Qs An element exist in the form of two isotope Y^{40} and Y^{42} then Calculate the %age occerance in nature If the avg. atomic wt. of element Y is 41.3,

$^{40}Y = x\%$

$^{42}Y = 100 - x\%$

$$\text{avg. at. wt} = \frac{40x + 42(100-x)}{100}$$

~~$= 40x + 42(100-x)$~~

$x = 35\%$

$^{42}Y = 100 - 35$

$= 65\%$

Application :—

\# Relation b/w no. of deflected particles (μ) & deflection angle(θ).

$$\boxed{\mu \propto \frac{1}{\sin\left(\frac{\theta}{2}\right)^4}}$$

Ques. Calculate the radius of nucleus of atom that have 64 nuclean in it.

$R_N = R_0 \cdot (A)^{1/3}$

$= 1.33 \times 10^{-13} (64)^{1/3}$

$= 1.33 \times 10^{-13} \times 4$

$= 5.32 \times 10^{-13}$ cm

Qs If 120 α-particles deflected at an angle of 60° then find out the no. of deflected particles at 90°.

$$\mu \propto \frac{1}{\left(\sin\left(\frac{90}{2}\right)\right)^4}$$

~~$\mu \propto \frac{1}{(\sin 45)^4}$~~

~~$\mu \propto \frac{1}{(1/\sqrt{2})^4}$~~

$$\frac{\mu_1}{\mu_2} = \frac{\sin\left(\frac{\theta_2}{2}\right)^4}{\sin\left(\frac{\theta_1}{2}\right)^4}$$

$$= \frac{\sin\left(\frac{90}{2}\right)^4}{\sin\left(\frac{60}{2}\right)^4} = \frac{(\sin 45)^4}{(\sin 30)^4} = \frac{(1/\sqrt{2})^4}{\left(\frac{1}{2}\right)^4}$$

$$\frac{120}{\mu_2} = \frac{1/4}{1/16}$$

~~$\mu_2 = \frac{120}{4}$~~

~~$\mu_2 = 30$ pati.~~

$\mu_2 = \frac{120}{4} = 30$ particles.

ⓐ Amplitude (a) :—

As we know,

$V \propto \frac{1}{\lambda}$

$\boxed{V \propto \frac{c}{\lambda}}$ —— (i)

$\boxed{\bar{\nu} = \frac{1}{\lambda}}$ —— (ii)

$\boxed{V = c\bar{\nu}}$ —— (iii)

Ques Calculate the frequency and wavelength of a radiation where wave no. is 400cm^{-1}

$\bar{\nu} = 400 cm^{-1}$

$\lambda = \frac{1}{\bar{\nu}} = \frac{1}{400}$

$= \lambda = 2.5 \times 10^{-3} cm$

$= 2.5 \times 10^{-5} m$

$= 25000 \times 10^{-9} m$

$= 25000 nm$

$= 2.5 \times 10^{4} nm$

$\nu = c\bar{\nu}$

$= 3 \times 10^{10} \times 400$

$= 1.2 \times 10^{13} s^{-1}$

Ques Calculate the frequency and wave no. of a yellow radiation having a wavelength of 5800A°

$\bar{\nu} = \frac{1}{\lambda}$

$= \frac{1}{5800A^\circ} = \frac{1}{5800 \times 10^{8}} = \frac{10^{8}}{5800}$

$= 17241.37 cm^{-1}$

$= 1.7 \times 10^{4} cm^{-1}$

$\nu = c\bar{\nu}$

$= 3 \times 10^{10} \times 1.7 \times 10^{4}$

$= 5.1 \times 10^{14} s^{-1}$

Unit of energy:

$1 Cal = 4.2 J$

$1 J = 10^7 erg$

$1 eV = 1.6 \times 10^{-19} J$

$E = nh\nu$

Ques. Calculate the frequency of and energy of a poton of a radiation having a wavelength of 4000 A°. (energy J)

$\nu = \frac{c}{\lambda}$

$= \frac{3 \times 10^8}{4 \times 10^{-7}}$

$= 0.75 \times 10^{15}$

$= 7.5 \times 10^{14} s^{-1}$

$E = h\nu$

$= 6.6 \times 10^{-34} \times 7.5 \times 10^{14}$

~~$= 4.95 \times 10^{-19} s^{-1}$~~

$= 49.5 \times 10^{-19}$

$= 4.95 \times 10^{-19} J.$

Ques The wavelength of poton having energy E is 6000 A° then find out the wavelength of poton having energy 3E

$\frac{E_1}{E_2} = \frac{\lambda_2}{\lambda_1}$

$\frac{E}{3E} = \frac{\lambda_2}{6000}$

$\boxed{\lambda_2 = 2000 A°}$

Q. 3×10^8 photon of a certain light radiation ~~having~~ have of a energy of 1.5 J then calculate the wavelength of photon of ~~[illegible]~~ radiation.

$$E = \frac{nhc}{\lambda}$$

$$\lambda = \frac{nhc}{E}$$

$$= \frac{(3\times10^{8})(6.6\times10^{-34})(3\times10^{8})}{1.5}$$

$$= 3.9\times10^{-17}\,m$$

Ques A bulb emits of light of wavelength of 4500 A° If the bulb is rated at 150watt and only 8% of their energy is emitted as light then find out the no. of photon emitted by the bulb per second.

↳

$$P = \frac{E}{T} \qquad 150\,watt \longrightarrow 150\,J\,s^{-1}$$

$$E = 15\cancel{0}\times\frac{8}{10\cancel{0}} = 12\,J$$

$$E = \frac{nhc}{\lambda}$$

$$n = \frac{E\lambda}{hc} = \frac{12\times4500\times10^{-10}}{6.63\times10^{-34}\times3\times10^{8}}$$

$$= 2.7\times10^{19}\ photons$$

Ques The value of planck constant is $6.63\times10^{-34}\,J\,s^{-1}$ the value of speed of light is $3\times10^{17}\,nm\,s^{-1}$ which value is closest to the wavelength in nm for a quantum of light having a frequency of $6\times10^{15}\,s^{-1}$.

(I) 75 [✓ (III) 50]

(II) 10 (IV) 25

↳ $\lambda = \frac{c}{\nu}$

$= \frac{3\times10^{17}\ nm\ s^{-1}}{6\times10^{15}}$

$\boxed{= 50 nm}$

Bohr's Atomic model :—

Note :- In each transition only a single photon is absorbed or emitted.

$1 \xrightarrow{①} 4$

$1 \xrightarrow{①} 2 \xrightarrow{①} 3 \xrightarrow{①} 4$

Application :—

① Radius of n^{th} orbit (r_n) :—

$$\boxed{r_n = 0.529 \frac{n^2}{Z} Å}$$

n = orbit no

Z = Atomic no.

$\left(r_n \propto \frac{n^2}{Z}\right)$ n↑ ⇒ r_n ↕
Z ↑ ⇒ r_n ↕

$$\boxed{\frac{r_{n_1}}{r_{n_2}} = \frac{n_1^2}{n_2^2} \times \frac{Z_2}{Z_1}}$$

② Velocity of e^- in n^{th} orbit (v_n) :—

$$\boxed{\begin{array}{l} v_n = 2.18\times10^{6}\ m s^{-1} \\ v_n = 2.18\times10^{8}\ cm s^{-1} \end{array}}$$

$\left(v_n \propto \frac{Z}{n}\right)$ $Z \uparrow \Rightarrow v_n \uparrow$

$n \uparrow \Rightarrow v_n \downarrow$

$$\boxed{\frac{(v_n)_1}{(v_n)_2} = \frac{Z_1}{Z_2} \times \frac{n_2}{n_1}}$$

③ Time Period of revolution (T_n) :—

Time taken by an e^- for one complete revolution in nth orbit. $\Longrightarrow$ $\boxed{T_n = \frac{2\pi r_n}{v_n}}$

④ Frequency of revolution (ν_n) :—

No. of revolution taken by an e^- in one second in nth orbit. $\boxed{\nu_n \Longrightarrow \frac{v_n}{2\pi r_n}}$

⑤ Total energy of an e^- in nth orbit (E_n)

$\boxed{T.E. = K.E. + P.E.}$ $\boxed{T.E. = -K.E. = \frac{P.E.}{2}}$

$$\boxed{E_n = -13.6 \frac{Z^2}{n^2} \text{ eV/atom}}$$

$$E_n = -2.18 \times 10^{-18} \frac{Z^2}{n^2} \text{ J/atom}$$

$$E_n = -1312 \frac{Z^2}{n^2} \text{ KJ mol}^{-1} = -313.6 \frac{Z^2}{n^2} \text{ Kcal mol}^{-1}$$

$$E_n \propto -\frac{Z^2}{n^2}$$

$$Z\uparrow \Rightarrow E_n\downarrow$$

$$n\uparrow \Rightarrow E_n\uparrow$$

$$\boxed{\frac{(E_n)_1}{(E_n)_2} = \frac{Z_1^2}{n_1^2} \times \frac{n_2^2}{Z_2^2}}$$

Ques. Calculate the energy of e^- 1st, 2nd, 3rd 4th orbit and also at ∞ for H-atom.

I. $E_n = -13.6\,\frac{Z^2}{n^2}$

$= -13.6\,\frac{(1)^2}{(1)^2} = -13.6$ eV

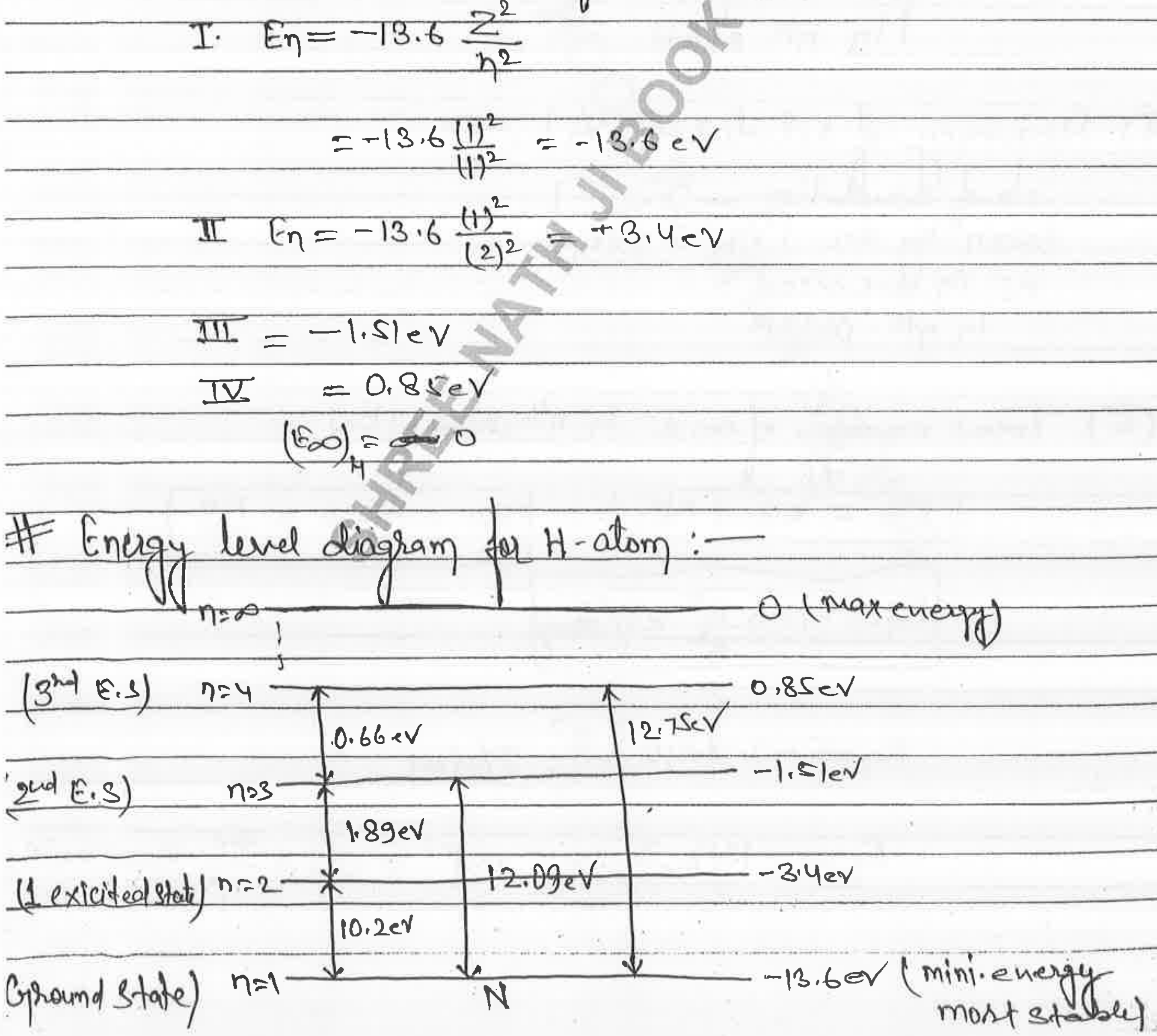
II $E_n = -13.6\,\frac{(1)^2}{(2)^2} = +3.4$ eV

III $= -1.51$ eV

IV $= 0.85$ eV

$(E_\infty)_H = \cancel{\infty}\ 0$

Energy level diagram for H-atom :—



n^{th} energy level = $(n-1)$ excited state.

(1) Ionisation energy (I.E.) :—

$$I.E. = E_\infty - E_1$$

$$\boxed{I.E = -E_1}$$

Ex- for H-atom

$$I.E. = -E_1 = -(-13.6) = 13.6\,eV$$

(2) Seperation energy (S.E.) :—

$$S.E. = E_\infty - E_n$$

$$\boxed{S.E. = -E_n} \quad n = 1, 2, 3 \ldots$$

Eg :- for H-atom

$$1^{st}\ S.E. = E_\infty - E_2 = -(-3.4) = 3.4\,eV$$

$$2^{nd}\ S.E. = E_\infty - E_3 = -(-1.51) = 1.51\,eV$$

(3) Excitation energy (E.E.) :—

$$\boxed{E.E. = E_n - E_1} \quad n = 1, 2, 3 \ldots$$

Eg :- for H-atom

$$1^{st}\ E.E. = E_2 - E_1 = (3.4) - (-13.6)$$
$$= 10.2\,eV$$

$$2^{nd}\ E.E. = E_3 - E_1 = (-1.51) - (-13.6)$$
$$= 12.09\,eV$$

Note :—

Ionisation, Seperation and Excitation are always positive.

Total energy of an e^- in a atom is Negative and its max. value is considered to be zero at infinity.

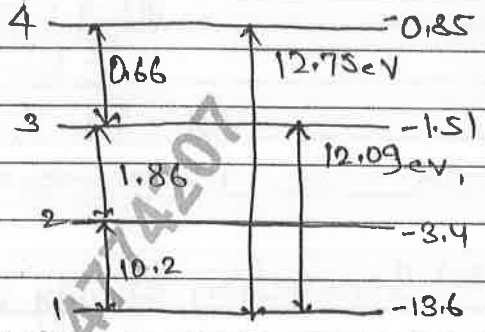
⇒ For any atom (Single e^- species)

$(T.E.)_1 < (T.E)_2 < (T.E)_3$

$(K.E)_1 > (K.E)_2 > (K.E)_3$

$(E_2 - E_1) > (E_3 - E_2) > (E_4 - E_3)$

$(P.E)_1 < (P.E)_2 < (P.E)_3$



★ $\boxed{E_n = \frac{E_1}{n^2}}$ ⇒ for same atom

$$\boxed{\underset{(\text{any atom})}{E_n} = \underset{(\text{H-atom})}{E_n} \times Z^2}$$

$$\boxed{\underset{(\text{any atom})}{\Delta E} = \underset{(\text{H-atom})}{\Delta E} \times Z^2}$$

Ques Calculate the radius ratio of second exitation state of H-atom to the first exitation state of Li^{+2}.

Soln:-

$$\frac{r_{n_1}}{r_{n_2}} = \frac{n_1^2}{Z_1} \times \frac{Z_2}{n_2^2}$$

$$\frac{(r_3)_H}{(r_2)_{Li^{+2}}} = \frac{3^2}{1} \times \frac{3}{2^2}$$

$$= \frac{9}{1} \times \frac{3}{4}$$

$$= \frac{27}{4}$$

Date ______ Page ______

Ques The radius ratio of 2 Bhor orbits of H-atom is found to 4:1 then the ~~ob~~ orbits will be.

(i) K & L
(ii) N & L
(iii) L & K
(iv) Both (ii) & (iii)

$$\frac{(r_n)_1}{(r_n)_2} = \frac{n_1^2}{\cancel{Z_1}} \times \frac{\cancel{Z_2}}{n_2^2} = \frac{4}{1}$$

$$\frac{n_1}{n_2} = \frac{2}{1}$$

	K	L	M	N
$n=$	1	2	3	4

Ques Calculate the ratio of the time period of e in second orbit of H-atom to the first orbit of He⁺-atom.

Sol:-

$$T_n = \frac{2\pi r_n}{v_n}$$

$$T_n \propto \frac{r_n}{v_n} \propto \frac{n^2/Z}{Z/n} \propto \frac{n^3}{Z^2}$$

$$\frac{(T_n)_1}{(T_n)_2} = \frac{n_1^3}{(Z_1)^2} \times \frac{Z_2^2}{n_2^3}$$

$$= \frac{2^3}{1^2} \times \frac{2^2}{1^3} \Rightarrow \frac{32}{1}$$

Ques. Calculate the energy of e present in 3nd exitation state of Li^{+2}.

Sol:-

$$\underset{\text{any atom}}{E_n} = \underset{\text{H-atom}}{-0.85} \times Z^2$$

$$= -0.85 \times 3^2$$

$$= -7.65\,eV$$

Ques. Calculate the 2nd exitation energy of an e present in ~~He~~ He^+

~~$E_n = -1.51 \times (Z)^2$~~
~~[illegible]~~

$$\Delta E = \underset{\text{(H-atom)}}{\Delta E} \times Z^2$$

$$= (E_3 - E_1)_H \times (Z)^2$$

$$= 12.09 \times 4$$

$$= 48.36\,eV$$

Ques If the Ionisation potential of a atom is 16V then find out its first exitation potential.

$$I.E. = -E_1 = 16V$$

$$E_1 = -16V$$

$$E_n = \frac{E_1}{n^2}$$

$$= \frac{-16}{2^2} = -4V$$

$$1^{st}\ E.E. = E_2 - E_1$$

$$= (-4) - (-16)$$

$$= \underline{12V}$$

Ques Calculate the ratio of the difference in energy in b/w the 3rd and 2nd orbit of He^+ to the 2nd and 1st orbit of Li^{+2}.

Soln:-

$$\frac{(E_3 - E_2)_{He^+}}{(E_2 - E_1)_{Li^{+2}}} = \frac{-13.6\frac{(z)^2}{3^2} + 13.6\frac{(z)^2}{(2)^2}}{-13.6\frac{(3)^2}{(2)^2} + 13.6\frac{(3)^2}{(1)^2}}$$

$$= \frac{-\frac{4}{9} + 1}{-\frac{9}{4} + 9} \Rightarrow \frac{5/9}{27/4} \Rightarrow \underline{\frac{20}{243}}$$

Ques. The 2nd existation energy of one e in a atom is 1209 eV then find out the atomic no. of the atom.

Soln:-

$$\Delta E = \Delta E_{(H atom)} \times Z^2$$

$$(E_3 - E_1)_Z = (E_3 - E_1)_H \times Z^2$$

$$1209 = 1209 \times Z^2$$

$$Z = 10$$

Ques In which of the following transition a photon of mini. frequency is absorbed.

(i) $n=1$ to $n=2$

(ii) $n=1$ to $n=3$

(iii) $n=4$ to $n=3$

(iv) $n=3$ to $n=2$

absorbed ⇒ Low to high

emit ⇒ High to low

$E \propto \nu \propto \frac{1}{\lambda}$

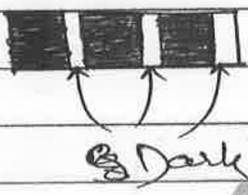
min. ν ⇒ min. E

Ques The total energy of an e^- in a orbit of H-atom is found to be -1.51eV then find out the K.E, P.E, the velocity of an e^- in that orbit.

Ques Calculate the angular momentum of an e^- and also the radius, circumference and diameter of the 3rd orbit of Li^{+2}

Spectrum :—

- → EMISSION
  - → Continous
  - → Discontinous → Line
    - → Band
- → ABSORPTION
  - → Discontinous
  - → Line
  - → Band



EMISSION Spectrum :—

- When a radiation from a light emitting source like sun, bulb a gas in discharge tube etc. is passed through a prism and mode to fall on photographic plate then the impression obtained is known as emission Spectrum.
- In a emission line sprectrum bright line are obtion in a dark ~~line~~ sprectrum.

ABSORPTION Spectrum :—

- When a radiation passed through an absorbing sample and then through the prism it is made to fall on a photographic plate then the impression obtained is known as absorption spectrum.
- In absorbtion spectrum dark line are obtained in bright sprectrum theire dark line correspond to the wavelength absorbed by the sample.
- Absorption spectrum is called as the photonegative of emision spectrum.

Note :

- The Spectrum of an element is called as the finger-print of that element.
- The Spectrum of same ~~ete~~ electron species can be similar but it cannot be same.

Emission line Spectrum of Hydrogen :

Series $(n_2) \longrightarrow (n_1)$

Higher orbit no.   Lower orbit no.

Total Spectral lines observed in a spectrum $= \frac{(n_2 - n_1)(n_2 - n_1 + 1)}{2}$

$$\boxed{\text{No. of lines in each series} = (n_2 - n_1)}$$

Lower fixed orbit no. of each series.

1st line = 'α' line
2nd line = 'β' line
3rd line = 'γ' line

for 'x' line of any series $\Rightarrow$ $\boxed{n_2 = n_1 + x}$

for last / marginal / Limiting line of any series $\Rightarrow$ $n_2 = \infty$

For a particular series :—

	1st line	Last line
E	Min.	Max.
ν	Min.	Max.
λ	Max.	Min.

Ques In hydrogen spectrum if the e^- moves 6th orbit to 2nd orbit by taking multiple transition then find out.

(i) Total No. of lines absorbed in the spectrum.
(ii) No. of line in each of series.
(iii) No. of lines in each region.

(i) $\text{Total} = \dfrac{(n_2-n_1)(n_2-n_1+1)}{2}$

$= \dfrac{(6-2)(6-2+1)}{2}$

$= \dfrac{4\times5}{2} = \dfrac{20}{2} = \underline{10}$

(ii) No. of lines in each series $= n_2 - n_1$

Lymen $= n_2 - 1 = \underline{0}$

Balmer $= (n_2-2) = 6-2 = 4$

Paschen $= 6-3 = 3$

Bracket $= 6-4 = 2$

Pfund $= (n_2-5) = 6-5 = 1$

Humphrey $= (n_2-6) = 0$

(iii) Region

U.V = 0
Visible = 4
I.R. 6

Ques In hydrogen atom e^- moves from n^{th} orbit to 1st orbit by taking multiple transition If the No. of lines absorbed in the spectrum are 10 then find the ~~?~~ value of n

$$n_2 = n ; \quad n_1 = 1$$

$$10 = \frac{(n-1)(n\cancel{-1}+1)}{2}$$

$$20 = n^2 - n$$

$$n^2 - n - 20 = 0$$

$$n^2 - 5n + 4n - 20 = 0$$

$$n(n-5) + 4(n-5) = 0$$

$$(n-5)(n+4) = 0$$

$$\boxed{n = 5} \quad \& \quad n = 4 \times$$

Ques A certain electronic transition from exitation state to ground state in H-atom in multiple state give ~~s~~ rise to 4 lines in U.V region then find out how many lines will be produces in I.R. region.

$$U.V = \text{lyman} \Rightarrow n_2 - 1 = 4$$

$$n_2 = 5$$

I.R.

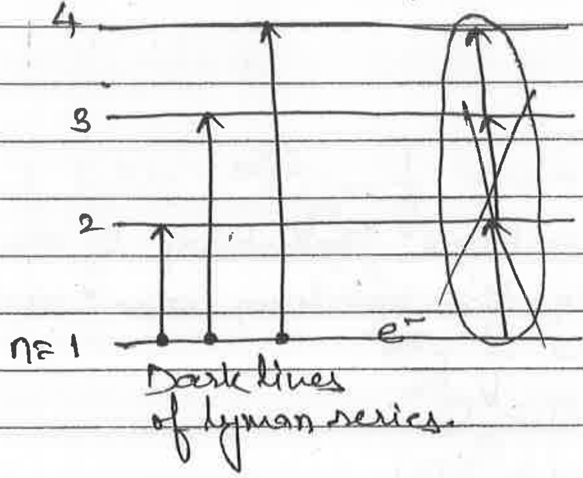
$$\text{Paschen} = (n_2 - 3) = (5-3) = 2$$

$$\text{Bracket} = (n_2 - 4) = (5-4) = 1$$

$$\boxed{3}$$

$$\text{Pfund} = (n_2 - 5) = 0$$

★ Note:— Absorption spectrum for Hydrogen



- In absorption spectrum of hydrogen only the dark lines ~~are~~ of lyman series are obtained this shows that e⁻ doesn't takes multiple transition during transition.

Ques In an atom five orbit are present then calculate the total no. of emission and absorption lines formed in the spectrum.

for emission

$$\text{Total no. of lines} = \frac{(5-1)(5-1+1)}{2}$$

$$= \underline{10}$$

for Absorption

$$\text{No. of lines} = (n_2 - 1)$$

$$= 5 - 1 = \underline{4}$$

Rydberg formula :—

$$\boxed{\bar{\nu} = \frac{1}{\lambda} = RZ^2\left(\frac{1}{n_1^2} \quad \frac{1}{n_2^2}\right)}$$

n_1 = lower orbit no.

n_2 = Higher orbit no.

Z = Atomic no.

R = Rydberg constant

$= 109678 \text{ cm}^{-1} \simeq 1.1 \times 10^5 \text{ cm}^{-1}$

$= 1.1 \times 10^7 \text{ m}^{-1}$

$$\boxed{\frac{1}{R} = 912 \text{ Å}}$$

As we know,

$$\boxed{\nu = c\bar{\nu}}$$

$$\therefore \boxed{\nu = RcZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)}$$

c = Speed of light

$$\Delta E = E_{n_2} - E_{n_1} = h\nu = \frac{hc}{\lambda}$$

→ Energy of e^- in nth orbit (in terms of Redberg constant)

$$\boxed{E_n = -\frac{RchZ^2}{n^2}} \text{ J/atom}$$

→ Energy of transition when an e^- moves from higher orbit (n_2) to lower orbit (n_1)

$$\boxed{\Delta E = Rch\, Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)}$$

Ques. Calculate the wavelength of γ lines of bracket series of H-atom. (Å)

[illegible]

$n_2 \to n_1$

$7 \to 4$

$n_2 = n_1 + x$

$= 4 + 3$

$= \underline{7}$

$$\frac{1}{\lambda} = R(1)^2\left(\frac{1}{4^2}-\frac{1}{7^2}\right)$$

$$= R\left(\frac{1}{16}-\frac{1}{49}\right)$$

$$\frac{1}{\lambda} = \frac{33R}{784}$$

$$\lambda = \frac{784}{33R} = \frac{784}{33}\times\left(\frac{1}{R}\right)$$

$$= \frac{784}{33}\times 912\ A^\circ$$

$$\boxed{\lambda = 21667\ A^\circ}$$

Q) Calculate the frequency of the last of paschen series of Li^{+2}

$n_2 = \infty$

$n_1 = 3$

$$\nu = RC\cancel{(3)^2}\left(\frac{1}{\cancel{3^2}}-\cancel{\frac{1}{(\infty)^2}}\right)$$

$$\nu = RC$$

$$= 1.1\times10^{7}\times3\times10^{8}$$

$$\nu = 3.3\times10^{15}\ s^{-1}$$

Q) Calculate the ratio of the max. frequency of Balmer series in H-atom. to the max. freqency of pashen series in He^+

$$\frac{(\nu_{max})_H}{(\nu_{max})_{He}} = \frac{RC(1)^2\left(\frac{1}{2^2}-\cancel{\frac{1}{\infty^2}}\right)}{RC(2)^2\left(\frac{1}{3^2}-\cancel{\frac{1}{(\infty)^2}}\right)}$$

$$= \frac{1/4}{4/9} = \boxed{\frac{9}{16}}$$

Que which transition in H- spectrum would have the same wavelength as the β-lines transition of Balmer series of He⁺.

Solⁿ:-

$$\left(\frac{1}{\lambda}\right)_H = \left(\frac{1}{\lambda}\right)_{He}$$

$$R(1)\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = R(2)^2\left(\frac{1}{2^2} - \frac{1}{4^2}\right)$$

$$\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 4\left(\frac{1}{4} - \frac{1}{16}\right) = \left(1 - \frac{1}{4}\right)$$

On Comparing

$n_1^2 = 1$ | $n_2^2 = 4$

$\boxed{n_1 = 1}$ | $\boxed{n_2 = 2}$

Que The mini. wavelength of lyman series of Li^{+2} is x A° than calculate the max. wavelength of Balmer series ~~of~~ in He^+

$Li^{+2} = (\lambda_{min.})_{lyman} \Rightarrow \infty - 1$

$H^+ = (\lambda_{max.})_{Balmer} \Rightarrow 3 - 2$

$$\frac{\left(\frac{1}{\lambda_{min.}}\right)_{Li^{+2}}}{\left(\frac{1}{\lambda_{max.}}\right)_{He^+}} = \frac{R(3)^2\left(\frac{1}{1^2} - \cancel{\frac{1}{\infty^2}}\right)}{R(2)^2\left(\frac{1}{2^2} - \frac{1}{3^2}\right)}$$

$$= \frac{9}{5/9} = \frac{81}{5}$$

$$\frac{(\lambda_{max.})_{He^+}}{(\lambda_{min})_{Li^{+2}}} = \frac{81}{5}$$

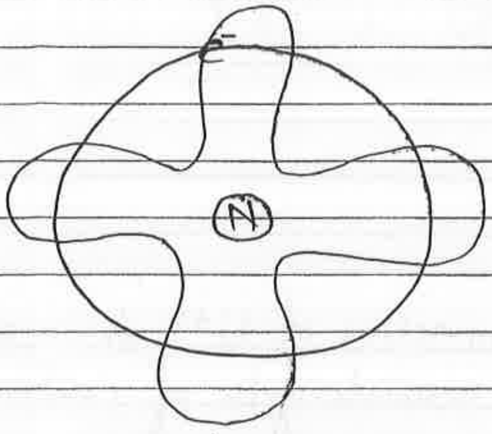
$$(\lambda_{max.})_{He} = \frac{81x}{5} A°$$

De-Broglie Concept :—

- Dual Nature of matter:

- Singnificance of De-broglie concept :—

Acc. to De-broglie for a circular orbit to exist of ~~a~~ circumference should be n intergral multiple of the wavelength of e^-.



no. of waves = 4
Orbit no. = 4

for a circuler orbit to exist:—

$$\boxed{2\pi r = n\lambda_e}$$

$$2\pi r = n\left(\frac{h}{mv}\right)$$

$$\boxed{mvr = n\left(\frac{h}{2\pi}\right)}$$

n = No. of waves
n = orbit no.

λ	h	m	v
m	Js	kg	ms^{-1}
cm	ergs	g	cms^{-1}

Ques Calculate the wavelength of e^- moving with a K.E of 2.5eV. (in Å)

$$\lambda = \frac{h}{\sqrt{2mK.E}}$$

$$= \frac{6.63\times10^{-34}}{\sqrt{2\times9.1\times10^{-31}\times2.5\times1.6\times10^{-19}}}$$

$$= \frac{6.63\times10^{-34}}{\sqrt{72.8\times10^{-50}}}$$

$$= \frac{6.63 \times 10^{-34}}{8.5 \times 10^{-25}}$$

$$= \frac{66.3 \times 10^{-10}}{8.5} = 7.8 \times 10^{-10} m$$

$$= 7.8 A'$$

OR

$$\lambda = \sqrt{\frac{150}{V}} = \sqrt{\frac{\cancel{1500}^{6}}{\cancel{25}}} = \sqrt{60} = 7.8 A'$$

Ques Two particle A and B are in a certain motion If the mass and velocity of particle B is 25% and 75% of particle A respectivily then calculate λ_B If λ_A is 1A'.

Solⁿ:-

$$\lambda = \frac{h}{mV}$$

$$\lambda \propto \frac{1}{mV}$$

$$\frac{\lambda_A}{\lambda_B} = \frac{m_B V_B}{m_A V_B} = \frac{\frac{\cancel{m_A}}{4} \times \frac{3\cancel{V_A}}{4}}{\cancel{m_A} \times \cancel{V_A}}$$

$$= \frac{3}{16}$$

$$\lambda_B = \frac{16}{3} \lambda_A \Rightarrow \frac{16}{3} \times 1A' = 5.33A'$$

Ques Calculate the wavelength of a photon If its velocity is 1/10th of its velocity light. (in meter)

Solⁿ:-

$$\lambda = \frac{h}{mV}$$

$$\lambda = \frac{6.63 \times 10^{-34}}{1.67 \times 10^{-27} \times \left(\frac{1}{10} \times 3 \times 10^{8}\right)}$$

$$= \frac{2.21}{1.67} \times 10^{-14} \Rightarrow 1.33 \times 10^{-14} m$$

Ques. Calculate the wavelength of an e^- present in 3rd orbit of H-atom. (in A°)

Solⁿ:- $2\pi r = n\lambda$

$2\pi (r_3)_H = 3\lambda_e$

$2\pi \times 0.53 \times \frac{(3)^{\cancel{2}}}{1} = \cancel{3}\lambda_e$

$\lambda_e = 2 \times 3.14 \times 1.59$

$\lambda_e =$ 9.98 A° ≃ 10 A°

Ques Calculate the De-broglie wavelength associated with an e^- accelerated with a potential diff. of 100 KV. (in Pm)

$\lambda_e = \sqrt{\frac{150}{V}}$ A°

$\lambda_e = \sqrt{\frac{15\cancel{0}}{100 \times 100\cancel{0}}}$

$= \frac{3.9}{100}$ A°

$= 3.9 \times 10^{-2} \times 10^{-10}$ m

$\lambda_e = 3.9$ Pm

- ~~By~~ Heisenberg's uncertainity principal conteradicts the Concept of ~~fixed~~ circular orbit given by Bohr acc. to ~~Heisenberg~~ we only define a region in space around the nuclei where

Ques. If the uncertainity in position of an e^- is 1Å then find out the uncertainity in its velocity? (ms^{-1})

Solⁿ :-

$$\Delta v = \frac{h}{4\pi m.\Delta x}$$

$$= \frac{0.527\times10^{-34}}{9.1\times10^{-31}\times10^{-10}}$$

$$= 5.7\times10^{5}\ ms^{-1}$$

Ques A dust particles has a mass of 10×10^{-10} g and ~~the~~ a velocity of 10^{-6} cm/sec. If the error in the measurement of velocity is 0.0001% then find out the uncertainity in position.

$$\Delta v = 10^{-6}\times\frac{0.0001}{100} = 10^{-12}\ cms^{-1}$$

$$\Delta x = \frac{h}{4\pi m.\Delta v}$$

$$= \frac{0.527\times10^{-27}}{10^{-10}\times10^{-12}}$$

$$= 5.27\times10^{-6}\ cm$$

Ques If the uncertainity in position and velocity same than uncertainity in momentum will be.

① $\sqrt{\frac{hm}{4\pi}}$ (iii) $\frac{h}{\sqrt{4\pi m}}$

(ii) $\sqrt{\frac{h}{4\pi m}}$ (iv) N.o.T.

$\Delta P = m.\Delta V$

$\Delta P = m.\Delta x$ (as $\Delta x = \Delta V$)

$\Delta P = m\frac{h}{4\pi\Delta P}$ ($\Delta x.\Delta P = \frac{h}{4\pi}$)

$\Delta P^2 = \frac{hm}{4\pi}$

$\Delta P = \sqrt{\frac{hm}{4\pi}}$

Ques An e^- has a speed of 40m/sec accurate upto 99.99% the Calculate the uncertainity in ~~to~~ locating its position.

~~$\Delta x = \frac{h}{4\pi m.\Delta v}$~~

$$\Delta v = 40 \times \frac{0.01}{100} = 4\times10^{-3} ms^{-1}$$

$$\Delta x = \frac{h}{4\pi m.\Delta v}$$

$$= \frac{0.527\times10^{-34}}{9.1\times10^{-31}\times4\times10^{-3}}$$

$$= \frac{0.527}{36.4} = 1.4\times10^{-2} m$$

Ques The uncertainity in position and velocity of a particle are 10^{-10} m and $5.27\times10^{-24} ms^{-1}$ respectively then determine the mass of the particles.

Ans = 0.11 kg

Quantum mechanical Model of atom :—

⇒ Given by Schrodinger

⇒ This model is based on dual nature of electron.

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

Ψ (Psi) = Wave function

ψ^2 = Probability density

E = $\underset{\text{Total}}{\text{energy}}$

V = Potential ~~diff~~ energy

- The solution of Schrodingers equation gives us a set of 3 quantum nos i.e. n, l, & m.

Note:- Orbital — It is define as the region in space where the probability in finding an e^- is max.^{n}

OR

An orbital is an e^- cloud that has a definite size, shape, and orintation.

An orbital is represented by the following symbol (ψ_{nlm}).

$$\psi_{\underset{\text{Size}}{\underset{\downarrow}{n}}\;\underset{\text{Shape}}{\underset{\downarrow}{l}}\;\underset{\text{Orientation}}{\underset{\downarrow}{m}}}$$

Quantum Numbers :—

The represent the address of an e^-.

They denote the position and energy of an e^-.

An orbitals is designated by 3 quantum nos i.e. n, l, & m.

An e^- is designated by 4 quantum no.s i.e. n, l, m & s.

① Principal Quantum no.(n):—

- Originated by Bohr.
- It denotes the name & energy of a shell.
- Possible values of 'n' are +ive integers.

$n=1 \Rightarrow$ K-shell
$n=2 \Rightarrow$ L-shell
$n=3 \Rightarrow$ M-shell
⋮ ⋮ ⋮

- It also denotes, the size of orbitals and distance of e^- from nucleus.
- As the value of n ↑es then energy of shell, size of orbital & distance of e^- from nucleus as ↑es.

— For n^{th} shell

No. of subshell = n
No. of orbital = n^2
No. of e^- = $2n^2$

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② Azimathal / Secondary / Subsidary :—
Angular Quantum No. (l) :

- Originated by Sommerfield
- It denotes the name of subshell & shape of orbital.
- Possible value of 'l' are—

$l = 0 \Rightarrow$ s- Subshell
$l = 1 \Rightarrow$ p- Subshell
$l = 2 \Rightarrow$ d- Subshell
⋮ ⋮ ⋮ ⋮

- Relation b/w n & l

In a particular n^{th} shell, the value of 'l' range from 0 to $(n-1)$

If $n = 1 \Rightarrow l = 0$ (1s- Subshell)
$n = 2 \Rightarrow l = 0, 1$ (2s, 2p- Subshell)
$n = 3 \Rightarrow l = 0, 1, 2$ (3s, 3p, 3d- Subshell)
$n = 4 \Rightarrow l = 0, 1, 2, 3$ (4s, 4p, 4d, 4f- Subshell)
⋮ ⋮ ⋮

* It determines the orbitals angular momentum (μ_l) as follows

$$\boxed{\mu_l = \sqrt{l(l+1)} \left(\frac{h}{2\pi}\right)}$$

- No. of orbitals in a subshell $= (2l+1)$
- No. of e^- in a subshell $= 2(2l+1)$
- 'l' depends the energy of a subshell in a particular n^{th} shell.

$l = 0 \quad 1 \quad 2 \quad 3$ } multi-e^-
$s < p < d < f$ } Species

{ As the value of l ↑res ⟹ Energy of subshell also ↑res }

Eg:— $4s < 4p < 4d < 4f$
$3s < 3p < 3d$

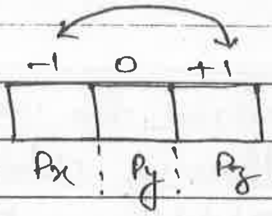
— But in case of single e^- species
$s = p = d = f$
Ex. $4s = 4p = 4d = 4f$
$3s = 3p = 3d$

Note:— Multi e^- species energy depends both n & l but for single e^- species ~~only~~ energy depends only on n.

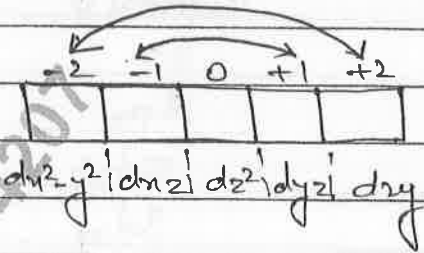
③ Magnetic Quantum no. (m):—
Given by Linde
— It represented the orientation of an orbital.
— Total no. of values of 'm' = Total no. of orbital
— Possible values of 'm' = $\underbrace{-l \text{ to } +l}$ including zero.

for $l = 0 \Rightarrow m = 0$
(s-subshell ⟹ 1 orbital)

for $l=1 \Rightarrow m = -1, 0, +1$
(P-subshell ⇒ 3 orbitals)



for $l=2 \Rightarrow m = -2, -1, 0, +1, +2$
(d-subshell ⇒ 5 orbitals)



④ Spin Quantum no. (S or m_s) :—

- Given by Uhlenbeck & Goudsmit
- It represents the rotation of an e^- about its own axis.
- Possible values of 's' = $\left(+\frac{1}{2}\right)$ & $\left(-\frac{1}{2}\right)$

(Represents clockwise and anti-clockwise rotation) $\boxed{\uparrow\downarrow}$

- It determines the spin angular momentum (μ_s) as follow :—

$$\boxed{\mu_s = \sqrt{S(S+1)}\left(\frac{h}{2\pi}\right)}$$

Put, $S = \frac{1}{2}$

$$\mu_s = \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}\left(\frac{h}{2\pi}\right)$$

$$\boxed{\mu_s = \frac{\sqrt{3}\,h}{4\pi}}$$

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Ques Determine the values of Quomtum no. n, l & m for the following orbitals:—

Orbital	n	l	m
3s	3	0	0
$4p_x$	4	1	±1
$5d_{z^2}$	5	2	0
$3d_{xy}$	3	2	±2

Ques Determine the orbitals from the following values of Quomtum no. —

n	l	m	Orbitals
2	1	−1	$2p_x$ / $2p_y$
4	0	0	4s
5	2	+1	$5d_{xz}$ / $5d_{yz}$
3	1	0	$3p_z$
ψ_{420}			$4d_{z^2}$

Ques Put out the correct sequence of Qunatum no. in the following:—

(i) $n=2$; $l=1$; $m=2$; $s=+\frac{1}{2}$

(ii) $n=3$; $l=3$; $m=1$; $s=-\frac{1}{2}$

(iii) $n=2$; $l=1$; $m=-1$; $s=+\frac{1}{2}$

(iv) $n=3$; $l=2$; $m=0$; $s=+1$

Ques Calculate the value of orbital angular momentum for a d-electrons.

~~No. of e~~

$$\mu_l = \sqrt{l(l+1)}\left(\frac{h}{2\pi}\right)$$

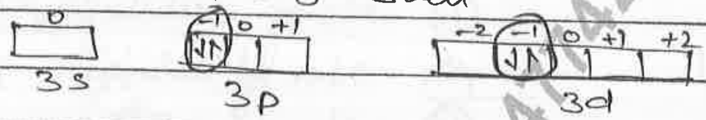
$$= \sqrt{2(2+1)}\left(\frac{h}{2\pi}\right.$$

$= \sqrt{6}\ \frac{h}{2\pi}$

$= \sqrt{6}\ \hbar$

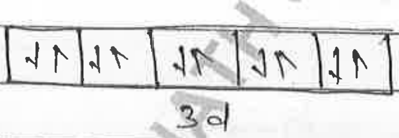
Ques Calculate the no. of e^- present in m-shell that have a value of magnetic Quantum no. equal to -1.

M-Shell = 3rd shell



no. of $e^- = 4$

Ques for $n=3$; $l=2$ orbitals Determine the no. of e^- having the value of spine quamtum no. equal to $-\frac{1}{2}$.



no. of $e^- = 5$

Ques Calculate the no. of orbital in 4th shell having an e^- with value of Spine Quamtum No. of $-\frac{1}{2}$

Solun:-

No. of orbitals in n^{th} shell $= n^2$

$= (4)^2$

$= 16$

Ques If the value of $(n+l)$ is not more than 4 then calculate ① no. of subshell (II) no. of orbitals (III) No. of e^-s.

$(n+l) \le 4$

$n+l=1$
$1+0=$ 1s
$0+1=X$

$n+l=2$
$2+0=$ 2s
$1+1=X$
$0+2=X$

$n+l=3$
$3+0=$ 3s
$2+1=$ 2p
$1+2 \neq x$
$0+3=x$

$n+l=4$
$4+0=$ 4s
$3+1=$ 3p
$2+2=x$
$1+3\neq x$

(I) No. of subshell = 6
(II) No. of orbital = 10
(III) No of e^- = 20

NODES :—

It is define as the region in space around the nucleus where the probability of finding an e^- is zero.

* There are of two types.

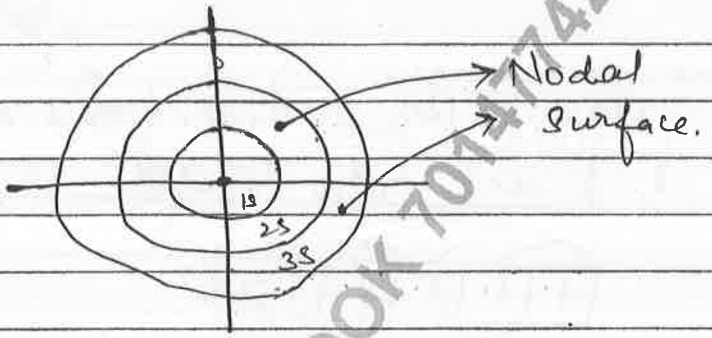
- Radical nodes / Spherical nodes / Nodal Surface $= (n-l-1)$

- Angular nodes / Non-spherical nodes / Nodes Plane $= (l)$

- Total nodes $= (n-1)$

P-Orbital	Nodal Plane (l)
P_x	yz
P_y	xz
P_z	xy

d-orbitals	Nodal Plane (l)
d_{xy}	yz & xz
d_{yz}	xy & xz
d_{xz}	xy & yz
$d_{x^2-y^2}$	2 (at an angle of 45°)
d_{z^2}	0



Ques Calculate the no. of radial, angular and Total nodes for 4s, 5p and 3d orbital :-

For 4s :-	For 5p	For 3d
Radial = 4-0-1 = 3	Radial = 3	= 0
Angular = 0	Angular = 1	= 2
Total nodes = 3	Total = 4	= 2

Rules for filling of e^- :—

② $(n+l)$ rule

- lowest value of $(n+l)$ = lowest energy subshell
- If value of $(n+l)$ is same = lower value of 'n' = lower energy subshell
- for H-atom = Single e^- species = energy depends only on 'n'

$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f$ —

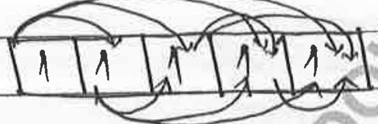
④ Hund's Rule of max^m multiplicity :-
(Many of same kind)

Reasons:—

① Symmetrical Distribution of e^-
(To minimize inter-electronic repulsion)

⑪ Exchange energy

Note:- Half filled and full filled orbitals are more stable.



d^5

No. of exchanges = 4+3+2+1 = 10

Note:—

- The atom having unpair e^- in them are called as paramagnetic. and the atom having no unpaired e^- in them are called as Dimagnetic.

- Magnetic moment $= \sqrt{n(n+2)}$ BM
BM = Bohr Magneton
$= 9.27 \times 10^{-24}$ J T^{-1}
n = No. of unpaired e^-

- Total spin $= \pm\frac{1}{2} \times$ no. of unpaired e^-

- Kernel → Remaining part of atom after the removal of outermost shell.

- Core cherge = z − (no of e^- in kernel)

Ex − $_{24}Cr$ = (Ar) $3d^5\ 4s^1$

kernel ⇒ (Ar) $3d^5$

Core cherge = 24 − 23

= <u>1</u>

<u>Ques</u> For which element of the period table the pauli's exclusion principal is not applicable.

<u>Ans</u> <u>H</u> → pauli's principal are applicable for two e^- but in Hydrogen only one e^-

<u>Ques</u> For which element of the period table the Hund's Rule is first applied.

<u>Ans.</u> C [↑↓] [↑↓] [↑ | ↑ |]

1s 2s 2p

<u>Ques</u> What are the maxm no. of electron that can be associated with the following set of Quantum no.

$n = 3$; $l = 1$; $m = -1$ ① 2 ② 4 ③ 6 ④ 10

<u>Ques</u> How many e^- can be accommodated in a atom in which the maxm value of principal Quantum no. is 4.

<u>Ans.</u> $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 3p^6$ ~~$5s^2$~~

= 36 e^-

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Ques In the following configⁿ. determine which rule are voilated.

Ans

1s² 2s 2p

ⓐ $\boxed{\uparrow}$ $\boxed{\uparrow\uparrow}$ $\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$ ⇒ Aufbau & Pauli's

ⓑ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}$ $\boxed{\uparrow}\boxed{\downarrow}\boxed{\uparrow}$ ⇒ Aufbau & Hund's

ⓒ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow\uparrow}$ $\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{}$ ⇒ Pauli's & Hund's

Ques Calculate the no. of unpaired e⁻, megnetic momentum & total Spin for Cr^{+3}.

Ans

	Unpaired e⁻	MM	Total spain
$_{24}Cr^{+3}$ $(Ar)\,3d^5 4s^1$	3	$\sqrt{3(3+2)}$ BM $= \sqrt{15}$ BM $= 3.9$ BM	$= \pm\frac{1}{2}\times 3$ $= \pm\frac{3}{2}$

Ques. An atom has 2K, 8L, 11M, 2N e⁻ then write down its electronic configⁿ and find out of

(I) No. of Subshell

(II) No. of orbital having unpaired e⁻

(III) No. of e⁻ having l = 1

(IV) No. of pairs of paired e⁻

Ⓐ 23 e⁻ = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$

(I) 7

(II) 3

(III) 12

(IV) 10

Que for Fe atom Calculate the following:—

(i) No. of e^-s with $(n+l)=5$

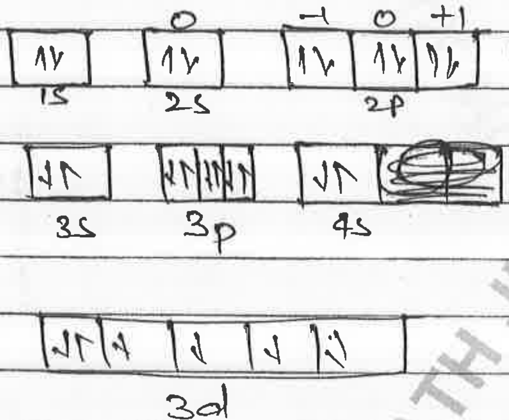
(ii) No. of with $l=1$; $m=0$

(iii) No. of e^-s with $l=0$; $s=+1/2$

(iv) No. of e^-s with $n=2$; $m=-1$

(v) Write down the set of 4 Quantum no. for the last e^- filled.

$_{26}Fe = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$



(i) $(n+l)=5 \Rightarrow 6e^-$

$(5+0) = \times$

$(4+1) = \times$

$(3+2) = \boxed{3d}$ ✓

(ii) $(l=1;\ m=0) \Rightarrow 4e^-$

(iii) $(l=0;\ s=+1/2) = 4e^-$

(iv) $(n=2;\ m=-1) \Rightarrow 2e^-$

(v) $n=3;\ l=2;\ m=-2$ to $+2$

$s=+1/2$

Surface Chemistry

Thermodynamic approach for Adsorption :—

As we known,

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

for adsorption,

$\Delta H_{ads.} = -ve$ [Due to decreare in surface evergy]

$\Delta S_{ads.} = -ve$ [Due to decreare in degree of movement of particles]

$$\therefore \boxed{\Delta G_{ads.} = -\Delta H + T\Delta S}$$

Case 1: $\Delta H > T\Delta S$ At low temp.

$\therefore \boxed{\Delta G = -ve}$

Adsorption is spontaneous

Case 2: At high temp. :

$\Delta H < T\Delta S$

$\therefore \boxed{\Delta G = +ve}$

Adsorption is non spontaneous.

Case 3: When $T = \frac{\Delta H}{\Delta S}$

$\therefore \boxed{\Delta G = 0}$

Adsorption & Desorption are at equilli^{m} with each other.

~~Adsorp~~ Adsorbate + Adsorbent $\underset{Desop^{n}}{\overset{Adsorp^{n}}{\rightleftharpoons}}$ Adsorbed

+Note:—

Physical adsorption at low temp may be converted into chemical adsorption at high temp.

Eg:- Nickel Hydride

Ⓐ Freundlich adsorption

Ⓑ Langmuir adsorption isotherm:—

① At low P

$1+bP \simeq 1$

So,

$\frac{x}{m} = aP$

$\therefore \boxed{\frac{x}{m} \propto P}$

1st order Rxn

Ⓘⓘ At high P

$1+bP \simeq bP$

So,

$\frac{x}{m} = \frac{aP}{bP} = \frac{a}{b} = \text{Const.}$

$\therefore \boxed{\frac{x}{m} \propto P^{\circ}}$

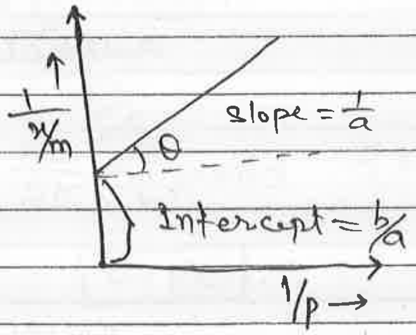
Zero order Rxn.

$$\frac{x}{m} = \frac{aP}{1+bP}$$

$$\frac{1}{x/m} = \frac{1+bP}{aP} = \frac{1}{aP} + \frac{bP}{aP}$$

$$\boxed{\frac{1}{x/m} = \frac{1}{aP} + \frac{b}{a}}$$

$$y = mx + c$$



Preferential adsorption theory:—

The charge on colloidal particles is due to the prefractional adsorption of a +ive or -ive common ~~ip~~ ion present in excess.

NCERT

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$$AgNO_3 + \underset{\text{excess}}{KI} \longrightarrow \underset{\text{-ive colloid}}{AgI/I^-}$$

$$\underset{\text{excess}}{AgNO_3} + KI \longrightarrow \underset{\text{+ive colloid}}{AgI/Ag^+}$$

Ques The graph b/w $\log x/m$ vs $\log p$ is straight line inclined at an angle of 45° with an intercept of 0.6 then determine the extent of adsorption at a pressure of 0.3 atm.

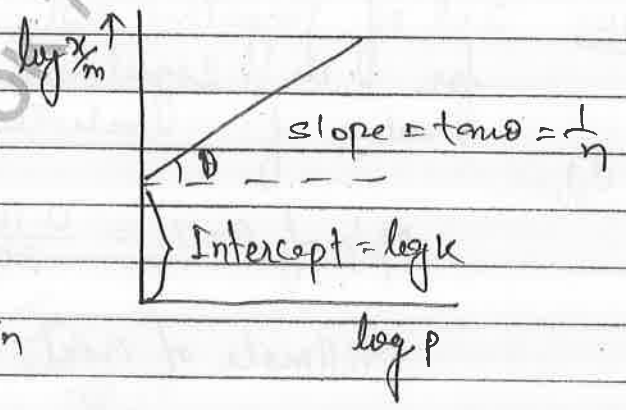
$\log k = 0.6$

$k = 4$

$\tan 45° = \frac{1}{n}$

$1 = 1/n$

$n = 1$



$$\frac{x}{m} = kP^{1/n}$$

$$\frac{x}{m} = 4(0.3)^1$$

$$= 1.2$$

Ques 2gm of charcoal having a surface area of $3.01 \times 10^2 m^2$ is mixed in 100ml of 0.25M acetic acid sol^n after same time conc. of solu^n become 0.24M what will be surface area accupied by 1 molecules of acetic acid.

Initial mole of $CH_3COOH = 0.25 \times \frac{100}{1000} = 25 \times 10^{-3}$ mol

final mole of $CH_3COOH = 0.24 \times \frac{100}{1000} = 24 \times 10^{-3}$ mol.

Adsorbed molecules of CH_3COOH = 1×10^{-3} mole.
Adsorbed molecules of " = $10^{-3} \times N_A$
= 6×10^{20} molecules

$\therefore$ Surface area occupied by 1 molecules = $\frac{\text{Total Surface area}}{\text{Total no. of ad. mole.}}$

$= \frac{3.01 \times 10^{2}}{6 \times 10^{20}} = 5 \times 10^{-19} m^2$

Ques 20l of Negative sol required 0.104g Barium chloride for its coagulation then Determine the coagulation value of electrolite.

Solu:-

Moles of $BeCl_2$ = $\frac{0.104}{208} = 5 \times 10^{-4}$ mol

Millmole of $BeCl_2$ = $5 \times 10^{-4} \times 10^{3}$
= 0.5 mmole

Coagulation value = $\frac{0.5 \text{ m mol}}{20L}$

= 0.025 mmolL^{-1}

Ques On Adding 1ml solun of 10% Nacl to 10ml gold sol in the presence of 0.025 gm starch so, that its Coagulation prevented then what will be the gold no. of starch.

(I) 0.25
(II) 2.5
(III) 25
(IV) 0.0025

Mass of starch = 0.025g
= 25g
(Gold no. is in mg)

Ques W.Of combination will lead to the formation of a negativily charged colloidal soln.

(i) 50mL 0.1M $AgNO_3$ + 50mL 0.1M KI
(ii) 50mL 0.2M $AgNO_3$ + 50mL 0.1M KI
(iii) 50mL 0.1M $AgNO_3$ + 50mL 0.2M KI
(iv) N.O.T.

Date ______ Page ______

Electrochemistry

Ques1. The resistance of a cell filled with 0.2M CaI_2 solu^n is 250Ω with cell constant of $0.9 cm^{-1}$ then find out conductivity and equivalent conductivity of solu^n.

Solu^n:—

(I) $K = G \times G^* = \frac{1}{R} \times G^*$

$= \frac{1}{250} \times 0.9$

$= 3.6 \times 10^{-3} ohm^{-1} cm^{-1}$

(II) $\Lambda_{eq.} = \frac{K \times 100}{N}$

$= \frac{3.6 \times 10^{-3} \times 100}{0.02 \times 2}$

$= 90 \; ohm^{-1} cm^2 eq^{-1}$

Ques 2. A cell with electrodes 0.5cm apart and $1.5cm^2$ area is filled with 0.1 N $MgCl_2$ Solu^n If the equient conductivity of the solu^n is $97.1 \Omega^{-1} cm^{-1}$ then find out how much current will flow when the potential diff. b/w the electrod is 5V.

Solu^n:—

$G^* = \frac{l}{A} = \frac{0.5}{1.5} = \frac{1}{3} cm^{-1}$

$\Lambda eq. = \frac{K \times 1000}{N}$

$97.1 = \frac{K \times 1000}{0.1}$

$K = 9.71 \times 10^{-3} ohm^{-1} cm^{-1}$

$K = G \times G^* = \frac{1}{R} \times G^*$

$R = \frac{1}{K} \times G^* = \frac{1}{9.71 \times 10^{-3}} \times \frac{1}{3}$

$R = \frac{1000}{29.13}$

As,

$V = IR$

$I = \frac{V}{R}$

$= \frac{5}{1000/29.13}$

$= 0.14565 A$

Ques 3. The resistance of a cell filled with 0.1M kcl soln is 100Ω and the conductivity (K) is $1.29\ S\ m^{-1}$ when the same cell is filled with 0.02M kcl soln then the resistance is found to be 520Ω then find out the molar conductivity of 0.02M KCl soln:-

Soln:-

0.1M kcl → $R_1 = 100\Omega$; → $K_1 = 1.29\ S m^{-1}$

0.02M KCl → $R_2 = 520\Omega$; → $K_2 = ?$

$K = G \times G^*$

$1.29 = \frac{1}{R} \times G^*$

$G^* = K \times R = 1.29 \times 100$

$G^* = 129\ m^{-1}$

$G^* = 129 \times 10^{-2}\ cm^{-1}$

$G^* = 1.29\ cm^{-1}$

0.02 KCl Soln

$K = G \times G^* = \frac{1}{R} \times G^*$

$= \frac{1}{520} \times 1.29$

$= \frac{1.29}{520}\ ohm^{-1} cm^{-1}$

$$\Lambda_m = \frac{K \times 1000}{M} = \frac{1.29 \times 1000}{520 \times 0.02}$$

$$= \underline{124\ ohm^{-1} cm^2 mol^{-1}}$$

Ques 4. The molar conductivity of 0.01M $AgNO_3$ soln is $144.8\ S\ cm^2\ mol^{-1}$ and the resistance is 1442Ω if the electrode are ~~present~~ placed 0.54cm apart then find out the area of cross section of electrodes.

⁑ Factor affecting Electrolytic Conductance :—

(I) Nature of electrolyte :—

Strong electrolyte(aq.) > Weak electrolyte(aq.)

(II) Nature ~~of~~ (Polarity) of Solvent :—

$\underbrace{\mu}_{\text{(Dielectric const.)}}\uparrow \Rightarrow \alpha$ of electrolyte ↑ ⇒ No. of ions in soln ↑ ⇒ G ↑

(III) Inter Ionic Attraction (IIA) :—

IIA ↑ ⇒ Mobility of ions ↓ ⇒ G ↓

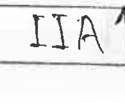
(IV) Viscosity of Medium :—

Viscosity ↑ mobility of ions ↓ ⇒ G ↓

(V) Temperature

T ↑ ⇒ K.E of ions ↑ ⇒ IIA ↓ ⇒ Mobility of ion ↑ ⇒ G ↑

(VI) Hydration or Solvation of ion :—



⇒ Hydration ↑ ⇒ Effective size of ion ↑ ⇒ Mobility of ion ↓ ⇒ G ↓

$$\boxed{\text{Hydration} \propto \frac{1}{\text{Size of Cation}}}$$

Order of

Size of Cation ⇒ $Li^+(g) < Na^+(g) < K^+(g) < Rb^+(g) < Cs^+(g)$

Size of hydrated ions ⇒ $Li^+(aq) < Na^+(aq) < K^+(aq) < Rb^+(aq) < Cs^+(aq)$

Order of Conductance ⇒ $Li^+(aq) < Na^+(aq) < K^+(aq) < Rb^+(aq) < Cs(aq)$

Note :—

On dilution, no. of ions in a solu^n of stronge electrolite remains same as it is already 100% dissociated.

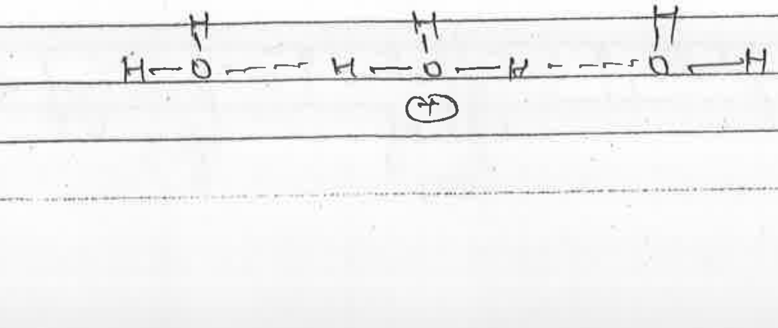
**

Dilution ↑ or Concentration ↓ } $G\uparrow, \Lambda_m\uparrow$ & $\Lambda_{eq}\uparrow$ but $K\downarrow$

Ques Arrange the following compd. in ↑ing order of there conductance in ageous solution.

NaCl, HCl, KCl, & LiCl

Ans LiCl < NaCl < KCl < HCl



↳★→ HCl has higher conductance due to proton transfer from one water molecule to another water molecule hence, the mobility of H^+ ions is very high in aqeous solution So, its conductances is also very high.

Ques WOF solution has max^m conductances.

① $HCl(aq)$
② $KCl(aq)$
③ $H_3PO_4(aq)$
[✓ ④ $H_2SO_4(aq)$]

Ques WOF solution will have max^m conductivity.

① 0.1M KCl
[✓ ② 1M KCl]
③ 0.02M KCl
④ Same

↑Conc ∝ K↑

dilution ka question

Ques In WOF solution the equivalent conductivity minim if all solution have identical value of conductivity.

① 0.05M HCl
[✓ ② 0.05 M $Al_2(SO_4)_3$]
③ 0.05M K_2SO_4
④ Same

$$\downarrow \Lambda_{eq} = \frac{K \times 1000}{N}\uparrow$$

$$\uparrow N = M \times v.f. \uparrow$$

~~Ques~~ #

↳ At ∞ dilution both W.E and S.E are 100% dissociated into there ion's and no IIA Hence each ion can migrate independetly in the soln of ~~[illegible]~~ electrolyte.

Date ______ Page ______

*** Hence Kohlrausch's law can be stated as follow:-
The equivalent conductivity of an electrolyte at ∞ dilution is equal to the sum of equivalent ionic Conductivity of each ions at ∞ dilution given by electrolyte.

→ The molar conductivity ~~an~~ of an electrolyte at ∞ dilution is equal to the sum of molar conductivity of each ion at ∞ dilution each multiplied by respectively no. of moles of ions given by 1 mole of electrolyte.

$$A_xB_y \longrightarrow xA^{+y} + yB^{-x}$$

$$\boxed{\Lambda^{\infty}_{eq}(A_xB_y) = \Lambda^{\infty}_{eq}(A^{+y}) + \Lambda^{\infty}_{eq}(B^{-x})} \quad \text{— (I)}$$

$$\boxed{\Lambda^{\infty}_{m}(A_xB_y) = x \cdot \Lambda^{\infty}_{m}(A^{+y}) + y \cdot \Lambda^{\infty}_{m}(B^{-x})} \quad \text{— (II)}$$

$x \rightarrow$ Moles of Cation; $y \rightarrow$ Moles of Anion

As,

$$\frac{\Lambda_m}{\Lambda_{eq}} = v.f \implies \Lambda_m = \Lambda_{eq} \times v.f$$

$$\boxed{\Lambda^{\infty}_{m} = \Lambda^{\infty}_{eq} \times v.f.} \quad \text{— (III)}$$

From eqn ①

$$\Lambda^{\infty}_{eq.}(\text{ion}) = \frac{\Lambda^{\infty}_{m}(\text{ion})}{v.f.\ \text{ion}}$$

$$\Lambda^{\infty}_{eq.}(A^{+y}) = \frac{\Lambda^{\infty}_{m}(A^{+y})}{y} \qquad \Lambda^{\infty}_{eq}(B^{-x}) = \frac{\Lambda^{\infty}_{m}(B^{-x})}{x}$$

Ques The limiting ionic conductivity of Al^{+3} and Cl^- ions are 63 and 65.5 $\Omega^{-1} cm^2 eq^{-1}$ respectivily then find out molar and equivalentent conductive of $AlCl_3$ at ∞ dilution.

$$\Lambda_{eq}(AlCl_3) = \Lambda_{eq}^{\infty}(Al^{+3}) + \Lambda_{eq}^{\infty}(Cl^-)$$
$$= 63 + 65.5 = 128.5\ \Omega^{-1} cm^2 eq^{-1}$$

$$\Lambda_m^{\infty}(AlCl_3) = \Lambda_{eq}(AlCl_3) \times V.f$$
$$= 128.5 \times 3$$
$$= 385.5\ \Omega^{-1} cm^2 mol^{-1}$$

Ques The limiting ionic conductivity of K^+ Al^{+3} and SO_4^{2-} are x, y and z $\Omega^{-1} cm^2 mol^{-1}$ respectivity then find out the molar and equivalent conductive of Potas alums. ($K_2SO_4 \cdot Al_2(SO_4) \cdot 24H_2O$

$$\Lambda_m^{\infty}(\text{Potash Alum}) = 2\Lambda_m^{\infty}(K^+) + 2\Lambda_m^{\infty}(Al^{+3}) + 4\Lambda_m^{\infty}(SO_4^{2-})$$
$$= (2x + 2y + 4z)\ \Omega^{-1} cm^2 mol^{-1}$$

$$\Lambda_{eq}^{\infty} = \frac{\Lambda_m^{\infty}}{V.F} = \left(\frac{2x + 2y + 4z}{8}\right) \Omega^{-1} cm^2 eq^{-1}$$

Application of Kohlrorch's law :—

① To determine Λ_m for W.E. :—

$$\Lambda_m^{\infty}(CH_3COOH) = ?$$

Given,

$\Lambda_m^\infty (CH_3COONa) = a \; S\,cm^2\,mol^{-1}$

$\Lambda_m^\infty (HCl) = b$ — ,, —

$\Lambda_m^\infty (NaCl) = c$ — ,, —

$CH_3COOH \longrightarrow CH_3COO^- + H^+$

Given,

$\Lambda_m^\infty (CH_3COONa) = \Lambda_m^\infty (CH_3COO^-) + \Lambda_m^\infty (Na^+)$ — ①

$\Lambda_m^\infty (HCl) = \Lambda_m^\infty (H^+) + \Lambda_m^\infty (Cl^-)$ — ⑪

$\Lambda^\infty (NaCl) = \underline{\Lambda_m^\infty (Na^+)} + \underline{\Lambda_m^\infty (Cl^-)}$ — (iii)

$\underline{\Lambda_m^\infty (CH_3COOH) = \Lambda_m^\infty (CH_3COO^-) + \Lambda_m^\infty (H^+)}$ — ④

④ = ① + ② − ③

$\Lambda_m^\infty (CH_3COOH) = (a + b - c) \; S\,cm^2\,mol^{-1}$

② To determine degree of dissociation of W.E. :—

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\infty} \quad \text{or} \quad \alpha = \frac{\Lambda_{eq}^c}{\Lambda_{eq}^\infty}$$

where,

$$\Lambda_m^c = \frac{K \times 1000}{M} \; ; \; \Lambda_{eq}^c = \frac{K \times 1000}{N}$$

③ To determine dissociation constant of W.E. :—

$$\boxed{K_a \text{ or } K_b = \frac{c\alpha^2}{1-\alpha}} \Rightarrow \text{If } \alpha > 5\% \text{ or } 0.05$$

$$\boxed{K_a \text{ or } K_b = c\alpha^2} \Rightarrow \text{If } \alpha < 5\% \text{ or } 0.05$$

④ To determine solubility of Sparingly soluble salt :—

⇒ For Saturated solⁿ ⇒ $S = M$

⇒ Saturated Solⁿ of sparingly soluble solt can be Considered as infinitely dilute solⁿ.

$$\therefore \Lambda_m = \Lambda_m^\infty$$

As we know ⇒ $\Lambda_m = \frac{K \times 1000}{M}$

∴ For saturated solⁿ ⇒ $\boxed{\Lambda_m^\infty = \frac{K \times 1000}{S}}$

Ques Calculate Λ_m^∞ for [illegible] AgOH If the ~~mol~~ Λ_m^∞ of [illegible] AgF, $Ca(OH)_2$ and CaF_2 are 104.6, 448 and 135 $S cm^2 mol^{-1}$ respectivity.

$$\Lambda_m^\infty(AgOH) = \Lambda_m^\infty(AgF) + \frac{\Lambda_m^\infty(Ca(OH)_2)}{2} - \frac{\Lambda_m^\infty(CaF_2)}{2}$$

$$= 104.6 + \frac{448}{2} - \frac{135}{2}$$

$$= 261.1 \, S cm^2 mol^{-1}$$

Ques $\Lambda_m^\infty(H_2CO_3) = ?$

$\Lambda_m^\infty(K_2CO_3) = 285.6 \, S cm^2 mol^{-1}$

$\Lambda_m^\infty(H_2SO_4) = 430 \, S cm^2 eq^{-1}$ ⇒ $\Lambda_m^\infty(H_2SO_4) = 430 \times 2 = 860 \, S cm^2 mol^{-1}$

$\Lambda_m^\infty(K_2SO_4) = 153.5 \, S cm^2 eq^{-1}$ ⇒ $\Lambda_m^\infty(K_2SO_4) = 153.5 \times 2 = 307 \, S cm^2 mol^{-1}$

$$\Lambda_m^\infty(H_2CO_3) = \Lambda_m^\infty(H_2SO_4) + \Lambda_m^\infty(K_2CO_3) - \Lambda_m^\infty(K_2SO_4)$$

$$= 860 + 285.6 - 307$$

$$= 838.6 \, S cm^2 mol^{-1}$$

<u>Ques</u> The Conductivity of 0.1M formic acid solution is $8\times10^{-3}\,Scm^{-1}$, then find the dissociation constent of formic acid by following data.

$$\Lambda_m^\infty[Mg(HCOO)_2] = 230\ Scm^2mol^{-1}$$

$$\Lambda_m^\infty[MgCl_2] = 280\ Scm^2mol^{-1}$$

$$\Lambda_m^\infty[HCl] = 425\ Scm^2mol^{-1}$$

$$\Lambda_m^\infty(HCOOH) = \frac{\Lambda_m^\infty[Mg(HCOO)_2]}{2} + \Lambda_m^\infty(HCl) - \frac{\Lambda_m^\infty[MgCl_2]}{2}$$

$$= \frac{230}{2} + \cancel{220}\ 425 + \frac{280}{2}$$

$$= 400\ Scm^2mol^{-1}$$

$$\Lambda_m^c = \frac{K\times1000}{M} = \frac{8\times10^{-3}\times1000}{0.1} = 80\ Scm^2\ mol^{-1}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\infty} = \frac{80}{400} = 0.2 \quad i.e \Rightarrow 20\%$$

$$Ka = \frac{C\alpha^2}{1-\alpha} \Big\} \quad As\ \alpha > 5\%$$

$$Ka = \frac{(0.1)(0.2)^2}{1-0.2} = 5\times10^{-3}$$

Date ________ Page ___

Ques The conductivity of a saturated solution of faric hydrooxy [$Fe(OH)_3$] is $8 \times 10^{-4}\ \Omega^{-1} cm^{-1}$ If the maxm molar conductivity of Fe^{+3} and OH^{-1} are 203 and 199 $\Omega^{-1} cm^{2} mol^{-1}$ then final out the solubility producted of $Fe(OH)_3$.

Solun:—

$$\Lambda^{m}_{\infty}[Fe(OH)_3] = \Lambda^{\infty}_{m}(Fe^{+3}) + 3 \cdot \Lambda^{\infty}_{m}(OH^{-})$$

$$= 203 + 3(199)$$

$$= 800\ S\,cm^2 mol^{-1}$$

$$\Lambda^{\infty}_{m} = \frac{K \times 1000}{S}$$

$$S = \frac{K \times 1000}{\Lambda^{\infty}_{m}} = \frac{\cancel{8} \times 10^{-4} \times 10\cancel{0}\cancel{0}}{\cancel{8}0\cancel{0}} = 10^{-3} M$$

$$Ksp = 27S^4 = 27(10^{-3})^4 = 2.7 \times 10^{-11}$$

Ques The Λ^{∞}_{m} of H^+ and CH_3COO^- are 340 and 44 $\Omega^{-1} cm^2 mol^{-1}$ respectivity if the molar conductivity of 0.008 M CH_3COOH solun of 48 $\Omega^{-1} cm^2 mol^{-1}$ then find out

(i) DOD (α) (i) 12.5%

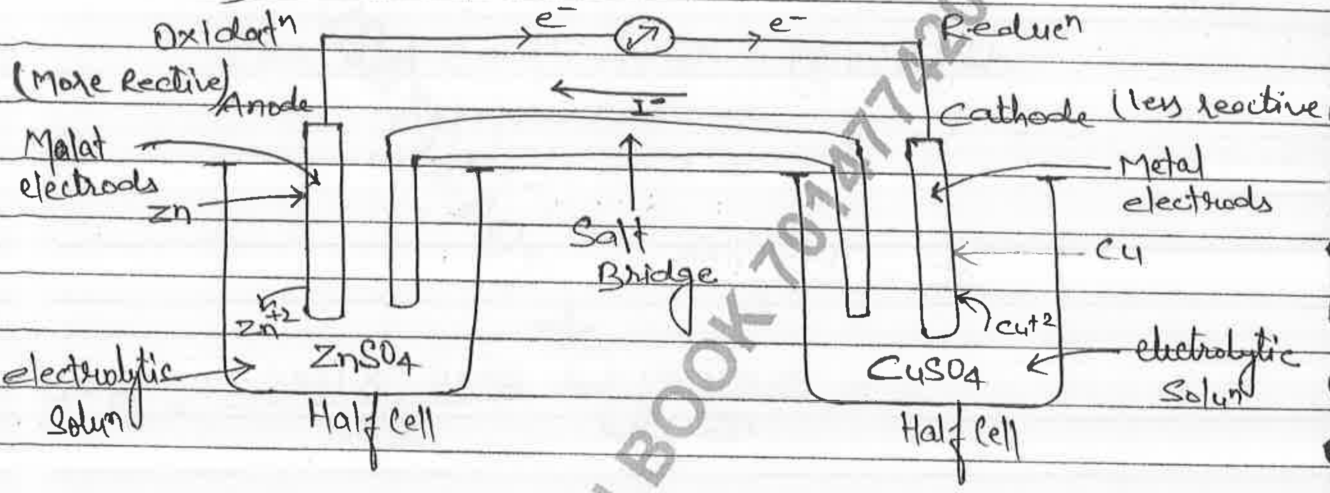
(ii) Dissociation const. (ii) $Ka = \frac{1}{7} \times 10^{-3}$.

(iii) P_H of 0.008 M CH_3COOH solu. pH = 3

Galvanic Cell/Voltaic Cell :—

It converts chemical energy into electrical energy by spon. redox rxn.

Ex — Daniell Cell



Anode :—

$Zn(s) \longrightarrow Zn^{+2}(aq.) + 2e^-$

(Oxidaⁿ half rxn)

Mass of Zn rod ↓ses and conc. of (Zn^{+2}) ↑ses.

Cathode :—

$Cu^{+2}(aq.) + 2e^- \longrightarrow Cu(s)$

(Reduction half Rxn)

Mass of Cu rod ↑ses. & Conc. of (Cu^{+2}) ↓ses

Complete cell Rxn :—

$Zn(s) + Cu^{+2}(aq.) \xrightarrow{n=2} Zn^{+2}(aq.) + Cu(s)$

Note :— On ↑sing the mass of Zn rod & ↑sing the conc. of (Cu^{+2}) in solun, then the diff of cell also ↑es.

Trick!!

L ⇒ Left O ⇒ Oxidation ⇒ A ⇒ Anode ⇒ N ⇒ Nega.

Salt Bridge & its functions:—

from Module

Representation of cell:—

(Oxidat^n) Anode A	(Salt) Bridge B	(Redu^n) Cathode C
Metal electrode | aq. Sol^n	||	aq. Sol^n | Metal electrode

Vertical line ⇔ | ⟹ Used for seperating out 2 diff. phases.

Electrode Potential:—

↳ It is the potential developed b/w the metal electrode and its ions in the solution.

There are of two types:—

① Oxidation potential (O.P. or E_{op}):—

↳ Electrode potential of oxidation half r^xn.

$$M_{(s)} \longrightarrow M^{n+}_{(aq.)} + ne^- ; \ O.P. = E_{M|M^{+n}}$$

* Tendency to get oxidised.

⇒ O.P. ∝ tendency to get oxidised.

Ex:- $Zn_{(s)} \longrightarrow Zn^{+2}_{(aq.)} + 2e^- \; ; \; E_{Zn|Zn^{+2}}$

$2Cl^-_{(aq.)} \longrightarrow Cl_2(g) + 2e^- \; ; \; E_{Cl^-|Cl_2}$

② Reduction potential (R.P. or $E_{R.P.}$) :—

↳ Electrode potential of reduction half r^xn.

$M^{n+}_{(aq.)} + ne^- \longrightarrow M_{(s)} \; ; \; R.P. = E_{M^{n+}|M}$

* Tendency to get reduced.

* R.P. ∝ Tendency to get reduced.

Ex. $Cu^{+2}_{(aq.)} + 2e^- \longrightarrow Cu(s) \; ; \; E_{Cu^{+2}|Cu}$

$Cl_2(g) + 2e^- \longrightarrow 2Cl^-_{(aq.)} \; ; \; E_{Cl_2|Cl^-}$

Electrode Potential depend on :—

(I) Nature of electrode

ernst eqn. { (II) Concentration of ions in soln
(III) Pressure
(IV) Temp.

Standard electrode potential :—

It is the potential developed b/w the metal electrode and its ions in soln and 1M concentration, 1 Bar pressure and 298 K temp.

$M_{(s)} \longrightarrow M^{n+}_{(aq.)} + ne^- \; ; \; SOP = E^\circ_{M|M^{+n}}$

$M^{n+}_{(aq.)} + ne^- \longrightarrow M_{(s)} \; ; \; SRP = E^\circ_{M^{n+}|M}$

for same electrode ⇒ (SRP = − SOP)

⇒ E° value of an ~~electro~~ element always remains constant.

⇒ Acc. to IUPAC, standard electrode potential is considered as SRP.

⇒ Standered Cell potential (E°_{cell})
or
Standard EMF of Cell

$$\boxed{E^\circ_{cell} = (SRP)_{cathode} - (SRP)_{Anode}}$$

Ques $Cr(s) \mid Cr^{+3}(aq.) \parallel Fe^{+2}(aq.) \mid Fe(s)$

$A \Rightarrow Cr(s) \longrightarrow Cr^{+3}(aq.) \quad \times 2$

$C \Rightarrow Fe^{+2}(aq) + 2e^- \longrightarrow Fe(s) \quad \times 3$

$2Cr(s) \longrightarrow 2Cr^{+3}(aq.) + 6e^-$

$3Fe^{+2}(aq.) + 6e^- \longrightarrow 3Fe(s)$

Overall $2Cr(s) + 3Fe^{+2}(aq) \xrightarrow{n=6} 2Cr^{+3}(aq) + 3Fe(s)$

Ques $Pt(s) \mid H_2(g) \mid H^+(aq) \parallel Cl^-(aq) \mid Cl_2(g) \mid Pt(s)$

$A \Rightarrow H_2(g) \longrightarrow 2H^+ + 2e^-$

$C \Rightarrow Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$

$H_2(g) + Cl_2(g) \xrightarrow{n=2} 2H^+(aq) + 2Cl^-(aq.)$

Ques $Pt(s) \mid I_2(g) \mid I^-(aq.) \parallel Br^-(aq) \mid Br_2(g) \mid Pt(s)$

~~$A \Rightarrow$ [illegible] $\longrightarrow 2I^- + 2e^-$~~

$A \Rightarrow 2I^-(aq.) \longrightarrow I_2(g) + 2e^-$

$C \Rightarrow Br_2(g) + 2e^- \longrightarrow 2Br^-(aq)$

$$2I^-(aq.) + Br_2(g) \xrightarrow{n=2} I_2(g) + 2Br^-(aq.)$$

Ques Determine the standard emf of the cell $Cr(s)|Cr^{+3}(aq.)||Fe^{+2}(aq.)|Fe(s)$ If $Cr(s) \longrightarrow Cr^{+3}(aq.) + 3e^-$; $E^\circ = 0.75V$ SOP

$Fe^{+2}(aq.) + 2e^- \longrightarrow Fe(s)$; $E^\circ = -0.45V$ SRP

SRP = −SOP = 0.75V

$E^\circ cell = (SRP)_C - (SRP)_A$

$= (-0.45) - (-0.75)$

$= +0.30V$

Ques find out the value of E°cell for the following rxn

$2Al + 3Sn^{+2} \longrightarrow 2Al^{+3} + 3Sn$

Given = $E^\circ_{Al^{+3}/Al} = -1.66V$ (A= SRP) ; $E^\circ_{Sn^{+2}/Sn} = -0.14V$ (C= SRP)

$E^\circ cell = (SRP)_C - (SRP)_A$

$= (-0.14) - (-1.60)$

$= 1.52V$

Ques Two Metals P and Q are connected to prepared a galvanic cell. If the standard electrode potential of P and Q are −0.28V and 1.40V respectively then find out standard electrode potential.

SEP = SRP

$(SRP)_P = -0.28V$ = SRP is less = SOP is more = easily oxid. ⇒ A.

$(SRP)_Q = 1.40V$ = SRP is more

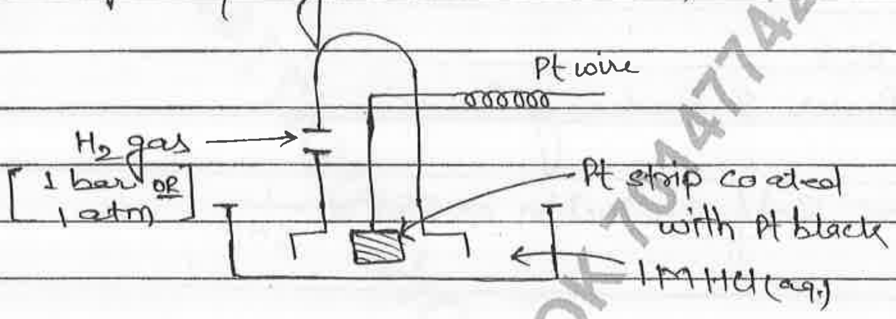
= SOP is less = catode

$$E^\circ_{cell} = (SRP)_C - (SRP)_A$$
$$= (1.40) - (-0.28) = 1.68 V$$

Reference Electrodes :—

① Primary reference electrodes

Standard Hydrogen electrode (SHE) :—



When act as Anode ;

$$H_2(g) \longrightarrow 2H^+(aq.) + 2e^-$$

Represatation

$$Pt(s) | H_2(g) | H^+(aq.)$$

When acts as a cathode

$$2H^+(aq.) + 2e^- \longrightarrow H_2(g)$$

Represatation

$$H^+(aq.) | H_2(g) | Pt(s)$$

Electrochemical Series :—

लेके भारत सरकार का नाम माँगे 'अली मकान पानी में जानकर फेके सीढ़ी कोई नीचे सुनो प्रभात है।

Cu

F_2

Hg → H

Ag → A

Br_2

Pt → P

Cl_2

Au → A

* In ECS, form top to bottom SRP $\uparrow$ses & SOP $\downarrow$ses

$\Rightarrow$ Li has min, SRP or max. SOP

$\Rightarrow$ F_2 has max. SRP or min. SOP

$\Rightarrow$ All elements above H_2 have (-)ive SRP value and below H_2 have (+)ive SRP.

Application of ECS

① Oxidising Power & Reducing Power:-

$$\text{Oxidising Power} \propto \text{Self Reduction} \propto SRP \propto \frac{1}{SOP}$$

$$\text{Reducing Power} \propto \text{Self-Oxidation} \propto SOP \propto \frac{1}{SRP}$$

$\Rightarrow$ Strongest O.A. = F_2

Strongest R.A. = Li

Remaning from module:-

(VI) Stability of metal oxides:-

Metal placed below Cu in ECS from less stable oxides & decomposes easily on heating.

Ex:- HgO, Ag_2O, etc.

Ex:- $Ag_2O \xrightarrow{\Delta} 2Ag(s) + \frac{1}{2}O_2(g)$

Ques Which of the following most reactive.

(i) Zn [✓ (ii) Mn] (iii) Hg (iv) Pb

$$\uparrow \text{Reactivity of metals} \propto SOP \propto \frac{1}{SRP\downarrow}$$

Ques WOF is strongest reducing agent.

(i) Na [✓ (ii) Ca] (iii) Ag (iv) Ni

$$\uparrow \text{Reducing Power} \propto SOP \propto \frac{1}{SRP}\downarrow$$

Ques WOF is strongest reducing agent.

(i) Li^+ (ii) Mg^{+2} [✓ (iii) Cu] (iv) Zn^{+2}

All element are allready oxidise.

Ques WOF is strongest reducing agent.

(i) Cl^- (ii) Br^- [✓ (iii) I^-] (iv) F^-

Ques WOF is strongest oxidising agent

(i) Cr^{+3} (ii) Sn^{+4} [✓ (iii) Ag^+] (iv) Fe^{+2}

$$\uparrow \text{Oxidising Power} \propto SRP \propto \frac{1}{SOP}\downarrow$$

Ques

[✓ (i) Cl_2] (ii) I^- (iii) Br_2^- (iv) F^-

Ques Arrange the following element in ↑ing order of reactivity and ↑ing order of oxidising power.

$$P^{2+} + 2e^- \longrightarrow P;\quad E^\circ = 1.90V$$

$$Q \longrightarrow Q^{2+} + 2e^-;\quad E^\circ = +0.7V = SOP = SRP = 0.72V$$

$R^{+2} + 2e^- \longrightarrow R$; $E^\circ = 0.53V$ = [illegible]

$S \longrightarrow S^{2+} + 2e^-$; $E^\circ = -0.88V$ = SOP ⇒ SRP ⇒ 0.88V

Solⁿ:- Ⓐ ↑ Reactivity of metals $\propto$ SOP $\propto \frac{1}{SRP}$ ↓

$P < S < Q < R$

Ⓑ ↑ Oxidising Power $\propto$ ↑SRP $\propto \frac{1}{SOP}$ ↓

$R < Q < S < P$

Nernst equation:—

It gives relation b/w electrode potential and conc. of electrolytic solution.

Nernst eqⁿ:- $\boxed{E = E^\circ - \frac{RT}{nF} \ln Q}$ — ①

$\therefore$ $\boxed{E = E^\circ - \frac{2.303RT}{nF} \log_{10} Q}$ — ② *

E = Electrode potential (in V)

E° = Standard electrode potential (in V)

R = Uni. gas Const.
(R = 8.314 J mol⁻¹ K⁻¹)

T = Temp. (in K)

n = No. of moles of e⁻ transfered in a balanced chemical rxn.

F = Faradays Const.
(F = 96500 C mol⁻¹) (charge on 1 mol e⁻)

Q = Reaction Quotient.

$$Q = \frac{[\text{Product}]_t^{s.c}}{[\text{Reactant}]_t^{s.c.}}$$

At 298K

$$\frac{2.303RT}{F} = \frac{2.303 \times 8.314 \times 298}{96500}$$

$$= 0.0591 \rightarrow \text{Put in ②}$$

$$\boxed{E = E^\circ - \frac{0.0591}{n}\log_{10}Q} \text{ — (iii)}$$

Application of Nernst Equation :—

from Modul —

Ques At 25°C Cr electrode is placed in 0.001M $Cr(NO_3)_3$ soln then determine the electrode potential of chromium (Cr).

given: ($E^\circ_{Cr^{+3}/Cr} = -0.75V$)

Soln —

E.P. = R.P.

$$Cr^{+3}_{(aq.)} + 3e^- \xrightarrow{n=3} Cr_{(s)} \qquad [0.001M\ Cr(NO_3)_3]$$

$$E_{RP} = E^\circ_{RP} - \frac{0.06}{3}\log_{10}\frac{1}{[Cr^{+3}]}$$

$$= -0.75 - 0.02\log_{10}\frac{1}{(10^{-3})}$$

$$= -0.75 - 0.02\log_{10}10^{3}$$

$$= -0.81V$$

Ques At 25°C Zn rod is placed in 0.1M $ZnSO_4$ solution in which the salt is 25% dicossiated then determine the reduction potential of zinc (given:- $E^\circ_{Zn/Zn^{+2}} = 0.76V$)

$E^\circ_{Zn^{+2}/Zn} = 0.76V = -0.76V$

$Zn^{+2}_{(aq)} + 2e^- \longrightarrow Zn(s)$

$E_{RP} = E^\circ_{RP} = \frac{-0.06}{2} \log_{10} \frac{1}{[Zn^{+2}]}$

$ZnSO_{4(aq)} \longrightarrow Zn^{+2}_{(aq)} + SO_{4(aq)}^{-2}$

$C \quad 0 \quad 0$

$C - C\alpha \quad C\alpha \quad C\alpha$

$[Zn^{+2}] = C\alpha = 0.1 \times \frac{20}{100}$

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

$= -0.76 - 0.03 \log_{10} \frac{1}{(2 \times 10^{-2})}$

$= -0.811$

Ques Determine the oxidation potential of hydrogen electrode which is dipped in a solution having a POH is 4.

$POH = 4 \quad pH = 10$

$E_{OP} = 0.0591 \times pH$
$= 0.0591 \times 10$
$= 0.591 V$

Ques Determine the reduction potential of the following half cell.

$Pt(s) | H_2(g, 4atm) | H_2SO_4(aq. 0.01M)$

$2H^+_{(aq)} + 2e^- \longrightarrow H_2(g)$

$E_{RP} = E^\circ_{RP} - \frac{0.06}{2} \log_{10} \frac{P_{H_2}}{(H^+)^2}$

For SHE ⇒ SRP = 0V = E°_{RP}

$E_{RP} = -0.03 \log_{10} \frac{4}{(2 \times 10^{-2})^2}$

$= -0.12V$

Ques Determine the reduction potential of the following half cell.

$Pt_{(s)} / Cl_2(g, 10atm) / HCl(aq, 0.1M)$

Given:- $E^\circ_{Cl_2}/Cl = 1.36V$

$Cl_{2(g)} + 2e^- \longrightarrow 2Cl^-_{(aq)}$

$$E_{RP} = E^\circ_{RP} - \frac{0.06}{2}\log_{10}\frac{(Cl^-)^2}{P_{Cl_2(g)}}$$

$$= 1.36 - 0.03\log_{10}\frac{(10^{-1})}{10}$$

$$= 1.45V$$

Ques A Ni rod is placed in Nickle sulphate ($NiSO_4$) solution. If the solution is 10times dilutaed then the electrodeed potential of nickel will be.

① ↑sed by 60mV
(II) ↓sed by 60mV
(III) ↑sed by 30mV
(IV) ↓sed by 30mV

ER = R.P.

$Ni^{+2}_{(aq.)} + 2e^- \longrightarrow Ni_{(s)}$

$$E_{RP} = E^\circ_{RP} - \frac{0.06}{2}\log_{10}\frac{1}{(Ni^{+2})}$$

Before Dilution

$(Ni^{+2})_i = 1M$

$$\therefore (E_{RP})_i = E^\circ_{RP} - 0.03\log\frac{1}{1}$$

$$(E_{RP})_i = E^\circ_{RP}$$

After Dilution

$(Ni^{+2})_f = \frac{1}{10}M$

$$(E_{RP})_f = E^\circ_{RP} - 0.03\log\left(\frac{1}{10}\right)$$

$(E_{RP})_f = (E_{RP})_{i} - 0.03$

$(E_{RP})_f - (E_R)_i = -0.03V$

$= -30mV$

Ques Determine the emf of the following cell.

$Cr_{(s)} | Cr^{+3} (0.1M) || Fe^{+2} (0.01M) | Fe_{(s)}$

Given :- $E^\circ_{Cr^{+3}/Cr} = -0.75V$

$E^\circ_{Fe^{+2}/Fe} = -0.45V$

$$2Cr_{(s)} + 3Fe^{+2}_{(aq.)} \xrightarrow{n=6} 2Cr^{+3}_{(aq.)} + 3Fe_{(s)}$$

$$E^\circ_{cell} = (SRP)_C - (SRP)_A$$
$$= (-0.45) - (-0.75)$$
$$= 0.30V$$

$$E_{cell} = E^\circ_{cell} - \frac{0.06}{6} \log_{10} \frac{(Cr^{+3})^2}{(Fe^{+2})^3}$$

$$= 0.30 - \frac{0.06}{6} \log_{10} \frac{(10^{-1})^2}{(10^{-2})^3}$$

$$= 0.26V$$

Ques Calculate the emf and the gibbs ~~enegy~~ energy change for the follasing cell.

$Pt_{(s)} | H_2(g) | H^+(0.01M) || Cl^-(0.01M) | Cl_2(g) | Pt_{(s)}$

Given :- $E^\circ_{Cl_2/Cl^-} = 1.36V$

$$H_{2(g)} + Cl_{(g)} \xrightarrow{n=2} 2H^+_{(aq.)} + 2Cl^-_{(aq.)}$$

$$E^\circ_{cell} = (SRP)_C - (SRP)_A$$

~~$= (SRP).$~~

$$= 1.36 - 0 = 1.36V$$

$$E_{cell} = E^\circ_{cell} - \frac{0.06}{2}\log_{10}\frac{(H^+)^2(Cl^-)^2}{P_{H_2} \times P_{Cl_2}}$$

$$= 1.36 - \frac{0.06}{2}\log_{10}\frac{(10^{-2})^2(10^{-2})^2}{1 \times 1}$$

$$= 1.60V$$

$$\Delta G = -nFE_{cell}$$

$$= \frac{-2 \times 96500 \times 1.60}{1000}$$

$$= -308.8 KJ$$

Que Calculate the value of equlbm constant and the standred gibbs energy change for the following cell.

$$Sr_{(s)} | Sr^{+2}_{(aq.)} || Mg^{+2}_{(aq.)} | Mg_{(s)}$$

~~$Sr_{(aq)} + 2e^- \rightarrow Sr_{(s)}$~~

~~$Sr_{(s)} + 2e^- \rightarrow Sr_{(aq.)}$~~

$$Sr_{(s)} + Mg^{+2}_{(aq.)} \xrightarrow{n=2} Sr^{+2}_{(aq.)} + Mg_{(s)}$$

$$E_{cell} = (SRP)_C - (SRP)_A$$

$$= (-2.37) - (2.89)$$

$$= 0.52V$$

Ⓐ $E^\circ_{cell} = \frac{0.0591}{n} \log_{10} K_{eq.}$ Ⓑ $\Delta G^\circ = nfE^\circ_{cell}$

$= \frac{-2 \times 96500 \times 0.52}{1000}$

$= -100.36 \text{ kJ}$

$0.52 = \frac{0.591}{2} \log_{10} k_{eq.}$

$\log_{10} k_{eq.} = \frac{0.52}{0.03} = 17.33$

$K_{eq.} = 10^{17.33} = 10^{17} \times 10^{0.33}$

$= 2.1 \times 10^{17}$

Ques The emf of the following rxn can be ↑ed by

$Sn^{+2}(aq.) + Cu^{+2}(aq.) \longrightarrow Sn^{+4}(aq.) + Cu(s)$

① ↑sing (Sn^{+2})

⑪ ↓sing (Sn^{+4})

⑪ ↑sing (Cu^{+2})

✓ ⑩ All of these

$E_{cell} = E^\circ_{cell} - \frac{0.06}{2} \log_{10} \frac{(Sn^{+4})}{(Sn^{+2})(Cu^{+2})}$

$\Downarrow$

$\uparrow E_{cell} = E^\circ_{cell} + \frac{0.06}{2} \log_{10} \frac{\uparrow(Sn^{+2})(Cu^{+2})\uparrow}{(Sn^{+4})\updownarrow}$

Ques $E^\circ_{Au^+/Au} = 1.69V$

$E^\circ_{Au^{+3}/Au} = 1.40V$

$E^\circ_{Au^{+3}/Au^+} = ?$

$Au^+ + e^- \xrightarrow{n=1} Au$ — ①

$Au^{+3} + 3e^- \xrightarrow{n=3} Au$ — ⑪

$Au^{+3} + 2e^- \xrightarrow{n=2} Au^+$ — ⑪

~~$E_3^\circ = \frac{3E_2^\circ - E_1}{2}$~~

~~$= \frac{3(1.40) - (1.69)}{2}$~~

③ = ② − ①

$\Delta G^\circ_3 = \Delta G^\circ_2 - \Delta G^\circ_1$

$(-2FE^\circ_3) = (-3FE^\circ_2) - (-1FE^\circ_1)$

$-2E^\circ_3 = -3E^\circ_2 + E_1$

$E^\circ_3 = \frac{3E^\circ_2 - E^\circ_1}{2}$

$$= \frac{3(1.40)-(1.69)}{2}$$

$$= 1.255V$$

Note:- Electrode potential is an intenive property so it is non-additive in nature but gibbs energy is an extensive nature so it is additive in nature.

Ques $E^\circ_{MnO_4^-/Mn^{+2}} = 1.51V$

$E_{MnO_2/Mn^{+2}} = 1.23V$

$E^\circ_{MnO_4^-/MnO_2} = ?$

$$MnO_4^- + 5e^- \xrightarrow{n=5} Mn^{+2}$$
$$MnO_2 + 2e^- \xrightarrow{n=2} Mn^{+2}$$
$$MnO_4^- + 3e^- \xrightarrow{n=3} MnO_2$$

③ = ① − ②

$$\Delta G^\circ_3 = \Delta G^\circ_1 - \Delta G^\circ_2$$
$$(-3FE^\circ_3) = (-5FE^\circ_1) - (-2FE^\circ_2)$$
$$-3E^\circ_3 = -5E^\circ_1 + 2E^\circ_2$$

$$E^\circ_3 = \frac{5E^\circ_1 - 2E^\circ_2}{3}$$

$$E^\circ_3 = \frac{5(1.51) - 2(1.23)}{3}$$

$$= 1.69V$$

Ques Determine the solubility product of AgI at 25°C with the help of following rxn.

$$Ag^+_{(aq)} + e^- \xrightarrow{n=1} Ag_{(s)},\ E^\circ = 0.80V$$
$$Ag_{(s)} + I^-_{(aq)} \xrightarrow{n=1} AgI,\ E = 0.15V$$

③ $AgI_{(s)} \xrightleftharpoons{n=1} Ag^+_{(aq.)} + I^-_{(aq)}$; $E^\circ = ?$

$E_{cell} = \underbrace{(SRP)_c}_{I} - \underbrace{(SRP)_A}_{Ag}$

$= (-0.152) - (0.80)$

$= -0.952$

~~Agl~~ ③ = −② − ①

$\Delta G^\circ_3 = -\Delta G^\circ_2 - \Delta G^\circ_1$

$-1FE^\circ_3 = -(-FE^\circ_2) - (-FE^\circ_1)$

$-E^\circ_3 = +E^\circ_2 + E^\circ_1$

$= (0.152 + 0.80)$

$E^\circ_3 = 0.952V$

$E_{cell} = \frac{0.0591}{n} \log_{10} k_{eq.}$

$0.952 = \frac{0.06}{1} \log_{10} Ksp$

$\log_{sp} = \frac{-0.952}{0.06} = -15.86$

$Ksp = 10^{-15.86} = 10^{-16} \times 10^{0.14}$

$= 1.5 \times 10^{-16}$

$\simeq 16.1$

$= 10^{-17} \times 10^{0.9}$

$= 8 \times 10^{-17}$

$= 0.8 \times 10^{-16}$

we consider = 0591
तो

Ques Determine the Ksp value of $PbI_{2(s)}$ at 25°c with the following rxn.

$Pb^{+2}_{(aq.)} + 2e^- \longrightarrow Pb_{(s)}$; $E^\circ = -0.121V$

$PbI_{2(s)} + 2e^- \longrightarrow Pb_{(s)} + 2I^-_{(aq)}$; $E^\circ = -0.365V$

$E^\circ = -0.244 = \frac{0.06}{2} \log ksp$

$$\log_{10} K_{sp} = -\frac{0.244}{0.03} = -8.13$$

$$K_{sp} = 10^{-8.13} = 10^{-9} \times 10^{0.87}$$

$$= 7.5 \times 10^{-9}$$

Ques If $E^\circ_{Fe^{+2}/Fe} = -0.441\,V$
$E^\circ_{Fe^{+3}/Fe^{+2}} = 0.771\,V$ then find out the standard emf of the following rxn.

$$Fe + 2Fe^{+3} \longrightarrow 3Fe^{+2}$$

~~$E_{cell} = (SRP)_c - (SRP)_a$~~

$$Fe + 2Fe^{+3} \longrightarrow 3Fe^{+2} \quad \text{— (iii)}$$

$$Fe^{+2} + 2e^- \xrightarrow{n=2} Fe \quad \text{— (1)}$$

$$Fe^{+3} + e^- \xrightarrow{n=1} Fe^{+2} \quad \text{— (2)}$$

$$(3) = -(1) + (2)$$

$$\Delta G^\circ_3 = -\Delta G^\circ_1 + 2(\Delta G^\circ_2)$$

$$-2FE^\circ_3 = -(-2FE^\circ_1) - 2(-1FE^\circ_2)$$

$$-E_1 = E^\circ_1 - E^\circ_2$$

$$E^\circ_3 = E^\circ_2 - E_1$$

$$= (0.771) - (0.441)$$

$$= 1.212\,V$$

OR

$$E^\circ_{cell} = (SRP)_c - (SRP)_A$$
$$= (0.771) - (0.441)$$
$$= 1.212\,V$$

Ques C ⇒ $E^\circ_{Cu^+/Cu} = 0.53V$
A ⇒ $E^\circ_{Cu^{+2}/Cu^+} = 0.15V$ then find out the standard emf of the following cell.

$$\overbrace{2Cu^+ \longrightarrow Cu}^{Red.} + Cu^{+2}$$
$$\underbrace{2Cu^+ \longrightarrow Cu + Cu^{+2}}_{oxdn.}$$

$$E^\circ_{cell} = (SRP)_c - (SRP)_A$$
$$= (0.53) - (0.15)$$
$$= 0.38$$

Ques If $E^\circ_{Cu^{+2}/Cu} = 0.34V$
$E^\circ_{Cu^{+2}/Cu^+} = 0.15V$ then calculate E°_{cell} for the following cell.

$$\overbrace{2Cu^+ \longrightarrow Cu + Cu^{+2}}^{oxide.}$$
$$\underbrace{2Cu^+ \longrightarrow Cu}_{Red^n}$$

$E^\circ_{Cu^+/Cu} = ?$

$\boxed{0.38}$

~~$E^\circ_{cell} = (SRP)_c - (SRP)_A$~~
~~$= (0.34) - (0.15)$~~
~~$= 0.19$~~

$$Cu^{+2} + 2e^- \longrightarrow Cu \quad — ①$$
$$Cu^{+2} + e^- \longrightarrow Cu^+ \quad — ②$$

③ = −2② + ①

$$\Delta G^\circ_3 = 2\Delta G^\circ_2 + \Delta G^\circ_1$$

~~* Conductivity :~~

* Concentration of Cell :—

It's a galvanic cell that comparises of 2 equivalent half cell of same material having diff. conc. of ion or pressure of gasses.

for a conc. cell as both cathod and anode are of same material i.e. $E^\circ_{cell} = 0$.

Ex. $Pt_{(s)} | H_2(g, P) | H^+(aq. c) || H^+(aq. c_2) | H_2(g, P_2) | Pt_{(s)}$

Que Determine the emf of the following cell.

$Zn_{(s)} | Zn^{+2}(aq. 0.01M) || Zn^{+2}(aq., 0.1M) | Zn_{(s)}$

$$Zn_{(s)} + Zn^{+2}(0.1M) \longrightarrow Zn^{+2}(0.01M) + Zn_{(s)}$$

$$E_{cell} = \underbrace{E^\circ_{cell}}_{0} - \frac{0.06}{2} \log_{10} \frac{(10^{-2})}{(10^{-1})}$$

$$E_{cell} = 0.03V$$

Que Determine the emf of the following cell.

$Pt_{(s)} | H_2(g, 10\,atm) | HCl(aq., pH = 2 | H_2(g, 2atm | Pt_{(s)}$

$$H_2(10\,atm) + 2H^+(10^{-2}M) \longrightarrow 2H^+(10^{-2}M) + H_2(2\,atm)$$

$$E_{cell} = \underbrace{E^\circ_{cell}}_{0} - \frac{0.06}{2} \log_{10} \frac{(10^{-2})^2(2)}{(10^{-2})^2(10)}$$

$$= 0.021V$$

Reversible Cells :—

from module

× — × — × — ×

Qualitative aspects of electrolysis :—

IV ① If more then one cation is present in electrolyti cell then that cation will be discharged (Reduced) at Cathode which has higher reduction potential.

ⓐ Cathode ⇒ Cations ⇒ Reduction

$Li^+, K^+, Ba^{+2} - - - - , H_2O, Zn^{+2} - - - - H^+, Cu^{+2}, Hg_2^{+2}, Ag^+, Pt^{+2}, Au^{+3}$

$\xrightarrow{\hspace{2cm}}$ SRP ↑ses.

Reduction ⇒ $2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq.)$; $E^\circ = -0.83V$

ⓑ If more than one anion is present in electrolytic cell then that anion will be discharge (oxidised) at anode which has higher oxidation potential or low reduction potential.

Anode ⇒ Anions ⇒ Oxidation

$SO_4^{2-}, NO_3^-, PO_4^{3-}, H_2O, Cl^-, Br^-, I^-$

$\xrightarrow{\hspace{2cm}}$ SOP ↑ses

Oxidation ⇒ $2H_2O \longrightarrow O_2(g) + 4H^+(aq.) + 4e^-$; $E^\circ = -1.23V$

Some examples :—

① Electrolysis of $AgNO_3(aq)$ using inert electrodes :—

$AgNO_3(aq) \Longrightarrow Ag^+, NO_3^-, H_2O$

Cathode ⇒ $Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$

Anode ⇒ $2H_2O \longrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$

Before electrolysis $AgNO_{3(aq)} \longrightarrow$ SAWB ~~⇒~~ Salt ⇒ Weakly acidic

After electrolysis formation of $HNO_{3(aq)}$ ⇒ SA ⇒ Strongly acidic
⇒ $P_H < 7$
⇒ P_H ↓es

④ Electrolysis of $AgNO_{3(aq)}$ using Ag electrodes: —
→ Reactive

$AgNO_{3(aq)} \Rightarrow Ag^+, NO_3^-, H_2O$

Cathode ⇒ $Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$

Anode ⇒ $Ag_{(s)} \longrightarrow Ag^+_{(aq)} + e^-$

⇒ P_H & conc. of solⁿ remains same.

Note: — If metals electrodes (reactive) is present in its electrolytic solⁿ, then —

Cathode ⇒ Metal cation is reduced.

Anode ⇒ Metal atom is oxidised.

p^H & conc. of solⁿ remains same.

⑤ Electrolysis of NaCl(aq.) using inert electrodes :-

$NaCl_{(aq.)} \Rightarrow Na^+, Cl^-, H_2O$

Cathode ⇒ $2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq.)$

Anode ⇒ $Cl^-(aq.) \longrightarrow \frac{1}{2}Cl_2(g) + e^-$

Before electrolysis $NaCl(aq.)$ ⇒ SASB Salt ⇒ Neutral ⇒ $pH = 7$

After electrolysis ⇒ Formation of $NaOH(aq.)$ ⇒ SB ⇒ Strongly Basic

⇒ $pH \Rightarrow 7$

⇒ pH ↑ses

⑥ Electrolysis of very dilute NaCl(aq.) using inert electrodes :-

$NaCl_{(aq.)} \Rightarrow Na^+, Cl^-, H_2O$

Cathode ⇒ $2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq.)$

Anode ⇒ $2H_2O \longrightarrow O_2(g) + 4H^+(aq.) + 4e^-$

On dilution ⇒ Vol. of soln ↑ ⇒ (Cl^-) ↓es

$$2Cl^-(aq.) \xrightarrow{n=2} Cl_2(g) + 2e^-$$

$$E_{op} = E^\circ_{op} - \frac{0.0591}{2}\log_{10}\frac{P_{Cl_2(g)}}{(Cl^-)^2}$$

$$\downarrow \therefore E_{op} = E^\circ_{op} + \frac{0.0591}{2}\log_{10}\frac{(Cl^-)^2}{P_{Cl_2(g)}} \downarrow$$

∴ Acc. to Nernst eqn.

$E_{op}(Cl^-) \downarrow$ es

∴ $E_{op}(H_2O) > E_{op}(Cl^-)$

So, H_2O will be oxidised.

⑦ Electrolysis of NaCl(aq.) using Hg Cathode and Graphite Anode:—

$NaCl(aq.) \Rightarrow Na^+, Cl^-, H_2O$

Anode $\Rightarrow 2Cl^-(aq.) \longrightarrow Cl_2(g) + 2e^-$

Cathode $\Rightarrow Na^+(aq.) + e^- \longrightarrow Na(s)$

$Na + Hg \longrightarrow$ Sodium Amalgam

Note :— Hg acts as a active electrode for Na^+ ion.

⑧ Electrolysis of dilute H_2SO_4 using inert electrodes:—

H^+, SO_4^{2-}, H_2O

Cathode $\Rightarrow 2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq.)$

Anode $\Rightarrow 2H_2O + \longrightarrow O_2(g) + 4H^+(aq.) + 4e^-$

⑨ Electrolysis of conc. H_2SO_4 using inert electrodes :—

H^+, SO_4^{2-}, H_2O

Cathode $\Rightarrow 2H^+(aq.) + 2e^- \longrightarrow H_2(g)$

Anode $\Rightarrow 2SO_4^{2-}(aq.) \longrightarrow S_2O_8^{2-}(aq.) + 2e^-$

Quantitative Aspects :—

$n F$ charge $\xrightarrow{\text{discharged}}$ 1 mol. of M^{n+}
$1 F$. charge $\longrightarrow \frac{1}{n}$ mol of M^{n+}

$\therefore$ No. of g eq. of M^{n+} = No. of mole × v.f.
(getting discharged by 1F charge) $= \frac{1}{n} \times n$
$= 1$ g eq.

$\because$ On farady is the charge required to discharged (deposit or liberate) 1g eq. or 'E' g (Eq. wt) of substance.

~~Note~~ .

$\boxed{1 \text{ mol. } e^- = N_A e^- = 96500C = 1F = 1 \text{geq.} = \text{'E' g of substa}}$

E = equivalent weight of substance.

First law of electrolysis :—

$W \propto Q$

$\boxed{W = ZQ = Zit}$ — ①

t → time (s)
i → Current (A)

If $Q = 1C \Rightarrow \boxed{W = Z}$

As we know,

If i.e. $96500C \xrightarrow{\text{Dicharged}}$ 'E' g of substance.

$1C \longrightarrow \frac{E}{96500}$ g of substance.

$$\therefore \boxed{Z = \frac{E}{96500}} \, g\, C^{-1} \Rightarrow \text{put in } ①$$

$$\boxed{w = \frac{EQ}{96500} = \frac{EIt}{96500}} \quad ②$$

$$\frac{w}{E} = \frac{It}{96500} = \text{No. of g eq.} = \text{No. of faraday.}$$

Second law of electrolysis:—

$$Na^{+} + e^{-} \longrightarrow Na_{(s)}$$
$$Mg^{+2} + 2e^{-} \longrightarrow Mg_{(s)}$$
$$Al^{+3} + 3e^{-} \longrightarrow Al_{(s)}$$

Na	Mg	Al
2F	2F	2F
46g	24g	18g
23 :	12 :	9

$$W \propto E$$

$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

Ques. Calculate the mass of Fe deposited when 4A current is passed for 15min. through $FeCl_2(aq.)$ solⁿ.

Solⁿ:-

$$Fe^{+2} + 2e^- \longrightarrow Fe_{(s)}$$

$$w = ZIt$$

$$w_{Fe} = \frac{56 \times 4 \times 15 \times 60}{2 \times 96500}$$

$$= \frac{56 \times 4 \times 900}{2 \times 96500}$$

$$= \underline{1.04g}$$

Ques How much current should be passed through molten Al_2O_3 for 10sec. to deposit 0.009 g Al metal.

$$w = ZIt \qquad 2Al^{+3} + 6e^- \xrightarrow{n=3} 2Al_{(s)}$$

$$0.009 = \frac{27 \times I \times 10}{3 \times 96500}$$

$$I = \underline{9.65A}$$

Ques Calculate the volume of $O_2(g)$ librated at STP when 5A current is passed for 80min. through $CdSO_4(aq.)$ solution.

Solⁿ:- Anode $= 2H_2O \longrightarrow O_2(g) + 4H^+(aq.) + 4e^-$

$$E_{O_2} = \frac{32}{4} = 8\,g\,eq.$$

~~w = 8 × [illegible] × [illegible] / 96500~~

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$$W = \frac{8 \times 5 \times 80 \times 60}{96500} = 1.99g \simeq 2g$$

$$n_{O_2} = \frac{2}{32} = \frac{1}{16} \text{ mol.}$$

$$\text{Vol. of } O_2 \text{ at STP} = \frac{1}{16} \times 22.4L = 1.4L$$

Ques When a certain amount of current is passed through NaCl(aq.) soln then 2.24 L of $Cl_2(g)$ is liberated at STP When the same amount of current passed through $AgNO_3$ (aq.) solution then determine the wt. of Ag metal deposited.

Soln:—

$$n_{Cl_2(g)} = \frac{2.24}{22.4} = 0.1 \text{ Mol}$$

$$W_{Cl_2(g)} = 0.1 \times 71 = 7.1g$$

$$\frac{W_{Cl_2}}{W_{Ag}} = \frac{E_{Cl_2}}{E_{Ag}}$$

NaCl(aq).

$$2Cl^-(aq.) \longrightarrow Cl_2(g) + 2e^-$$

$$E_{Cl_2} = \frac{71}{2} = 35.5$$

$$\frac{7.1}{W_{Ag}} = \frac{35.5}{108}$$

$$W_{Ag} = 21.6g$$

$AgNO_3(aq)$

$$Ag^+(aq.) + e^- \longrightarrow Ag(s)$$

$$E_{Ag} = \frac{108}{1} = 108.$$

Ques 3mol of e^- are passed through molten Al_2O_3, NaCl, and $CuSO_4$ then determine the ratio of No. of g.eq. No. of Mole & masses of respective metal.

63.5

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$2Al^{+3} + 6e^{-} \xrightarrow{n=3} 2Al_{(s)}$

[illegible]

3 mole e^{-} = 3F charge

① Ratio of no. of geq.

Al	Na	Cu
3	3	3
1 :	1 :	1

② Ratio of no. of moles

Al	Na	Cu
$\frac{3}{3}$	$\frac{3}{1}$	$\frac{3}{2}$

$\frac{1}{3} : 1 : \frac{1}{2}$ ×6

2 : 6 : 3

(III) Ratio of masses

Al	Na	Cu
3 :	3 :	3
1 :	1 :	1
$\frac{27}{3}$:	$\frac{23}{1}$:	$\frac{63.5}{2}$

9 : 23 : 31.75

Ques 96.5A current is passed for 10sec through 2l $CuSO_4$(aq.) solun then determine the pH of solun after electrolysis.

I = 96.5A

t = 10

Cathode ⇒ $Cu^{+2}_{(aq.)} + 2e^{-} \longrightarrow Cu_{(s)}$

Anode ⇒ $2H_2O \longrightarrow O_2(g) + 4H^{+}(aq.) + 4e^{-}$

After electrolysis ⇒ formation of H_2SO_4(aq.)

Amount of charge passed ⇒ Q = It

= 96.5×10

No. of faradays = No. of g.eq.

$\therefore$ No. of g. eq. of $(H^+) = 10^{-2}$ geq.

$$\text{Normality of } (H^+) = \frac{\text{No. of g eq.}}{\text{Vol. of solu}} = \frac{10^{-2}}{2} = 5\times10^{-3}\,N$$

$$\begin{aligned} pH &= -\log(H^+) \\ &= -\log(5\times10^{-3}) \\ &= 3 - \log 5 \\ &= 2.3 \end{aligned}$$

Ques 3.7A current is passed through 0.5L of 2M $CuSO_4$(aq.) solun for 6hr. then find out the molarity of solun after electrolysis.

Solun:-

Initial mole of Cu in Solun = M × Vol(L)
= 2 × 0.5 = 1 mol

Moles of cu deposited during electrolysis

$$W_{cu} = ZIt$$

$$= \frac{63.5 \times 3.7 \times 6 \times 60 \times 60}{2 \times 96500}$$

$$n_{cu} = \frac{63.5 \times 3.7 \times 6 \times 60 \times 60}{2 \times 96500 \times 63.5} = 0.4\ \text{mol}.$$

Remaining mole of Cu after electrolysis = 1 − 0.4
= 0.6 mol.

Conc. of solun after electrolysis $= \frac{0.6}{0.5} = 1.2M$

Ques Calculate the charge required to convert the following

(i) 5 mol BrO_3^- into Br^-

(ii) 200 ml 0.1M [illegible] MnO_4^- into Mn^{+2}

(iii) 2 mol Mn_3O_4 into ~~into~~ MnO_4^-

$$6H^+ + \overset{+5}{Br}O_3^- + 6e^- \longrightarrow Br^- + 3H_2O$$

1 mol ⟶ 6F Charge

(i) 5 mol ⟶ 6×5 = 30F Charge.

(ii) $MnO_4^- \longrightarrow Mn^{+2}$

Moles of MnO_4 = M × Vol.(L)

$= 0.1 \times \frac{200}{1000} =$

1 mol ⟶ 5F

0.02 mol ⟶ 5×0.02 = 0.1F

(iii) $\overset{+8/3}{Mn_3O_4} \longrightarrow 3\overset{+6}{MnO_4^{-2}}$

$6 - \frac{8}{3} = \frac{10}{3} \times 3 = 10$

1 mol ⟶ 10F

2 mol → 20F

Calculate the total vol. of gas produced at STP when dilute H_2SO_4 is electrolysis by using 2F charge.

C ⇒ $2H_2O + 2e^- \longrightarrow H_{2}(g) + 2OH^-(aq.)$

A ⇒ $2H_2O \longrightarrow O_2(g) + 4H^+(aq.) + 4e^-$

Mole of ~~eq~~ H_2 = $\frac{\text{no. of eq.}}{\text{V.f}} = \frac{2}{2}$ = 1 mol ⇒ 22.4L

Moles of O_2 = $\frac{\text{no. of eq.}}{\text{V.f}} = \frac{2}{4}$ = 0.5 mol = 11.2L

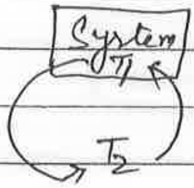
$\boxed{33.6L}$

Date ______ Page ___

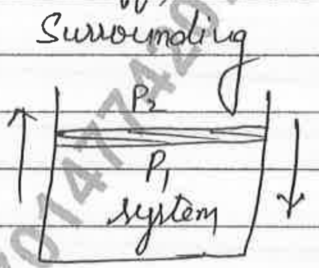
Thermodyamics

Modoes of transfer of energy :—

① Heat
(Due to temp. diff.)



(II) Work
(Due to pressure diff.)



① If $T_1 > T_2$
Heat is released or evolved by the system. (∴ energy of system ↓es)

∴ $q = -ve$

(II) If $T_1 < T_2$
Heat is absorbed by ~~its~~ the system. (∴ energy of system ↑es)

$q = +ve$

(III) If $T_1 = T_2$
Heat absorbed by the system = Heat released by the system.
(∴ Net heat flow is zero)
(Thermal eqm is attained)

① If $P_1 > P_2$

Work done by the system (∴ ~~work~~ energy of system ↓es)

(Expansion work)

∴ $W = -ve$

(II) If $P_1 < P_2$

Work is done ~~by~~ on the system (Compression work)

(∴ energy of system ↑es)

∴ $W = +ive$

(III) If $P_1 = P_2$

Work done by the system = W.D. on the system.

(∴ Net W.D. is zero)

(Mechanical eqm is attained)

Que A 2l gas expanded 12l against a const. external paressure of 2atm then Calculate W.D in Joule

$P_{ext.} = \text{const.}$ (Irr. process)

$$W = -P_{ext.}\,\Delta V$$
$$= 2 \times 10$$
$$= -20 \times 101.3 = 2026J$$

Que. 5l O_2 gas at 25°c temp. and 12atm pressure expands Isothermally against a constant ext. pressure of 2atm so that the finale pressure of gas become 2atm then calculate the W.D. in L-atm.

$P_{ext} = \text{const.}$ (Irr)

$$W = -P_{ext.}\,\Delta V$$
$$= -2(V_2 - V_1)$$
$$= -2(30 - 5)$$
$$= -50\ \text{L-atm}$$

$PV = nRT$

$P \propto \frac{1}{V}$

$\frac{P_1}{P_2} = \frac{V_2}{V_1}$

$12 = V_2$ ... $V_2 = 30l$

Internal energy (E/U) :—

⇒ E depends upon the physical state of a substance as follow:—

Solid < liquid < gas

$\longrightarrow$ E ↑ses

⇒ For an ideal gas, E is a function of temp. i.e. $E = f(T)$

for 1 mol ideal monoatomic gas $\Rightarrow E = \frac{3}{2}RT = K.E.$

$$\boxed{E \propto T}$$

Ques Calculate the change in internal energy of a system. If 100 cal. of heat is supplied to the system and 100 J of work is done on the surrounding.

$q = +100\,cal$
$= +420\,J$
$w = -100\,J$

$\Delta E = q + w$
$= +420 + (-100)$
$= \underline{320\,J}$

Ques If 4Kcal of heat is supplied to a gas and the volume of gas change from 5l to 55l against a constant external pressure 2atm then calculate the change in ΔE of gas. (cal)

$w = -P_{ext}\Delta V$

~~$\Delta E = q + w$~~

$= -2(55-5)$

$q = +4\,kcal = 4000\,cal$

$= -100\,L\,atm$

$= -100 \times 24.2$

$$\Delta E = q + w$$
$$= (4000) + (-2420)$$
$$= 1580 \text{ cal}$$

Que The change in internal energy of a gas when it expaind from a vol. of $0.001 m^3$ to $x\, m^3$ againt a constant a external pressure of $1 \times 10^5 N/m^2$ is 1KJ then determine the value of x If 100J of heat is release by the gas.

$$\Delta E = q + w$$
$$-1000 = -100 - 10^5 (x - 10^{-3})$$
$$-900 = -10^5 (x - 10^{-3})$$
$$9 \times 10^{-3} = x - 10^{-3}$$
$$x = 9 \times 10^{-3} + 10^{-3}$$
$$= 10 \times 10^{-3}$$
$$\boxed{x = 10^{-2} m^3}$$

Que find out the relation b/w ΔH and ΔE when 1 mole of propane undergoes complete cubustion at 25°c temp.

① $\Delta H > \Delta E$ (III) $\Delta H = \Delta E$
[✓ (II) $\Delta H < \Delta E$] (IV) N.O.T.

$$C_3H_8 + 5O_2(g) \longrightarrow 5CO_2(g) + 4H_2O(l)$$

$$\Delta n_g = 3 - 6 = -3$$

$$\Delta n_g < 0$$

Ques Calculate the diff. b/w heat at const. pressure and heat at const. volume when 1mole of liquid methenol undergoes complete combustion at 25°c temp.

$$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta ng = 1 - \frac{3}{2} = -\frac{1}{2}$$

$$\Delta H = \Delta E + \Delta ng RT$$

$$\Delta H - \Delta E = \Delta ng RT$$

$$= \frac{1}{2} \times 2 \times 298$$

$$= -298 \text{ kal}$$

Ques for a gasses rxn $2A + 3B \longrightarrow C + 2D$ If 20 KCal of heat is evolved at const. volume then determine the heat of rxn at constant pressure at 500°c temp.

(I) 18kcal

(II) -18kcal

(III) 22kcal

(IV) -22kcal

$$2A + 3B \longrightarrow C + 2D$$

$$\Delta ng = 3 - 5 = -2$$

$$\Delta H = \Delta E + \Delta ng RT$$

$$= -20 + (-2)\frac{(2)}{1000}500$$

$$= -22 \text{ Kcal}$$

★★★★

Ques The heat of vaporisation of water is 40.63 KJ/mol then determine the change in internal ~~eng~~ energy for the vapourisation of water.

$$H_2O(l) \xrightarrow[100°C]{1atm} H_2O(g)$$

$$\Delta H = \Delta E + \Delta ng RT$$

$$\Delta ng = 1 - 0 = 1$$

$$\Delta E = \Delta H - \Delta n_g RT$$
$$= 40.63 - \frac{(1)(8.314)(373)}{1000}$$
$$= 37.53\, KJ\, mol^{-1}$$

Ques The heat of vapourisation of liquid is 20Kcal mol⁻¹ then find out then change in internal energy for the vapourisation 4 moles of liquid at 500K temp.

(I) 16Kcal (III) 76Kcal ✓

(II) 19Kcal (IV) 79 kcal

Liquid ⟶ Gas

$\Delta n_g = 4 - 0 = 4$

for 4 moles = $\Delta H = 20 \times 4 = 80$ Kcal.

$$\Delta H = \Delta E + \Delta n_g RT$$
$$\Delta E = \Delta H - \Delta n_g RT$$
$$= 80 - \frac{4(2)\,50\cancel{0}}{100\cancel{0}}$$
$$= 76\, Kcal$$

Ques A non-ideal gas undergoes a changes of state from (2atm, 3Lit., 80K) to (4atm, 5L, 245K) If the change in internal energy is 30Lit atm, then determine the change in enthalpy of gas.

$$\Delta H = \Delta E + (P_2V_2 - P_1V_1)$$
$$= 30 + (4 \times 5 - 2 \times 3)$$
$$= 44\, L\, atm$$

Ques 1L of an ideal gas is heated at a constant pressure until its vol. double If the external pressure was 1atm and 300J of heat was supplied to the gas then determine the value of ΔH & ΔE for the gas.

$q_p = \Delta H = 300J$

$\Delta H = \Delta E + P\Delta V$

$\Delta E = \Delta H - P\Delta V$

$= 300J - 1(2-1)L\,atm$

$= 300J - 101.3J$

$= \underline{198.7J}$

H.W

Ques The heat of combution of benzene in bomb calorimeter at 27'C is $-100KJ\,mol^{-1}$ then calculate the heat of combution of benzene at const. pressure at the same temp.

Heat Capacity :—

Que The specific heat capacity of Ar at const volume is 0.075 cal $g^{-1} K^{-1}$ then determine its molar heat capacity at const. P & V.

(M.w = 40 Ar)

$(C_s)_v = 0.075 \, cal \, g^{-1} K^{-1}$

$(C_m)_v = (C_s)_v \times$ Molar mass

$= 0.075 \times 40$

$(C_m)_v = 3 \, cal \, mol^{-1} K^{-1}$

$C_p - C_v = R$

$C_p = R + C_v$

$= 2 + 3 = 5 \, cal \, mol^{-1} K^{-1}$

Que 5 mole of O_2 gas was heated to raise its temp from 25°C to 35°C then determine ~~the~~ Change in internal energy of O_2 gas If its molar heat capacity at constant pressure is $7 \, cal \, mol^{-1} K^{-1}$

~~ΔE~~ $\Delta E = n (C_m)_v \Delta T$

$= 5 \times 5 \times 10$

$= 250$ Cal

$(C_m)_p = 7$

$C_p - C_v = R$

$C_v = C_p - R$

$= 7 - 2 = 5 \, cal \, mol^{-1} K^{-1}$

Que Calculate the amount of heat requi to raise the temp of 9g of water from 298K to 308K If its heat Capacity is ~~kg~~

(i) $1 \, J/K \Rightarrow 10$

(ii) $1 \, J \, mol^{-1} K^{-1} \Rightarrow 5$

(iii) $1 \, J g^{-1} K^{-1} \Rightarrow 90$

(i)

$q = C \cdot \Delta T$

$= 1 \times 10$

$= 10 J$

(ii)

$q = n C_m \Delta T$

$= \frac{9}{18} \times 1 \times 10$

$= 5 J$

(iii)

$q = m C_s \Delta T$

$= 9 \times 1 \times 10$

$= 90 J$

Ques The capacity of water at const. pressure is $75\ J\ mol^{-1} K^{-1}$ If 1KJ of heat is supplied to 100gm of water at const. pressure then determine the change the temp. of water.

$$(C_M)_p = 75\ J mol^{-1} K^{-1}$$

$$q_p = \Delta H = 1KJ$$

$$\Delta H = n (C_m)_p \Delta T$$

$$1000 = \frac{100}{18} \times 75 \times \Delta T$$

$$\Delta T = 2.4°c \text{ or } K$$

Ques Calculate the value of ΔH & ΔE for a solid of mass 1kg when it is heated from 30°c to 80°c Considered the the vol. Change is negliable and heat capacity is $2 g^{-1} °c^{-1}$

$$\cancel{\Delta H}\ q = q_v = \Delta E$$

$$\Delta E = m (C_s)_v \Delta T$$

$$= 1000 \times 2 \times 50$$

$$= 10^5 J = 100 KJ$$

Vol. change is negligible.

$$\Delta H = \Delta E + \underset{0}{\underset{\Downarrow}{P\Delta V}}$$

$$\therefore \Delta H = \Delta E = 100KJ$$

Ques At 300°c temp. 60g of ethene gas was heated If 900 cal of heat was supplied to the gas then determine the final temp. of the gas If the vessel has (given $C_p = 7 cal\ mol^{-1} k^{-1}$)

① Closed, rigid wall

(ii) freely movable piston

① V = Const.

$$q = q_v = \Delta E$$

$$\Delta E = n (C_m)_v \Delta T$$

$$900 = \frac{60}{28} \times 5 \times \Delta T$$

$$\Delta T = 84$$

$$T_f - 300 = 84$$

$$T_f = 384K$$

⑪ $q = q_p = \Delta H$ (P=const.)

$\Delta H = n c_p \Delta T$

$900 = \frac{60}{28} \times 7 \times \Delta T$

$\Delta T = 60$

$T_f - 300 = 60$

$T_f = 360K$

Work done in diff. Process :-

Ques At 27°c 3mole of an ideal gas undergoes a change in volume from 10l to 20l reversibly and isothermally then Calculate the value of W.D., heat and change in internal energy for the gas (in KJ)

$$W = -2.303\, nRT \log_{10}\left(\frac{V_2}{V_1}\right)$$

$$= -2.303 \times 3 \times \frac{8.314}{1000} \times 300 \log_{10}\left(\frac{20}{10}\right)$$

$$= \frac{-19.15 \times 9 \times 0.3}{10} = -5.17\ KJ$$

Isothermal Ideal As $\Delta T = 0$ $\Delta E = 0$

So, $q = -W = -(-5.17)$

$$\boxed{q = 5.17\ KJ}$$

Ques At 27°c temp. 2mole of an ideal gas at an initial pressure of 2atm are compress isothermally against a constant external pressure to half of its initial vol. then Calculate the value of W.D., heat and I.E.?

Pext. = Const.

Irr. process $W = \cancel{2.303 nRT}$

$= \cancel{2.303(2)(8.314)(300)}$

~~$W = -P_{ext} \Delta V$~~

Acc to Boyles law

$$\frac{P_1}{P_2} = \frac{V_2}{V_1}$$

$$\frac{2}{P_2} = \frac{12.3}{24.6}$$

$$P_2 = 4 atm = P_{ext}$$

$$V_1 = \frac{nRT}{P_1} = \frac{(2)(0.0821)(300)}{(2)}$$

$$V_1 = 24.6L$$

$$V_2 = \frac{V_1}{2} = 12.3L$$

$$W = -P_{ext} \cdot \Delta V = 4(12.3 - 24.6) = 49.2 \; Latm$$

As $\Delta T = 0$; $\Delta E = 0$

$$q = -w = -49.2 \; Latm$$

OR

$$W = -nRT\left(1 - \frac{P_2}{P_1}\right)$$

$$= -(2)(0.0821)(300)\left(1 - \frac{2P_1}{P_1}\right)$$

$$= 49.2 \; Latm$$

Ques At 27°c temp. 1mole of an ideal gas expands reversally and adibatically. If 3KJ of work is obtained from a gas then determine the final temp. of the gas. (Given $C_v = 20 J mol^{-1} K^{-1}$)

~~(I) 150K~~
(II) 300K
(III) 450K
(IV) N.O.T.

$$W = nC_v \Delta T$$

$$-3000 = 1 \times 20 \Delta T$$

$$\Delta T = \frac{-3000}{20}$$

$$= -150$$

$$T_f - 300 = -150$$

$$T_f = 150K$$

Ques Calculate the W.D. for the vapourisation 1 mole of water.

Solⁿ:—

$$H_2O(l) \xrightarrow[100^\circ C]{1atm} H_2O(g)$$

~~W.D. =~~

$$\Delta n_g = 1-0 = 1$$

$$W = -\Delta n_g RT$$

$$= -1(2)(373$$

$$= -746 Cal.$$

Q An ideal gas compressied reversilbily and isothermally from a state of (0.5 atm, 40l) to (1atm, 20l) than Calculate the value of W.D.

$$W.D. = -2.303\, nRT \left(\frac{V_2}{V_1}\right)$$

$$= -2.303 \times 20 \left(\frac{20}{40}\right)$$

$$= 13.8\ L\,atm$$

$$T = \frac{P_1V_1}{nR} = \frac{P_2V_2}{nR}$$

$$= \frac{0.5 \times 40}{} = 20$$

Acc. to Boyle law

PV = const.

$$P_1V_1 = P_2V_2 = nRT$$

$$\boxed{20 = nRT}$$

Ques At 300K temp. 1 mole of an ideal gas undergoes a change pressure from 2atm to 1atm isothermally. then Calculate the W.D. If

① P change gradually (slow)

(II) P change ~~[illegible]~~ steply. (Sudden large change.)

①

$$W.D. = -2.303\, nRT \log_{10}\left(\frac{P_1}{P_2}\right)$$

$$= -2.303(1)\left(\frac{8.314}{1000}\right)(300) \log_{10}\left(\frac{2}{1}\right)$$

$$= -1.7\ KJ$$

(ii) $W = -nRT\left(1-\frac{P_2}{P_1}\right)$

$= -(1)\frac{(8.314)}{1000}\left(1-\frac{1}{2}\right)$

$= -1.24\,KJ$

Expansion $2\,atm \longrightarrow 1\,atm$

$(P\downarrow\ V\uparrow)$

$|W_{rev.\ iso.}| > |W_{irr.\ iso.}|$

Compression $1\,atm \longrightarrow 2\,atm$

$(P\uparrow\ V\downarrow)$

$|W_{rev.\ iso}| < |W_{irr.\ iso}|$

ENTROPY

Ques Calculate the entropy change of when 10 mole of an ideal gas undergoes a change in pressure from 10 atm to 1 atm rev. and isothermally at 300 K temp.

$\Delta S = 2.303\,nR\log\left(\frac{10}{1}\right)$

$= 2.303\times10\times2\log_{10}\left(\frac{10}{1}\right)$

$= 2.303\times20\log_{10}10$

$= 2.303\times20\times1 = 46.06\ Cal^{-1}K^{-1}$

Ques Calculate the entropy change for the conversion of 1 g of ice into water if the enthalpy of fusion of water is 6 KJ/mol.

$\Delta S = \frac{\Delta H}{T}$

$= \frac{6000}{273} = 21.97\ J\,mol^{-1}K^{-1}$

for 1g of H_2O :-

$$\Delta S = \frac{6000}{273} \times \frac{1}{18} = 1.2 JK^{-1}$$

Ques The heat of vapourisation of liquid is 60 KJ mol^{-1} and its entropy of vapourisation is 200 J $mol^{-1}K^{-1}$ then determine the bolloing point of liquid.

$$\Delta S = \frac{\Delta H}{T_{B.P.}}$$

$$T_{B.P.} = \frac{\Delta H_{vap.}}{\Delta S_{vap.}} = \frac{\overset{3}{\cancel{6}0} \times 10\cancel{0}\cancel{0}}{\cancel{2}\cancel{0}\cancel{0}} = 300K$$

Ques The entropy of H_2, O_2 & H_2O is 192, 205 and 210 J $mol^{-1}K^{-1}$ respecti.. then determine the entropy change for the formation of 2 mole of water

~~ΔS~~ $2H_2 + O_2 \longrightarrow 2H_2O$

$$\Delta S_{RXN} = \sum S_{(prod.)} - \sum S_{(React.)}$$

$$= [2(210) - [2(192) + 205]$$

$$= -169 JK^{-1}$$

Ques for an ideal gas $C_p = 2.5R$ then determine the entropy change for 3 mole of gas ~~where it is~~ when it is heated from 300K to 600K at (cal.)

① Const. P.

⑪ Const. Volume

~~$\Delta S = nC_p \log$~~

① $\Delta S = 2.303\, nC_p \log\left(\frac{T_2}{T_1}\right)$

$= 2.303 \times 3\, (2.5R) \log_{10}\left(\frac{600}{300}\right)$

$= 2.303 (3) (2.5R) \log 2$

$= 10.35\ Cal\,K^{-1}$

⑪ $\Delta S = 2.303\, nC_v \log\left(\frac{T_2}{T_1}\right)$

$= 2.303 (3) (1.5R) \log\left(\frac{600}{300}\right)$

$= 2.303 (3) (1.5R) \log (2) (0.3)$

$= 6.2\ Cal\,K^{-1}$

Ques: If 900J of heat is required for the vapourisation of 1g of water then Calculate the entropy of vapourisation of water.

$$\Delta S = \frac{\Delta H_{vap}}{T_{B.P.}} = \frac{900 \times 18}{373}$$

$$= \frac{16200}{373} = 43.45 \, mol^{-1} K^{-1}$$

Gibb's energy (G or F):—

$$\boxed{G = H - TS}$$

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

$$\boxed{\Delta G_{sys.} = -T\Delta S_{total}}$$

ΔG & Temp. dependence:—

Case-1 $\Delta H = -ve$

$\Delta S = +ve$

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

$= -ve - ve$

$\therefore \boxed{\Delta G = -ve}$

Process is spontaneous at all temp.

Case-2 $\Delta H = +ve$

$\Delta S = -ve$

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

$= +ve - (-ve)$

$\therefore \boxed{\Delta G = +ve}$

Process is non spontaneous at all temp.

Case-3 $\Delta H = -ve$

$\Delta S = -ve$

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

$= -ve + ve$

(a) At low temp.

$\Delta H > T\Delta S$

$\therefore \boxed{\Delta G = -ve}$

Spontaneous at low temp.

(b) At high temp.

$\Delta H < T\Delta S$

$\therefore \boxed{\Delta G = +ve}$

Case 4 $\Delta H = +ve$

$\Delta S = +ve$

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

$= +ve + ve$

ⓐ At low temp.

$\Delta H > T\Delta S$

$\Delta G = +ve$

Non-spontaneous

ⓑ At high temp.

$\Delta H < T\Delta S$

$\Delta G = -ve$

Spontaneous

Note:—

Endo — High temp. is favourble.

Exo. — low temp is favourble.

Ques for a rxn $2A + B \longrightarrow C$ then enthapy and entropy charge are 400KJ and $200\,J\,\cancel{K}^{-1}$ respect. then determine the temp above which the rxn will become spontaneous.

$\Delta G < 0$

$\Delta H - T\Delta S < 0$

$\Delta H < T\Delta S$

$T > \frac{\Delta H}{\Delta S}$

$\boxed{T = \frac{\Delta H}{\Delta S}}$

ये Eqm का temp. है

Endo → above which

Exo → below which.

$T > \frac{400 \times 1000}{200}$

$\boxed{T > 2000\,K}$

Ques for a rxn the values of ΔH & ΔS are found to be 15KJ and 20 Cal K^{-1} respectiv. at 500 K temp. then determine the rxn will be spontaneous or not at the given temp.

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

$= \cancel{15}\,15 - 500\left(\frac{20}{1000}\right)$

$= 5\,kcal.$

$\boxed{\Delta G > 0}$ Non-Spon.

Ques At 300K for a rxn $N_2 + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$ If the equilliᵐ partical pressure of each reactant & product is found to be 0.1Atm then Calculate the standred gibb energy of the rxn.

जब भी gases की बात होगी तब Kp से ही बात करेंगे।

$$\cancel{\Delta G} \quad K_p = \frac{(0.1)^2}{(0.1)(0.1)^3} = 100$$

$$\Delta G^\circ = -2.303\, RT \log_{10} K_p$$

$$= -2.303 \frac{(8.314)}{1000} (300) \log_{10}(100)$$

$$= -11.5\, KJ$$

Ques Calculate the standered gibb energy change for the following rxn.

$$2SO_{2(g)} + O_{2(g)} \longrightarrow 2SO_{3(g)}$$

$$\Delta G^\circ [SO_{2(g)}] = -300.2\, KJmol^{-1}$$

$$\Delta G^\circ [SO_{3(g)}] = -371.1\, KJmol^{-1}$$

$$\Delta G^\circ_{Rxn} = \sum \Delta G_{(prod.)} - \sum \Delta G_{(React.)}$$

$$= [2(-371.1)] - [2-(-300.2)]$$

$$= -141.8\, KJ$$

Ques for the rxn the value of enthalpy change & entropy change are found to 29KJ and $-35JK^{-1}$ respectivily. then determine the temp above of which the rxn will become spontaneous.

the rxn will Non-spontaneous at all temp.

Ques for a rxn $2A_{(g)} \longrightarrow B_{(g)} + 3C_{(l)}$ If the value of ΔE is equal to 4.2Kcal and $\Delta S = 40\, cal\, K^{-1}$ respectively at 300K temp. then Calculate the value of ΔG for the rxn.

$\Delta n_g = 4-2 = \underline{2}$

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

$= 5.4 - 300 \times \frac{40}{1000}$

$= -6.6\ KCal$

$\Delta H = \Delta E + \Delta n_g RT$

$= 4.2 + \frac{2 \times 2}{1000}(300)$

$= 5.4\ KCal.$

Ques for a process $\Delta S_{total} = 20\ KJ\ mol^{-1} K^{-1}$ & $\Delta H_{system} = 1000\ KJ\ mol^{-1}$ at 300K temp then determine ΔS for the ~~system~~ process.

~~$\Delta S =$~~ $\Delta G_{sys.} = -T\Delta S$

$= -300(20)$

$= -6000\ KJ\ mol^{-1}$

$\Delta G_{sys.} = \Delta H_{sys.} - T\Delta S_{sys.}$

$T\Delta S_{sys} = \Delta H_{sys.} - \Delta G_{sys.}$

$\Delta S_{sys.} = \frac{\Delta H_{sys.} - \Delta G_{sys.}}{T}$

$= \frac{1000 - (-6000)}{300} = \frac{7000}{300} = 23.3\ KJ\ mol^{-1} K^{-1}$

Ques Calculate the stadred for the following ~~the~~ rxn at 300K temp.

$V_{(s)} + 2Br_{2(l)} \longrightarrow VBr_{4(s)}$; $\Delta H = -820\ KJ$

Given :- $S^\circ[V(s)] = 50\ J\ mol^{-1} K^{-1}$

$S^\circ(Br_{2}(l)) = 152$

$S^\circ(VBr_4(s)) = 242$