atomic number 112, 114 and 118.

Ans. 112 - un-un-bium, 118 - Ununoctium, 114 - Ununquadium (Uuq)

Q.25. Explain the electron affinity of Cl is more than F.

Ans. The irregularity in the electron affinity trend between Cl and F is due to the small size of the F atom. Although F definitely has a higher attraction for an electron than Cl (as evidenced by its high electronegativity value), the small size of the F atom means that adding an electron creates significant repulsion. Since electron affinity is an energy measurement, the total energy associated with electron affinity winds up being the energy that is released by the electron binding to the nucleus, minus the energy involved in overcoming the electrical repulsion in the outer shell.

By the way, you might notice that when you look at atomic radius Ne is slightly larger than F, another irregularity in the trend which is caused by needing more room for the eight electrons in the valence shell relative to seven in F.

Q.26. Define lattice energy and hydration energy? How these two affect the comparative solubility of ionic compounds?

Other Related Questions -

Q. Comment on lattice energy and hydration energy.

Q. Write short note on Lattice energy.

Ans. The lattice energy (U) of a crystal is the energy evolved when one-gram molecule of the crystal is formed from gaseous state.

$$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow NaCl_{(crystal)} \qquad U = -782\ KJmol^{-1}$$

Lattice energy cannot be measured directly; they are either determined indirectly by using Born Haber Cycle or calculated theoretically by the formula.

$$U_0 = -\frac{N_0 A Z^+ Z^- .e^2}{r}\left(1 - \frac{1}{n}\right)$$

Where A = Madelung constant, e = charge on an electron, N = Avoga
number, r = inter ionic distance, Z^+ = cationic charge, n = Born exponent, Z^-
anionic charge.

Above equation is called Born-Lande equation. It allows the latt
energy to be calculated from knowledge of the geometry of the cryst
According the lattice, energy is expected to increase ionic charge and decre
ionic radius (since inter ionic distance = $r^+ + r^-$).

Thus between NaCl and $MgCl_2$, the lattice energy will be expected
be higher $MgCl_2$ since Mg^{++} is more highly charged and smaller size than N

Importance: -

(i) Stability of ionic solid: - In general higher the lattice energy greater will
the stability of ionic solid.

(ii) Melting point and hardness of ionic solids: - In general higher the lat
energy greater will be melting point and hardness.

(iii) Solubility of the ionic solids in water: - In general higher the lat
energy lower the solubility.

Hydration Energy [H_0] (Solvation Energy): -

Let us take one example

It is the energy released when one or more of a given ion passes fr
the isolate gaseous state into the state of hydration in aqueous solution.

$$Cl^-_{(g)} + \text{water} \longrightarrow \left[Cl(H_2O)_n\right]^- + H_0$$

$$H_0(NaCl) = H_0(Na^+) + H_0(Cl^-)$$

The hydration energy of an ionic solid is equal to the sum of the hydra
energy of its ions.

Factors Influence H_0: -

(i) Ionic charge. **(ii)** Ionic radius.

Hydration energy in general increases with increase in a ionic charge
decreasing ionic radius. For example

$Na^+ Mg^{++} Al^{+++}$ →

Ionic charge increase →

Radius decrease →

Hydration energy increases →

It is to note that, for solubility of particular compound it mu
posses greater hydration energy as compared to lattice energy.

Q.27. Define lattice energy of ionic crystals.

Ans. Lattice Energy: -

It may be defined as the energy released when the co
number of gaseous cation M^+ and anion X^- are brought together fro

nfinite distance to form one gram mole of the solid crystal.

$$M^+(g) + X^-(g) \rightarrow M^+X^- + \text{Energy released (lattice energy)}$$

Ionic crystal

may be defined as the energy required to move ions of one gm. mole of an
onic solid crystal separated from each other from their equilibrium in the crys-
l to infinity.

$$M^+X^- + \text{Energy required} \rightarrow M^+(g) + M^-(g)$$

reater the value of lattice energy, greater is the energy required to decompose
e ionic crystal (M^+X^-) into its constituent jons M^+ and X^-. Lattice rnergy
aries inversely as inter nuclear distance between oppositely charged ions,
t varies directly as the product of charges on ions in an ionic crystal.

LiF LiCl LiBr LiI

$U_0 = -24 > -213 > -193 > -180 K.cal / mol.$

pplication of Lattice Energy:-

) In determination of electron affinities, proton affinities and heat of forma-
n.

) Explaining solubilities of metal hydrides, polyhalides, peroxides and super-
ides

28. Amongst F^-, Cl^-, Br^- and I^- which is the strongest reducing agent? (2015)

s. I^-, Order of reducing agent are as follows -

$I^- > Br^- > Cl^- > F^-$

29. Which one of the following transition metals shows highest oxidation te? Mn, Cr, Fe, Ru. (2015)

s. Ru

30. Which one of the following silver salts has maximum solubility in ter?

$AgNO_3$, AgI, AgBr, AgCl, $AgClO_4$ (2015)

s. $AgClO_4$

31. Write short on Electron Affinity. (2016)

s. Electron Affinity -

The amount of energy released when an electron is added to
eutral atom to form an anion. The first electron affinity is always exothermic
negative, the second electron affinity of the same element will be positive or
dothermic. This is so because second electron has to be forced to enter the
gative ion.

$$O_{(g)} + e^- \xrightarrow{-EA_1} O^-_{(g)}$$

$$O^-_{(g)} + e^- \xrightarrow{+EA_2} O^{2-}_{(g)}$$

The electron affinity cannot be determined directly, but is obtained indir from **Bron-Haber cycle.**

Q.32. The ionic radii of Ca^{2+} and Hg^{2+} ions are almost similar in size bu melting point of $CaCl_2$ is higher than that of $HgCl_2$. Explain.

Other Related Questions -

Q. Which one of Ca^{2+} and Hg^{2+} has more polarzing power and why? (2014, 17, 1

Ans. Covalent character is greater for cations with a non-noble gas el configuration (i.e., 18-electron, pseudo-noble-gas cations) than for ca with a true noble-gas configuration (8-electron cations). This effect m shows up in transition-metal and post-transition metal cations in which or more d-electrons ineffectively shield the outer electrons, or the electro an adjacent ion, from the nuclear charge. Thus, for two ions of similar siz charge, a transition metal ion with a $(n-1)d^x\ ns^0$ configuration will be polarizing and more polarizable than an alkali or alkaline earth metal w noble gas configuration $(n-1)s^2(n-1)p^6ns^0$. So that Hg^{2+} (r = 102 is more polarizing power than Ca^{2+} (r = 100 pm). Therefore, $CaCl_2$ show h melting point than that of $HgCl_2$. $HgCl_2$ (mp 276°C, Hg^{2+} is $4f^{14}3d^{10}$, r = 1 with $CaCl_2$ (mp 782°C, Ca^{2+} is $3s^23p^6$, r = 114 $\overset{0}{A}$)

Q.33. The hydrogen is displaced from dilute acids by Zn and not by Cu

Ans. All those metals which are more reactive than hydrogen, that is, metals which lose electron more easily than hydrogen, displace hydrogen dilute acids to produce hydrogen gas. This is due to the fact that the reactive metals give electrons easily and these electrons reduce the hyd ions of acid to hydrogen gas. The metals like copper and silver which ar reactive than hydrogen, do not displace hydrogen from dilute acid. Be they do not give out electrons required for the reduction of hydrogen present in acids. Thus, all the metals which are above hydrogen in the a series, displace hydrogen from dilute acids (like dil. HCl and dil. H_2SO_4). metals which are below hydrogen in the activity series, do not displace gen from dilute acids.

$$Zn(s) + H_2SO_4(aq) \longrightarrow ZnSO_4(aq) + H_2(g)$$

Q.34. Electron affinity value of noble gases are zero and those of ha are the highest in each period.

Other Related Questions -

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Why electron affinities of nobel gases are zero? (2017)

ns. Nobel gases has no affinity for addition of electron in valance shell as y have full filled orbital electronic configuration. While in case of halogen one ctron is needed for their full filled electronic configuration. From moving top bottom due to decrease in size the electron affinity of halogen increases.

35. Write short note on factors affecting stability of nucleus. (2017)

ns. Factor Affecting Nuclear Stability:-

An element is radioactive when its nucleus will spontaneously emit diation to achieve nuclear stability. That radiation can be emitted in the form particles, photons or both. The two factors that directly influence whether a ecific nuclear configuration will be stable or radioactive are the proton-to-utron ratio and the binding energy per nucleon.

e Proton-to-Neutron Ratio: -

In the periodic table, as elements build up, more protons are added to nucleus (i.e., the Z-number increases). As a result strong electrical forces of pulsion result inside the nucleus due to the repulsive force that exists be-een the like positive charges. The addition of neutrons to the nucleus adds degree of stability because they are uncharged particles that take up space d allow the positive charges of the protons to be placed further from each her to lower the repulsive forces between protons. Generally, the same num-r of neutrons and protons form a stable nuclear configuration for elements to Z= 20. For Z > 20, there must be more neutrons than protons in order to ve a stable nuclear configuration. However, there can be too many neutrons too many protons in a nucleus, which will cause the nucleus to become nstable (or radioactive). For instance, carbon-13 (i.e., 6 protons plus 7 neu-ons) is stable isotopes of carbon that has an extra neutron, but just the dition of one more neutron produces carbon-14, which is radioactive.

uclear Binding Energy per Nucleon: -

The nuclear binding energy is the energy that holds nuclear compo-nts together. Recall that, by the law of conservation of matter, matter can be nverted into energy. It is this mass-energy conservation process that pro-des the energy that holds the nucleus together (i.e., the nuclear binding ergy). It is important to note that the binding energy per nucleon alone nnot be used to determine whether a particular nuclear configuration will be able or radioactive. However, when we compare the binding energies per ucleon of two different isotopes of an element, the one having the greater nding energy per nucleon will most likely be stable and the one having the wer binding energy per nucleon will most likely be radioactive. In summary, e greater the nuclear binding energy per nucleon, the more likely a particular uclear configuration will be stable (or not radioactive).

.36. Write short note on London forces. (2017)

ns. The **London** dispersion **force** is the weakest intermolecular **force**. The

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London dispersion force is a temporary attractive force that results when t
electrons in two adjacent atoms occupy positions that make the atoms for
temporary dipoles. This force is sometimes called an induced dipole-induc
dipole attraction. Found in both polar and nonpolar molecules, it can be attri
uted to the fact that an atom that usually is nonpolar sometimes becom
polar because the constant motion of its electrons may cause uneven char
distribution at any one instant. When this occurs, the atom has a tempora
dipole. This dipole can then cause a second, adjacent atom to be distorte
and to have its nucleus attracted to the negative end of the first atom. Lond
forces are about one tenth the force of most dipole interactions and are t
weakest of all the electrical forces that act between atoms or molecules. The
forces help to explain why nonpolar substances such as nobel gases and h
halogens condense into liquids and then freeze into solids when the tempe
ture is lowered sufficiently. In general, they also explain why liquids co
posed of discrete molecules with no permanent dipole attraction have l
boiling points relative to their molecular masses. It is also true that co
pounds in the solid state that are bound mainly by this type of attraction ha
rather soft crystals, are easily deformed, and vaporize easily. Because of t
low intermolecular forces, the melting points are low and evaporation tak
place so easily that it may occur at room temperature. Examples of such soli
are iodine crystals and mothballs (paradichlorobenzene and napthalene).

**Q.37. Define lattice energy and hydration energy. How these two effect t
comparative solubility of ionic compounds. (201**

Ans: Hydration energy is the energy that is released when the lattice
dissolved in water. Both formation and hydration of a lattice release ener
because both processes involve chemical bond (or chemical interacti
formation. The key difference between lattice energy and hydration energ
that lattice energy is the amount of energy released when a mole of tne lat
is formed from infinitely separated ions whereas hydration energy is the amo
of energy released when a lattice is separated into ions by solvation in wa
Lattice energy relates to the formation of a lattice whereas hydration ener
relates to the destruction of a lattice. The difference between lattice ene
and hydration energy is that lattice energy is the amount of energy releas
when a mole of the lattice is formed from infinitely separated ions wher
hydration energy is the amount of energy released when a lattice is separa
into ions by solvation in water.

Relationship Between Lattice Energy and Hydration Energy:

The energy of dissolution is equal to the sum of lattice energy
hydration energy. That is because, in order to dissolve a lattice in water,
lattice should undergo dissociation and hydration. The lattice should
provided with an amount of energy that can dissociate the lattice into ic
This is equal to the lattice energy.

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Chapter 3 - Chemical Bonding

Q.1 Discuss Fajan's rules of ionic polarizability. (2007, 2009)

Related Questions -

2. **Write short notes on Fajan's rule. (2012, 13, 18)**
2. **Write short notes on odd electron bonds. (2015)**
2. **Write short note on covalent character in ionic bonds (Fanjan's rules). (2015, 16)**
2. **What are Fajan's rules? Explain with examples. (2016)**
2. **Give example of molecules involving odd electron bond. (2010)**

ns. Fajan's rule:-

If the electron is shared between the two atoms and hence imparts a ight covalent character to the ionic bond, i.e. ionic bond, assume some valent nature due to polarization of anion by cation. Greater the polarization anion, higher will be covalent character in ionic bond.

Fajan studied the development of covalent character in ionic bond and ve rules known as Fajan's rules. The following are the factors on which valent nature in ionic bond depends:-

) High charge:-

High charge on cation or anion or on both favour the covalent nature, increase polarizability. e.g.

$$\overset{+}{NaCl} < \overset{+2}{MgCl_2} < \overset{+3}{AlCl_3}$$

Covalent nature increase

) Small size

all size of cation favour high polarisability, thus favour covalent nature of ic bond. e.g.

$$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$$

imum polarization power, smaller size

) Large size of anions:-

Large size of anions favour high polarizability, thus favour covalent re of ionic bond. e.g.

$$F^- < Cl^- < Br^- < I^-$$

size incrases polarising power increases

$$LiF < LiCl < LiBr < LiI$$

minimum covalent more covalent

Cation with a pseudo noble gas type structure:-

This types of cations has high polarizing power because of its high lear charge but comparatively low screening effects.

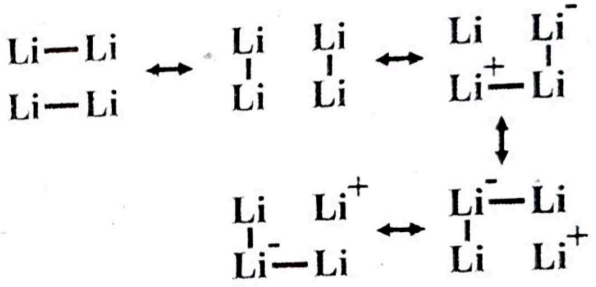
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tal ions (kernels) are immersed in electron-sea and held together by electrons. ce the valence electrons are not attached to any individual ions but belong he crystal as a whole, they are free to more throughout the lattice from one t of the crystal to the other. Thus they conduct electricity easily.

Resonance or Valance Bond Theory: -

This theory was introduced by Pauling. According to this theory the tallic bond is covalent in nature and involves resonance of electron-pair ıds. Between each atom and its nearest neighbours.

Consider the case of lithium metal in which each Li atom is surrounded eight nearest Li atoms. Because of the presence of only one valance electron, h Li atom is capable of forming only one normal covalent bond with one of nearest Li atoms. This Li – Li covalent bond is assumed to resonate mainly tween all the eight neighbours and to some extent between the six next to nearest neighbours. In this way each Li atom would bind all its neighbours. us it stabilizes metallic bond.

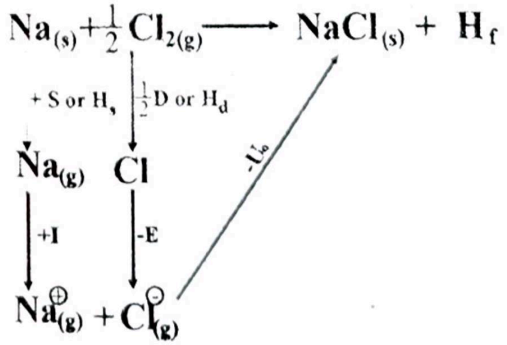


3. Why $BeCl_2$ shows more covalent character than $MgCl_2$? (2006)

ıl. Small size of cation favour high polarisability, thus favour covalent ture of ionic bond.

4. Write short notes on Born-haber Cycle . (2012)

ns: This cycle devised by Born and Haber in 1919, relates the lattice ergy of a crystal to other thermo chemical data. The energy terms involved building of a crystal lattice such as sodium chloride may be taken in steps. ıe element in their standard states are first converted to gaseous atoms and en to ions, and finally packed into crystal lattice.



ere s = Sublimation energy, I = Ionization energy, D = Dissociation energy, E electron affinity

ccording to Hess's law of heat summation

$$-\Delta H_f = S + I + \frac{1}{2} - E - U_0$$

It is a theoretical approach to the formation of an ionic compou from it's elements by involving thermo type energy.

Applications: -

(i) Determination of lattice energy: -

In thermo chemical equation related Born Haber Cycle, all energ except lattice energy can be determined by direct experiment and hence lattic energy is indirectly obtained.

(ii) Determination of electron affinity: -

In case of elements for which lattice energy cannot be determine directly, it is indirectly obtained by using the calculated lattice energy. Sinc all other energies can be determined experimentally.

Q. 5. Which one of K^+ and Ag^+ has more polarising power and why? (2012, 16

Ans. According to Fajan rule smaller the cation size larger will be th polarising power. So that, the polarising power of K^+ is larger compared to th Ag^+.

Q.6. On the basis of Fajan's rule explain which compound of each of th following pair is more covalent.

(i) CuO or CuS (ii) LiCl or KCl (iii) $SnCl_2$ or $SnCl_4$ (iv) CuCl or KCl (v) AgCl or NaCl. (2012, 14, 17, 18, 19

Ans: According to Fajan's rule

(i) CuS (ii) LiCl (iii) $SnCl_4$ (iv) CuCl (v) AgCl

Remark: -

The molecule having cations with 18-electrons valance she configurations are more covalent than those having 8-electrons valance she configuration.

Q.7. Calcium hydroxide is less soluble in water than berium hydroxide

Ans. Metals react with water to form metal hydroxides and hydrogen.

e.g. $Ca(s) + 2H_2O(l) \longrightarrow Ca^{2+}(aq) + 2OH^-(aq) + H_2(g)$

The vigour of these reactions depends on two factors:

- how easily two electrons can be removed from an atom
- how soluble the hydroxides of the metals are formed

Since ionisation energies decrease down a group, the electrons a more easily removed from the atoms and the reaction with water becom increasingly vigorous on descending group II.

Since $Be(OH)_2$ is insoluble in water, the hydroxide formed remains o the surface of the metal, preventing further reaction. Thus the reactions o

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beryllium with water are very slow. So since hydroxide solubility increases down group II, so does the rate of reaction with water.

Q.8 Write short note on van der Waal's forces. (2013, 18)

Sol. van der Waal's forces:- The forces which bind together the atoms forming a molecule are called interatomic forces. These are interperted as electrostatic forces and covalent bond forces in case of ionic and covalent compounds respectively. These forces are of a very high order, as indicated by the large values of bond dissociation energies. Other forces exist between molecule of substances and these additional forces are different for different molecular species and relatively weaker than the interatomic forces of chemical bonds. Under these conditions molecules remain intact though the inter molecular distance increases. The residual very short lived inter-molecular attractive forces which are believed to exist between molecules, atoms and ions when they are sufficiently close to each other are known as Van der waal's forces.

The existence of van der Waal's attraction between atoms, and molecules is indicated by

(i) Even through inter gases are incapable of forming normal valency bonds, they release energy when condensed to liquid or solid states at a certain pressure.

(ii) When a gas is allowed to expand through a porous plug, suffers decrease in temperature.

The energy of the bond due to van der waal's attraction is very weak, seldom exceeding more than a few Kcal per mole. These forces are short range and non-directional in nature. It is proportional to polarizability and inversely propotional to the ionization potential of the atoms concerned. Van der waal's attraction exists between all atoms and molecules irrespective of any other types of bonds present between them. The molecules attached with only Van der waal's forces possess low melting point and boiling point. The strength of this force depends upon the size of the molecule, and usually increases with increasing molecular weight.

London in 1937 proposed that molecules held together with van der Waal's forces possess rapidly fluctuating dipoles so that when two molecules approach each other the dipole at that instant comes into phase and there is always a resultant attractive force. Since the dipoles are rapidly changing there is no permanent dipole moment. These forces are called London dispersion forces. These dispersion forces provide major contribution to Van der waal's forces in case of non-polar molecules. The magnitude of these forces increases in proportion to the heaviness of the atom and polarizability. These reason is very simple: The chances of induced dipole increase more and can more appreciably disturb the balance of neighbouring atoms which have greater degree of polarizability. This argument seems quite rational by observing the striking increase in the boiling points of noblegases and halogens with heaviness.

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ganic molecules such as water and in organic molecules like DNA and proteins.

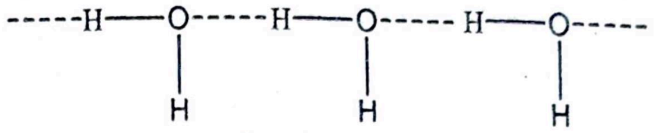
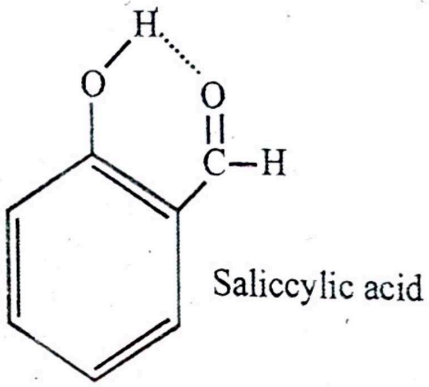


Fig. - Intermolecular hydrogen bonding



Saliccylic acid

Fig. - Intramolecular Hydrogen Bonding

Intermolecular hydrogen bonding is responsible for the high boiling point of water (100°C) compared to the other group 16 hydrides that have much weaker hydrogen bonds. Intramolecular hydrogen bonding is partly responsible for the secondary and tertiary structures of proteins and nucleic acids. It also plays an important role in the structure of polymers, both synthetic and natural.

In 2011, an IUPAC Task Group recommended a modern evidence-based definition of hydrogen bonding, which was published in the IUPAC journal Pure and Applied Chemistry. This definition specifies:

The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation.

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Chapter 4 - Co-Ordination Chemistry

Co-ordination chemistry

Double salt: -

There are addition compounds, which are stable in the solid state b their constituent ion when dissolved in water or any other ionic solvent. these compounds the individual properties of the constituent ions are lo For e.g. –

$$FeSO_4 + (NH_4)_2SO_4 + 6H_2O \xrightarrow[\text{Till dryness}]{\Delta} FeSO_4(NH_4)_2SO_4.6H_2O$$

Mohr's Salt (light green crystal)

Dissolve in water

$$Fe^{2+} + 2NH_4^+ + 2SO_4^{2-} + 6H_2O$$

$$KCl + MgCl_2 \cdot 6H_2O \xrightarrow[\text{Till dryness}]{\Delta} KClMgCl_2.6H_2O$$

White crystal Carnalite

Dissolve in water

$$K^+ + Mg^{2+} + 3Cl^- + 6H_2O$$

Give positive test

Complex: -

The molecular compounds, which retain their identity in solid as well a solution phase. When these compounds are dissolve in their polar solve then they do not dissociated into a simple species [Cl^-Br, SO_4^{2-}] and are ve big species called the complex species.

$$CuSO_4 + NH_4OH \xrightarrow[\text{dryness}]{\text{Heated till}} [Cu(NH_3)_4]SO_4$$

Dark blue crystal

Dissolve into water

$$[Cu(NH_3)_4]^{2+} + SO_4^{2-}$$

Complex Simple species

Central atom: -

All element having small size vacant orbitals of right energy can act Central Metal Ion (CMI). In general both condition fulfill by Transition eleme and hence in most of the complex compound CM belong to Transition eleme

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Ligands: -

All molecular or ionic species having one or more lone pair of electron can act as ligands. For e.g. :NH, donor atom is N while $C_2O_4^{2-}$ the donor atom is O, mono denate bidenatate

Co-ordination number: -

The total number of ligands attached to CMI is called the co-ordination number of CMI for e.g. $Cu(NH_3)_4^{2+}$. The C.N. of Cu^{2+} is 4. $[Ag(S_2O_3)_2]^{3-}$ the CN of Ag^+ is 2.

Q.1. What is 'theory of coordination chemistry' of Alfred Werner, the Nobel Laurate? Give the number of primary and secondary valencies in the following coordination compounds:

$Co(NH_3)_6Cl_3$, $Co(NH_3)_3Cl_3$, $Co(en)_2Cl_3$ and $Co(NH_3)_5Cl(NO_3)_2$. (2009, 14)

Related Questions -

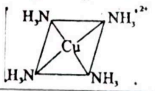
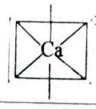
Q. Explain Sidgwick's concept of Effective Atomic Number (EAN) of the central metal atom/ion in complexes and calculate its value in the following: Atomic number of: V = 23, F = 26, Ni = 28). $[Ni(CO)_4]$ (2015)

Q. Explain Sidgwick concept of Effective Atomic Number (EAN) of the central metal atom/ion in complexes. (2016)

Q. Write short note on Effective Atomic Number (EAN) of central metal atoms in complexes. (2018)

Ans. Werner's theory of co-ordination compounds: -

To explain the formation of co-ordination compounds and structures Verner proposed following points –

Example	Geometry
$Ag(CN)_2]^{2-}$	Linear $[NC - Ag - CN]^{2-}$
$u(NH_3)_4]^{2+}$	Square planer 
$o(NH_3)_6]^{3+}$	Octahedral 

) All elements (C.M.I.) have two types of valencies namely primary and condary.

) Primary valencies are ionisable while secondary valency are non ionisable.

) Every element has always fixed number of secondary valencies. The ligands t attached to CMI through secondary valencies of CMI. The total number

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of ligands attached to CMI in complex species is known as co-ordina
number of CMI.

For e.g. $[Cu(NH_3)_4]SO_4$

SO_4^{2-} is attached to central metal copper ion through ionisable pri
valancies while four ammonia molecule are attached to copper ion thr
nonionisable secondary valancies.

$$[Cu(NH_3)_4]SO_4 \rightleftharpoons [Cu(NH_3)_4]^{2+} + SO_4^{2-}$$

All secondary valancies are always directed in particular direction aroun
nucleus of CMI. Thus all secondary valancies have a definite spatial arrang
due to this reason every complex species always acquires a definite geo
for e.g. given in table.

Sidewick's concept of EAN. (2006,

Effective atomic number: -

Sidwick extended the lewis theory to explain the bonding in th
ordination compounds. He consider the formation of complexes by don
of an electron from the ligand to the metal ion. The donor atom act as a
base and the metal ion act as a lewis acid. He suggested that the metal io
continue to accept electron pairs till it achieves the next inert gas configur
This is known as the **effective atomic number rule (ENA).**

ENA = atomic number of metal (Z) – electrons lost in ion forma
electrons gained from the donor ligands.

Metal complex	Formula applied	ENA
$Fe(CN)_6^{+}$	26 – 2 + 12	=36
$[Co(NH_3)_6]^{3+}$	27 – 3 + 12	=36
$[Ni(CO)_4]$	28 – 0 + 8	=36
$[Cu(CN)_4]^{3-}$	29 – 1 + 8	=35
$[Fe(CN)_6]^{3-}$	26 – 3 + 12	=38
$[Ni(NH_3)_6]^{2+}$	28 – 2 + 12	=52
$[Pd(Cl)_4]^{2-}$	46 – 2 + 8	=84
$[Pt(NH_3)_4]^{2+}$	78 – 2 + 8	=36
$[Co(en)_2Cl(ONO)]^{1+}$	27 – 3 + 6 x 12	=30
$Na_2[CrOF_4]$	24 – 4 + 5x 2	=54
$K_4[Mo(CN)_8]$	42 – 4 + 8 x 2	=10
$K[BF_4]$	5 – 3 + 4 x 2	=84
$Pt(NH_3)_2Cl_2$	78 – 2 + 8	=35
$K_3[FeF_6]$	26 – 3 + 12	=58
$[SbCl_5^{2-}]$	51 – 3 + 10	=3
$Na_3[Cr(C_2O_4)_3]$	24 – 3 + 12	=33
$[Cr(SCN)_3(H_2O)_3]$	24 – 3 + 12	=35
$[Mn_2(CO)_{10}]$	(50 – 0 + 20)/2	=38
$Fe(H_2O)_5NO$	26 – 0 + 12	=84
BiOCl	83 – 3 + 4	=84
$[Pt(Pg)_2Cl_2]$	78 – 2 + 8	

. Calculate the effective atomic number (EAN) of the central metal atom
he following : (ii) $K_3[Fe(C_2O_4)_3]$ (2005, 14)

$Ni(CN)_4]^{2-}$

EAN of $[Ni(CN)_4]^{2-}$, 28-2+8=34

EAN of $K_3[Fe(C_2O_4)_3]$, 26-3+12=35

Name the following according to the IUPAC system of nomenclature
also calculate the effective atomic number (EAN) of the central metalion

$Pt(NH_3)_4NO_2Cl]SO_4$

$NH_4)_3[Cr(NCS)_6]$ (2008)

$[Co(en)_2Cl_2]^{+}$

(i) EAN = 78-4+12=86

EAN= 24-3+12=33

EAN=27-1+12=38

(At. No. : Pt = 78 ; Cr = 24, en = ethylenediamine)

Calculate the effective atomic number (EAN) of the central metal in (2009)
$CoF_6]$ **Complex.**

EAN=27-3+12=36

Calculate the effective atomic number of the central metal atom/iron
e following complex: $[Co(en)_2Cl_2]Cl$. (2009)

EAN=27-1+10=36

AC Nomenclature of co-ordination compound (Some Facts): -

ame of cation is written first followed by the name of anion.

$$K_4[Fe(CN)_6] \rightleftharpoons 4K^{\oplus} + [Fe(CN)_6]^{4-}$$

potassium hexacynoferrate (II)

ame of complex species is written in one single word and not as Hexa,
, Ferate, II $[Fe(CN)_6]^{4-}$ Hexacynoferate(II)

ng of complex species: -

The name of ligand is written first followed by the name of CMI.

ming of CMI: -

It depends on nature of complex species i.e. on its charged.

hen the complex species is anionic then the ending "ate" is added the
f the naming of CMI.

$e(CN)_6]^{4-}$ Hexacyanoferrate II ion.

special ending is used for CMI if complex species is cationic or neutral.

For e.g. $[Cu(NH_3)_4]^{2+}$ - tetraanmincopper(II)ion

$[Ni(CO)_4]$ - Tetracarbonylnickel(0)

co-ordination compound is acid then ending i.e. is added to the name of

$$H_4[Fe(CN)_4] \longrightarrow 4H^{\oplus} + [Fe(CN)_6]^{4+}$$

yanoferric(II)ion

(iv) The oxidation state of CMI is written after the name of CMI in parenth using Roman numerals. If O.S. is negative then (-) sign is mentioned inside parenthesis before OS as (-I)(-II)

(b) Naming of legends: -

(i) There can be anionic or cationic or neutral ligands. Negatively cha ligends end in suffix – O and positively charged ligands end in the suffix –

Monodenate =

(1) Negative ligands

- CN^- Cyno
- Cl^- Chloro
- Br^- Brmo
- NO_2^- Nitro
- NC^- Isocyno
- S^{2-} Sulphido
- SO_4^{2-} Sulphato
- $S_2O_3^{2-}$ Thiosulphato
- NO_2^- Nitro
- ONO Nitrito
- SCN^- Thiocynato
- NCS- Isothiocynato

(2) Positive ligands

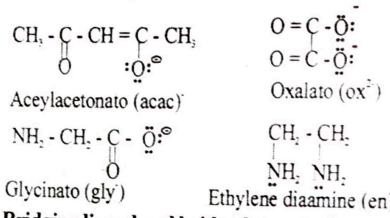
$N_2H_5^+$ Hydrazinium
NO^+ Nitrosonium
NO_2^+ Nitronium

(3) Neutral ligends

CH_3NH_2 Methylamine
$(C_2H_5)_3N$ Trimethylphosphine
$(CH_3)_3P$ Trimethylphosphine
$NH_2CH_2CH_2NH_2$ Ethylenediamine

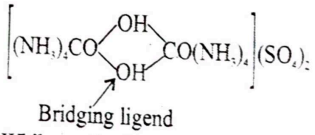
There are four important exceptions –
CO (Carbonyl), NO (Nitrosyl), NH_3 (Amine), H_2O (Aquo)

(b)Bidentate ligand: -



Bridging ligend and bridged complexes: -

For example -



While naming the bridging ligends, the prefix m is used before the na of each of bridging ligend. For two similer bridging ligand di m or m di is

N_2 = dinitrogen, O_2^{2-} = peroxo, NH_2NH_2 = hydrazine, O_2^- = super NH_2^- = amidoor amino, NH^{2-} = Imido, O^{2-} = oxo

(2) If the ligends are present in a complex they are named in alphabetical of their charge or complexity thus $[Mn(NH_3)_4Cl_2]^+$ Tetraammine**dichloro**magnease (III) nitate.

(3) When more than one simple ligand of a particular kind are present, prefix di, tri, tetra, pentra and hexa are used for 2, 3, 4, 5 and 6 ligands respectively before their names.

For e.g. $[Cr(H_2O)_4Cl_2]NO_3$ dichlorotetraaquochromium(III)nitate

Prefix bis, tris, tetrakis, pentakis and hexakis are used before the name of 2, 3, 4, 5 and 6 number of complex ligands respectively.

$[Ni(dmg)_2]$ bis (dimethylglyoximato) nickel (II)

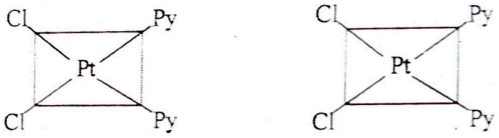
(4) For neutral catonic and nonionic complexes the name of the metal ends in ate. The oxidation number of the metal is given by a Roman numeral in parentheses after the name of the material.

$Ag(NH_3)_2Cl$	diamminesilver(I)chloride
$Na_3(AlF_6)$	Sodiumhexafluoroaluminate(III)

Nomenclature of geometrical isomerism: -

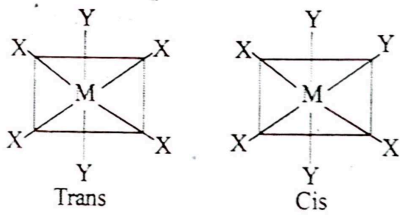
The geometrical isomers are denoted by cis and trans peffers separated by hyphen.

For e.g. – $[Pt(Cl)_2(Py)_2]$



When identical ligands are "adjacent" to each other.

$[M(X)_4(Y)_2]$



Application: -

$K_3[Fe(Cn)_6]$	Potassiumhexacynoferrate(III)
$NH_4[Cr(NH_3)_2(NCS)_4]$	Ammoniumdiaminethiocyanato-N chromateate(III)
$K_3[Al(C_2O_4)_3]$	Pottasiumtrisoxalatoaluminate(III)
$[Co(NH_3)_3NO_2(Cl)(CN)]$	Triaminechlorocyantonitro cibalt(III)
$[Co(NH_3)_5H_2O]I_3$	Pentaamineaquo cobalt(III)iodiade
$[Co(en)_2Cl(NO_2)]^+$	Chlorobis(ehtylendiamine) nitrocobalt(III)ion
$(CO)_3Fe \langle Co \rangle Co \rangle Fe(CO)_3$	μ tricarbonyl hexacarbonyl di ioron(0)
$[Fe(H_2O)_5(NO)]^{2+}$	Pentaqua nitrosyl iron(I)
$Na_2[Fe(Cn)_5NO]$	Sodium pentacynonitrosyl ferrate(II)

$K_2[Cr(Cn)_2(O)_2(O_2)(NH_3)]$ Potassiumamminedicyano dioxopexoxochromate(VI)

$H[BF_4]$ Tetrafluroboxicacid(III)

$H[AuCl_4]$ Tetrachloroanicacid(III)

Q.6 Define the term ligand. **(2005)**

Ans: Ligands: -

All molecular or ionic species having one or more lone pair of electron can act as ligands. For e.g. :NH_3 donor atom is N while $C_2O_4^{2-}$ the donor atom is O, mono denate bidenatate.

Q.7 Give the oxidation state of the metal, its coordination number and geometry of the following complex:

$[Co(en)_3]Cl_3$ **(2009)**

Ans. Oxidation state of Co is +III coordination number is 6

Q.8 Explain the Valance Bond Theory (VBT) of metal complexes with suitable complexes. Mention its limitation also.

Related Questions -

Q. Explain the Valance Bond Theory (VBT) of the co-ordinate bond with suitable examples. Mention its limitation also. **(V. Imp.)**

Ans: Valence Bond Theory (VBT) of the metal complexes: -

In 1931 **Linus Pauling introduced** the concept of hybridization, in the valance bond theory of **Heitler & London**. This improved valance bond theory (VBT) replaced the **Sidgewick's theory of co-ordinate bond**, which was not able to explain many-many complexes in the light of **Octet theory**.

The valance bond theory of complexes given by **Linus Pauling** was instrumental for two decades for the standard discussion about stereochemistry and magnetic properties of the complexes, although this theory has little to offer about electronic spectra, thermodynamics and the kinetics of the complexes about this theory was so simple that several forms of this theory are still retained.

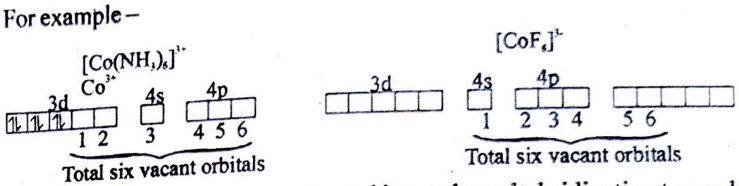
In this theory we examine how the empty orbitals on a central metal ion undergo hybridization to produce a set of new hybrid orbitals with better overlapping power. How these hybrid orbitals undergo effective overlap with the suitable orbitals having an electron pair of the donor atom of suitable ligand. How the hybrid orbitals having electron pair of the donor atoms of suitable ligand. How the hybrid orbitals of the central metal ion loaded with electron pairs orient themselves around the central metal ion to provide definite shape for a particular complex.

Silent features of Valance Bond Theory (VBT) of the complexes: -

(1) The central metal ion / central metals make available vacant orbitals of suitable energy in appropriate number for ligands.

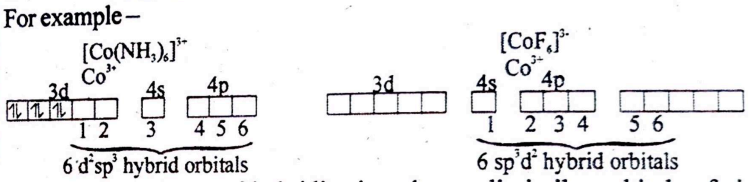
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For example –



(2) These orbitals of the central metal ion undergo hybridization to produce a set of new hybrid orbitals of equivalent energy in equivalent number with better overlapping power.

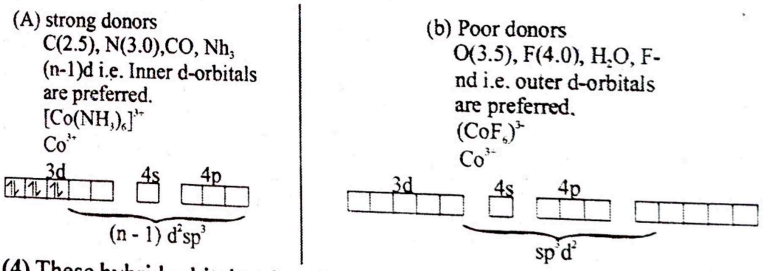
For example –



In the process of hybridization always-dissimilar orbitals of similar energy are involved.

(3) If d-orbitals are involved in hybridization then this may be either (n - 1)d i.e. inner d-orbitla or nd i.e. outer d orbitals. The choice of inner and outer d-orbitals depend upon the donor behaviour of the donor atom of a particular ligand.

For example –

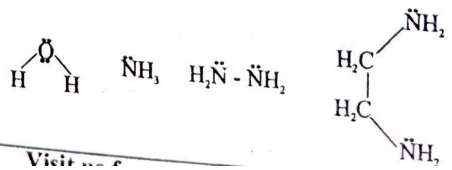


(4) These hybrid orbitals orient themselves in three-dimentional space around the central metal ion according to the geometry of the complex.

The six d^2sp^3 hybrid orbitals orient themselves along the six corners of an octahedral given as follows –

(5) The ligand must contain atleast one electron pair in suitable orbital, which may be donated to the empty vacant orbitals of the central metal ions. In other words the ligand must be electron rich species i.e. either negatively charged or neutral with lone pairs. Only a very few ligands are positively charged. e.g. -

CN^-, F^-, NO^{3-}, SO_4^{2-}

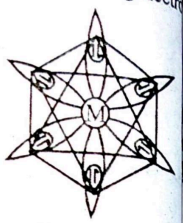


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(6) The empty hybrid orbitals of the central metal ion oriented in fixed directio undergo effective overlap with the suitable orbitals of the ligand having electr pair.

Due to this overlap between the filled orbitals of the ligand and empty hybrid orbitals of central metal ion. The very first bond between ligand and metal is established. This is known as σ bond i.e.

L to M ($M \xleftarrow{\sigma} L$).

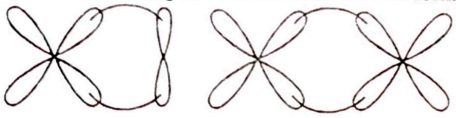


M = Metal, L = Ligan

Q.9 Describe the sigma donor and pi-acceptor ligands. Give two exampl of each type.

Ans. In the process of donation of electron pair in the form of effective overla between the orbitals of the ligand and metal. A large amount of electron densi is accumulated over the central metal ion, which is incontrast to the nature matel ion. Therefore in order to get rid off this excess electron density t central metal ion returns to the fraction of electron density to the ligand. In th way an additional bond is formed between metal and ligand. This is nothing b

$M \rightarrow L$ i.e. p bond. Thus overall $M \underset{\sigma}{\overset{\pi}{\rightleftarrows}} L$ this M to L π bond overla specially under following two circumstances in the form of $d_\pi - p_\pi$ or $d_\pi - d_\pi$.



dπ - pπ dπ - pπ

(i) The central metal of the complex should be in low oxidation state e.g. (zero) oxidation state.

$Na[V^{-1}(CO)_6]$ $[Ni(CO)_4]$

V(-1) Ni(O)

(ii) The ligands must posses vacant orbitals of suitable energy in appropria number e.g. CO, NO etc. such ligands are known as π acid ligand.

Q.10 Explain the utility of coordination compounds in qualitative analysi giving two examples. (2005

Related Questions -

Q. Write down the application of Coordination Compounds in qualitativ analysis. (2011, 12

Ans. (i) Sulphide (S^{2-}) test sodium nitroprusside reacts with sulphide ion t give a purple complex $[Fe(CN)_5(NOS)]^{4-}$. This is used as a sensitive qualitativ test for sulphides

$$2[Fe(CN)_5(NO)]^{2-} + S^{2-} \rightarrow 2[Fe(CN)_5(NOS)]^{4-}$$

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$CdSO_4$ form Complex with NH_4OH

$CdSO_4 + 4NH_4OH$ —à $[Cd(NH_3)_4]SO_4 + 4H_2O$

Colourless

11 Write the name and the structural formula of a tridentate chelating and and indicate the liganding sites. (2006)

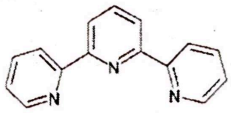
lated Question -

Write name and structure of a bidentate or a tridentate chelating ligand. (2016)

Give suitable examples of bidentate and tridentate chelating ligands. (2018)

s. Tridetate ligand are the ligand that have three site for co-ordination, mple as followes

2,2',2"-Terpyridine





acyclononane, known as "TACN" which is ck-en," is a cyclic organic compound with $_{12}(NH)_3$. series include diazacyclohexane,

12 Discuss with equations, the role of the following in qualitative or lumetric analysis :

Ammonium molybdat (ii) Borax (iii) $K_4[Fe(CN)_6]$ (2008)

s. Ammonium molybdat used as for test of PO_4^{3-}. When a mixture is warm th conc. HNO_3 and ammonium Molybdate a bright yellow precipate of mmonium phosphate is form.

13 Two moles of AgCl is precipitated when $AgNO_3$ solution is added into aqueous solution of containing one mole of the complex, $CO(NH_3)_XCl_3$. ve the value of x and the correct structural formula of this complex. (2009)

ns. X=5 and correct formula is $[CO(NH_3)_5Cl]Cl_2$

14. Discuss limitations of Sidgwick's EAN concept. (2017)

ns. Limitations of Sidgwick's EAN concept are as:

Many complexes are stable but do not follow EAN rule.

Theory doesn't predict the geometry of the complexes.

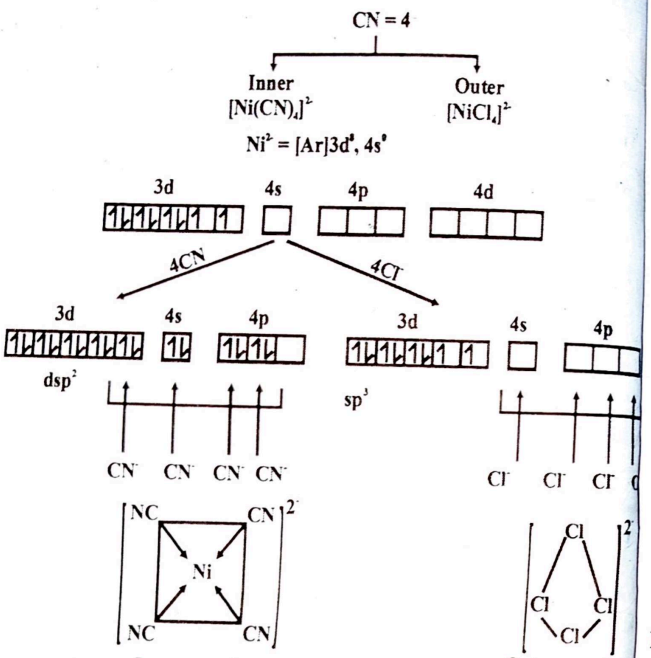
Theory doesn't predict the magnetic behavior of the complexes.

.15 Write a short notes on outer and inner orbital complexes. (Imp.)

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Ans: In 1931 Linus Pauling put forward a new idea of hybridization **Valance Bond Theory** of Heiler and Londonand then applied this theory explanation of the bonding and structures of a variety of the complexes. brief this theory involves the process of mixing of dissimilar orbitals of energy on a particular transition metal in a particular transition metal co

$$\left\{\begin{matrix}[Ni(CN)_4]^{2-} \\ [NiCl_4]^{2-}\end{matrix}\right\} = CN = 4$$

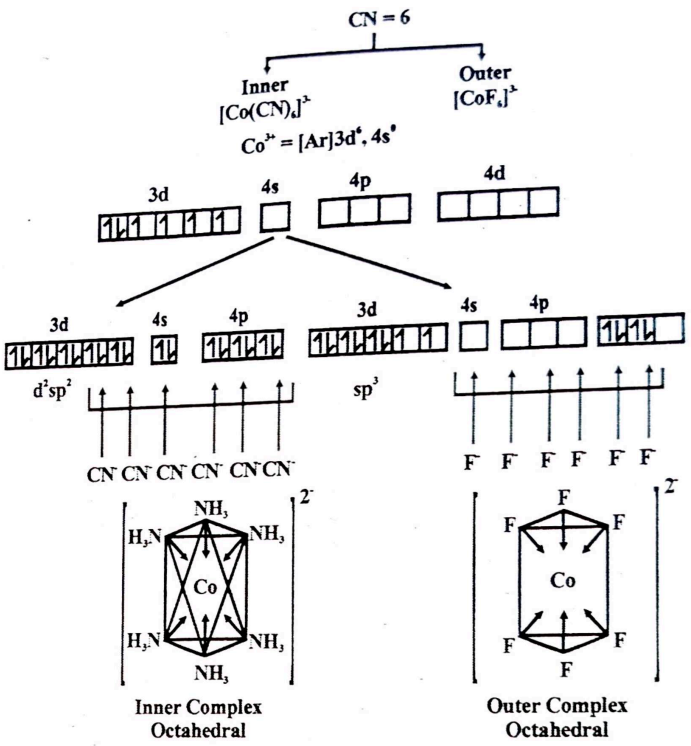


In this process of hybridization, most of the times d orbitals ar involved. Now there is a option for the central metal to use either in orbitals i.e. (n – 1) d orbitals with s and p orbitals of n[th] level or involvem nd orbitals i.e. outer dorbitals with ns and np orbitals.

When the inner orbitals are used in the process of hybridizatio the resulting complex is known as **inner orbital complex** or **low spin co** or **spin paired complex** or **covalent complex** or several time **diamag complex**. On the other hand if outer d orbitals i.e. nd orbitlals are used w and np orbitals for the process of hybridization then the resulting comp known as **outer orbital complex** or **high spin complex** or **spin free comp** ionic complex or most of the times **paramagnetic complex**.

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$$\left\{\begin{matrix}[Co(CN)_6]^{3-} \\ [NiCl_4]^{2-}\end{matrix}\right\} = CN = 6$$



Thus in inner complexes the bond is strong since here in the hybridization process the d orbitals, which are used are more close to the nucleus. On the other hand the outer orbital complexes where the outer d orbitals i.e. nd orbitals are used the bonds are comparatively weaker.

Let us have survey in 3d series of the transition metals in their divalent states.

(b) Ligend with donor and acceptor properties both: -

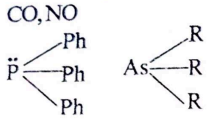
There are some ligands which are capable to accept excess electron density from the central metal in the form of M → L bond i.e. π bond. Such ligand possesses vacant orbitals especially vacant π orbitals of suitable energy in appropriate number, for such type of acceptance quite naturally. Such type of ligand possesses donor properties as usual in order to stabilized L → M σ bonds. Such types of donor form the complexes with those metals which are in low oxidation state either zero or negative oxidation state. Thus here we have two types of bonds in between metal and ligand.

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$L \underset{\sigma}{\overset{\pi}{\rightleftarrows}} M$

These π bonds may be $p_\pi - p_\pi$, $p_\pi - d_\pi$, $d_\pi - d_\pi$. A few examples of such type of ligands are as given –

CO, NO



Q.16. Calculate the effective atomic number of central atom in following complexes $[Fe(CO)_5]$ and $Na[V(CO)_6]$. (Atomic No. Fe = 26; V = 23). (201

Sol. EAN of metal in a complex

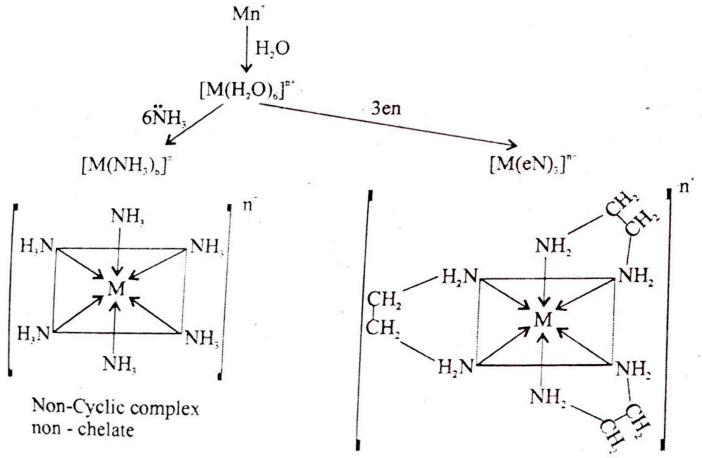
= At. No. - Oxidation state + 2 × cordination number

(i) $[Fe(CO)_5]$ EAN = (26 - 0) + 2 × 5 = 36

(ii) $Na[V(CO)_6]$ EAN = (26 - 1) + 2 × 6 = 37

Q.17. Define chelates with suitable examples and mention their importan applications.

Ans. Chelates: -



Non-Cyclic complex
non - chelate

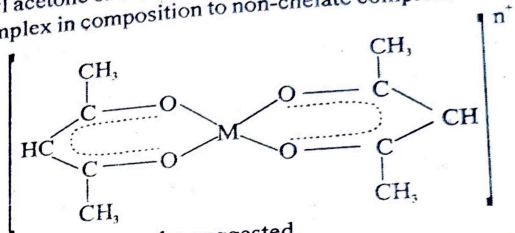
Cyclic complex
chelate complex

When a particular metal ion especially transition metal ion undergoes complex formation with polydentate ligands then the closed chain i.e. cyclic complexes are formed. These cyclic complexes are nothing but the chelate complexes. For e.g. –

• Among the chelates complex the 5 and 6 membered chelates are more stable due to same steric factors.

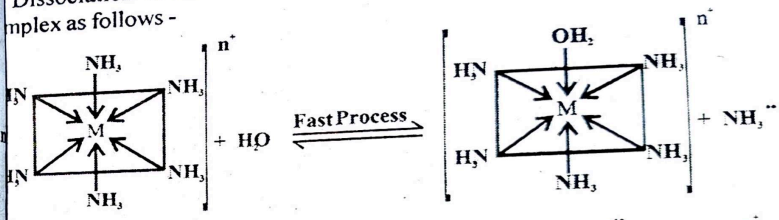
Few more examples of chelates are as follows –

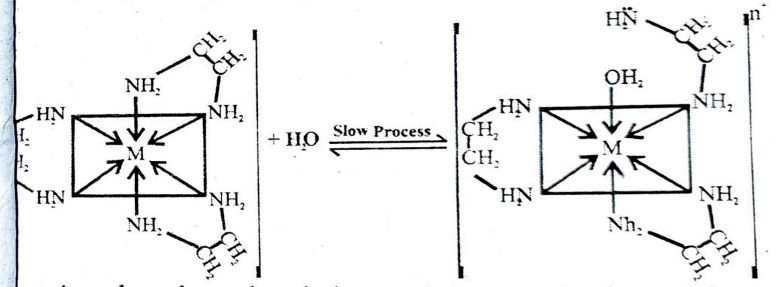
Acetyl acetone of a transition metal ion (6 membered) over stability of chelate complex in composition to non-chelate complex.



llowing two reasons may be suggested.

Dissociation of non chelate compex is faster in comparison to chelate mplex as follows -





As we have shown above in the **non-chelate complex** the monodentatate and water totally replaces one monodentate ligand ammonia from the co-lination sphere of the central metal ion in the single step, suggesting that dissociation of a non-chelate complex is an easier job. On the other hand he chelate complex where the ligand is bidenatate, the ligand substitution monodentate ligand water is not complete in to single step.

As we have shown above in the chelate complex the bidentate ligand s not leave the co-ordination sphere of the central metal ion in the single p. Thus dissociation of a chelate complex is a relatively tough job.

Yet another reason for the over stability of the chelate complex over the n-chelate complex has been given in terms of **thermodynamics.**

$$\underbrace{[M(H_2O)_6]^{n+}}_{7\ Mole} + 6\ddot{N}H_3 \rightleftharpoons \underbrace{[M(NH_3)_6]^{n+}}_{7\ Mole} + 6H_2O$$

$$\underbrace{[M(H_2O)_6]^{n+}}_{4\ Mole} + 3en \rightleftharpoons \underbrace{[M(en)_3]^{n+}}_{7\ Mole} + 6H_2O$$

Thus we have shown above the formation of a chelate co accompanied a large order of randomness. Since on the product side w more number of moles as compared to the reactant side. In the other wo ΔS i.e. change in entropy is positive here which leads to high negativ of ΔG leading to more chelate formation.

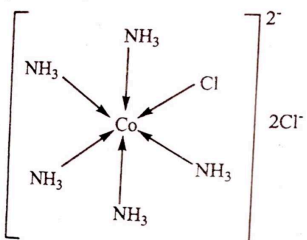
Since $\Delta G = \Delta H - T.\Delta S$

Large positive value of ΔS leads to negative value of ΔG on th hand in the non-chelate formation the change in entropy i.e. ΔS favourable. Since on the both sides we have same number of moles.

Therefore ΔG posses low negative value, which leads to low fea of chelate complex formation.

Q.18 Represent $CoCl_3.5NH_3$ according to Werner's Co-ordination if two third of its chloride ions are precipitated as silver chloride fr aqueous solution when reacted with silver nitrate solution. Write do IUPAC name of the compound and calculate the effective atomic numb central metal atom.

Ans: The structure of $CoCl_3.5NH_3$ according to Werner's Co-ordi theory -



IUPAC name = Pentaamminechlorocobalt(III)chloride

EAN=27-3+12=36

Central metal is Co

Q.19. Calculate the Effective Atomic Number (EAN) of the central at in the following complex species:

$[Cu(NH_3)_4]$; $[Co(NH_3)_6]^{3+}$; $[Fe(Cn)_6]^{4-}$ $Ni(Co)_4$

$[Pt(NH_3)_2Cl]$; $[PdCl_4]^{2-}$ **(Atomic number of: Cu = 29, Co = 27, Ni = 28, Pt = 78, Pd = 46)**

Ans. EAN = (Atomic number - oxidation state) + Total number of e

eved by ligand

$[Cu(NH_3)_4] = (29-2)+2\times4 = 27+8 = 35$

$[Co(NH_3)_6]^{3+} = (27-3)+2\times6 = 24+12 = 36$

$[Fe(CH)_6]^{4-} = (26-2)+2\times6 = 24+12 = 36$

$Ni(Co)_4 = (28-0)+8 = 28+8 = 36$

$[Pt(NH_3)_2Cl] = (78-4)+2\times3 = 74+6 = 80$

$[PdCl_4]^{2+} = (46-2)+2\times4 = 44+8 = 52$

D. Name the following complex compound according to IUPAC system omenclature :

$(C_2O_4)_2Cr\begin{matrix}OH\\OH\end{matrix}Cr(C_2O_4)_2]^{4-}$ (ii) $[Co(en)_2(ONO)Cl]Cl$

$[Pt(NH_3)_4(NO_2)Cl]SO_4$ **(2010)**

ere, en = ethylenediamine

(i) μ - dihydroxotetraoxalatodicromate (II) ion

B is (ethylenediamine) nitritochloride cobaltate (III)

$Pt(NH_3)_4(NO_2)Cl]SO_4$ - Tetraaminonitrochlorosulphateplatinum (II)

1. Find out the normality of solutions containing in one litre (i) 0.49g O_4 (ii) 0.90g. $NaHSO_4$. (2011)

(i)

$$\text{Normality (N)} = \frac{\text{Number of gram equivalents of solute}}{\text{Volume of the solution in litre}}$$

$$\frac{0.49/49}{1} = 0.01N \qquad \therefore \text{ Number of } g_{eq.} = \frac{\text{Mass of substance}}{\text{Equivalent wt.}}$$

$(H_2SO_4 = 98)$

$$\text{Normality (N)} = \frac{\text{Number of gram equivalents of solute}}{\text{Volume of the solution in litre}}$$

$$= \frac{0.90/120}{1} = 0.007N$$

2. Explain the difference between iodometry and iodimetry.

Iodimetry: - (2011, 14, 19)

Iodine is an oxidizing agent and can be used to titrate reduc- gents. Titrations with iodine are called iodimetric methods. These titrations performed in neutral or mildly alkaline to weakly acid solutions.

Since Iodine is not a strong oxidizing agent the number of reducing ts that can be titrated is limited. Few cases are listed below.

Substance determined	Reaction with I_2	Solution
H_2S	$H_2S+I_2 \longrightarrow S + 2I^- + 2H^+$	Acidic
SO_3^{2-}	$SO_3^{2-} + I_2 \longrightarrow SO_4^{2-}+2I+2H^+$	
Sn^{2+}	$Sn^{2+}+I_2 \longrightarrow Sn^4+2I^-$	Acidic
As (III)	$H_2AsO_3^-+I_2+H_2O \longrightarrow HAsO_4^{2-}+2I^-+3H^+$	pH_8

Iodometry:-

Iodide is a weak reading agent and will reduce strong oxidizing *when n excess of iodide is added to the solution of an oxidizing agent, io* *produced in an amount equivalent to the oxidizing agent present. This io* *ce be titrated with a reducing agent. The result will be the same as* *oxidizing agent is titrated directly. The titrating agent is sodium thiosul* *With iodine thiosulphate ion is oxidized quanitatively to tetra thionate*

$$2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e$$

Some example of this procedure are

Determination of sodium hypochlorite in bleaches. The reactions invo *are:*

$$OCl^- + 2I^- + 2H^+ \longrightarrow Cl^- + I_2 + H_2O$$

$$I_2 + 2S_2O_3^{2-}\ 2I^- + S_4O_6^{2-}$$

Determination of dichromate:

$$Cr_2O_7^{2-}6I+14H^+2Cr^{3+}+3I_2+7H_2O$$

$$I_2 + 2S_2O_3^{2-}\ 2I^- + S_4O_6^{2-}$$

Titrations involving iodine are performed with a suspension of s as the indicator. The deep blue colour that develops in presence of iodi due to the absorption of iodine in to the helical chain of -amylos macromolecular Component of most starches. Disappearance of this blue st colour indicates the end pint of this titration.

Q.23. Discuss the merits and demerits of the long form of the periodic T Write down the IUPAC nomenclature of elements having atomic number 112, 113 and 118.

Ans. Merits Of Long Form Of Periodic Table:-

1. Long form periodic table is based upon atomic number which is a f fundamental property of the atom.
2. It relates the position of an element in the periodic table with its electr configuration.
3. It removed the anomalies about the position of isotopes which existe the Mendeleev's table.
4. It removed the abomalies of inversions which existed in the Mendele table. Thus, $^{39}_{19}K$ precedes $^{40}_{18}Kr$ in the periodic table because it h

lower atomic number.

5. It also removed the other anomalies found in Mendleev's periodic table, such as grouping of the chemically dissimilar elements, and separation of chemically similar elements, etc.
6. It reflects more clearly the changes in the properties of various elements while moving across a period or down a group.
7. Typically (representative), and transition elements have been assigned separate locations in this form of the period table.
8. It also separates metals and non-metals.

Demerits in Long Form Of Periodic Table:-

Although the long form of periodic table gives an almost perfect arrangment of elements, but it yet suffers from the following drawbacks:

1. Position of hydrogen - Hydrogen resembles both the alkali metals as well the halogens. As in the earlier periodic tables, hydrogen has not been allocated an exclusive location of its own even in the long form periodic table. However, it is placed in a separate box just above the group 1.

2. Location of Helium - The location of helium (He) amongst the p-block elements is not fully justfied as its electronic configuration justifies it to be included in the s-block.

IUPAC Name-

Atomic Number	Name
111	Unununium
112	Ununbium
113	Ununtrium
118	Ununoctium

Note and remark:-

In accordance with the 2016 IUPAC guideline for naming new elements, the discoverers were invited to propose names and symbols for the elements. Claims have been assigned to them and the following are proposed: (a) nihonium and symbol Nh, for the element with Z = 113, (b) moscovium with the symbol Mc, for the element with Z = 115, (c) tennessine with the symbol Ts, for the element with Z = 117, and oganesson with the symbol Og, for the element with Z = 118.

Q.24. Write the name of following complexes according to IUPAC system:

(i) $Na_2[Fe(CN)_5NO]$ **(2011, 12, 14)**

(ii) $[Fe(CO)_5]$ **(2011)**

(iii) $K_4[Ni(CN)_4]$ **(2011, 12, 15, 16)**

(iv) $K_2[Ni(CN)_4]$ **(2013)**

(v) $K_4[Fe(CN)_6]$ **(2013, 19)**

$H_3)_3Cl]_2[PtCl_4]$,

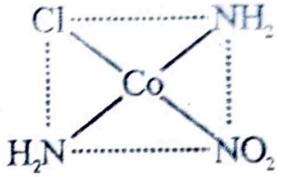
F_6.

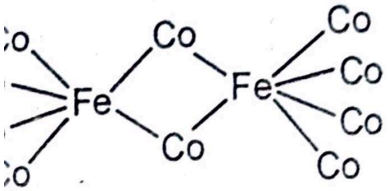
gF_4)

(viii) $[Co(NO_2)_3(NH_3)_3]$

(x) $Cu(NH_3)_4SO_4.H_2O$.

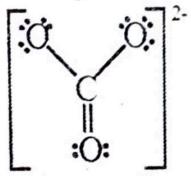
(xii)





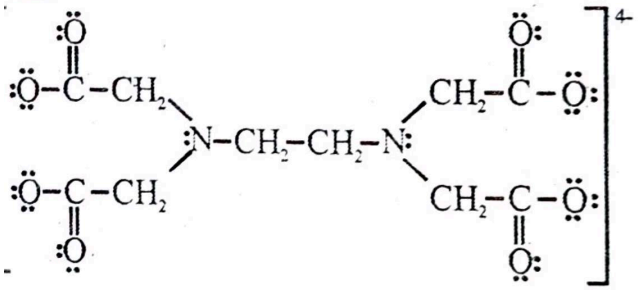
ive suitable examples of bidentate and hexadentate chelating ligands. eir name and structural formulae. **(2015, 18)**

inate ligand -



Carbonate ion

ıtate -



EDTA^{4-}, ethylenediaminetera acetate ion

Write down the IUPAC nomenclature of elements having atomic 108, 110 and 112. **(2014, 15)**

Go through Q.23 page no. 26. for 112.

PAC Commission on the Nomenclature of Inorganic Chemistry that it is necessary to have a systematic naming for the elements mic number greater than 100 ($Z > 100$), even for those which had not covered. The Commission decided that these elements would be ned systematically and that names should accord with the following

name is derived directly from the atomic number of the element using following Latin numerical roots:

roots are put together in the order of the digits which make up the mic number and terminated by 'ium' to spell out the name. The final 'n'

of 'enn' is elided when it occurs before 'nil', and the final 'i' of 'tri' when it occurs before 'ium'.

3. The symbol of the element is composed of the initial letters of the roots which make up the name.
4. The root 'un' is pronounced with a long 'u', to rhyme with 'moon' element names each root is to be pronounced separately.

Number	Root
0	nil
1	un
2	bi
3	tri
4	quad
5	pent
6	hex
7	sept
8	oct
9	enn

Here are examples of the names generated for elements with numbers 101 to110.

Atomic number	Name	Symbol
101	Unnilunium	Unu
102	Unnilbium	Unb
103	Unniltrium	Unt
104	Unnilquadium	Unq
105	Unnilpentium	Unp
106	Unnilhexium	Unh
107	Unnilseptium	Uns
108	Unniloctium	Uno
109	Unnilennium	Une
110	Ununnilium	Uun

Q.29. Addition of strong ammonium hydroxide solution into cupri gives deep blue solution. Why?

Ans. $[Cu(NH_3)_4(H_2O)_2]^{2+}$ formation of a soluble deep blue comple ammonia ion.

Q.30. Write short note on application of coordination compounds in tive analysis. **(2015,**

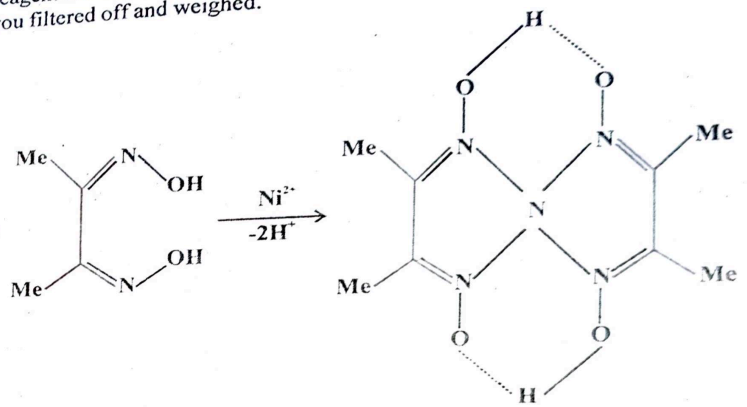
Related Question -

Q. Write Application of co-ordination componds in qualitative an

Ans. Number of coordination compounds are known that are used fo tative analysis. For example thiocyanate ions to solutions contain gives rise to a characteristic red colour of the thiocyanate

$[Fe(H_2O)_5(SCN)]^{2+}$ (often just written as $Fe(SCN)^{2+}$). This can be used as a qualitative test, but it can also be used to give a quantitative measure of the Fe(III) concentration by constructing a calibration curve from solutions of known Fe(III) concentration.

Similarly gravimetric determination of nickel is another application **quali-tative analysis.** This involved treating a solution containing Ni^{2+} ions with the reagent dimethylglyoxime to produce a virtually insoluble red complex which you filtered off and weighed.



Another common example of this is the gravimetric determination of aluminium using 8-hydroxyquinoline, often called oxine and abbreviated as Hox; in this case the complex formed is octahedral $Al(ox)_3$ with the ligand binding through the nitrogen of the quinoline ring and the deprotonated hydroxy group.

Q.31. Calculate EAN value in the following.

Atomic number of : V = 23, Fe = 26, Co = 27, Ni = 28

$K_4[Fe(CN)_6]$, $K_3[CoF_6]$. **(2016)**

Ans. EAN of Iron in $K_4[Fe(CN)_6] = 26 - 2 + 12 = 36$

EAN of Iron in $K_3[CoF_6]$ - Go through Q. No. 4 Page No. 44.

Chapter 5 - Electrode Potential

Q.1. On the basis of given EMF diagram represent : (200

E^0 Acid Mn $\xrightarrow{1.19} Mn^{2+} \xrightarrow{-0.95} Mn^{3+} \xrightarrow{-0.95} Mn^{4+}$

E^0 Base Mn $\xrightarrow{1.55} Mn^{2+} \xrightarrow{-0.10} Mn^{3+} \xrightarrow{-0.20} Mn^{4+}$

(i) In which medium Mn^{2+} is more stable

Ans. Basic medium

Q.2. Write a brief note on the importance of electrochemical series, (2007, 14, 1

Related Question -

Q. Discuss the importance of electro chemical series. (2016, 1

Ans. Enormous use may be mode of reduction for summarizing what spec will oxidies or reduce something else, what product will be and what oxidati states are stable with respect to solvent and also with to disproportionati

A great deal of useful information about an element can be shown the appropriate half reactions and reduction potential. Consider some h reaction –

$Fe^{2+} + 2e^- \longrightarrow Fe$ $\quad E^0 = -0.47\ V$

$Fe^{3+} + 3e^- \longrightarrow Fe$ $\quad E^0 = -0.057\ V$

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$ $\quad E^0 = +0.77\ V$

$FeO_4^{2-} + 3e^- + 8H^+ \longrightarrow Fe^{3+} + 4H_2O$ $\quad E^0 = +2.20\ V$

Above half-cell reaction arrange in R.P. Diagram. In this the high oxidation state is written at the left and the lowest state at the right species such as electron H^+ and OH_2 are omitted.

$$\overset{VI}{FeO_4^{2-}} \ \underline{2.20}\ \overset{III}{Fe^{3+}} \ \underline{0.77}\ \overset{II}{Fe^{2-}} \ \underline{-0.47}\ \overset{0}{Fe} \qquad Fe^{3+}$$

$\longleftarrow 0.057 \longrightarrow$

One of the most important facts, which can be obtained form reduc potential diagram, is whether any of oxidation states are unstable with re to disproportionation. Disproportionation is where one oxidation s decomposes, forming some ions in a higher oxidation state, and some in lo oxidation state.

Q.3 On the basis of given standard electrode potential data, predict whet aluminium may be used to prevent corroision of iron pipes : (20

$E^0_{Fe^{2+}/Fe} = -0.44$ Volt, $\quad E^0_{Al^{3+}/Al} = -1.66$ Volt

Sol. $E^0 = E_{cathod} - E_{anode} = -1.66 - (-0.44)$

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$= -1.22$volt

Q.4. A cadminium foil is put into a lead (II) nitrate solution, predict products? Given that $E^0(Cd^{2+}/Cd) = -0.40$ V and $E^0(Pb^{2+}/Pb) = -0.13$ V. (2009)

Ans. $E^0 = E_{cathod} - E_{anode}$

$= -0.40 - (-0.13)$

$= -0.27$volt

Q.5. What is electrochemical Series? Describe its uses in explaining chemical reaction. (1999, 2003, 2011)

Related Questions -

Q. Write short notes on Electrochemical series. (2012, 13, 17)

Ans. If the elements are arranged in order of increasing standard electrode potential, the resulting series is called electrochemical series. In the electrochemical series the most electropositive elements are at top and the least electropositive at the bottom. Greater the negative value of the potential greater will be tendency for a metal to ionize. Thus a metal, which is high in electrochemical series, will displace another metal low down the series from solution.

Half Cell Reduction Reaction	E^0 (Standard Electrode Potential)
$Li^+ + e^-$ ⟹ Li	= - 3.045 {Best reduction agent, worst oxiding agent}
$K^+ + e^-$ ⟹ K	= - 2.923
$Ca^{++} + 2e^-$ ⟹ Ca	
$Na^+ + e^-$ ⟹ Na	
$Mg^{++} + 2e^-$ ⟹ Mg	
$Al^{3+} + 3e^-$ ⟹ Al	
$Zn^{2+} + 2e^-$ ⟹ Zn	
$Fe^{2+} + 2e^-$ ⟹ Fe	
$Sn^{++} + 2e^-$ ⟹ Sn	
$Pb^{++} + 2e^-$ ⟹ Pb	
$2H^+ + 2e^-$ ⟹ H_2	= 0
$Cu^{++} + 2e^-$ ⟹ Cu	
$Ag^+ + 2e^-$ ⟹ Ag	
$Cl_2 + 2e^-$ ⟹ $2Cl^-$	
$Au^{+++} + 3e^-$ ⟹ Au	
$F_2 + 2e^-$ ⟹ $2F^-$	+ 2.870 {Best oxiding agent, worst reducing agent}

Table – Electrochemical Series

{Remark – Above table given in reduction potential as the IUPAC consider}

Application of Electrochemical Series or Application (Significance) Of Standard Electrode Potential: -

A number of applications, which is given below –

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(i) Forecasting, the relative ease with which species would be oxidized reduced: - As the higher the +ve E^0 value greater will be tendency towa reduction and on the other hand the – ve sign of reduction potential indic the electrode reaction occurs in opposite direction. It means the reduct form has grater tendency to lose the electrons and get oxidized. Thus floar is best oxidizing agent and Li is best reducing agent.

(ii) Displacement of One Species By Other: -

The metals with more negative reduction potentials can displace tho with leaser negative or positive reduction potential forms their solution.

(iii) Calculation of Standard emf of The Cell: -

We can calculate the E^0 value by knowing E^0_{anode} and E^0_{cathod} value following reduction.

$$E^0_{Cell} = E^0_{Anode} + E^0_{Cathode}$$

in oxidation form, both anode and cathode.

(iv) Predicting Feasibility Of Cell Reaction: -

By following formula we can predicate the pathway of reaction.

$$\Delta G^0 = -nFE^0$$ Where ΔG = free energy, F = Faraday

From above equation we can also calculate the standard free energy chang

ΔG	E	Cell reaction
-	+	Spontaneous
0	0	Equilibrium
+	-	Non spontaneous

(v) Determination of Equilibrium Constant of The Reaction: -

$$2.303\ RT\ \log K = nFE^0$$

Where E^0 = standard electrode potential

With the help of above equation we can calculate equilibrium constant of t reaction.

(vi) Prediction of Reactions of Metals With Acids to Liberate Hydrogen: -

With the help of the standard electrode potentials of metals it can b predicted whether a given metal would react with the acid to produce hydroge or not.

Q.6. Given : $Li(g) + Br(g) \rightarrow LiBr(s)$, $\Delta H = -607$ KJ mol^{-1}

$Li(g) \rightarrow Li^+ + e^-$ $\Delta H = +527$ KJ mol^{-1}

$Li^+(g) + Br^-(g) \rightarrow LiBr(s)$ $\Delta H = -787$ KJ mol^{-1}

Calculate the value of ΔH for $Br(g) + e^- \rightarrow Br^-(g)$. **(2009)**

Ans. $Li(g) + Br(g) \rightarrow LiBr(s)$, $\Delta H = -607$ KJ mol^{-1} .....(1)

$\Delta H = +527$ KJ mol^{-1} .....(2)

$\Delta H = -787$ KJ mol^{-1} .....(3)

$Li(g) \rightarrow Li^+ + e^-$

$Li^+(g) + Br^-(g) \rightarrow LiBr(s)$

$r(g) + e^- \rightarrow Br^-(g)$. We invert the equation 2 and 3 and we get

ΔH = Product – reactant

$= 787.0 - (-607.0 - 527.0)$

$= -1921$ KJ mol^{-1}

$E^0_{Co/Co^{2+}} = 0.28$

$E^0_{Sn/Sn^{2+}} = 0.14$ } Oxidation

$= -0.14 - (-0.28) = -0.14$ V

value is – ve hence reaction is not spontaneous.

Predict whether the following reactions will occur spontaneously or

$o^{2+} + Sn \longrightarrow Sn^{2+}$, **Given $E^0_{Co/Co^{2+}} = +0.28$ V, $E^0 = +0.14$ V**

$i + Cu^{2+} \longrightarrow Ni^{2+} + Cu$, **Given $E^0_{Ni/Ni^{2+}}$**

$= 0.25$ V, $E^0_{Cu/Cu^{2+}} = -0.34$ V **(2014)**

(i) As we know ,

$$E_{Cell} = \left(E^0_{red}\right)_{cathode} - \left(E^0_{red}\right)_{anode}$$

$$= -0.14 - (-0.28) = -0.14 + 0.28 = +0.14 \text{ V}$$

use of E^0_{cell} is positive hence reaction is spontaneous.

s we know

$$E_{Cell} = \left(E^0_{red}\right)_{cathode} - \left(E^0_{red}\right)_{anode}$$

$$= 0.34 - (-0.25) = 0.34 + 0.25 = 0.59 \text{ V}$$

one is also spontaneous.

F. (Electromotive Force) or Electrode Potential: -

ark: -

Give below some term and definition then application.

ation: -

Removal of e^- from the substance

$A \longrightarrow A^+ + e^-$

e.g., $Zn \longrightarrow Zn^{2+} + 2e^-$

ucing agent a substance which itself undergoes oxidation and thus ces to the other substance.

Reduction: -

Addition of e^- to a substance

$$A + e^- \longrightarrow A^-$$

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

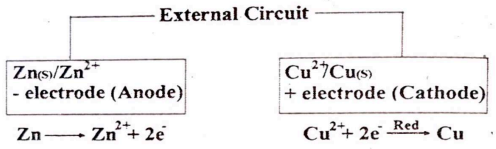
Oxidising agent – A substance which itself undergoes reduction a oxidized to the other substance.

$K_2Cr_2O_7$ Vs $FeSO_4(NH_4)_2SO_4.6H_2O$ in acidic med

$$\underset{\text{oxidising agent}}{Cr_2O_7^{2-}} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$\left[\underset{\text{reducing agent}}{Fe^{2+}} \longrightarrow Fe^{3+} + e^-\right] \times 6$$

Oxidation and reduction reaction takes place simultaneously there known as redox reaction.



Q.8. What is electrode potential of an electrode [Electrode or E]?

Related Questions -

Q. What is standard electrode potential? (2014,

Ans. The electrical potential difference set up between a metal an in solution is called potential of the electrode or simply as electrode po Electrode potential can also be defined as the tendency of an elemen or gain electrons when it is in contact with its own ions in solution su electrode represents a half-cell; electrode potential is also called pote the half-cell.

What Is Standard Electrode Potential (E^0): -

If in a half-cell, the metal rod is suspended in a solution of having 1-M conc. and the temperature is 298 K, the electrode potenti half-cell or electrode is called standard electrode potential.

Electrode Potential: -

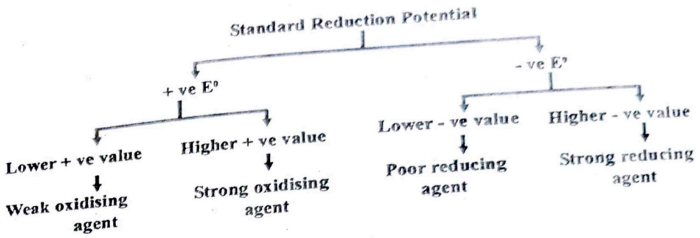
Nernst equation –

$$E = E^0 - \frac{RT}{nF} \ln \frac{\text{oxidation}}{\text{Reduction}}$$

$$E = E^0 - \frac{RT}{nF} \ln \frac{\text{Reduction}}{\text{Oxidation}}$$

$$\boxed{E = E^0 - \frac{2.303}{n} \log K}$$

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Meaning Of Stability: -

Stability with respect to disproportion. In the reduction potential diagram the E^0 value on the right hand side of the species is more than the E^0 value of the left hand side then this type of species will undergo dispornation.

Work out the relative stabilities of specie formed by the nitrogen in acidic and basic medium solution from following reduction potential.

Acidic Solution: -

$$NO_3^- \xrightarrow{0.94\ V} HNO_2 \xrightarrow{1.00\ V} NO \xrightarrow{1.59\ V} N_2O \xrightarrow{1.77\ V} N_2 \xrightarrow{0.27} NH_3$$

Oxidising agent order – $N_2O > NO > HNO_2 > NO_3^- > N_2$

Basic Solution: -

$$NO_3^- \xrightarrow{0.01\ V} NO_2^- \xrightarrow{0.46\ V} NO \xrightarrow{0.76\ V} N_2O \xrightarrow{0.94\ V} N_2 \longrightarrow NH_3$$

(0.15 spans $NO_3^- \to NO$; 0.01 spans $NO_3^- \to N_2O$)

Oxidising agent order – $N_2O > NO > N_2 > NO_2^- > NO_3^-$

For Acidic Medium: -

HNO_2, NO and H_2O species are unstable with respect to dispropornation rest of element are stable because the value of standard reduction potential on their right hand side is more than their left hand side viz. NO_3^-, N_2 and NH_4^+ are stable with respect to disproportation.

$$[2e^- + 2H^+ + 2HNO_2 \longrightarrow 2NO + 2H_2O]_2 \qquad E^0 = 1.0$$

$$2HNO_2 + 2H_2O \longrightarrow 2NO_3^- + 6H^+ + 4e^- \qquad E^0 = 0.94$$

$$6HNO_2 \longrightarrow 4NO_2 + 2NO_3^- + 2H^+ + 2H_2O \qquad E^0 = 0.06\ V$$

$$2NO + 2H^+ + 2e^- \longrightarrow N_2O + H_2O \qquad E^0 = 1.59$$

$$2NO + 2H_2O\ 2HNO_2 ++ \qquad E^0 = -1$$

$$4NO + H_2O\ 2HNO_2 + NO_2 \qquad E^0 = 0.59$$

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$N_2O + 2H^+ + 2e^- \longrightarrow N_2 + H_2O$ $\quad E^0 = 1.77$

$N_2O + H_2O \longrightarrow 2NO + 2H^+ + 2e^-$ $\quad E^0 = -1.59$

$2N_2O \longrightarrow N_2 + 2NO$ $\quad E^0 = 0.18$

Stability - $\underset{\text{most unstable}}{NO} > N_2O > \underset{\text{least unstable}}{HNO_2}$

In Basic Medium: -

$[NO_2^- + H_2O + e^- \longrightarrow NO + 2OH^-] \times 2$ $\quad E^0 = +0.46$

$NO_2^- + 2OH^- \longrightarrow NO_3^- + H_2O + 2e^-$ $\quad E^0 = -0.94$

$3NO_2^- + H_2O \longrightarrow 2NO + 2OH^- + NO_3^-$ $\quad E^0 = 0.45$

$2NO + H_2O + 2e^- \longrightarrow N_2O + 2OH^-$ $\quad E^0 = 0.76$

$[NO + 2OH^- \longrightarrow NO_2^- + H_2O + e^-] \times 2$ $\quad E^0 = 0.46$

$4NO + 2OH^- \longrightarrow N_2O + 2NO_2^- + H_2O$ $\quad E^0 = 0.30$

$[N_2O + H_2O + 2e^- \longrightarrow N_2 + 2OH^-] \times 4$ $\quad E^0 = 0.94$

$N_2O + 10OH^- \longrightarrow 2NO_3^- + 5H_2O + 2e^-$ $\quad E^0 = 0.10$

$5N_2O + 2OH^- \longrightarrow 4N_2 + 2NO_3^- + H_2O$ $\quad E^0 = 0.84$

$\underset{\text{most stable}}{N_2O} > NO > \underset{\text{least stable}}{NO_2}$

Q.9. Describe the important factors, which influence the magnitude o electrode potential. **(2002**

Ans: Factors Affecting The E^0: -

Several factors affect the value of the standard potential. Th conversion of M to M^+ in aqueous solution may be considered in series o steps.

(i) Sublimation of solid metal

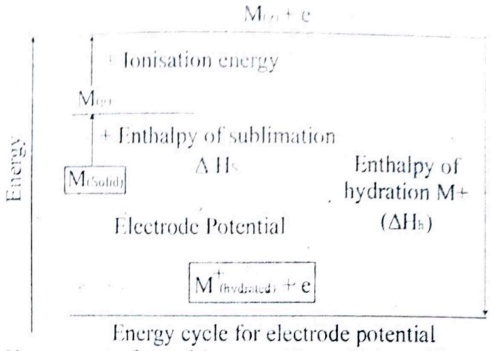
(ii) Ionisation of a gaseous metal atom.

(iii) Hydration of a gaseous ion.

There are best considered in a Born-Haber type of cycle. The enthalp of sublimation and the ionisation energy are positive since energy must b put into the system and the enthalpy of hydration is negative since energy i evolved thus,

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$I \quad \Delta H_s + I + \Delta H_h$



Energy cycle for electrode potential

Hence most of transition metal have high melting point. Hence the halpy of sublimation is high. Similarly they are fairly small atoms and have h ionisation energies. Thus the value for the electrode potential E is low the metal has little tendency to form ions.

oblem: -

idic Medium: -

$SO_4^{2-} \xrightarrow{0.17} \overset{IV}{SO_2} \xrightarrow{0.40} \overset{III}{S_2O_3} \xrightarrow{0.50} \overset{0}{S} \xrightarrow{0.14} \overset{-II}{H_2S}$

$S_4O_6^{2-}$ (0.51, 0.08)

sic Medium: -

$\overset{VI}{SO_4^{2-}} \xrightarrow{-0.98} \overset{IV}{SO_3^{2-}} \xrightarrow{-0.58} \overset{-II}{S_2O_3^{2-}} \xrightarrow{-0.74} \overset{0}{S} \xrightarrow{-0.28} \overset{-II}{S^{2-}}$

-0.59

mment on oxidising and the power and the relative stabilities of the various cies formed by sulphur acidic and basic form the reduction potential gram. Higher E^0 value most oxidizing agent.

Oxidising Power In Acidic Medium: -

$\underset{IV}{SO_2} > \underset{III}{S_2O_3} > \underset{VI}{SO_4^{2-}} > \underset{0}{S} > S_4O_6^{2-}$

sic Medium: -

$\underset{\text{most poor}}{SO_4^{2-}} < S_2O_3^{2-} < SO_3^{2-} \xrightarrow[\text{OXIDISING AGENT}]{} \underset{\text{least poor}}{S}$

0. Write a brief note on Redox indicators. **(2011, 17)**

s. A **redox indicator** (also called an **oxidation-reduction indicator**) is an icator that undergoes a definite color change at a specific electrode ential. The requirement for fast and reversible color change means that the dation-reduction equilibrium for an indicator redox system needs to be

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established very fast. Therefore only a few classes of organic redo
can be used for indicator purposes.
There are two common type of redox indicators:
• metal-organic complexes (Ex. phenanthroline)
• true organic redox systems (Ex. Methylene blue)
Sometimes colored inorganic oxidants or reductants (Ex. Potassium ma
Potassium dichromate) are also *incorrectly* called redox indicators. Th
be classified as **true** redox indicators because of their **irreversibility**. A
redox indicators with true organic redox systems involve a proton as a pa
in their electrochemical reaction. Therefore sometimes redox indicator
divided into two general groups: independent or dependent on pH.

Q.11. Explain the separation of Cu^{2+} and Cd^{2+} on the basis of f formation in qualitative analysis.

Ans. With H_2S, CuS is precipitated as black color. However prec soluble on oxidation.

$$CuS + 4[O] \xrightarrow{HNO_3} CuSO_4$$

With NH_4OH. $CuSO_4$ forms deep blue coloured complex solution.

$$CuSO_4 + 4NH_4OH \longrightarrow \left[Cu(NH_3)_4\right]S_4 + 4H_2O$$

Tetraammine copper (II) sulphate

On adding $K_4Fe(CN)_6$ to copper sulphate, a chocolate brown prec formed.

$$2CuSO_4 + K_4Fe(CN)_6 \longrightarrow Cu_2\left[Fe(CN)_6\right] + 2K_2SO_4$$

Chocolate Brown

Cadmium Cation:
$CdSO_4$ form complex with NH_4OH

$$CdSO_4 + 4NH_4OH \longrightarrow \left[Cd(NH_3)_4\right]SO_4 + 4H_2O$$

Tetrammine Cadmium (II) sulphate (colou

When KCN is added to above complex solution then white precipitate in excess KCN is formed.

$$\left[Cd(NH_3)_4\right]SO_4 + 2KCN + 4H_2O \longrightarrow Cd(CN)_2 + K_2SO_4 + 4N$$

White Precipitate

$$Cd(CN)_2 + 2KCN \longrightarrow K_2\left[Cd(CN)_4\right]$$

Soluable

Q.12. Fe displaces Cu from $CuSO_4$ solution but Ag does not. Expl (2014)

Ans. The higher position of the metal in the electrochemical se tion is

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reactive it is and the more vigorously it reacts with water, oxygen and
A metal in the activity series can displace any metal below it in the series
its compound. Copper Hence Fe displaces Cu from $CuSO_4$ solution
use of Fe is present above to the Cu in electrochemical series. Ag^{2+}
ted below to the Cu in electrochemical series. Hence, Fe displaces Cu
$CuSO_4$ solution but Ag does not.

. Explain the chemical reactions involved in the confirmatory test of (2015, 19)
and Mn^{2+}.

Addition of the ammonia water to precipitate the bismuth hydroxide converts any copper II ion present to the deep blue complex ion, $Cu(NH_3)^{2+}$.

$$Cu^{2+} + 4NH_3 \leftrightarrow Cu(NH_3)_4^{2+} \qquad \left\{\left(Cu(NH_3)_4^{2+}\right) \text{ is deep blue}\right\}$$

The occurrence of the deep blue solution confirms the presence of er II ion.

The test for manganese involves an oxidation reduction reaction e Mn^{2+} reacts with bismuthate ion (BiO_3^-). The bismuthate ion is reduced accompanied by the oxidation of Mn^{2+} to form the purple permanganate MnO^-. This test requires the manganese ion to be in its +2 oxidation ; the +4 oxidation state cannot be oxidized by BiO^{3-}.

. What is the principle of redox titration? How do you determine the (2015)
valent weight of oxidant/raductant.

Redox Titration: -

The potential of a redox electrode depends on the ratio of the activi- of the oxidised and reduced species with which it is in contact. For ex- le, the potential of a paltinum wire in contact with solution of iron (III) and (II) ions has potential given by eq.(i) replicated here:

$$E_{Fe^{3+}/Fe^{2+}} = E^0_{Fe^{3+}/Fe^{2+}} - \frac{RT}{F}\ln\frac{\left[a_{Fe^{2+}}\right]}{\left[a_{Fe^{3+}}\right]} \qquad \text{.....(i)}$$

re $E^0_{Fe^{3+}/Fe^{2+}}$ is known as the formal redox potential of the Fe^{3+}/Fe^{2+} sys-

half cell reaction is

$$Fe^{3+} + e^- \leftrightarrow Fe^{2+} \qquad E^0_{Fe^{3+}/Fe^{2+}} = 0.771V$$

clear from eq.(i) that when the iron(III) and iron(II) ions are present in equal unts, the potential of the electrode will become equal to the formal redox ntial of the system. This is the principle on which redox titrations are ed.

An example is the titration of an iron(II) salt with a cerium (IV) salt. The

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vessel and a platinum electrode is dipped in it. This half-cell is ... salt solution is taken in ... reference electrode like the Saturated Calomel Electrode. The cell is ... sented as

$$\text{S.C.E.} \parallel Fe^{3+}(aq), Fe^{3+}(aq) \mid Pt(s)$$

The emf of the cell is given by the equation

$$E_{cell} = E_{Fe^{3+}, Fe^{2+}} - E_{S.C.E}$$

$$E_{cell} = E_{Fe^{3+}, Fe^{2+}} - \frac{RT}{F} \ln \frac{\left[a_{Fe^{2+}}\right]}{\left[a_{Fe^{3+}}\right]} - E_{S.C.E}$$

Initially there are only iron(II) ions in the solution, making ... of platinum electrode practically zero. As cerium (IV) ions are ... solution, iron(III) ions are formed. The redox couple formed causes ... trode potential to increase gradually. At the end point there is a ... increase in the electrode potential. The end point of titration is de... graphically from the first and second derivative curves. At the po... iron (II) ions present have been oxidised to iron (III) ions. Therefore ... halfway to end point, the iron(II) and iron(III) ions should be prese... amounts. The cell emf corresponding to half the volumen of titrant re... end point, $(E_{cell})_{e.p./2}$, is determined. [here e.p. = end point]

$$(E_{cell})_{e.p./2} = E^0_{Fe^{3+}/Fe^{2+}} - E_{S.C.E.}$$

$$E^0_{Fe^{3+}/Fe^{2+}} = (E_{cell})_{e.p./2} + E_{S.C.E.}$$

A similar technique is employed for determining the formal redox pote... the Ce^{4+}/Ce^{3+} system.

$$Ce^{4+} + e^- \longrightarrow Ce^{3+} \qquad E^0_{ce^{4+}/ce^{3+}} = 1.61V$$

Cerium(IV) ions are taken in the titration vessel and iron(II) ions are add... the burette. The cell can be represented as

$$\text{S.C.E.} \parallel Ce^{4+}(aq), Ce^{3+}(aq) \mid Pt(s)$$

The emf of the cell is given by the equation

$$E_{cell} = E_{Ce^{4+}/Ce^{3+}} - E_{S.C.E.}$$

$$E_{cell} = E^0_{Ce^{4+}/Ce^{3+}} - \frac{RT}{F} \ln \frac{\left[a_{Ce^{3+}}\right]}{\left[a_{Ce^{4+}}\right]} - E_{S.C.E.} \quad \text{.....(i}$$

During the titration, the cell emf drops slowly at first and very sharply ... end point. At end point,

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$$E^0_{Ce^{4+}/Ce^{3+}} = (E_{cell})_{e.p./2} + E_{S.C.E.}$$

In a redox potentiometric titration the formal redox potentials of the two redox system should be very different in order to obtain a sharp change in the emf at the end point.

Equivalent weight of a substance (oxidant or reductant) is equal to molecular weight divided by number of electrons lost or gained by one molecule of the substance in a redox reaction.

$$\text{Eq. wt. of O.A.} = \frac{\text{Molecular weight}}{\text{No. of electrons gained by one molecule}}$$

$$= \frac{\text{Molecular weight}}{\text{Change in O.N. per mole}}$$

$$\text{Eq. wt. of R.A.} = \frac{\text{Molecular weight}}{\text{No. of electrons lost by one molecule}}$$

$$= \frac{\text{Molecular weight}}{\text{Change in O.N. per mole}}$$

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