Cu will pass into soln with greater ease.
Therefore if a Cu wire is dipped into an aq. soln of $AgNO_3$, Cu will pass into soln as Cu^{2+} leaving electron on its surface. These electrons react with Ag^+ ion to produce Ag. Hence there will be a deposit of Ag on the Cu wire and the colourless aqueous solution will assume a blue colour due to Cu^{2+} ions. On the contrary when Ag wire is dipped into Cu^{2+} soln, no rxn occurs.
Similarly,
When a Zn rod is placed in a soln containing Cu^{2+} ions. There is a deposite of metallic Cu on the Zn rod. On the other hand if Cu rod is dipped in a soln of Zn^{2+} ion, NO rxn occurs.

(2) Calculation of cell potential:

With the help of $E^\circ_{(red)}$ values we can calculate the value of standard potential of a given Galvanic cell.
The value of E°_{cell} is given by $E^\circ_{cell} = E^\circ_{red\,(right)} - E^\circ_{red\,(left)}$
Let us consider the standard electrode potentials of the following two couples;

$$Zn^{2+} + 2e \rightleftharpoons Zn; \quad E^\circ = -0.763 \text{ volt.}$$
$$Ag^+ + e \longrightarrow Ag; \quad E^\circ = 0.799 \text{ volt.}$$

Thus for the cell $Zn/Zn^{2+} \,||\, Ag^+/Ag$, the cell potential $= 1.562$.

⊛ It is not necessary to consider the no. of electrons involved in the change.

(3) Determination of eqm. constant of a redox rxn.

The relation betn the standard free energy change and eqm. constant of a given rxn is given by $\Delta G^\circ = -RT \ln K_{eq.}$ ..... (1)
Where $K_{eq.}$ = eqm. constant of a redox rxn.
R = Molar gas constant
T = absolute Temperature.
and ΔG° = standard free energy change of the rxn.
Again, we know that, $\Delta G^\circ = -nFE^\circ$ ..... (2)
where E° = standard e.m.f of the cell.
n = no. of electrons involved in the overall cell rxn
F = Faraday.
(comparing equn (1) and (2) we get,

$RT \ln K_{eq} = -nFE^\circ$

or, $\ln K_{eq} = \frac{nFE^\circ}{RT}$

or, $2.303 \log K_{eq} = \frac{nFE^\circ}{RT}$

or, $K_{eq} = 10^{\frac{nFE^\circ}{2.303RT}}$

or, $\boxed{K_{eq} = 10^{\frac{nE^\circ}{0.059}} \text{ at } 25^\circ C}$

Thus knowing E° as well as 'n' we may calculate the value of eqm. constant of a redox rxn.

Q. 2002 E° value of Fe^{3+}/Fe^{2+} is 0.77 V at 25°C. Calculate the K_{eq} for the reaction Fe^{2+} and Sn^{4+} in Kelvin at this temp.

Q. Calculate the K_{eq} for the overall equn of the cell,

$Sn^{2+} \mid Sn^{4+} \parallel Fe^{3+} \mid Fe^{2+}$

given, $E^\circ_{Sn^{4+}/Sn^{2+}} = 0.15$ volt and $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77$ volt

Ans:- The above cell rxn will be written as

$Sn^{2+} + 2Fe^{3+} \rightleftharpoons Sn^{4+} + 2Fe^{2+}$

$E^\circ_{cell} = E^\circ_{Cathode} - E^\circ_{anode}$

$= 0.77 - 0.15$

$= 0.62$ volt

We know that, $K_{eq} = 10^{\frac{nE^\circ}{0.059}}$ at 25°C [where n = no. of electrons involved in the overall rxn.]

or, $K_{eq} = 10^{\frac{2 \times 0.62}{0.059}}$

$= 1.03 \times 10^{21}$

④ potentiometric determination of P_H :-

The fundamental rxn for the hydrogen electrode is

$2H^+ + 2e \rightleftharpoons H_2$ ∴ Its single electrode potential at 1 atm hydrogen pressure is

$E_H = E^\circ_H + \frac{0.059}{2} \log \frac{a_{H^+}}{a_{H_2}}$

where E°_H = standard potential of hydrogen electrode = 0

At 1 atm hydrogen pressure $P_{H_2} = 1$, here $n = 2$.

For dilute solution it can be written as

$E_H = 0.059 \log [H^+]$

8. 2006 Calculate potential for H^+/H_2 system at pH = 2 and pH 2.4.

or, $\boxed{E_H = -0.059\,pH}$ $[\because pH = -\log[H^+]]$.

This equⁿ is utilised in determining the pH of an solⁿ for this, hydrogen electrode is dipped into the unknown solⁿ and combine with a calomel electrode through a salt bridge of 1N KCl solⁿ.

The cell set up is

$Pt, H_2(g, 1\,atm) \,|\, \underset{pH(X)}{\text{solⁿ}} \,\|\, \text{calomel (1N) electrode.}$

↓ salt bridge of 1 (N) KCl solⁿ.

The emf of the cell is measured with a potentiometer. The potential of the 1(N) calomel electrode = 0.280 volt.

Hence $E_{cell} = E_{cal.} - E_H$

$= 0.280 - (-0.059\,pH)$

$= 0.280 + 0.059\,pH$

or, $E_{cell} - 0.280 = 0.059\,pH$

or, $\boxed{pH = \dfrac{E_{cell} - 0.280}{0.059}}$

From this equⁿ the pH of the unknown solⁿ can be measured.

(5) Relative stability of oxidation states and disproportionation

The relative stability of different oxidation states of an element may be predicted from the knowledge of standard potentials.

Examples:— ① - ② Disproportionation of $Au^{(+)}$ takes place according to the equⁿ

$3Au^{(+)} \rightleftharpoons 2Au + Au^{3+}$

This is explained as follows;

$2Au^{(+)} + 2e \rightleftharpoons 2Au$; $E^\circ = 1.68$ volt; $\Delta G^\circ = -2 \times 96500 \times 1.68$ joule

$Au^{(+)} \rightleftharpoons Au^{3+} + 2e$; $E^\circ = -1.41$ volt ; $\Delta G^\circ = -2 \times 96500 \times (-1.41)$ joule

Adding, $3Au^{(+)} \rightleftharpoons 2Au + Au^{3+}$; $E^\circ = 0.27$ volt; $\Delta G^\circ = -0.54 \times 96500$ joule

This gives a positive E° of 0.27 volt for the total cell rxn and the free energy of the process is negative (−0.54F). Hence Au^+ proportionate to Au^0 and Au^{3+} in the solⁿ.

The potential in the series

$Au^{3+} \xrightarrow{1.41\ volt} Au^+ \xrightarrow{1.68\ volt} Au^0$

The species in the middle (Au^+) in such a case is unstable and disproportionates.

(2) 2007 $E^\circ_{Cu^+/Cu} = 0.521$ volt.

$E^\circ_{Cu^{2+}/Cu^+} = 0.153$ volt

Disproportionation of Cu^+ takes place according to the equn

$$2Cu^+ \rightleftharpoons Cu + Cu^{2+}$$

This is explained as follows

$Cu^+ + e \rightleftharpoons Cu$; $E^\circ = 0.521$ volt $\Delta G^\circ = -1.F.(0.521)$

$Cu^+ - e \rightleftharpoons Cu^{2+}$; $E^\circ = -0.153$ volt $\Delta G^\circ = -1.F.(-0.153)$

Adding, $2Cu^+ \rightleftharpoons Cu + Cu^{2+}$; $E^\circ = 0.368$ volt $\Delta G^\circ = -0.368F$

This gives a positive E° of 0.368 volt for the total cell rxn and the free energy of the process is negative (−0.368). Hence Cu^+ proportionate to Cu^0 and Cu^{2+} in the solution.

The potential in the series

$$Cu^{2+} \xleftarrow{0.153} Cu^+ \xrightarrow{0.521} Cu^0$$

The species in the middle (Cu^+) in such a case is unstable and disproportionates.

(3) 2007 $E^\circ_{Ag^+/Ag} = 0.799$ volt

$E^\circ_{Ag^{2+}/Ag^+} = 1.98$ volt

Disproportionation of Ag^+ takes place according to the equn

$$2Ag^+ \rightleftharpoons Ag + Ag^{2+}$$

This is explained as follows

$Ag^+ + e \rightleftharpoons Ag$; $E^\circ = 0.799$ volt $\Delta G^\circ = -1.F.(0.799)$

$Ag^+ - e \rightleftharpoons Ag^{2+}$; $E^\circ = -1.98$ volt $\Delta G^\circ = -1.F.(-1.98)$

Adding $2Ag^+ \rightleftharpoons Ag + Ag^{2+}$; $E^\circ = -1.181$ V $\Delta G^\circ = 1.181$ V

This gives a negative E° of (−1.181) for the total cell rxn and the free energy of the process is positive (1.181).