

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,

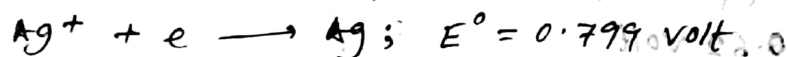
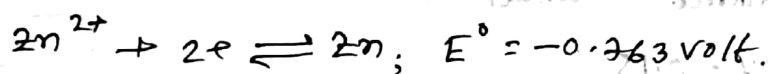
When a Zn rod is placed in a soln containing Cu^{2+} ions. There is a deposit of metallic Cu on the Zn rod. On the other hand if Cu rod is dipped in a soln of Zn^{2+} ion, no rxn occurs.

(2) Calculation of cell potential:

With the help of E°_{red} values we can calculate the value of standard potential of a given Galvanic cell.

The value of E°_{cell} is given by $E^\circ_{\text{cell}} = E^\circ_{\text{red}}(\text{right}) - E^\circ_{\text{red}}(\text{left})$

Let us consider the standard electrode potentials of the following two couples;



Thus for the cell $\text{Zn}|\text{Zn}^{2+}||\text{Ag}^+|\text{Ag}$, 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 $\Delta G^\circ = -RT \ln K_{\text{eq}}$.

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 eqn (1) and (2) we get,

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

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

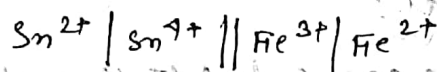
$$\text{or, } 2.303 \log K_{eq} = \frac{nFE^{\circ}}{RT}$$

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

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

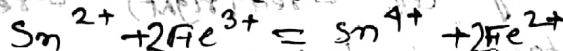
Thus knowing E° as well as n , we may calculate the value of eqm. constant of a redox rxn.

8. Calculate the K_{eq} for the overall eqn of the cell,



Given, $E^{\circ}_{\text{Sn}^{4+}/\text{Sn}^{2+}} = 0.15 \text{ volt}$ and $E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ volt}$

Ans:- The above cell rxn will be written as,



$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

$$= 0.77 - 0.15$$

$$= 0.62 \text{ volt}$$

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

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

$$= 1.03 \times 10^{21}$$

9. Potentiometric determination of P_{H^+} :

The fundamental rxn for the hydrogen electrode is

$2\text{H}^+ + 2e \rightleftharpoons \text{H}_2$: Its single electrode potential at 1 atm hydrogen pressure is

$$E_{\text{H}} = E^{\circ}_{\text{H}} + \frac{0.059}{2} \log \frac{a_{\text{H}^+}}{a_{\text{H}_2}}$$

Where $E^{\circ}_{\text{H}} = \text{standard potential of hydrogen electrode} = 0$

At 1 atm hydrogen pressure $P_{\text{H}_2} = 1$, here $n = 2$.

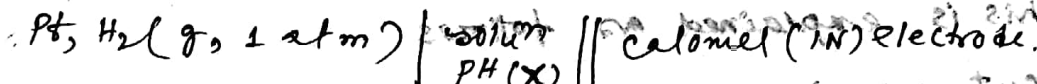
For dilute soln it can be written as

$$E_{\text{H}} = 0.059 \log [\text{H}^+]$$

or, $E_H = -0.059 \text{ pH}$ [∵ $\text{pH} = -\log [\text{H}^+]$]

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

The cell set up is



salt bridge of 1(N) KCl solⁿ

The e.m.f. of the cell is measured with a potentiometer.

The potential of the 1(N) calomel electrode = 0.280 volt.

Hence $E_{\text{cell}} = E_{\text{cal}} - E_H$

$$= 0.280 - (-0.059 \text{ pH})$$

$$= 0.280 + 0.059 \text{ pH}$$

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

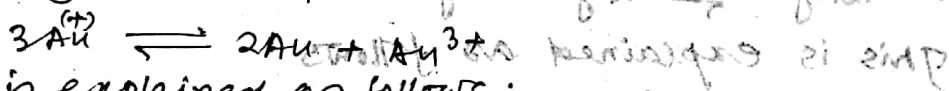
or, $\text{pH} = \frac{E_{\text{cell}} - 0.280}{0.059}$

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

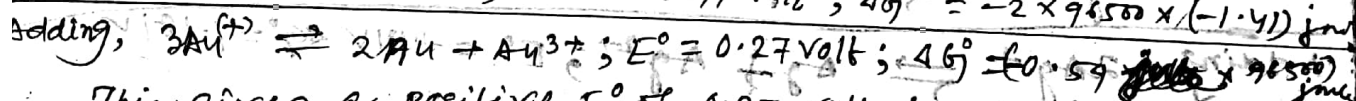
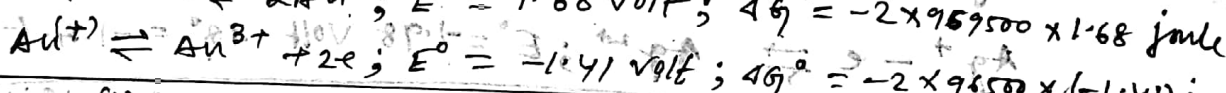
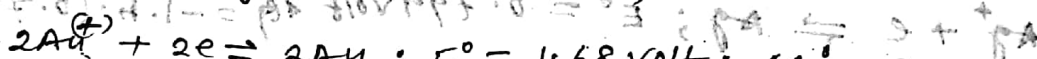
(5) Relative stability of oxidation states and disproportionation

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

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



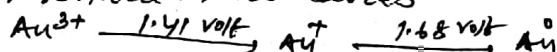
This is explained as follows;



This gives a positive E° of 0.27 volt for the total cell rxn and the free energy of the process is negative (-0.59 J).

Hence Au^{+} is proportional to Au^0 and Au^{3+} in the solⁿ.

The potential in the series



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

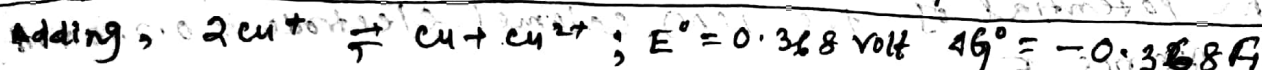
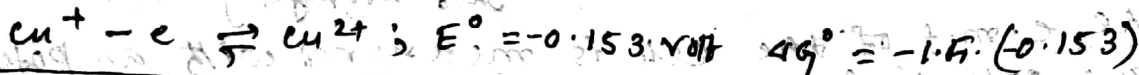
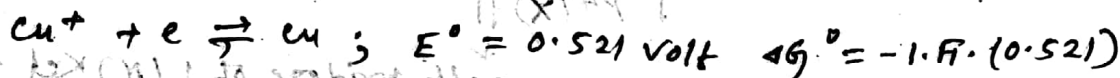
(2) $E^\circ_{Cu^+/Cu} = 0.521 \text{ volt}$

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

Disproportionation of Cu^+ takes place according to the eqn



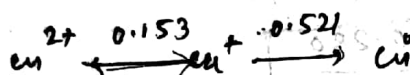
This is explained as follows



This gives a positive E° of 0.368 volt for the total cell rxn and the free energy of the process is negative (-0.368F)

Hence Cu^+ is proportional to Cu^0 and Cu^{2+} in the soln.

The potential in the series

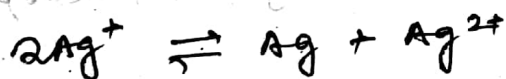


The species in the middle (Cu^+) in such a case is unstable and disproportionates.

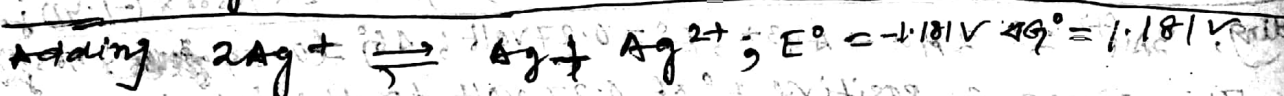
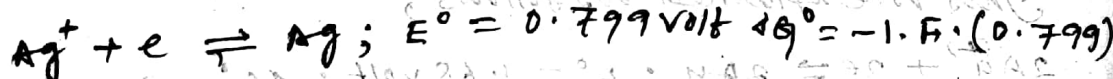
(3) $E^\circ_{Ag^+/Ag} = 0.799 \text{ volt}$

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

Disproportionation of Ag^+ takes place according to the eqn



This is explained as follows



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