Hence the potential is raised from 0.36 volt (in neutral soln) to 0.71 volt (in 1M HCl, H_2SO_4 or $HClO_4$ soln^n). The formal potential is now above than that of $I^{(-)}/I_2$ couple. Hence the oxidation of $I^{(-)}$ to I_2 by $[Fe(CN)_6]^{3-}$ ion takes place by the following eqn^n;

$$2[Fe(CN)_6]^{3-} + 2I^{(-)} \longrightarrow 2[Fe(CN)_6]^{4-} + I_2$$

Hence we may concluded that formal potential comment over standard normal potential.

Influence of different factors on redox potential:-

(1) Influence of pH of the medium:-

(a) The standard reduction potential of AsO_4^{3-}/AsO_3^{3-} and $I_2/I^{(-)}$ systems are 0.56 V and 0.54 volt respectively. Hence the rxn should occur as $AsO_4^{3-} + 2H^+ + 2I^{(-)} \rightarrow AsO_3^{3-} + I_2 + H_2O$. But in reality the direction of rxn depends on the pH of the soln^n. The potential of the AsO_4^{3-}/AsO_3^{3-} couple depends on pH.

$$AsO_4^{3-} + 2H^+ + 2e \rightleftharpoons AsO_3^{3-} + H_2O.$$

According to Nernst eqn^n, we can write.

$$\text{Therefore, } E = E^\circ + \frac{0.059}{2}\log\frac{[AsO_4^{3-}][H^+]^2}{[AsO_3^{3-}]}$$

$$= E^\circ + 0.059\log[H^+] + \frac{0.059}{2}\log\frac{[AsO_4^{3-}]}{[AsO_3^{3-}]}$$

$$= E^\circ - 0.059\,pH + \frac{0.059}{2}\log\frac{[AsO_4^{3-}]}{[AsO_3^{3-}]}$$

$$= E^{\circ\prime} + \frac{0.059}{2}\log\frac{[AsO_4^{3-}]}{[AsO_3^{3-}]}$$

where $E^{\circ\prime}$ = formal potential.

Thus the formal potential ($E^{\circ\prime}$) decreases with increase of pH. On presence of excess $NaHCO_3$ soln^n (pH $\simeq$ 8), $E^{\circ\prime}$ becomes 0.088 V which is less than 0.54 volt (standard potential of $I_2/I^{(-)}$ system) under the comparable condition. Thus at pH $\simeq$ 8, AsO_4^{3-} can not oxidise $I^{(-)}$ to I_2 But I_2 can oxidise AsO_3^{3-} to AsO_4^{3-} i.e.,

$AsO_3^{3-} + I_2 + H_2O \rightleftharpoons AsO_4^{3-} + 2I^- + 2H^+$

(b) The redox potential of MnO_4^-/Mn^{2+} couple depends on the pH of the soln.

Explain $MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$.

Why Cl^- is oxidised by permanganate soln only at low pH below 1.5 but not in neutral medium.

$$E = E^\circ + \frac{0.059}{5} \log \frac{[MnO_4^-][H^+]^8}{[Mn^{2+}]}$$

$$= E^\circ + \frac{0.059 \times 8}{5} \log[H^+] + \frac{0.059}{5} \log \frac{[MnO_4^-]}{[Mn^{2+}]}$$

$$= E^\circ - \frac{0.059 \times 8}{5} pH + \frac{0.059}{5} \log \frac{[MnO_4^-]}{[Mn^{2+}]}$$

Given: $E^\circ (MnO_4^-/Mn^{2+}) = 1.51\ V$

$E^\circ (Cl_2/Cl^-) = 1.36\ V$

$$= 1.51 - 0.094\, pH + \frac{0.059}{5} \log \frac{[MnO_4^-]}{[Mn^{2+}]}$$

$$E^\circ (Cl_2/Cl^-) = E^{\circ\prime} + \frac{0.059}{5} \log \frac{[MnO_4^-]}{[Mn^{2+}]}$$

Where $E^{\circ\prime}$ = formal potential.

Though the standard potential (E°) at pH = 0 is 1.51 V, the increase of pH the formal potential ($E^{\circ\prime}$) decreases. At pH = 6, $E^{\circ\prime} = 0.95$ V, Hence among the halides only I^- can be oxidised ($E^\circ_{I_2/I^-} = 0.54$ V, $E^\circ_{Br_2/Br^-} = 1.07$ volt, $E^\circ_{Cl_2/Cl^-} = 1.36$ V). At pH = 3, $E^{\circ\prime} = 1.23$ V and Br^- can be oxidised but Cl^- can not be oxidised. Thus to oxidise Cl^- a much higher conc. of H^+ is required ($pH < 1.5$)

B. 2005. The E° values of Cu^{2+}/Cu^+ (0.15 V) and I_2/I^- (0.54 V) suggest the iodometric titration of copper (II) is not possible. Explain why it is found otherwise in practice.

(2) Influence of precipitation on redox potential:-

(a) The volumetric estimation of Cu by an iodometric method is based on the rxn.

$$2Cu^{2+} + 4I^- \rightleftharpoons 2CuI + I_2$$

But the standard potentials of the systems Cu^{2+}/Cu^+ ($E^\circ = 0.15$ V) and I_2/I^- ($E^\circ = 0.54$ V) suggest that reverse rxn should take place.

Explain why iodine is liberated when KI is added to an aqueous soln of $CuSO_4$. ($E^\circ_{Cu^{2+}/Cu^+} = 0.15$ V and $E^\circ_{I_2/I^-} = 0.54$ V)

Now let us consider the effect of