Assignment [Chemistry]

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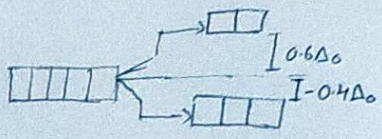
1) Calculate the CFSE for high spin and low spin octahedral complexes having d^5, d^6, d^8 configurations and comment on the magnetic nature

d^5 → high spin

$t_{2g}^3\ eg^2$

$-0.4\times3 + 0.6\times2 = -1.2 + 1.2$

$= 0\ \Delta_o$



If is paramagnetic

→ Low spin

$t_{2g}^5\ eg^0$

$-0.4\times5 + 0\times0.6 = -2\Delta_o$

If is paramagnetic

d^6 high spin

$t_{2g}^4\ eg^2$

$= -0.4\times4 + 0.6\times2 = -1.6 + 1.2 = -0.4\Delta_o$

If is paramagnetic

Low spin

$t_{2g}^6\ eg^0$

$= -0.4\times6 + 0.6\times0 = -2.4\Delta_o$

It is diamagnetic

d^8

high spin

$t_{2g}^6\ eg^2$

$= -0.4\times6 + 0.6\times2 = -2.4 + 1.2 = -1.2\Delta_o$

If is paramagnetic

Low spin

$t_{2g}^6\ eg^2$

$= (-0.4)\times6 + (0.6)\times2$

$= -1.2\Delta_o$

If is paramagnetic

2) Arrange the following in the increasing order of atomic radii and give reasons
N, S, P, O

Atomic radii increasing down the group and decreases left to right across the period.

Oxygen < Nitrogen < Sulphur < Phosphorus

Nitrogen and phosphorus is of same group (15) N < P, oxygen and sulphur is of same group 16, O < S, Nitrogen & oxygen is of same period 2, Phosphorus and sulphur is of same period 3

3) Calculate the difference between

a) Zeff for a 2p and a 3d electron in Nickel

$[Ni] = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$

In 2p $\Rightarrow S = 0.35 \times 7 + 0.85 \times 2 = 4.15$

$\therefore Zeff = Z - S = 28 - 4.15$

$= 23.85$

In 3d

$S = .1 \times 18 + 0.35 \times 7$

$= 20.45$

$\therefore Zeff = Z - S = 28 - 20.45$

$= 7.55$

The difference $= 23.85 - 7.55$

$= 16.3$

b) 1s And 3d Electron in Scandium

$[Sc] = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$

In 1s $\Rightarrow S = 0.35 \times = 0.35$

$Zeff = 21 - 0.35$

$= 20.65$

In 3d $\Rightarrow S = 1 \times 18 + 0.35 \times 6 = 18$

$= 18$

$Zeff = 21 - 18$

$= 3$

The difference $= 20.65 - 3$

$= 17.65$

4) Derive Nernst Equation

$E^\circ = \mathcal{E}^\circ_{red} - \mathcal{E}^\circ_{oxi}$

$\Delta G^\circ = -nF\mathcal{E}^\circ$ [under standard condition]

Gibbs Energy change under non-standard condition can be related to Gibbs Energy change under standard condition via

$\Delta G = \Delta G^\circ + RT\ln Q$

$-nF\mathcal{E} = -nF\mathcal{E}^\circ + RT\ln Q$

$\mathcal{E} = \mathcal{E}^\circ - \frac{2.303RT}{nF}\log_{10} Q$

$\mathcal{E} = \mathcal{E}^\circ - \frac{0.0592V}{n}\log_{10} Q$

b) Explain the significance of Gibbs-Helmholtz Equation

Significance of Gibbs-Helmholtz Equation

The Gibbs-Helmholtz equation is a thermodynamic equation used for calculating changes in the Gibbs energy of a system as a function of temperature where H is the enthalpy, T is the absolute temperature and G is the Gibbs free energy of the system, all at constant pressure P

$$\left[\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right]_P = \frac{-H}{T^2}$$

The Equation states that the change in the G/T ratio at constant pressure as a result of an infinitely small change in temperature is a factor of H/T^2

5) Hydrochloric Acid (HCl) reacts with potassium hydroxide (KOH) to form Potassium chloride (KCl) and water. If $\Delta H^\circ = -56.13$ KJ/mol And $\Delta S = 79.11$ J/mol.K what is ΔG° for this reaction at 20°C?

$HCl + KOH \longrightarrow KCl + H_2O$

$\Delta H^\circ = -56.13$ KJ/mol $\quad \Delta S^\circ = 79.11$ J/mol·K. $\quad T = (273.15 + 20)K = 293.15K$.

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

$= -56130 - (293.15) \times (79.11)$

$= -56130 - 23191.09$ J/mol.

$= 79321.09$ J/mol

$= 79.32$ KJ/mol

Q6

Give reasons for the following

(a) Ongoing from C to N in the second period, the values electron affinity decrease instead of increasing

The Electron affinity decreases because going from C to N in the second period because the configuration of N i.e $1s^2 2s^2 2p^3$ is more stable than of C i.e $(1s^2 2s^2 2p^2)$ as Nitrogen has half filled p-orbital which is stable.

(b) Ca^{2+} has smaller ionic radius than K^+

Ca^{2+} has smaller ionic radius than K^+ because Ca^{2+} has higher Effective nuclear charge due to which electron are attracted towards nucleus of atom. Thus reducing size of atom or ionic radius.

Q7

With a neat sketch Explain all the salient features seen in Pourbaix diagram for iron

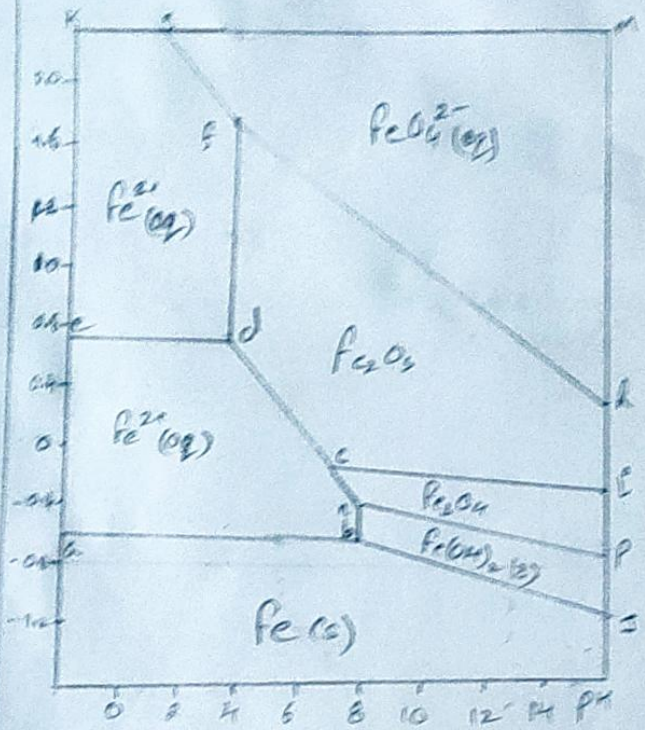
Pourbaix diagrams are used to determine the corrosion behaviour of a metal in metal solution. Normally, the Pourbaix diagrams are built for the water solutions with the concentration of metal ion 10^{-6} M and at the temperature 298K

The Main objectives of the Pourbaix diagram are :-

- To show the directions of the various reactions at given pH and potential
- To make a basis for estimation of the corrosion product composition at various pH and potential combinations
- To show which environment pH and potential changes will reduce or prevent corrosion

The characteristics of the Pourbaix diagram are :-

- pH is plotted on the horizontal axis and potential E on the vertical axis
- The horizontal lines represent electron transfer reaction. They are pH-independent but potential-dependent
- The vertical lines are potential-independent but pH-dependant and not accompanied by any electron transfer
- The sloping, straight lines give the redox potentials of a solution in equilibrium with hydrogen and oxygen, respectively. This equilibrium indicates electron transfer as well as pH
- The concentrated of all metal ions is assumed to be 10^{-6} mol per litre of solution.
- The diagram is computed for the equilibrium conditions at 25°C
- The hydrogen and oxygen lines are indicated in Pourbaix diagrams by dotted line.



- Below the line a-b-g: solid iron. The electrochemical reactions in this zone proceed in the direction of reduction of iron ions into corrosion occurs in this zone
- a-b-m-e-d-e: Aqueous solution of ion Fe^{2+} [Corrosion zone] metallic ion oxides in this zone
- c-d-f-g-k: Aqueous solution of ion Fe^{3+} [Corrosion zone] metallic iron oxides in this zone

- h-f-g-m:- Aqueous solution of iron FeO_4^{2-} (passivation zone)
- c-d-f-h-i:- Solid ferrous oxide Fe_2O_3. Iron oxides in this zone. However the resulted oxide film depresses the oxidation process causing passivation (corrosion protection of the metal due to formation of a film of a solid product of the oxidation reaction.
- n-c-i-p: Solid oxide Fe_3O_4 ($Fe_2O_3.FeO$) Passivation zone
- b-n-p-j: Solid hydroxide $Fe(OH)_2$ (Greenrust) Passivation zone

Q8

a) A reaction with a low enthalpy of reaction value is not spontaneous at low temperature but becomes spontaneous at high temperatures. What are the sign for $\Delta H°$ and $\Delta S°$ respectively?

ΔS is positive

ΔH is positive

b) Dinitrogen tetroxide (N_2O_4) decomposes to nitrogen dioxide (NO_2). If $\Delta H° = 58.02\ KJ/mol$ and $\Delta S° = 176.1\ J/mol.K$, at what temperature are reactants and products in their standard states at equilibrium?

At Equilibrium $\Delta G° = 0$

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

$$\Delta H° = T\Delta S°$$

$$T = \frac{\Delta H°}{\Delta S°} \quad \{\Delta H = 58.02\ KJ/mol\ ;\ \Delta S = 176.1\ J/mol\}$$

$$T = \frac{58.02 \times 10^3}{176.1} = \frac{58020}{176} = 329.47\ K$$

The required temperature is $329.47\ K\ [56.32\ °C]$

Q9

What is the entropy change if 4.5g of $CaCO_3(s)$ is placed in a container and allowed to decomposes to $CaO(s)$ and $CO_2(g)$, according to the following reaction?

$CaCO_3(s)$ in equilibrium with $CaO(s) + CO_2(g)$. Substance $S°(J/mol.K)$ is given below

$CaCO_3(s)$ 92.88, $CaO(s)$ 39.75, $CO_2(g)$ 213.6

$$CaCO_3 \underset{(s)}{\rightleftharpoons} CaO(s) + CO_2(g)$$

$\Delta S°(CaCO_3) = 92.88$

$\Delta S°(CaO) = 39.75$

$\Delta S°(CO_2) = 213.6$

$$\Delta S°_{(g)} = \Delta S°_{Product} - \Delta S°_{Reactant}$$

$$= (39.75 + 213.6) - 92.88$$

$$= 160.47\ J/mol$$

No. of moles of $CaCO_3 = \frac{4.5}{100} = 0.044$

$\Delta S°$ for 0.044 moles $= (160.47 \times 0.044)\ J$

$= 7.06\ J$

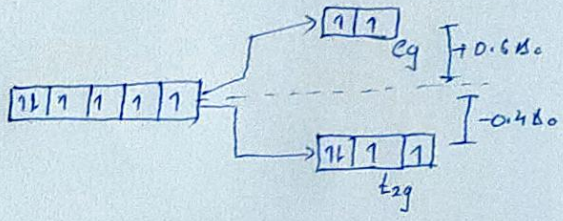
Q10 Write the oxidation number, d-orbital occupation, co-ordination number and expected magnetic moment of the central metal ion in the following complexes:

1) $K_3[Co(C_2O_4)_3]$

Central metal ion = Co^{3+}

It is a octahedral complex

$(C_2O_4)^{2-}$ is a weak ligand



$K_3[Co(C_2O_4)_3]$

$3 + x - 6 = 0$

$x = 3$

$Co \rightarrow 3d^7 4s^2$

$Co^{3+} \rightarrow 3d^6 \ (t_{2g}^4 \ eg^2)$

Co-ordination No. = 6

Magnet moment $= \sqrt{4(4+2)} = \sqrt{(4 \times 6)}$

$= \sqrt{24}$

$= 4.89$ BM

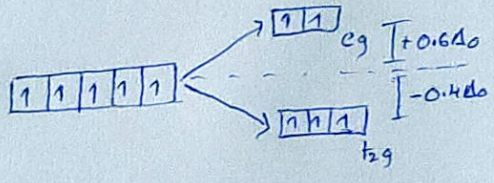
2) $[Mn(H_2O)_6]SO_4$

Central metal ion = Mn^{2+}

It is a octahedral complex.

Co-ordination No = 6

(H_2O) is a weak ligand



$[Mn(H_2O)_6]SO_4$

$x + 0 - 2 = 0$

$x = 2$

$Mn^{2+} \ 3d^5 4s^2$

$Mn^{2+} = 3d^5 \ [t_{2g}^3 eg^2]$

Magnet moment $= \sqrt{5(5+2)}$

$= \sqrt{35}$

$= 5.98$ M

3) ~~$[Ni(CO)_4]$~~ $[Cu(NH_3)_4]SO_4$

It is Weak ligand (NH_3) Cu^{2+} is central metal ion

It is a tetrahedral complex

$x + 0 + (-2) = 0$

$x = +2$

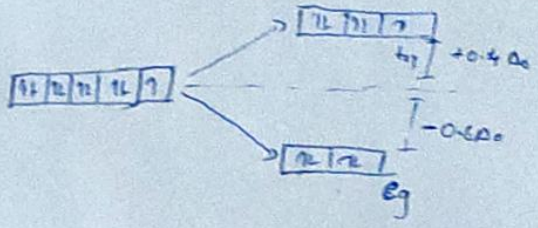
$Cu^{2+} \rightarrow 3d^9 [t_{2g}^5 eg^4]$

Coordination number = 4

Magnet moment = $\sqrt{1(1+2)}$

$= \sqrt{3}$

$= 1.73$ BM



3) $[Ni(CO)_4]$

$x + 0 = 0$

coordination No - 4

$Ni \rightarrow 3d^8 4s^2$

$(t_{2g}^4 \; eg^4)$

It is a tetrahedral complex

Ni is central metal ion

Magnet moment = $\sqrt{(2)(4)}$

$= \sqrt{8} = 2.828$ BM