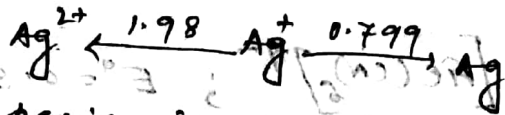


Hence  $\text{Ag}^+$  does not disproportionate to  $\text{Ag}$  and  $\text{Ag}^{2+}$  in the soln.

The potential in the series



The species in the middle ( $\text{Ag}^+$ ) in such a case is stable and does not disproportionate.

Formal potential :- what is meant by formal potential.

In the process,  $\text{ox} + n\text{e} \rightleftharpoons \text{red}$ ,  
According to Nernst eqn the potential is given by

$$E = E^\circ + \frac{0.059}{n} \log \frac{a_{\text{ox}}}{a_{\text{red}}} \quad \text{at } 25^\circ\text{C}$$

When  $a_{\text{ox}} = a_{\text{red}}$ , then  $E = E^\circ$

Here it is believed that all the involved species will remain in their simple forms and the activity equal to one and such a situation may only exist in a very dilute condition. In practice, the soln is sufficiently concentrated and the ions may not exist in simple forms in the presence of other electrolytes. Under these conditions the activity and concentration widely differ. In such cases the concept of standard potential is of no practical use and it requires another parameter called formal potential. The formal potential takes care of actual situation existing in soln.

(The formal potential of a system is the experimentally observed potential of the system in soln where the formal concentration (formality) of the oxidised and reduced forms are the same. The formal potential covers the effect of the conc. of the species, pH of the soln, the possibility of complexation and other factors.

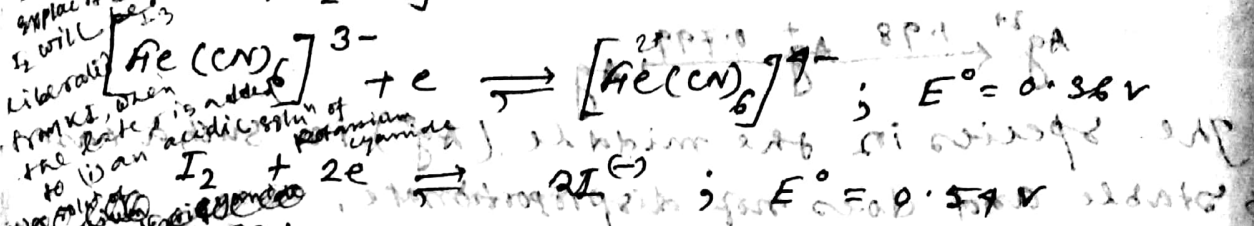
The modified form of the Nernst eqn is given by

$$E = E^\circ + \frac{0.059}{n} \log \frac{[\text{ox}]}{[\text{red}]} \quad \text{at } 25^\circ\text{C}$$

where  $E^\circ = \text{formal potential}$

2007 Utility of formal potential and formal potential which is more useful - discuss

2008 The standard potentials of  $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$  and  $I^{\ominus}/I_2$  couples are



Since  $I^{\ominus}/I_2$  has a greater red. potential than the  $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$  couple, it would be expected that  $I_2$  would oxidise  $[Fe(CN)_6]^{4-}$  to  $[Fe(CN)_6]^{3-}$  ion.

i.e;  $2[Fe(CN)_6]^{4-} + I_2 \rightarrow 2[Fe(CN)_6]^{3-} + 2I^{\ominus}$

In reality, it is the  $[Fe(CN)_6]^{3-}$  that oxidises  $I^{\ominus}$  ion to  $I_2$  in acid medium, it is explained in terms of formal potential.

The expression for redox potential of  $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$  can be written as follows:

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

$$= 0.36 + 0.059 \log \frac{[Fe(CN)_6]^{3-}}{[Fe(CN)_6]^{4-}}$$

In soln<sup>n</sup> of low pH ( $1M, H^+$ ),  $[Fe(CN)_6]^{4-}$  ions combine with one or more  $H^+$  ions to form hydroferrocyanic and hydroferricyanic acids.

$[Fe(CN)_6]^{4-}$  ion is a stronger base than  $[Fe(CN)_6]^{3-}$  and hence the reactivity of  $[Fe(CN)_6]^{4-}$  ion with  $H^+$  ion is more than the reactivity of  $[Fe(CN)_6]^{3-}$  ion with  $H^+$  ion.

Thus the conc. of  $[Fe(CN)_6]^{4-}$  ion is appreciably diminished in acid solution.