

The change in free energy for the overall cell rxn is expressed as

$$\Delta G = \sum G_{\text{product}} - \sum G_{\text{reactant}}$$

$$= \Delta G^\circ + RT \ln \frac{a_C^\gamma \cdot a_D^\delta}{a_A^\alpha \cdot a_B^\beta} \quad \text{--- (1)}$$

[where ΔG° = standard free energy change]
 we know,

$$\Delta G = -nFE \text{ and } \Delta G^\circ = -nFE^\circ$$

[where E° = standard e.m.f of the cell]

Thus equation (1) becomes

$$-nFE = -nFE^\circ + RT \ln \frac{a_C^\gamma \cdot a_D^\delta}{a_A^\alpha \cdot a_B^\beta}$$

$$\text{or, } E = E^\circ - \frac{RT}{nF} \ln \frac{a_C^\gamma \cdot a_D^\delta}{a_A^\alpha \cdot a_B^\beta} \quad \text{--- (2)}$$

This equation is known as Nernst equⁿ.
 From equation (2) we can write

$$E = E^\circ - \frac{2.303RT}{nF} \log \frac{a_C^\gamma \cdot a_D^\delta}{a_A^\alpha \cdot a_B^\beta}$$

$$\text{or, } E = E^\circ - \frac{0.059}{n} \log \frac{a_C^\gamma \cdot a_D^\delta}{a_A^\alpha \cdot a_B^\beta} \quad \text{[at 25°C]}$$

[where $\frac{2.303RT}{F} = 0.059$ at 25°C]

This is also the another form of Nernst equⁿ.

For dilute solun equⁿ (2) can be written as

$$E = E^\circ - \frac{0.059}{nF} \log \frac{[C]^\gamma [D]^\delta}{[A]^\alpha [B]^\beta} \quad \text{--- (3)}$$

Since at equilibrium, the cell could not perform any work, e.m.f will be zero.

Hence equⁿ (3) becomes

$$E^\circ = \frac{RT}{nF} \ln K_{eq.} \quad \text{[where } K_{eq.} = \frac{[C]^\gamma [D]^\delta}{[A]^\alpha [B]^\beta}]$$

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

$$\text{or, } -\Delta G^\circ = RT \ln K_{eq.}$$

or, $\Delta G^\circ = -RT \ln K_{eq}$ ————— (4)

This is the relation betⁿ standard free energy change and eqm. constant for a given cell rxn.

⊗ For a rxn oxidant + ne ⇌ reductant

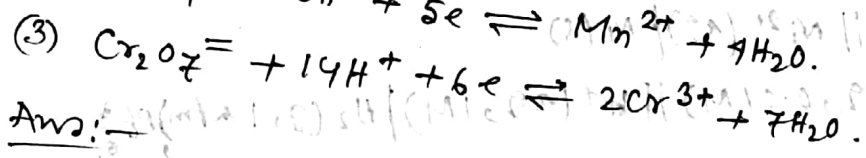
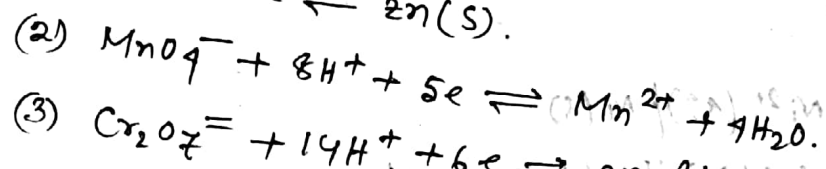
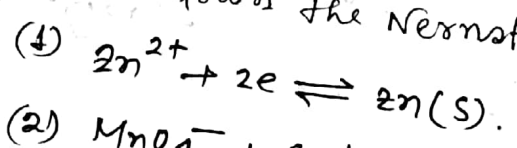
The Nernst eqn can be written as

$$E = E^\circ + \frac{0.059}{n} \log \frac{[\text{oxidant}]}{[\text{reductant}]}$$

at 25°C

or, $E = E^\circ - \frac{0.059}{n} \log \frac{[\text{reductant}]}{[\text{oxidant}]}$ at 25°C

§. write down the Nernst eqn's for the following equations:



Ans:—

(1) For the rxn $2n^{2+} + 2e \rightleftharpoons 2n(s)$, the Nernst eqn can be written as

$$E_{2n^{2+}/2n(s)} = E^\circ_{2n^{2+}/2n(s)} + \frac{RT}{nF} \ln \frac{a_{2n^{2+}}}{a_{2n(s)}}$$

Since 2n is in the solid state its activity = 1.

$$E_{2n^{2+}/2n(s)} = E^\circ_{2n^{2+}/2n(s)} + \frac{0.059}{2} \log [2n^{2+}]$$

[where n = 2 and $\frac{2.303RT}{nF} = 0.059$ at 25°C and for dilute soln activity = concentrations and

$E^\circ_{2n^{2+}/2n(s)}$ = standard reduction potential of $2n^{2+}/2n$ electrode

(2) For the rxn $MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$. The Nernst eqn can be written as

$$E_{MnO_4^-/Mn^{2+}} = E^\circ_{MnO_4^-/Mn^{2+}} + \frac{RT}{nF} \ln \frac{a_{MnO_4^-} \cdot a_{H^+}^8}{a_{Mn^{2+}} \cdot a_{H_2O}^4}$$

or, $E_{MnO_4^-/Mn^{2+}} = E^\circ_{MnO_4^-/Mn^{2+}} + \frac{0.059}{5} \log \frac{[MnO_4^-] [H^+]^8}{[Mn^{2+}] \cdot 1}$

[where n = 5 and $\frac{2.303RT}{nF} = 0.059$ at 25°C and for dilute soln activity = conc. and the activity of $H_2O = 1$ For 1(M) H^+ (on soln this eqn become

$$E_{MnO_4^-/Mn^{2+}} = E^\circ_{MnO_4^-/Mn^{2+}} + \frac{0.059}{5} \log \frac{[MnO_4^-] \cdot [1]^8}{[Mn^{2+}]}$$

(3) For the rxn $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$,
 The Nernst eqn can be written as

$$E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}}^{\circ} + \frac{RT}{nF} \ln \frac{a_{\text{Cr}_2\text{O}_7^{2-}} \cdot a_{\text{H}^+}^{14}}{a_{\text{Cr}^{3+}}^2 \cdot a_{\text{H}_2\text{O}}^7}$$

$$\text{or, } E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}}^{\circ} + \frac{0.059}{6} \log \frac{[\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^{14}}{[\text{Cr}^{3+}]^2 \cdot 1}$$

Where $n=6$, $\frac{2.303RT}{F} = 0.059$ at 25°C and for dilute soln activity = conc., and the activity of $\text{H}_2\text{O} = 1$

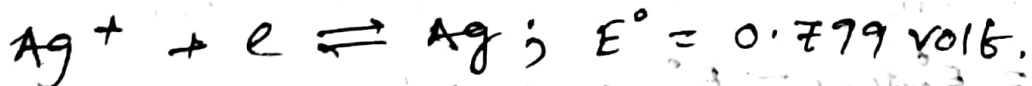
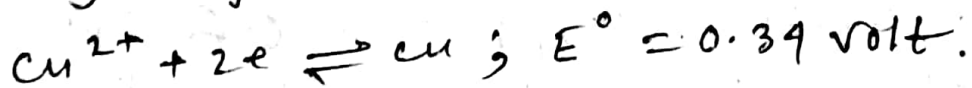
For 1 (M) H^+ soln this eqn becomes.

$$\text{or, } E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = E_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}}^{\circ} + \frac{0.059}{6} \log \frac{[\text{Cr}_2\text{O}_7^{2-}][1]^{14}}{[\text{Cr}^{3+}]^2}$$

Application of Standard redox potential values:

- (1) Prediction of rxns: - The oxidant of a couple with a more positive standard potential (red) value will in general, oxidise the reductant of a couple with a less positive or negative standard potential (red) value.

Consider the standard electrode potential of the following couple,



The less positive potential of the couple, the more effective the metal as a reducing agent.

Since the Cu^{2+}/Cu couple has a less positive potential, Cu will serve as a better reducing agent.