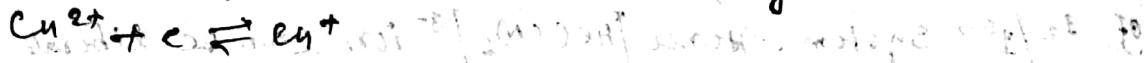


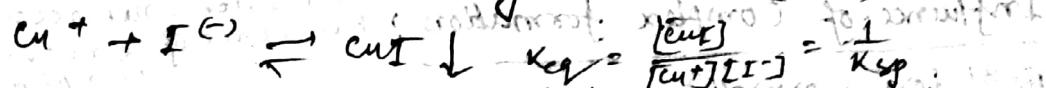
Precipitation of Cu⁺ on the Cu²⁺/Cu⁺ system.



According to Nernst eqn, the above reaction is written as

$$E = E^\circ + \frac{0.059}{T} \log \frac{[\text{Cu}^{2+}]}{[\text{Cu}^+]}$$
 (1)

In presence of I^(e), Cu⁺ is precipitated as CuI, having the low solubility product (10^{-12})



$$\text{Hence } K_{\text{sp}} = [\text{Cu}^+][\text{I}^{(e)}] = 10^{-12} \Rightarrow 10^{-12} = \frac{1}{K_{\text{sp}}} \Rightarrow K_{\text{sp}} = 10^{-12}$$

$$\therefore [\text{Cu}^+] = \frac{10^{-12}}{[\text{I}^{(e)}]}$$

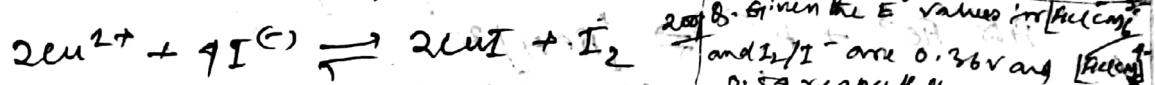
Therefore eqn (1) becomes

$$E = 0.15 + \frac{0.059}{T} \log [\text{Cu}^{2+}][\text{I}^{(e)}] + 10^{-12} \quad (2)$$
$$= 0.86 + 0.059 \log [\text{Cu}^{2+}][\text{I}^{(e)}]$$

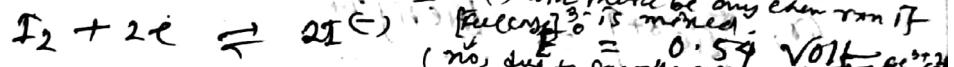
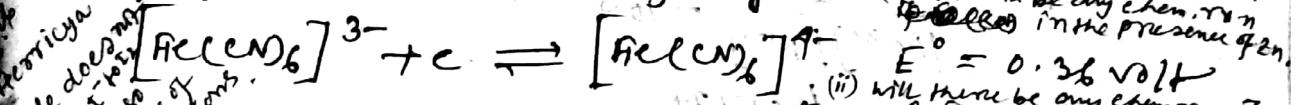
Thus for the system $\text{Cu}^{2+} + \text{I}^{(e)} + e \rightleftharpoons \text{CuI}$

we get the standard potential, 0.86 V.

Now we see though the Cu²⁺/Cu⁺ couple can not oxidise I^(e) to I₂ ($E^\circ_{\text{I}_2/\text{I}^{(e)}} = 0.54 \text{ V}$), But in the presence of I^(e) ion the oxidation becomes possible and to do metric estimation of Cu⁺, the following rxn is utilised

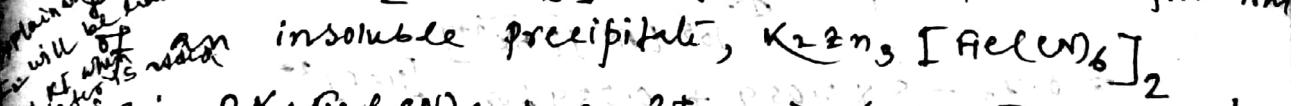


Q. Let us consider the following systems in the presence of Cu²⁺.



From the above values it is expected that $[\text{Fe}(\text{CN})_6]^{3-}$

should not be able to oxidise I^(e) to I₂. But in presence of Cu²⁺ ions, $[\text{Fe}(\text{CN})_6]^{4-}$ gets removed due to formation



According to Nernst eqn,

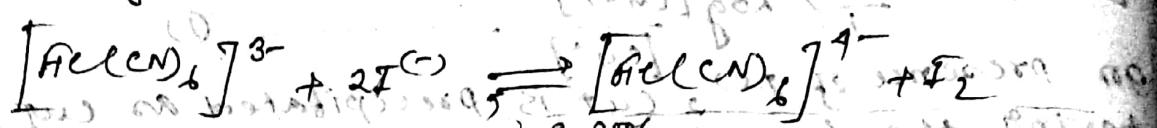
Reduction potential of $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ can be

expressed as

$$E = 0.36 + 0.059 \log \frac{[\text{Fe}(\text{CN})_6]^{3-}}{[\text{Fe}(\text{CN})_6]^{4-}} \text{ at } 25^\circ\text{C}$$

Due to the removal of $[\text{Fe}(\text{CN})_6]^{4-}$ through this precipitate, the formal potential of the system increases and it

exceeds from 0.59 volt, which is the standard potential of Fe/Fe^{2+} system. Hence $[\text{Fe}(\text{CN})_6]^{3-}$ ion can be liberated iodine by the following reaction:



(3) Influence of complex formation: presence of excess fluoride ions explain

Fe^{3+} ion normally oxidises I^- ion to I_2 in aqueous solution. Since the standard potential values of the two couples are $\text{Fe}^{3+}/\text{Fe}^{2+} = 0.77 \text{ V}$ and $\text{I}_2/\text{I}^- = 0.59 \text{ V}$

But in presence of $\text{Fe}(\text{CN})_6^{4-}$, Fe^{3+} is removed as the complex ion $[\text{Fe}(\text{CN})_6]^{4-}$ and the ratio $[\text{Fe}^{3+}]^{2+}/[\text{Fe}^{2+}]$ decreases.

For the system, $\text{Fe}^{3+} + e \rightleftharpoons \text{Fe}^{2+}$,

According to Nernst eqn, we can write

$$E = E^0 + 0.059 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

or, $E = 0.77 + 0.059 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$ (1)

For $\text{Fe}^{3+} + \text{F}^- \rightleftharpoons [\text{FeF}]^{2+}$,

$$\text{K}_{\text{eq.}} = \frac{[\text{FeF}]^{2+}}{[\text{Fe}^{3+}][\text{F}^-]} = 10^5$$

$$\text{or, } [\text{Fe}^{3+}] = \frac{[\text{FeF}]^{2+}}{10^5 [\text{F}^-]}$$

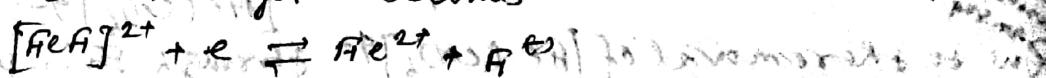
Substituting the value of $[\text{Fe}^{3+}]$ in eqn (1), we get,

$$E = 0.77 + 0.059 \log \frac{[\text{FeF}]^{2+}}{[\text{F}^-][\text{Fe}^{2+}]}$$

$$= 0.77 - 5 \times 0.059 + 0.059 \log \frac{[\text{FeF}]^{2+}}{[\text{F}^-][\text{Fe}^{2+}]}$$

$$= 0.77 - 0.059 \log \frac{[\text{FeF}]^{2+}}{[\text{F}^-][\text{Fe}^{2+}]}$$

Therefore the system becomes



As the reduction potential decreases, the oxidising power of Fe^{3+} decreases and it can no more oxidise I^- ion.

On the other hand Cu^{2+} does not form any such stable complex with I^- ion. Thus Cu may be estimated selectively in an Fe and Cu mixture by titrating the iodine liberated from KI in presence of Fe^{3+} .

Question: The E° value of $[\text{Co}^{3+}]^+$ couple is 1.82 volt at 25°C.

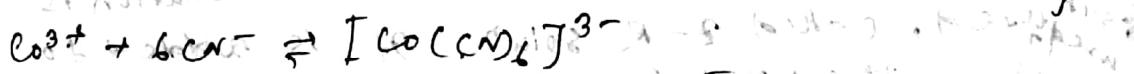
Calculate the E° value of $[\text{Co}(\text{CN})_6]^{3-}/[\text{Co}(\text{CN})_6]^{9-}$ couple given stability constants for the species $[\text{Co}(\text{CN})_6]^{3-}$ and $[\text{Co}(\text{CN})_6]^{9-}$ ions are 10^{64} and 10^{20} respectively.

Ans: For the system $\text{Co}^{3+} + e \rightleftharpoons \text{Co}^{2+}$, $E^\circ = 1.82$ volt.

According to Nernst equation, we can write:

$$E = E^\circ + \frac{0.059}{1} \log \frac{[\text{Co}^{3+}]}{[\text{Co}^{2+}]} \quad (1)$$

on adding of CN^- ions, both Co^{3+} and Co^{2+} form complexes



given the stability constant (K_1) for $[\text{Co}(\text{CN})_6]^{3-}$ ion = 10^{64}

$$\text{Hence } K_1 = \frac{[\text{Co}(\text{CN})_6]^{3-}}{[\text{Co}^{3+}][\text{CN}^-]^6} = 10^{64}$$

$$[\text{Co}^{3+}][\text{CN}^-]^6 = \frac{[\text{Co}(\text{CN})_6]^{3-}}{10^{64}}$$

$$\text{or, } [\text{Co}^{3+}] = \frac{[\text{Co}(\text{CN})_6]^{3-}}{10^{64} [\text{CN}^-]^6}$$

Similarly, $\text{Co}^{2+} + 6\text{CN}^- \rightleftharpoons [\text{Co}(\text{CN})_6]^{9-}$

given the stability constant (K_2) for $[\text{Co}(\text{CN})_6]^{9-}$ ion = 10^{20}

$$\text{Hence } K_2 = \frac{[\text{Co}(\text{CN})_6]^{9-}}{[\text{Co}^{2+}][\text{CN}^-]^6} = 10^{20}$$

$$\text{or, } [\text{Co}^{2+}] = \frac{[\text{Co}(\text{CN})_6]^{9-}}{10^{20} [\text{CN}^-]^6}$$

putting the values of $[\text{Co}^{3+}]$ and $[\text{Co}^{2+}]$ in eqn (1), we get,

$$E = 1.82 + \frac{0.059}{1} \log \frac{[\text{Co}(\text{CN})_6]^{3-}}{[\text{Co}(\text{CN})_6]^{9-}}$$

$$= 1.82 - 0.059 \times 99 + 0.059 \log \frac{[\text{Co}(\text{CN})_6]^{3-}}{[\text{Co}(\text{CN})_6]^{9-}}$$

$$= 1.82 - 0.776 + 0.059 \log \frac{[\text{Co}(\text{CN})_6]^{3-}}{[\text{Co}(\text{CN})_6]^{9-}}$$

Therefore the E° value of $[\text{Co}(\text{CN})_6]^{3-}/[\text{Co}(\text{CN})_6]^{9-}$ couple is -0.776

Lattice diagram: It can be defined as a compact form of the different species of an element involving different oxidation states. The different species have arrows between them and the standard potentials involving two species are written over the arrows. The O.S. of the element concerned is specified under each species. The species with highest O.S. is placed at extreme left, and the lowest is placed at the extreme right. Two examples are given below.

