

where the small energy of the initial thermal neutron has been ignored. (m_N denotes the nuclear mass.) Now

$$m_N(^{235}\text{U}) = m(^{235}\text{U}) - 92m_e$$

ignoring the small electronic binding energies compared to rest mass energies. Similarly for other nuclear masses.

$$Q = [m(^{235}\text{U}) - m(^{94}\text{Zr}) - m(^{140}\text{Ce}) - m_n] c^2$$

Using the given data,

$$Q = 213.3 \text{ MeV}$$

c. $1 \text{ MWd} = 10^6 \text{ Js}^{-1} \times 24 \times 3600 \text{ s} = 8.64 \times 10^{10} \text{ J}$

$$\text{No. of atoms of } ^{235}\text{U} \text{ fissioned} = \frac{8.64 \times 10^{10}}{213.3 \times 1.60 \times 10^{-13}} = 2.53 \times 10^{21}$$

$$\text{Mass of } ^{235}\text{U} \text{ fissioned} = \frac{2.53 \times 10^{21} \times 235}{6.02 \times 10^{23}} = 0.99 \text{ g}$$

$$\text{Mass of } ^{235}\text{U} \text{ in 1 kg uranium removed from the reactor} = 7.2 - 0.99 = 6.2 \text{ g}$$

Abundance of ^{235}U is 0.62 %

8. Radioactive decay

a. $1 \mu\text{Ci} = 3.7 \times 10^4 \text{ disintegrations per second (dps)}$.

$$\text{Initial } \beta \text{-activity} = 3.7 \times 10^6 \text{ dps}$$

$$\left. \frac{-dN_1}{dt} \right|_{t=0} = N_1^0 \lambda_1 = 3.7 \times 10^6 \text{ dps}$$

where N_1^0 is the number of atoms of ^{210}Bi at $t = 0$ and λ_1 is its decay constant.

$$\frac{0.693}{5.01 \times 24 \times 3600} N_1^0 = 3.7 \times 10^6$$

$$N_1^0 = 2.31 \times 10^{12}$$

$$\text{Initial mass of } ^{210}\text{Bi} = 2.31 \times 10^{12} \times \frac{210}{6.02 \times 10^{23}} \text{ g}$$

$$= 8.06 \times 10^{-10} \text{ g}$$

b. Number of atoms of ^{210}Bi at time t is given by

$$N_1 = N_1^0 e^{-\lambda_1 t}$$

The number of atoms of ^{210}Po , N_2 , is given by equation

$$\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2$$

where λ_2 is the decay constant of ^{210}Po .

$$\frac{dN_2}{dt} = \lambda_1 N_1^0 e^{-\lambda_1 t} - \lambda_2 N_2$$

Using the integrating factor $e^{\lambda_2 t}$

$$e^{\lambda_2 t} \frac{dN_2}{dt} + \lambda_2 N_2 e^{\lambda_2 t} = \lambda_1 N_1^0 e^{(\lambda_2 - \lambda_1)t}$$

$$\frac{d}{dt}(N_2 e^{\lambda_2 t}) = \lambda_1 N_1^0 e^{(\lambda_2 - \lambda_1)t}$$

Integrating

$$N_2 e^{\lambda_2 t} = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 e^{(\lambda_2 - \lambda_1)t} + C$$

To calculate C , use the condition that at $t = 0$, $N_2 = 0$

$$C = -\frac{\lambda_1 N_1^0}{\lambda_2 - \lambda_1}$$

This gives

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 (e^{-\lambda_1 t} - e^{-\lambda_2 t})$$

The time $t = T$ when N_2 is maximum is given by the condition

$$\left. \frac{dN_2}{dt} \right|_{t=T} = 0$$

which gives

$$T = \frac{\ln \frac{\lambda_1}{\lambda_2}}{\lambda_1 - \lambda_2} = 24.9 \text{ d}$$

At $t = T$, N_2 can be calculated from above.

$$N_2 = 2.04 \times 10^{12}$$

Mass of ^{210}Po at $t = T$,

$$= 7.11 \times 10^{-10} \text{ g}$$

c. α -disintegration rate of ^{210}Po at $t = T$

$$= 1.18 \times 10^5 \text{ dps}$$

At $t = T$

β - disintegration rate of ^{210}Bi

$$= \alpha\text{-disintegration rate of } ^{210}\text{Po} = 1.18 \times 10^5 \text{ dps}$$

9. Redox reactions

a.

i. Over-all reaction



$$\begin{aligned} \Delta G^\circ &= -nFE^\circ = -2FE^\circ \\ &= -2 \times 96485 \times 0.617 \text{ V} \\ &= -119 \text{ KJ} \end{aligned}$$

ii.
$$E^{\circ} = \frac{0.0592}{n} \log K$$

$$\log K = \frac{(2 \times 0.617)}{0.0592} \cong 20.84$$

$$K = 6.92 \times 10^{20}$$

b. Before the equivalence point, E of the cell is given by following equation

$$\begin{aligned} E_{\text{cell}} &= \text{ox } E_{\text{S.C.E}}^{\circ} + \text{red } E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^{\circ} - \frac{0.0592}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Sn}^{4+}]} \\ &= -0.242 + 0.154 - \frac{0.0592}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Sn}^{4+}]} \end{aligned}$$

i. The addition of 5.00 mL of Fe^{3+} converts 5.00/20.00 of the Sn^{2+} to Sn^{4+} ; thus

$$\frac{[\text{Sn}^{2+}]}{[\text{Sn}^{4+}]} = \frac{15.0/20.0}{5.0/20.0} = 3.00$$

$$E_{\text{cell}} = -0.102 \text{ V.}$$

ii. At the equivalence point, add the two expressions corresponding to $\text{Sn}^{4+}/\text{Sn}^{2+}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$.

$$2 E_{\text{cell}} = 2 \text{ ox } E_{\text{S.C.E}}^{\circ} + 2 \text{ red } E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^{\circ} - 0.0592 \log \frac{[\text{Sn}^{2+}]}{[\text{Sn}^{4+}]}$$

$$1 E_{\text{cell}} = \text{ox } E_{\text{S.C.E}}^{\circ} + \text{red } E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} - 0.0592 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

to get

$$3 E_{\text{cell}} = 3 \text{ ox } E_{\text{S.C.E}}^{\circ} + 2 \text{ red } E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^{\circ} + \text{red } E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} - 0.0592 \log \frac{[\text{Sn}^{2+}][\text{Fe}^{2+}]}{[\text{Sn}^{4+}][\text{Fe}^{3+}]}$$

At the equivalence point, $[\text{Fe}^{3+}] = 2 [\text{Sn}^{2+}]$ and $[\text{Fe}^{2+}] = 2 [\text{Sn}^{4+}]$

Thus,

$$E_{\text{cell}} = E_{\text{S.C.E.}}^{\circ} + \frac{2 E_{\text{red Sn}^{4+}/\text{Sn}^{2+}}^{\circ} + E_{\text{red Fe}^{2+}/\text{Fe}^{3+}}^{\circ}}{3}$$

$$= -0.242 + \frac{(2)(0.154) + 0.771}{3} = +0.118 \text{ V}$$

Beyond the equivalence point, E of the cell is given by following equation

$$E_{\text{cell}} = E_{\text{S.C.E.}}^{\circ} + E_{\text{red Fe}^{3+}/\text{Fe}^{2+}}^{\circ} - 0.0592 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

When 30 mL of Fe^{3+} is added, 10 mL of Fe^{3+} is in excess. i.e.

$$\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = \frac{20.0}{10.0} = 2.00$$

$$E_{\text{cell}} = 0.511 \text{ V}$$

c.

$$\text{i. } \Delta G^{\circ} = -RT \ln K_{\text{sp}}$$

$$= 68.27 \text{ KJ}$$

$$\Delta G^{\circ} = -nFE^{\circ}, \quad n=1$$

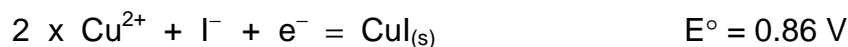
$$E^{\circ} = -0.707 \text{ V}$$



The overall reaction for reduction of Cu^{2+} by I^{-} is



The E° value for the reduction of Cu^{2+} by I^{-} can now be calculated



The over-all reaction is



The positive value of effective E° indicates that the reduction reaction is spontaneous. This has come about since in this reaction, I^{-} is not only a reducing agent, but is also a precipitating agent. Precipitation of Cu^{+} as CuI is the key step of the reaction, as it practically removes the product Cu^{+} from the solution, driving the reaction in the forward direction.

iii. $\Delta G^{\circ} = -nFE^{\circ}$

Here $n = 1$, $E^{\circ} = 0.325 \text{ V}$

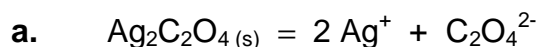
$$\Delta G^{\circ} = -31.3 \text{ kJ}$$

$$\Delta G^{\circ} = -RT \ln K$$

$$\log K = 5.47$$

$$K = 2.9 \times 10^5$$

10. Solubility of sparingly soluble salts



The solubility product K_{sp} is given by

$$K_{sp} = [\text{Ag}^{+}]^2 [\text{C}_2\text{O}_4^{2-}]$$

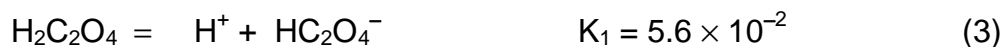
If S is the solubility of $\text{Ag}_2\text{C}_2\text{O}_4$

$$[\text{Ag}^{+}] = 2S \quad (1)$$

The total oxalate concentration, denoted by C_{ox} , is

$$C_{ox} = S = [\text{C}_2\text{O}_4^{2-}] + [\text{HC}_2\text{O}_4^{-}] + [\text{H}_2\text{C}_2\text{O}_4] \quad (2)$$

The dissociation reactions are:



Eqs. (2), (3) and (4) give

$$C_{\text{ox}} = S = [\text{C}_2\text{O}_4^{2-}] + \frac{[\text{C}_2\text{O}_4^{2-}][\text{H}^+]}{K_2} + \frac{[\text{C}_2\text{O}_4^{2-}][\text{H}^+]^2}{K_1K_2}$$

$$\therefore [\text{C}_2\text{O}_4^{2-}] = \alpha C_{\text{ox}} = \alpha S$$

$$\text{where } \alpha = \frac{K_1K_2}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2} \quad (5)$$

At pH = 7, $[\text{H}^+] = 10^{-7}$ and $\alpha \cong 1$

$$K_{\text{sp}} = 4S^3 = 3.5 \times 10^{-11}$$

At pH = 5.0, $[\text{H}^+] = 10^{-5}$

From the values of K_1 , K_2 and $[\text{H}^+]$, we get

$$\alpha = 0.861 \quad (6)$$

$$K_{\text{sp}} = [2S]^2 [\alpha S]$$

$$\therefore S = \left(\frac{K_{\text{sp}}}{4\alpha} \right)^{\frac{1}{3}} = 2.17 \times 10^{-4}$$

b. $[\text{NH}_3] = 0.002$

At pH = 10.8, $[\text{H}^+] = 1.585 \times 10^{-11}$

Eq. (5) implies

$$\alpha = 1$$

$$\text{i.e. } C_{\text{ox}} = S = [\text{C}_2\text{O}_4^{2-}] \quad (7)$$

The total silver ion in the solution is given by

$$C_{\text{Ag}} = 2S = [\text{Ag}^+] + [\text{AgNH}_3^+] + [\text{Ag}(\text{NH}_3)_2^+] \quad (8)$$

The complex formation reactions are



From eqs. (8), (9) and (10)

$$C_{\text{Ag}} = 2S = [\text{Ag}^+]\{1 + K_3[\text{NH}_3] + K_3K_4[\text{NH}_3]^2\}$$

$$\therefore [\text{Ag}^+] = \beta \times C_{\text{Ag}} = \beta \times 2S$$

$$\text{where } \beta = \frac{1}{1 + K_3[\text{NH}_3] + K_3K_4[\text{NH}_3]^2}$$

Using the values of K_3 , K_4 and $[\text{NH}_3]$,

$$\beta = 2.31 \times 10^{-4}$$

$$\begin{aligned} K_{\text{sp}} &= [\text{Ag}^+]^2 [\text{C}_2\text{O}_4^{2-}] \\ &= [\beta \times 2S]^2 [S] \end{aligned}$$

$$\therefore S = \left(\frac{K_{\text{sp}}}{4\beta^2}\right)^{\frac{1}{3}}$$

$$= 5.47 \times 10^{-2}$$

11. Spectrophotometry

- a. Denote the molar absorptivity of MnO_4^- at 440 nm and 545 nm by ϵ_1 and ϵ_2 and that of Cr_2O_7^- by ϵ_3 and ϵ_4 :

$$\epsilon_1 = 95 \text{ Lmol}^{-1}\text{cm}^{-1}, \quad \epsilon_2 = 2350 \text{ Lmol}^{-1}\text{cm}^{-1}$$

$$\epsilon_3 = 370 \text{ Lmol}^{-1}\text{cm}^{-1}, \quad \epsilon_4 = 11 \text{ Lmol}^{-1}\text{cm}^{-1}$$

The absorbance A is related to % transmittance T by

$$A = 2 - \log T$$

From the values given for the sample solution

$$A_{440} = 2 - \log 35.5 = 0.45$$

$$A_{545} = 2 - \log 16.6 = 0.78$$

Now if one denotes the molar concentrations of MnO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ in the steel sample solution by C_1 and C_2 respectively, we have

$$A_{440} = \epsilon_1 \times C_1 \times 1 + \epsilon_3 \times C_2 \times 1$$

$$A_{545} = \epsilon_2 \times C_1 \times 1 + \epsilon_4 \times C_2 \times 1$$

Using the given data, we get

$$C_1 = 0.0003266 \text{ M}$$

$$C_2 = 0.001132 \text{ M}$$

Amount of Mn in 100 mL solution

$$= 0.0003266 \text{ mol L}^{-1} \times 54.94 \text{ g mol}^{-1} \times 0.1 \text{ L}$$

$$= 0.001794 \text{ g}$$

$$\% \text{ Mn in steel sample} = \frac{0.001794 \times 100}{1.374} = 0.13\%$$

Amount of Cr present in 100 mL solution

$$= 0.001132 \text{ mol L}^{-1} \times 2 \times 52.00 \text{ g mol}^{-1} \times 0.1 \text{ L}$$

$$= 0.0118 \text{ g}$$

$$\% \text{ Cr in steel sample} = \frac{0.0118 \times 100}{1.374} = 0.86\%$$

- b.** In solution 1, since all the ligand is consumed in the formation of the complex,

$$[\text{CoL}_3^{2+}] = \frac{2 \times 10^{-5}}{3} = 0.667 \times 10^{-5}$$

Absorptivity of the complex CoL_3^{2+} is

$$\epsilon = \frac{0.203}{0.667 \times 10^{-5} \text{ mol L}^{-1} \times 1.0 \text{ cm}} = 3.045 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$$

If the concentration of the complex CoL_3^{2+} in solution 2 is C,

$$C = \frac{0.68}{3.045 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1} \times 1.0 \text{ cm}}$$

$$= 2.233 \times 10^{-5} \text{ M}$$

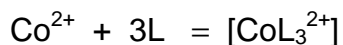
$$[\text{Co}^{2+}] = [\text{Co}^{2+}]_{\text{total}} - [\text{CoL}_3^{2+}]$$

$$= 3 \times 10^{-5} - 2.233 \times 10^{-5} = 0.767 \times 10^{-5}$$

$$\text{Similarly, } [\text{L}] = [\text{L}]_{\text{total}} - 3[\text{CoL}_3^{2+}]$$

$$= 7 \times 10^{-5} - 3 \times 2.233 \times 10^{-5} = 0.300 \times 10^{-5}$$

The complex formation reaction is

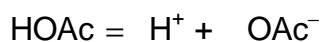
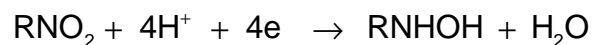


The stability constant K is given by

$$K = \frac{[\text{CoL}_3^{2+}]}{[\text{Co}^{2+}][\text{L}]^3}$$

$$= 1.08 \times 10^{17}$$

12. Reactions in buffer medium



$$K_a = \frac{[\text{H}^+][\text{OAc}^-]}{[\text{HOAc}]}$$

i.e

$$\text{p}K_a = \text{pH} + \log \frac{[\text{HOAc}]}{[\text{OAc}^-]}$$

$$4.76 = 5.0 + \log \frac{[\text{HOAc}]}{[\text{OAc}^-]}$$

$$\frac{[\text{HOAc}]}{[\text{OAc}^-]} = 0.5715$$

$$[\text{HOAc}] + [\text{OAc}^-] = 0.500$$

$$[\text{OAc}^-] = 0.3182$$

$$[\text{HOAc}] = 0.5 - 0.3182 = 0.1818$$

mmoles of acetate (OAc^-) present initially in 300 mL

$$= 0.3182 \times 300 = 95.45$$

mmoles of acetic acid (HOAc) present initially in 300 mL

$$= 0.1818 \times 300 = 54.55$$

mmoles of RNO_2 reduced

$$= 300 \times 0.0100 = 3$$

From the stoichiometry of the equation, 3 mmoles of RNO_2 will consume 12 moles of H^+ for reduction. The H^+ is obtained from dissociation of HOAc .

On complete electrolytic reduction of RNO_2 ,

$$\text{mmoles of HOAc} = 54.55 - 12.00 = 42.55$$

$$\text{mmoles of OAc}^- = 95.45 + 12.00 = 107.45$$

$$4.76 = \text{pH} + \log \frac{42.55}{107.45}$$

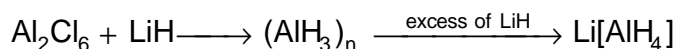
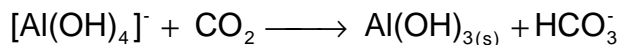
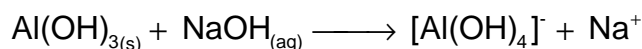
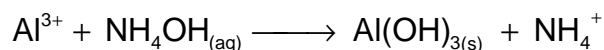
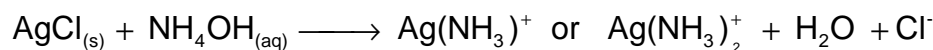
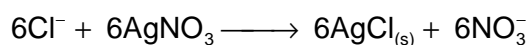
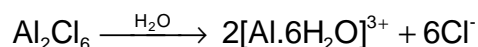
$$\text{pH} = 5.16$$

13. Identification of an inorganic compound

- a. The white gelatinous precipitate in group (III) obtained by qualitative analysis of solution **B** indicates the presence of Al^{3+} ions. The white precipitate with AgNO_3 indicates the presence of Cl^- ions.

From the above data the compound **A** must be a dimer of aluminium chloride Al_2Cl_6 .

- b. The reactions are as follows



14. Ionic and metallic structures

- a.
- i. The lattice of NaCl consist of interpenetrating *fcc* lattices of Na^+ and Cl^-
 - ii. The co-ordination number of sodium is six since, it is surrounded by six nearest chloride ions.
 - iii. For NaCl, the number of Na^+ ions is: twelve at the edge centres shared equally by four unit cells thereby effectively contributing $12 \times 1/4 =$

3Na^+ ions per unit cell and one at body center. Thus, a total of $3 + 1 = 4$ Na^+ ions per unit cell.

Number of Cl^- ions is: six at the center of the faces shared equally by two unit cells, thereby effectively contributing $6 \times 1/2 = 3$ Cl^- ions per unit cell and eight at the corners of the unit cell shared equally by eight unit cells thereby effectively contributing $8 \times 1/8 = 1$ Cl^- ion per unit cell. Thus, a total of $3 + 1 = 4$ Cl^- ions per unit cell.

Hence, the number of formula units of NaCl per unit cell = $4\text{Na}^+ + 4\text{Cl}^-$
= 4NaCl

- iv. The face diagonal of the cube is equal to $\sqrt{2}$ times 'a' the lattice constant for NaCl . The anions/anions touch each other along the face diagonal. The anion/cations touch each other along the cell edge.

$$\text{Thus, } a = 2 (r_{\text{Na}^+} + r_{\text{Cl}^-}) \quad \dots\dots\dots(1)$$

$$\text{Face diagonal } \sqrt{2} a = 4 r_{\text{Cl}^-} \quad \dots\dots\dots(2)$$

Substituting for 'a' from (1) into (2) we get :

$$\sqrt{2} \times 2 (r_{\text{Na}^+} + r_{\text{Cl}^-}) = 4 r_{\text{Cl}^-} \text{ from which,}$$

the limiting radius ratio $r_{\text{Na}^+} / r_{\text{Cl}^-} = \underline{0.414}$

- v. The chloride ion array is expanded to make the octahedral holes large enough to accommodate the sodium ions since, the $r_{\text{Na}^+} / r_{\text{Cl}^-}$ ratio of 0.564 is larger than the ideal limiting value of 0.414 for octahedral six coordination number.
- vi. As the cation radius is progressively increased, the anions will no longer touch each other and the structure becomes progressively less stable. There is insufficient room for more anions till the cation / anion radius ratio equals 0.732 when, eight anions can just be grouped around the cation resulting in a cubic eight coordination number as in CsCl .

- vii. Generally, the *fcc* structure with a six coordination number is stable in the cation/anion radius ratio range 0.414 to 0.732. That is, if $0.414 < r^+/r^- < 0.732$ then, the resulting ionic structure will generally be NaCl type *fcc*.

b.

- i. Bragg's law states $\lambda = 2d_{hkl} \sin(\theta)$

$$154 \text{ pm} = 2 \times d_{200} \sin(15.8^\circ)$$

$$d_{200} = \frac{154 \text{ pm}}{2 \times \sin(15.8^\circ)} = \frac{154 \text{ pm}}{2 \times 0.272} = 283 \text{ pm}$$

Thus, the separation between the (200) planes of NaCl is 283 pm.

- ii. Length of the unit cell edge, $a = d_{100} = 2 \times d_{200}$

$$a = 2 \times 283 \text{ pm} = \underline{566 \text{ pm}}$$

- iii. Since it is an *fcc* lattice,

$$\text{cell edge, } a = 2(r_{\text{Na}^+} + r_{\text{Cl}^-})$$

$$\text{radius of sodium ion } r_{\text{Na}^+} = \frac{a - 2 r_{\text{Cl}^-}}{2} = \frac{566 - 362}{2} = \underline{102 \text{ pm}}$$

c.

- i. The difference in an *hcp* and a *ccp* arrangement is as follows:

The two 'A' layers in a *hcp* arrangement are oriented in the same direction making the packing of successive layers ABAB.. and the pattern repeats after the second layer whereas, they are oriented in the opposite direction in a *ccp* arrangement resulting in a ABCABC... packing pattern which repeats after the third layer.

The unit cell in a *ccp* arrangement is based on a cubic lattice whereas in a *hcp* arrangement it is based on a hexagonal lattice.

- ii. Packing fraction = $\frac{\text{Volume occupied by 4 atoms}}{\text{Volume of unit cell}}$

Let 'a' be the length of the unit cell edge

Since it is an *fcc* lattice, face diagonal = $\sqrt{2}a = 4r$ (1)

Volume of the unit cell = a^3

$$\text{Packing fraction} = \frac{4 \times 4 \pi r^3}{3 \times a^3} \dots\dots\dots(2)$$

Substituting for 'a' from (1) into (2), we get

$$\text{Packing fraction} = \frac{4 \times 4 \times 22 \times (\sqrt{2})^3 \times r^3}{3 \times 7 \times (4r)^3} = 0.74$$

Thus, packing fraction in a *ccp* arrangement = 0.74

- iii. The coordination number(12) and the packing fraction (0.74) remain the same in a *hcp* as in a *ccp* arrangement.

d.

- i. For an *fcc*, face diagonal = $\sqrt{2}a = 4r_{\text{Ni}}$

where a = lattice constant

r_{Ni} = radius of the nickel atom

$$r_{\text{Ni}} = \frac{\sqrt{2} \times a}{4} = \frac{\sqrt{2} \times 352.4 \text{ pm}}{4} = \underline{124.6 \text{ pm}}$$

- ii. Volume of unit cell = $a^3 = (3.524 \text{ \AA})^3 = 43.76 \text{ \AA}^3$

- iii. Density of Nickel, $\rho_{\text{Ni}} = \frac{Z \times M / N}{V}$

No. of Ni atoms, $Z = 4$ for an *fcc* lattice

Avogadro constant

$$N = \frac{Z \times M}{\rho_{\text{Ni}} V} = \frac{4 \times 58.69 \text{ g mol}^{-1}}{8.902 \text{ g cm}^{-3} \times 43.76 \times 10^{-24} \text{ cm}^3}$$

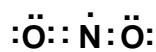
$$N = \underline{6.02 \times 10^{23} \text{ mol}^{-1}}$$

15. Compounds of nitrogen

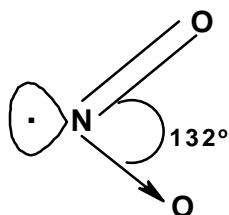
a.

- i. NO_2 : No. of electrons in the valence shell around nitrogen
 $= 5 + 0 + 2 = 7$

The Lewis structure for NO_2 is as shown below.

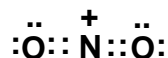


According to VSEPR, the molecule ideally should have linear geometry. However, this molecule has one single unpaired electron present on nitrogen. Due to the repulsion between the unpaired electron and the other two bonded pairs of electrons, the observed bond angle is less than 180° (132°). Thus, the shape of the molecule is angular as shown below.

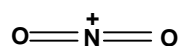


- ii. NO_2^+ : No. of electrons in the valence shell around nitrogen
 $= (5 + 2 + 2 - 1) = 8$

The Lewis structure is as shown below



Thus, there are no non-bonded electrons present on nitrogen. The two σ - bonds will prefer to stay at 180° to minimize repulsion between bonded electron pairs giving a linear geometry (180°). The π -bonds do not influence the shape.



NO_2^- : No. of electron in the valence shell around nitrogen
 $= 5 + 2 + 1 = 8$

The Lewis structure is as shown below

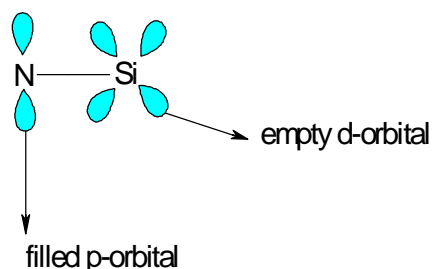


In case of NO_2^- , there is a lone pair of electrons present on nitrogen. Due to strong repulsion between the lone pair of electrons and the bonded pairs of electrons the angle between the two bond pairs shrinks from the ideal 120° to 115° .

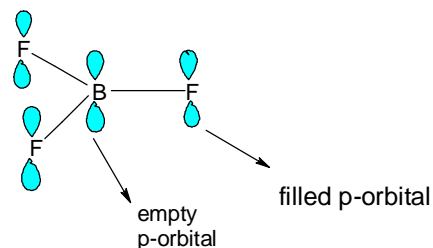
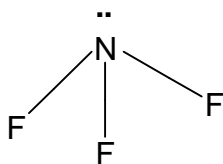
- b. In case of trimethylamine, the shape of the molecule is pyramidal with a lone pair present on nitrogen. Due to the lone pair Me-N-Me angle is reduced from $109^\circ 4'$ to 108° .



However, in case of trisilylamine, d orbital of silicon and p orbital of nitrogen overlaps giving double bond character to the N-Si bond. Thus, delocalisation of the lone electron pair of nitrogen takes place and the resultant molecule is planar with 120° bond angle.



- c. Both N and B are trivalent. However, NF_3 is pyramidal in shape. In case of BF_3 , the B-F bond gets double bond character due to the overlapping of p orbitals present on boron and fluorine. The observed bond energy is, therefore, much greater in BF_3



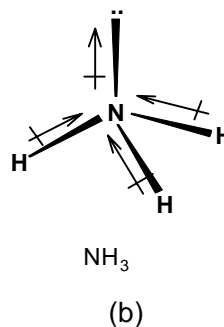
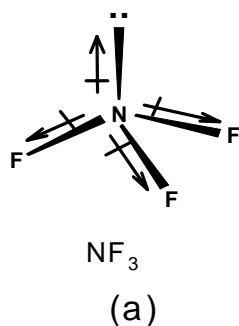
d.

- i. The difference in boiling points of NF_3 and NH_3 is due to hydrogen bonding which is present in ammonia.

High electronegativity of fluorine decreases the basicity of nitrogen in NF_3 . Thus, NF_3 does not act as a Lewis base.

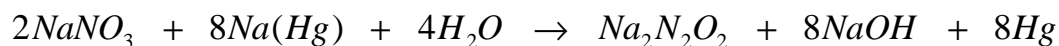
- ii. In NF_3 , the unshared pair of electrons contributes to a dipole moment in the direction opposite to that of the net dipole moment of the

N-F bonds. See figure (a).



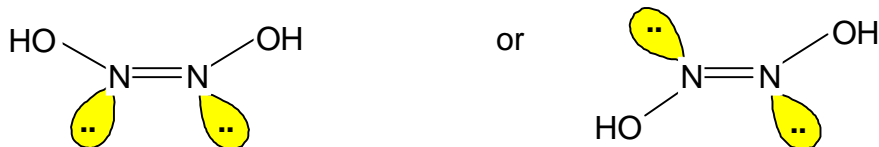
In NH_3 , the net dipole moment of the N-H bonds and the dipole moment due to the unshared pair of electrons are in the same direction. See figure (b).

e.

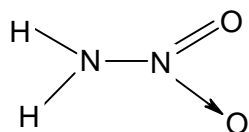


$\text{Na}_2\text{N}_2\text{O}_2$ is the salt of $\text{H}_2\text{N}_2\text{O}_2$ (Hyponitrous acid).

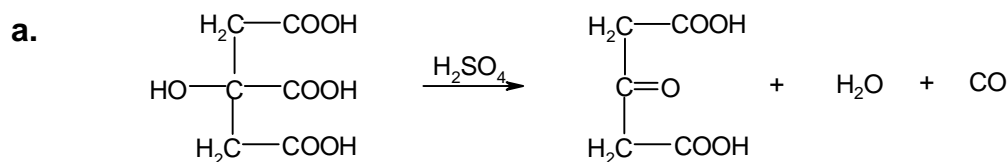
Structure :



Isomer is: $\text{H}_2\text{N}-\text{NO}_2$ (Nitramide)



16. Structure elucidation with stereochemistry



3-oxo-1,3-pentanedioic acid

α - Hydroxy carboxylic acids undergo similar reaction.

- b. Molecular weight of **A** = 236
 20 mL 0.05 M KOH \equiv 118 mg **A**
 1000 mL 1 M KOH \equiv 118 g **A**

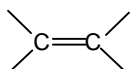
\therefore The acid is dibasic

Molecular weight of **A** = 236

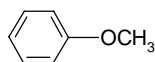
80 mg Br₂ \equiv 118 mg **A**

160 gm Br₂ \equiv 236 g **A**

A contains one double bond



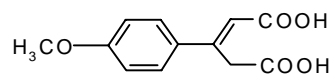
It has anisole ring in the molecule



It is formed from HOOC-CH₂-CO-CH₂-COOH

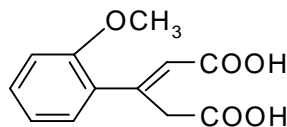
It has molecular formula **C₁₂H₁₂O₅**

Due to steric hindrance the attachment of the aliphatic portion on the anisole ring will be para with respect to -OCH₃. Hence the structure will be

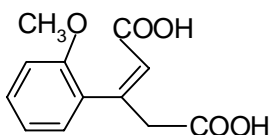


As **A** forms anhydride the two COOH groups should be on the same side of the double bond.

- c. Isomers of **A**



(E) 3-(2-methoxyphenyl)-2-pentenedioic acid



(Z) 3-(2-methoxyphenyl)-2-pentenedioic acid