Thermodynamics of the Cells : 6.

The e.m.f. of the cell is related to free energy by equation (1) i.e. $\Delta G = -nFE$(1) Now $\left(\frac{\partial \Delta G}{\partial T}\right)_{R} = -\Delta S$ $\left(\frac{\partial \Delta G}{\partial T}\right)_{\rm p} = -nF\left(\frac{\partial E}{\partial T}\right)_{\rm p} = -\Delta S$ So $\Delta S = nF \left(\frac{\partial E}{\partial T}\right)_{P}$ e enthalpy of the cell reaction will be $\Delta H = \Delta G + T\Delta S$ or(2) Tł

$$\mathbf{H} = \Delta \mathbf{G} + \mathbf{T} \Delta \mathbf{S}$$

$$= -nFE + TnF\left(\frac{\partial E}{\partial T}\right)_{P} \qquad \dots \dots (3)$$

The thermodynamic quantities of the cell reaction can be calculated by equations (1), (2)and (3) provided one knows the emf of cell and its dependence on temperature.

The heat effects in the system can be calculated as follows. If the process is irreversible (i.e. by mixing the reactants together), heat flow to the system can be given by the reaction, $\Delta H = Q_p$. If the process is reversible the heat flow to system is given by $Q_p = T\Delta S$.

Example 15.

Consider the cell Cd | $CdCl_{,2}H_{,0}$ | $AgCl_{,0}$ | Hg The emf of the cell at 15°C is 0.67531V and temperature coefficient of emf is 0.00065V deg⁻¹. Calculate the value of ΔH at 15°V and heat flow if the process is carried reversibly.

Solution :

The cell reaction is $\begin{array}{l} \mathrm{Cd}_{(\mathrm{s})}+2\mathrm{Cl}^{-} \longrightarrow \mathrm{CdCl}_{2(\mathrm{s})}+2\mathrm{e}^{-} \\ \mathrm{2AgCl}_{(\mathrm{s})}+2\mathrm{e}^{-} \longrightarrow \mathrm{2Ag}_{(\mathrm{s})}+2\mathrm{Cl}^{-} \end{array}$ At anode At cathode $Cd_{(s)} + 2AgCl_{(s)} \longrightarrow CdCl_{2(s)} + 2Ag_{(s)}$ The number of electrons involved are two So, ΔG = - nFE= -(2) (96500C) (0.67531V)= -130.335 kJ $= (2) (96500C) (-0.0065V deg^{-1})$ ΔS $= -125.45 \text{ J deg}^{-1}$ $= \Delta G + T \Delta S$ ΔH $= (-130.335 \text{ kJ}) + (288 \text{ K}) (-125.45 \text{ JK}^{-1}) (10^{-3} \text{ kJ J}^{-1})$ = -166.465 kJ $= (288 \text{K}) (-125.45 \text{ JK}^{-1} \text{ mol}^{-1}) = 36.$ Q_D

Condition of Equilibrium : (E_{cell} = 0.0V)

When $E_{cell} = 0.0 V$, i.e., no potential difference is obtained between the terminals of cell (battery), the cell reaction in such a state is said to be in equilibrium. So in such cases,

When
$$E_{cell} = Q = K_{eq} = equilibrium constant.$$

 $E_{cell} = E_{cell}^0 - \frac{0.059}{n} \log Q$ $0.0 = E_{cell}^0 - \frac{0.059}{n} \log K_{eq}$
 $E_{cell}^0 = \frac{0.059}{n} \log K_{eq}$

Example 16.

Calculate the equilibrium constant for the reaction, $Zn^{2+} + 4NH_{3} \longrightarrow [Zn(NH_{2})_{3}]^{2+}$ $E^{0}(Zn^{2+}/Zn) = -0.763 \text{ and } E^{0} [Zn(NH_{3})_{3}]^{2+}/Zn + NH_{3}] = 1.03V$ Solution : The electrode reactions for the given electrodes, can be written as $Zn^{2+} + 2e^{-} \longrightarrow Zn \qquad E_{1}^{0} = -0.763V$ $[Zn(NH_{3})_{4}]^{2+} + 2e^{-} \longrightarrow Zn + 4NH_{3} \qquad E_{1}^{0} = -1.03V$ Reaction (1) - (2) $Zn^{2+} + 4NH_{3} \longrightarrow [Zn(NH_{3})_{4}]^{2-}$ The standard emf of this reaction = $E_{1}^{0} - E_{2}^{0} = -0.763V - (-1.03) = 0.267V$ According to Nernst equation $E = E^{0} - \frac{RT}{2F} \ln \frac{a_{[Zn(NH_{3})_{4}]^{2+}}}{a_{Zn^{2+}} \cdot a}$ If the process is equilibrium, E = 0 at 25°C $\frac{0.0591}{2} \log K = 0.267$ $\log K = \frac{(0.267)(2)}{(0.059)} = 9.036$

 $K = 10^{-0.36}10^9 = 1.09 \times 10^9$ The equilibrium constant is also called the "Stability Constant" of the complex. If the reaction is written in a reverse manner, it will be "instability constant".

Example 17.

To find the standard potential of M^{3+}/M electrode, the following cell is constituted. $Pt \mid M \mid M^{3+} (0.0018 \text{ mol}^{-1}L) \mid Ag^{+} (0.01 \text{ mol}^{-1}L) \mid Ag$

The emf of this cell is found to be 0.42 volt. Calculate the standard potential of the

half reaction, $M^{3+} + 3e^- \longrightarrow M E^0_{Ag^+/Ag} = 0.80$ volt.

Solution :

The cell reaction is : $M + 3Ag^+ \longrightarrow 3Ag + M^{3+}$ Applying Nernst equation,

$$E_{cell} = E_{cell}^{0} - \frac{0.0591}{3} \log \frac{|M^{3+}|}{|Ag^{+}|^{3}}$$

$$0.42 = E_{cell}^{0} - \frac{0.0591}{3} \log \frac{(0.0018)}{(0.01)^{3}}$$

$$= E_{cell}^{0} - 0.064$$

$$E_{cell}^{0} = E_{cathode}^{0} - E_{anode}^{0}$$

$$E_{anode}^{0} = E_{cathode}^{0} - E_{cell}^{0}$$

$$= (0.80 - 0.484) = 0.32 \text{ volt}$$

Example 19.
Calculate the pH of the following half cells solutions.
(a)
$$Pt(H_2) | H^+ (HCl) = 0.25$$
 volt
latm
(b) $Pt(H_2) | H^+ (H_2SO_4)E = 0.3$ volt
latm
Solution :
(a) $H_2 \longrightarrow 2H^+ + 2 e^-$
 $E_{H_2/H^+} = E_{H_2/H^+}^0 - \frac{0.0591}{2} \log \frac{[H^+]^2}{P_{H_2}}$
 $= 0.0 - 0.0591 \log \frac{[H^+]}{1}$
 $0.25 = 0.0591 \text{ pH}$
 $pH = \frac{0.25}{0.0591} = 4.23$
(b) $E_{H_2/H^+} = E_{H_2/H^+}^0 - \frac{0.0591}{2} \log \frac{[H^+]^2}{P_{H_2}}$
 $= 0.0 - 0.0591 \log \frac{[H^+]}{1}$
 $0.3 = 0.0591 \text{ pH}$
 $pH = \frac{0.3}{0.591} = 5.076$

Example 20.

What is the standard potential of the Tl^{3+}/Tl electrode? $Tl^{3+} + 2e^- \longrightarrow Tl^+$ $E^o = 1.26 \text{ volt}$] $Tl^+ + e^- \longrightarrow Tl$ $E^o = -0.335 \text{ volt}$ Solution : $Tl^{3+} + 2e^- \longrightarrow Tl^+$ $nFE^0 = 2 \times 1.26 \times F = 2.52 \text{ F}$ $Tl + e^- \longrightarrow Tl$ $nFE^0 = 1 \times (-0.336) \times F = -0.336 \text{ F}$ addition $Tl^{3+} + 3e^- \longrightarrow Tl$ $E^0 = \frac{2.52F - 0.336F}{nF} = \frac{2.184}{3} = 0.728 \text{ volt}$

Example 21.

Calculate the emf of the following cell at 25 °C. Pt $H_2 \mid HCl \mid H_2Pt$ 2atm 10atm Solution : $E_{cell} = \frac{0.0591}{2} \log \frac{2}{10}$ $= \frac{0.0591}{2} \log \frac{2}{10}$ = -0.0206 volt

7. Solubility Product :

The solubility product of sparingly soluble salt MX can be discussed in terms of the equilibrium of the kind

$$MX_{(s)} \longrightarrow M^+_{(aq)} + X^-_{(aq)}$$

Since the activity of the pure solid is always unity, the equilibrium constant of the solubility product can be written.

$$K_{sp} = a_{M^+} a_{x^-}$$
(1)

When the solubility of the salt is very small, the solution is ideal and thus $a_1 = c_1$ of ions. The equation (1) can be written as

$$E = E^{0} - \frac{RT}{nF} \ln \frac{a_{M^{+}}}{a_{MX}} a_{MX}$$

Under equilibrium conditions the emf of the cell will be zero i.e., E = 0 and also the activity of pure solid is unity. Further $K_{sp} = a_{M^+} \cdot a_{X^-}$, the above equation at 25 °C can be written as :

$$\log K_{sp} = \frac{E^0 \cdot n}{0.0591}$$
(2)

The solubility product thus can be calculated from the standard emf of one cell, formed in such a way that the final reaction is the type given above.

Example 22.

Calculate the K_{sp} of AgI by forming proper cell.

	Given $E_{\Gamma/Ag_{(s)}/Ag}^{0} = -0.151$	V and $E^{0}_{Ag^{+}/Ag} = 0.7991V$	
Solution :	The cell can be written as : At left electrode	$Ag Ag^{+} I^{-} AgI Ag$ $Ag_{(s)} \longrightarrow Ag^{+} + e^{-}$	$E^0 = 0.7991V$
	At right electrode	$AgI_{(s)} + e^{-} \longrightarrow Ag_{(s)} + I^{-}$	$E^0 = -0.151V$
		$AgI_{(s)} \longrightarrow Ag^+ + I^-$	
The standard emf of the cell is		$E^{0} = E^{0}_{R} - E^{0}_{L} = -0.151 - 0.79$	991
		= -0.9501V	
Using	g relation (1) at 25°C		
log K	$F_{\rm sp} = -\frac{(0.9501)(1)}{0.059} = -16.1$	$K_{sp} = 10^{-16.1} = 7.94 \times 10^{-17}$	

8. Concentration Cells :

In concentration cell, the two electrodes are of the same material and they are dipping in the solutions of their respective ions at different concentrations. The two solutions are separated by salt bridge. The electrode dipping in a solution of higher concentration of positive ions is positive and the electrode dipping in lower concentration of positive ions is negative. The overall cell reaction is nothing but a transference of material from higher activity to lower activity. The emf of the cell is given by :

$$\mathbf{E} = -\frac{\mathbf{RT}}{\mathbf{nF}} \ln \frac{\mathbf{a}_1}{\mathbf{a}_2}$$

where a_1 and a_2 are the activities of the ion in two solutions. The term E^0 cancels but because both the electrodes are same and will have the same standard electrode potential at unit activity. The E is positive if $a_2 > a_1$ and negative if $a_1 > a_2$.

Concentration Cell in which Electrodes is Reversible with Respect to Cation

(a) $Zn | Zn^{2+} (C_1) || Zn^{2+} (C_2) | Zn$ At L.H.S. half cell $Zn \longrightarrow Zn^{2+} (C_1) + 2e^ E^0 = 0.76V$ At R.H.S. half cell $Zn^{2+} (C_2) + 2e^- \longrightarrow Zn$ $E^0_R = -0.76V$ Net $Zn^{2+} (C_2) \longrightarrow Zn^{2+} (C_1)$ $E^0_{cell} = 0.00V$

$$E_{cell} = E_{cell}^{0} - \frac{0.0591}{2} \log \left(\frac{C_{1}}{C_{2}}\right)$$
$$E_{cell} = \frac{0.0591}{2} \log \frac{C_{2}}{C_{1}}$$

Cell reaction is spontaneous in forward direction if $(C_2 > C_1)$

(b) Pt $(H_2) | HCl (C_1) || HCl (C_2) | Pt (H_2)$ 1 atm 1 atm

$$E_{cell} = E_{cell}^{0} - \frac{0.0591}{2} \log \left(\frac{C_{1}}{C_{2}} \right)$$
$$E_{cell} = 0.0591 \log \frac{C_{2}}{C_{1}}$$

Concentration Cell in which Electrode is Reversible with Respect to Anion

Pt (Cl₂) | Cl⁻ (C₁) || Cl⁻ (C₂) | Pt (Cl₂) 1 atm $E_{1} = E_{1}^{0} = 0.0591_{100} (C_{2})$

$$E_{cell} = E_{cell}^0 - \frac{0.0571}{2} \log\left(\frac{C_2}{C_1}\right)$$

For such cases, cell reaction is spontaneous in forward reaction if $C_1 > C_2$

Concentration Cell having Electrodes at Different Concentration Dipped into Same Electrolyte

$$\operatorname{Pt}(\operatorname{H}_{2}) | \operatorname{HCl}_{\operatorname{1M}} | \operatorname{Pt}(\operatorname{H}_{2})_{\operatorname{at } p_{2}}$$

Two half cells are joined by two salt - bridges since they have common electrolyte

L.H.S. half cell
$$\frac{1}{2}$$
 H₂ \longrightarrow H⁺ + e⁻

$$\begin{array}{c} \mathrm{H^{\scriptscriptstyle +}} + \mathrm{e^{\scriptscriptstyle -}} \longrightarrow \frac{1}{2} \mathrm{~H_{_2}} \\ 1 \mathrm{~M} \end{array}$$

 $E_{cell}^{0} = 0.00V$

Net

$$E_{cell} = E_{cell}^{0} - \frac{0.0591}{2} \log\left(\frac{p_2}{p_1}\right)$$
$$E_{cell} = 0.591 \log \frac{p_1}{p_2}$$

Cell reaction is spontaneous in forward direction if, p_1 (L.H.S.) > p_2 (R.H.S.)

 $H_2(P_1) \longrightarrow H_2(P_2)$

Example 23.

Calculate the emf of the cell Zn-Hg $(C_1)/Zn^{2+}$ (aq) | Zn – Hg (C_2) at 25°C, if the concentration of the zinc amalgam are $C_1 = 2$ gm per 100 gm of Hg and $C_2 = 1$ gm per 100 gm of Hg.

Solution :

At cathode : $Zn^{2+} + 2e^{-} \longrightarrow Zn(C_2)$ At anode : $Zn(C_1) \longrightarrow Zn^{2+} + 2e^{-}$ Net reaction $Zn(C_1) \longrightarrow Zn(C_2)$ $\therefore \qquad E = \frac{0.059}{2} \log \frac{C_2}{C_1} = -0.295 \log \left(\frac{1}{2}\right) = 8.8 \times 10^{-3} \text{ V}$

Electrolyte Concentration Cells :

Two electrodes of the same metal are dipping in solutions of metal ions of different concentrations :

e.g. $Zn | Zn^{2+} (C_1) || Zn^{2+} (C_2) | Zn$ At A^+ cathode $Zn^{2+} (C_2) + 2e^- \longrightarrow Zn(s)$ At A^+ anode $Zn(s) + 2e^- \longrightarrow Zn^{2+} (C_1) + 2e^ \overline{Zn^{2+} (C_2)} \longrightarrow Zn^{2+} (C_1)$ $\therefore E_{cell} = \frac{RT}{nF} ln \frac{C_2}{C_1}$

For the process to be spontaneous, emf should be +ve . Hence, $C_2 > C_1$.

9. Some Commercial Cells :

The commercial cells are actually portable source of electrical energy. These cells are also known as Batteries. There are mainly two types of commercial cells :

(a) Primary Cells :

These cells cannot be used for longer period of time because they are not chargeable. Some common examples of primary cells are:

(i) Dry cell (ii) Mercury Cell

(i) Dry Cell :

It is used in torches, toys and in other electronic devices. Leclanche cell is the compact form of the dry cell.

In this cell zinc cylinder acts as an anode. The cylinder is filled with the paste of NH_4Cl and little amount of $ZnCl_2$ in the form of paste in water. A graphite rod surrounded by a black paste of MnO_2 and carbon powder acts as a cathode.

The cathodic reaction of the cell is represented as

 $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH)^- + NH_3$

And the anodic reaction is $Zn \longrightarrow Zn^{2+} + 2e^{-1}$

It gives voltage of approximately 1.2 to 1.5V

Since, the NH_4Cl in slightly aqueous medium is acidic, it will corrode the Zn and the cell stops its functioning. Due to the corrosion and the consumption of Zn in the process, this cell cannot be reused.

(ii) Mercury Cell :

It consists of Zn anode and $HgO_{(s)}$ as a cathode. The electrolyte of this cell is a paste of KOH and ZnO.

The anodic reaction of the cell: $Zn(Hg) + 2OH^{-} \longrightarrow ZnO_{(s)} + H_2O + 2e^{-}$

And the cathodic reaction is $HgO_{(s)} + H_2O + 2e^- \longrightarrow Hg_{(l)} + 2OH^-$

The voltage of the mercury cell is 1.35V. The cell shows constancy in its potential throughout its life. This cell is used in small electrical circuits e.g., watches, hearing aids etc.

(b) Secondary Cells :

They are rechargeable by passing direct current in them, and, therefore, they can be used again and again. These cell are also known as accumulators or storage cells.

Most common accumulators are Lead Accumulators and Nickel Cadmium Accumulators. Lead Accumulators : In lead accumulators three to six voltaic cells are connected in series to get 6 to 12 volt.

The anode of this cell is made of spongy lead and cathode is a grid of lead packed with PbO_2 . The electrolyte used in the cell is 38% H_2SO_4 by weight having a density of 1.30 g/ml. When the Pb plates are placed for sometimes, a deposit of $PbSO_4$ is formed on them.

The cell (voltaic) is represented as :

$$\begin{array}{l} \mbox{Pb} \mid \mbox{PbSO}_4 \mid \mbox{H}_2 SO_{4(aq)} \mid \mbox{PbSO}_4 \mid \mbox{PbSO}_2 \mid \mbox{Pb} \\ \mbox{Pb}_{(s)} + \mbox{SO}_4^{2-} \longrightarrow \mbox{PbSO}_4 + 2e^- \\ \mbox{2e}^- + \mbox{PbO}_{2(s)} + \mbox{4H}^+_{(aq)} + \mbox{SO}_4^{2-} \longrightarrow \mbox{PbSO}_{4(s)} + \mbox{2H}_2 O \\ \mbox{Pb}_{(s)} + \mbox{PbO}_{2(s)} + \mbox{2H}_2 SO_{4(aq)} \longrightarrow \mbox{PbSO}_{4(s)} + \mbox{2H}_2 O \end{tabular} (overall reactions)$$

It is clear from the net cell reaction that H_2SO_4 is consumed during the operation of the cell and its density regularly decreases. When the density of the H_2SO_4 solution falls below 1.2g/ml, the recharging of the battery is required .

Recharging of the Cell : When D.C. passed directly in this battery, the reactions of its voltaic cells are reversed and this will slowly increase the density of the H_2SO_4 solution. The recharging reaction is represented as :

 $2PbSO_{4(s)} + 2H_2O \longrightarrow Pb_{(s)} + PbO_{2(s)} + 2H_2SO_4$

The discharging process of the storage cell is based on the principles of electrochemical cell, whereas the charging process is based upon the principles of electrolytic cells.

Example 24.

If a completely charged lead storage cell is found to have 1.6 litre of $6 M H_2 SO_4$ 3.5 ampere of current is consumed for 6 hours, what is the concentration of sulphuric acid and moles of sulphuric acid?

Solution :

The overall reaction is : $Pb_{(S)} + PbO_{2(S)} + 2H_2SO_4 \longrightarrow 2PbSO_{4(S)} + 2H_2O$ \therefore Moles of electron used = $\frac{3.5 \times 6 \times 60 \times 60}{96500} = 0.783$ This equals moles of H_2SO_4 used. \therefore Moles of H_2SO_4 , left = 9.6 - 0.783 = 8.817

:. Molarity of H₂ SO₄ left =
$$\frac{8.817}{1.6}$$
 = 5.51

Daily Practice Problem Sheet 3.

Q.1 A galvanic cell is constructed with 2 metals P and Q. Electrolysis used in the galvanic cell are sulphates of the metals. If $E_{p^{+m}|p}^{0} = a$ and $E_{O^{+n}|Q}^{o} = b$ and a > b then find out :

Direction of flow of current

- Cathode of the cell Anode of the cell **(a) (b)** Reaction at anode Reaction at cathode (d) (c)
- Redox change Nernst equation for both half cell and for complete cell **(e)** (f)
- Direction of flow of electron (h) **(g)**
- **Q.2** Calculate e.m.f. of the half cell given below :

(a)	Fe FeSO ₄	$E_{0P}^{o} = 0.44 \text{ V}$	(b)	$Zn ZnSO_4$	$E_{0}^{o} = 0.76 V$
	0.1M			0.2 M	
(c)	$Cu Cu(NO_3)_2$	$E_{0P}^{o} = -0.34 \text{ V}$	(d)	$Ag Ag^+$	$E_{RP}^{o} = 0.8 V$
	2M		0	.5 M	
(e)	Co ⁺² Co	$E_{0P}^{o} = 0.28 V$	(f)	$Cd \mid Cd^{+2}$	$E_{RP}^{o} = -0.4 V$
	0.01 M	01	0.0	05 M	
(g)	Ni ⁺² Ni	$E_{RP}^{o} = -0.24 V$	(h)	${ m Hg} { m Hg_2}^{+2}$	$E_{OP}^{o} = -0.792 V$
	0.12 M		0.01	5 M	01
(i)	Pb PbSO ₄	$E_{0P}^{o} = -0.126 V$	(j)	SnCl ₂ Sn	$E_{OP}^{o} = -0.136 V$
	0.004 M		0.	006 M	

- Q.3 The standard electrode potential of Cu|Cu²⁺ is -0.34 volt. At what concentration of Cu²⁺ ions, will this electrode potential be zero?
- A zinc electrode is dipped in a 0.1 M solution at 25°C. Assuming that salt is dissociated to **Q.4** 20 % at this dilution, calculate the electrode potential . $E^{o}_{Zn+2/Zn}$ = -0.76 V
- K_{sn} of Cu(OH)₂ is 1.0×10^{-19} . Calculate the reduction potential at pH = 8 for the couple Q.5 $C\tilde{u}^{2+}/Cu$. Given: E_{RP}^{o} of $Cu^{2+}/Cu = 0.34$ V.
- Using oxidation potential and reduction potential of various metals in Q.2 determine anode Q.6 and cathode of the cell, E^{o}_{cell} , E_{cell} when galvanic cell is composed of
 - (2) Ag Cu (4) Hg - Sn (1) Zn-Fe (3) Cd - Co (8) Hg - Ag (5) Pb - Ni (6) Zn - Cu (7) Pb - Ag
- **Q.7** The potential for the reaction, $O_2(g) + 4H^+ + 4e \longrightarrow 2H_2O$ is 1.23 V in 0.1 N strong acid solution. Calculate the potential of this couple in aqueous solution of : (i) pH = 10(ii) pH = 14
- Standard reduction potential of Cu and Ag are 0.34 and 0.8 respectively. A galvenic cell is **Q.8** constructed using Cu-Ag. Determine :
 - Anode and cathode of the cell (i)
 - Anode and cathode of the cell (ii) E^{o}_{cell} Cell potential when concentration of Cu⁺² and Ag⁺ are 3×10^{-2} M and 1.73×10^{-3} M (iii) respectively
- Calculate the values for cell, $Zn | Zn^{2+}(aq.) | Cu^{2+}(aq.) | Cu$ Q.9
 - (i) Cell reaction
 - E.m.f. of cell if Zn^{2+} and Cu^{+2} are 1 M each (ii)
 - The minimum concentration of Cu2+ at which the cell reaction, (iii)
 - $Zn + Cu^{2+} (aq.) \longrightarrow Zn^{+2} (aq.) + Cu$ will be spontaneous if Zn²⁺ is 1 M
 - (iv) Does the displacement of Cu^{2+} (aq.) by Zn goes to completion.

- **Q.10** Consider the reaction, $2Ag^+ + Cd \longrightarrow 2Ag + Cd^{2+}$. The standard reduction potential of Ag^+/Ag and Cd^{2+}/Cd couples are +0.80 and -0.40 volt respectively.
 - (a) What is the standard cell e.m.f., E° ?
 - (b) Will the total e.m.f. of the reaction be more +ve or -ve, if conc. of Cd²⁺ is 0.10 M rather than 1 M?
- **Q.11** A graph is plotted between E_{cell} and $\log_{10} \frac{[Zn^{2+}]}{[Cu^{2+}]}$. The curve was linear with intercept on

$$E_{cell}$$
 axis equal to 1.10 V. Calculate E_{cell} for $Zn \begin{vmatrix} Zn^{2+} \\ 0.1 M \end{vmatrix} \begin{vmatrix} Cu^{2+} \\ 0.01 M \end{vmatrix} Cu^{2+}$

- **Q.12** Which of the following hydrogen gas ion electrodes are in standard state? Also calculate their electrode potential if they are not in standard state.
 - (1) Pt $(H_2) | H_2 SO_4$
 - (3) $\begin{array}{c} 1 \text{ atm} & 0.5 \text{ M} \\ \text{Pt} (\text{H}_2) \mid \text{H}_2\text{O} \\ 10^{-14} \text{ atm} \end{array}$
 - (5) $CH_3COONH_4 | Pt(H_2)$ 10⁻³ M 10⁻¹⁴ atm
 - (7) $Mg(OH)_2 | Pt(H_2)$ (sat. sol.) 10 atm
- (2) $CH_3COOH | Pt(H_2)$ 0.1 M 0.1 atm(4) $Pt(H_2) | HCOOH + HCOONa$ $10^{-5} atm 1 M 1 M$ (6) $NH_4OH | Pt(H_2)$ $10^{-3} M$ (8) $H_2SO_4 + HCl + CH_3COOH | Pt(H_2)$ 0.1 M 0.2 M 1M

 $[K_{sp} \text{ of } Mg(OH)_2 = 4 \times 10^{-6} \text{ K}_a (CH_3COOH) = 10^{-5}, K_b(NH_4OH) = 10^{-5} \text{ K}_a(HCOOH) = 10^{-4}$

- **Q.13** If the electrode potential for the half cell, HA \mid Pt(H₂) is -0.236 V, then calculate the dissociation constant of HA. 0.1M 2 atm
- **Q.14** The standard oxidation potential of Ni/Ni²⁺ electrode is 0.236 V. If this is combined with a hydrogen electrode in acid solution, at what pH of the solution will the measured e.m.f. be zero at 25°C? Assume $[Ni^{2+}] = 1$ M and $p_{H_2} = 1$ atm.
- **Q.15** If $NO_3^- \longrightarrow NO_2$ (acidic medium); $E^\circ = 0.790 V \& NO_3^- \longrightarrow NH_2OH$ (acidic medium); $E^\circ = 0.731 V$. At what pH the above two half reaction will have same E values. Assume the concentrations of all the species to the unity.
- Q.16 What ratio of Pb⁺² to Sn⁺² concentration is needed to reverse the following cell reaction? Sn (s) + Pb(aq)⁺² \implies Sn(aq.)⁺² + pb(s) E^o_{Sn+2/Sn} = -0.136 V and E^o_{Pb+2/Pb} = -0.126 V
- Q.17 A cell is set up where the overall reaction is , $H_2(g) + Sn^{4+} \longrightarrow 2H^+ + Sn^{2+}$ The hydrogen electrode is under standard condition and E_{cell} is found to be +0.20 V. What is the ratio of Sn²⁺ to Sn⁴⁺ around the other electrode? Given $E_{Sn^{4+}/Sn^{2+}}^{\circ} = 0.15$ V.
- **Q.18** A galvanic cell is constructed with Ag^+/Ag and Fe^{3+}/Fe^{2+} electrodes. Find the concentration of Ag^+ at which the e.m.f. of cell is zero at equimolar concentration of Fe^{2+} and Fe^{3+} . Given : E°_{-} , $\mu = 0.80$ V and E°_{-} and Fe^{-}_{-} V.

iven :
$$E_{Ag^{+}/Ag}^{\circ} = 0.80$$
 v and $E_{Fe^{3+}/Fe^{2+}}^{\circ} = 0.77$

- Q.19 The e.m.f. of the cell $Pt(H_2)$ $\begin{vmatrix} HOCN \\ 1 atm \end{vmatrix} \begin{vmatrix} Ag^+ \\ 0.8 M \end{vmatrix} \begin{vmatrix} Ag(s) \text{ is } 0.982 \text{ V} \ Calculate the K_a for \\ HOCN \ Ag^+ + e \longrightarrow Ag(s) \ ; \quad E^o = 0.80 \text{ V}.$
- **Q.20** The standard reduction potential of $E^{o}_{Bi3+/Bi}$ and $E^{o}_{Cu2+/Cu}$ are 0.226 V and 0.344 V respectively. A mixture of salts of Bi^{3+} and Cu^{2+} at unit concentration each is electrolysed at 25°C. To what value can [Cu²⁺] be brought down before bismuth starts to deposit during electrolysis.

Daily Practice Problem Sheet 4.

- Q.1 Identify the type of the given half cells and write corresponding half cell reactions. Also write nernst equation for each half cell
 - $Pt(Cl_2) | HCl$ **(a)**
 - $Zn | Zn^{+2}$ (c)
 - $MnO_4^{-}, Mn^{+2}, H^+ \mid Pt$ **(e)**
 - **(g)** Cl^{-} | Hg₂Cl₂ | Hg

(i) Cl⁻ |AgCl | Hg

- $\begin{array}{c|c} \Pr(\mathrm{Cl}_2) & \mathrm{HCl} & \Pr(\mathrm{Cl}_2) \\ \mathbb{P}_1 & & \mathbb{P}_2 \end{array}$ (k)
- (m) Pb | saturated PbSO₄
- $Pt | Au^{+3}, Au^{+}$ $(\mathbf{0})$
- (q) $Pt(H_2) | H_2SO_4 || HCl | Pt(H_2)$
- CNS⁻ | CuCNS | Cu **(s)**
- $CaBr_{2}|AgBr|Ag$ **(u)**

- $Pt | Fe^{+2}, Fe^{+3}$ **(b)**
- $Pt(H_{2}) \mid H^{+}$ (d)
- Ag | Saturated. AgCl (f)
- Bi⁺⁵, Bi⁺³ | Pt **(h)**
- (j)
- $Pb \mid PbSO_4 \mid SO_4^{-2}$ **(l)**
- $CaCl_{2} | Pt(Cl_{2})$ **(n)**
- $Cr_{2}O_{7}^{-2}, Cr^{+3}, OH^{-} | Pt$ **(p)**
- **(r)** Ag|AgCl, KCl || KBr, AgBr | Ag
- $SnCl_2 | Sn$ (t)
- $Pb | \bar{P}bSO_4, K_2SO_4$ **(v)**
- Write chemical reaction for anodic half cell, cathodic half cell and for complete cell. Also Q.2 write nernst equation for each galvanic cell
 - Pt | Fe⁺², Fe⁺³ || Cr₂O₇⁻², Cr⁺³, H⁺ | Pt **(a)**
 - Ag | AgI, KI || KBr, AgBr | Ag **(b)**
 - (c)
 - $\begin{array}{c|c} Cu \mid CuSO_4 & \parallel CuSO_4 \mid Cu\\ Pt \mid C_2O_4^{-2}, CO_2 \parallel MnO_4^{-}, Mn^{+2}, H^+ \mid Pt \end{array}$ (d)
 - $Zn | ZnSO_4 || HCl | Pt(H_2)$ (e)
 - $Hg | Hg_{2}Cl_{2} | KCl \parallel NaCl | Pt(Cl_{2})$ (f)
 - Pt | $Fe(CN)_{6}^{-4}$, $Fe(CN)_{6}^{-3} \parallel CrO_{4}^{-2}$, Cr^{+3} , $OH^{-} \mid Pt$ (g)
 - Ag | AgBr, $CN^{-} \parallel AgCl, NH_{3} \mid Ag$ **(h)**
 - Pt (H₂) | HSO₃^{-,}, SO₃⁻² || ZnSO₄ | Zn (i)
 - $Cu | CuSO_4, NH_3 || AgCl, NH_3 |Ag$ (j)
 - Pb | Pb⁺² || $[Co(en)_3]^{+3}$, $[Co(en)_3]^{+2}$ | Pt (k)
 - $Pt (Cl_2) | HCl || NH_4Cl + NH_4OH + (NH_4)_2SO_4 | Pt(H_2)$ **(l)**
 - Pt | Mn^{+2} , $MnO_{2} \parallel MnO_{4}^{-}$, Mn^{+2} , H^{+} | Pt (m)
 - $Ag | Ag^+ \parallel KC\bar{l}, AgCl | Ag$ **(n)**
 - Pt | $Co(CN)_{6}^{-4}$, $Co(CN)_{6}^{-3}$ || Co^{+3} , Co^{+2} | Pt (0)
- Q.3 The e.m.f. of the cell obtained by combining Zn and Cu electrodes of a Daniel cell with N calomel electrodes are 1.083 V and -0.018 V respectively at 25°C. If the potential of N calomel electrode is -0.28 V, find e.m.f. of Daniel cell.
- Q.4 Calculate the potential of an indicator electrode versus the standard hydrogen electrode, which originally contains 0.1 M MnO_4^- and 0.8 M H⁺ and which was treated with Fe²⁺ necessary to reduce 90 % of MnO_4^- to Mn^{2+} . $E_{MnO4-/Mn2+}^{o} = 1.51$ V.
- Determine potential for the cell , Pt $|Fe^{+2}, Fe^{+3}||Cl_2O_7^{-2}, Cr^{+3}, OH^-|Pt|$ Q.5

$$E_{Fe^{+3}|Fe^{+2}}^{0} = 0.7 \text{ V}, \quad E_{Cr,O_{7}^{-2}|Cr^{+3}}^{0} = 1.35 \text{ V}$$

in which $[Fe^{+2}]$ and $[Fe^{+3}]$ are 1 M and 2 M respectively and $[Cr_2O_7^{-2}]$, $[Cr^{+3}]$ and $[H^+]$ are 2M, 4M and 10⁻¹³ M respectively.

- **Q.6** How much is the oxidizing power of $(0.1 \text{ M}, \text{MnO}_4^-/\text{Mn}^{+2}, 0.2\text{ M})$ couple decreased if the H⁺ concentration is decreased from 0.1M to 10⁻⁶ M at 25°C ?
- **Q.7** The cell $Pt(H_2)(1atm) | H^+(pH=X) | |$ Normal calomel electrode has e.m.f. of 0.67 V at 25°C. Calculate pH of solution. The oxidation potential of calomel electrode on H scale is -0.28 V.
- **Q.8** A hydrogen electrode having pressure is equal to 1.00 atm is combined with a standard calomel electrode, whose half-reaction is

 $Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(2\overline{2}) + 2Cl^- E^o = 0.242 V$

If the cell potential is 0.800 V, what is the pH of the solution around the hydrogen electrode? What will the cell potential be if the hydrogen electrode is immersed in a neutral solution?

- **Q.9** What is the e.m.f. of a cell containing two H electrodes, the negative one in contact with 10^{-8} molar OH⁻ and the positive one in contact with 10^{-3} molar H⁺?
- Q.10 Neglecting the liquid junction potential, calculate the e.m.f. of the following cell at 25 °C.

$Pt(H_2)$	НСООН	CH ₃ COOH	$Pt(H_2)$
1 atm	10-3 M	10-2 M	1 atm

- K_a for HCOOH and CH₃COOH are 1.77×10^{-4} and 1.8×10^{-5} respectively.
- **Q.11** Write the cell reaction and calculate the e.m.f. of the cell for $Pt(Cl_2)$ NaCl (aq) $Pt(Cl_2)$. 10 atm 1 atm

Will the cell reaction be spontaneous

- Q.12 The e.m.f. of a galvanic cell composed of two H electrodes is 272 millivolt. What is the pH of the solution in which the anode is immersed if the cathode is in the solution of pH = 3?
- **Q.13** Calculate the potential of a cell in which H electrodes are immersed in a solution with a pH of 3.5 and in a solution with a pH of 10.7 at 30 °C.
- Q.14 The reversible reduction potential of water is -0.414 V under 1 atm H₂ pressure. If the reduction is 2H⁺+2e \longrightarrow H₂, calculate [H⁺] in pure water.
- **Q.15** A cell designed below contains one litre of buffer mixture of CH_3COOH and CH_3COONa each 1 M in two compartments using platinum electrodes. pK_a for $CH_3COOH = 4.74$.

$$\begin{array}{c|c} Pt(H_2) & CH_3COOH + CH_3COONa \\ 1 \text{ atm} & 1 \text{ M} & 1 \text{ M} \end{array} \begin{array}{c|c} CH_3COOH + CH_3COONa \\ 1 \text{ M} & 1 \text{ M} \end{array} \begin{array}{c|c} Pt(H_2) \\ 1 \text{ M} & 1 \text{ M} \end{array} \begin{array}{c|c} Pt(H_2) \\ 1 \text{ atm} \end{array}$$

Calculate :

- (i) the pH in the each compartment
- (ii) the e.m.f. of cell
- (iii) the pH and e.m.f. of the cell each compartment after passage of 1.25 A current for 241.25 minute.
- Q.16 Calculate the e.m.f. of the cell at 18 °C for :

 $\begin{array}{c|c} Pt(H_2) & HCl & KOH & Pt(H_2) \\ 1 atm & N/10 & N & 1 atm \end{array}$

HCl is 90 % dissociated and KOH is 75 % ionised.

5. Daily Practice Problem Sheet

Q.1	The equilibrium conchange for this reaction	nstant for a reaction on is :	t is 1×10^{20} at 300 K.	The standard free energy
	(A)-115 kJ	(B) +115 kJ	(C) +166 kJ	(D) –166 kJ
Q.2	Standard electrode p -0.036 V respectivel (A) -0.476 V	ootentials of Fe ²⁺ + 2e ly. The standard electro (B) -0.404 V	$\longrightarrow Fe and Fe^{3+} + 3e$ ode potential (E°) for F (C) +0.404 V	
Q.3	Consider the cell, N	$Mg(s) \mid Mg^{2+} \parallel Ag^+ \mid Ag^+ \mid Ag^+$	g	
	(0. Given $E^{\circ}_{Ag+ Ag} = 0.8$ (i) What will the (A) decreased (C) remains s (ii) In the above of (A) 611.8 kJ	2M) (10^{-3} M) volt; $E^{o}_{Mg+2 Mg} = -2.37$ effect on emf if conce d to 3.022 V ame juestion maximum wo (B) 61.18 kJ	volt ntration of Mg ²⁺ ion is (B) increased by 3.0 (D) none rk that can be obtained (C) 107.2 kJ	decreased to 0.1 M 22 V by operating the cell is : (D) 1072.5 kJ
Q.4	Consider the following	ng cell reaction :		
	$Tl^{+3} + 2e^{-}$		1.26 V	
	The standard potential $T = C$	al of the Tl^{+3} Tl electro	- 0.550 V ode is :	
	(A) 0.728 V	(B) 0.824 V	(C) 1.596 V	(D) 2.52 V
Q.5	Two electro chemical	cells are assembled in	which the following rea	actions occur,
	$V^{2+} + VO^{2+} + 2H^+ - V^{3+} + A g^+ + H O$	$\rightarrow 2V^{3+} + H_2O$ $\rightarrow VO^{2+} + 2H^+ + \Delta \sigma(s)$; $E_{cell}^{o} = 0.616$; $F_{cell}^{o} = 0.439$	V V
	then E° for the half	reaction, $V^{3+} + e^{-}$	V^{2+} , is : [Given : E	$e_{A_{\alpha+ A_{\alpha}}} = 0.799 \text{ V}$
	(A) -0.256 V	(B) +0.256 V	(C) –1.05 V	(D) + 1.05 V
Q.6	For the reaction, H ₂ at 25 °C, the standar 109.7, -237.2 and - (A) - 43 kJ, 0.22 V (C) - 21.5 kJ, 0.11 V	$g(g) + 2AgCl(s) + 2H_2$ rd free energy of form 368.4 kJ mol ⁻¹ respect	$O(l) \longrightarrow 2Ag(s) + 2H$ ation of AgCl(s), H ₂ O tively. Then ΔG° and H (B) + 43 kJ, 0.22 V (D) + 21.5 kJ, 0.22 V	$I_{3}O^{+}(aq) + 2CI^{-}(aq)$ $O(l)$ and $(H_{3}O^{+} + CI^{-})$ are : E° for the reaction is : V
Q.7	Given : $Cu^{2+} + e^{-}$	\rightarrow Cu ⁺ ; E ^o = 0.15 V		
	$Cu^+ + e^-$	→ Cu; E ^o =0.5 V 2e ⁻ → Cu: is:		
	(A) 0.325 V	(B) 0.650 V	(C) 0.050 V	(D) 1.30 V
Q.8	Which of the follow	ving is always true reg	arding the spontaneity	of reaction occurring in a
	galvanic cell? (A) $F^{\circ} > 0$ A $G^{\circ} <$	0 and 0 > K	(B) $F^{0} < 0$ $AG^{0} <$	0 and 0 < K
	(C) $E_{cell}^{\circ} > 0, \Delta G^{\circ} >$	0 and $Q > K_c$	(D) $E^{\circ}_{cell} > 0, \Delta G^{\circ} <$	0 and $Q < K_c$
Q.9	If $E^{o}_{Fe2+ Fe} = x_1$ volt an	$d E^{o}_{Fe3+ Fe2+} = x_2 \text{ volt, th}$	hen $E^{o}_{Fe3+ Fe}$ will be :	
	(A) $(2x_1 + x_2)V$	(B) $(3x_2 - x_1)V$	(C) $\frac{(2x_1 + x_2)}{3}$ V	(D) $\frac{(x_1 + 2x_2)}{3}$ V
Q.10	Given that $E^{o}_{Cu2+/Cu} =$	$= 0.34 \text{ V}; \text{E}^{\circ}_{\text{Ag+ Ag}} = 0.5$	80 V; $E^{o}_{Mg2+ Mg} = -2.3$	7 and $E^{o}_{Al3+ Al} = -1.66 V$
	in which of the follow (A) Mg $ $ Mg ²⁺ (1M)	ving cells the standard f $\ Cu^{2+}(1M)\ Cu$	The energy decrease is r (B) $M\alpha + M\alpha^{2+}$ (1M)	maximum : $\ A \sigma^+ (1M) \ C u$
	$(C) Ag Ag^+ (1M) _A$	$ Cu^{(1M)} Cu^{(1M)} $	(D) $\operatorname{Cu} \operatorname{Cu}^{2+}(1M) $	$ Ag^+(1M) Cu $
		× / I	× / / / / / / / / / / / / / / / / / / /	

ELECT	FROCHEM	MISTRY						37
Q.11	The el given (A) 21 (C) 42	ectrical work d that : $E^{\circ}_{Cl2 Cl-}$ 0.37 kJ mol ⁻¹ 20.74 kJ mol ⁻¹	one during the $= 1.36 \text{ V}$; E°	Hg2Cl2 Hg, C	$\begin{array}{l} \text{at } 298 \text{ K} : 21 \\ \text{CH} = 0.27 \text{ V} : \\ \text{(B) } 105.185 \\ \text{(D) } 110.37 \text{ k} \end{array}$	Hg(l) + C $p_{C12} = 1$ $kJ mol^{-1}$ $kJ mol^{-1}$	$\operatorname{cl}_2(g) \longrightarrow H$ atm,	$[g_2Cl_2(s) \text{ is :}$
Q.12	Which (A) (B) (C) (D)	the following of the following $Zn ZnSO_4(ad)$ increase in the increase in pro- increase in mo- decrease in mo-	ng changes will q) $(x_1M) \parallel HCl$ volume of HC essure of hydro plarity x_2 from olarity x_1 from	cause th (aq) (x_2) I solution ogen from 0.1 to 1 I 1M to 0	the free energy M) $ H_2(g) , Pt$ n from 100 m n 1 atm to 2 at M .1 M	of the ce t 1 to 200 r tm	ll reaction to nl	decrease :
Q.13	If (A) (B) (C)	$Sn^{2+} + 2e^-$ $Sn^{4+} + 2e^-$ Sn^{2+} is unstab Sn^{2+} is stable a Sn^{4+} is easily to	→ Sn → Sn ²⁺ le and disprope and disproporti reduced to Sn	$E^{o} = -$ $E^{o} = 0$ ortionate onation	0.14 V .13 V es to Sn ⁴⁺ and reaction is no (D)	then : Sn t spontan none o	eous of these	
Q.14	For the	e reactions , or the reaction ,	$MnO_{4}^{-} + 8H^{+}$ $MnO_{2}^{-} + 4H^{+}$ $MnO_{4}^{-} + 4H^{-}$	+ + 5e ⁻ + 2e ⁻ + + 3e ⁻	$ \longrightarrow Mn^{2+} + 4 \rightarrow Mn^{2+} + 21 \rightarrow MnO_2 + $	H_2O, E° H_2O, E° $2H_2O,$	= 1.51 V = 1.23 V E° is :	
Q.15	(A) 1.For th(A) 1.	70 V e fuel–cell read 23 V	(B) 5.09 V etion : $2\text{H}_2 + \text{O}$ (B) 2.46 V	$_2 \longrightarrow 2$	(C) 0.28 V H ₂ O, $\Delta G = -4$ (C) 0.615 V	475 kJ. H	(D) 0.84 V Ience E _{cell} is (D) 0.31 V	:
Q.16	(i) (ii)	For the follow E_{cell} is 0.46 V (A) 193 JK ⁻¹ The temperatu (A) 0.02 VK ⁻¹	ving cell-react at 300 K and (B) 38 are coefficient of (B) 0.	ion, Cu 0.48 V a 86 JK ⁻¹ of the e.r .2 VK ⁻¹	$a(s) + 2Ag^{+}$ (a at 310 K. Her (C) 5 m.f. of the cell (C) 6	$\begin{array}{l} \text{in (q)} \longrightarrow \\ \text{for (r)} \\ \text{for (r)}$	$2Ag(s) + Cuopy change i(D)e question is\chi^{-1} (D)$	²⁺ (aq). is :) -193 JK ⁻¹ :) 2VK ⁻¹
Q.17	For th (A) C	is cell $Zn Zn^2$ $_1 = C_2$	+ $(C_1 M) Zn^{2+}$ (B) $C_1 > C_2$	(C ₂ M)	Zn. ΔG is ne (C) $C_2 > C_1$	gative if	: (D) none o	fthese
Q.18	For a A $\Delta G_f(A)$ Hence (A) 3.	Ag–Zn button c $ag_2O) = -11.21$ c, E°_{cell} of the but 182 V	tell, net reaction kJ mol ⁻¹ ΔG_{f} tton cell is : (B) 1.71 V	on is , Zr ZnO)=-	$h(s) + Ag_2O(s)$ -318.3 kJ mo (C) -1.591	$) \longrightarrow Z_{l}$ l^{-1} V	nO(s) + 2Ag (D) 1.591	(s) V
Q.19	Zn + Q value Q	$Cu^{+2} \longrightarrow Zn$ of equilibrium c 95×10^{37}	$E^{+2} + Cu; E^{o}_{cell} =$ constant for the (B) 4 4 × 10 ¹	= 1.1V above re	eaction: (C) 2×10^{35}		(D) 4 4 ×	1020
Q.20	(A) x (C) x	der the followin A + B = 2A + 2B = 2B $= y, K_1 = K_2$ $= y, K_1^2 = K_2$	equations for C + D 2C + 2D	$ E^{o} = x $ $ E^{o} = y $	action, ; $K_{eq} =$; $K_{eq} =$ (B) $x = 2y$, (D) $x_2 = y$,	$= \mathbf{K}_{1}$ $= \mathbf{K}_{2}$ $\mathbf{K}_{1} = 2\mathbf{K}$ $\mathbf{K}_{1}^{2} = \mathbf{K}_{2}$	2	
Q.21	For a Hence (A) 10	reaction, A + equilibrium co)	$B^{+2} \longrightarrow B + A$ nstant of the res (B) 10 ¹⁰	A ⁺² ; action is	E° = 0.2955 : (C) -10		(D) 10 ⁻¹⁰	

ELECT	FROCHEMISTRY			38
Q.22	If for a half cell re Cu ⁺² + e ⁻ - Cu ⁺² + 2e ⁻ Predict which exist (A) copper (I) sulf (C) both	actions . E ^o values are k $\longrightarrow Cu^+$; E ^o = $\longrightarrow Cu$; E ^o = t in aqueous solution : phate	nown , = 0.15 V = 0.34 V (B) copper (II) sulj (D) none of these	phate
Q.23	For the half-cell Hence, autoprotol (A) 1×10^{-10}	1 reaction, $2 H_2O + 2$ ysis constant for water i (B) 1×10^{-12}	$\begin{array}{l} \text{Re}^{-} \longrightarrow \text{H}_{2} + 2\text{OH}^{-},\\ \text{s:}\\ \text{(C) } 1 \times 10^{-13} \end{array}$	$E^{o} = -0.8277 \text{ V} \text{ at } 298 \text{ K}$. (D) 1×10^{-14}
Q.24	If a chemical read can be obtained fr	ction is carried out in a om the cell is :	fuel cell, the maximun	n amount of useful work that
	$(A)\Delta G$	$(B) \Delta H$	(C) $\frac{\Delta G}{\Delta H}$	(D) $T\Delta S$
Q.25	For electrosynthes (A) $\Delta G = +$ ve ar (C) $\Delta G = -$ ve an	sis of a substance : nd $E_{cell} = -ve$ d $E_{cell} = -ve$	(B) $\Delta G = -ve$ and (D) $\Delta G = +ve$ and	
Q.26	For hydrogen-oxy $\Delta G_{f}^{o}(H_{2}O) = -23'$ (A) +2.46 V	ygen fuel cell with react 7.2 kJ mol ⁻¹ . Hence e.m (B) –2.46 V	ion, $2H_2(g) + O_2(g) -$.f. of the fuel cell is : (C) +1.23 V	$\rightarrow 2H_2O(l)$ (D) -1.23 V
Q.27	For the reaction, (i) If free end formation (A) -3.16 (C) -0.262 (ii) $\Delta G^{o}_{f}[A](C)$ (A) -1.32 (C) -5.21	$4Al(s) + 3O_{2}(g) + 6H,$ ergy of formation of O of H ₂ O = -237.2 kJ motor × 10 ³ kJ mol ⁻¹ 3 ×10 ³ kJ mol ⁻¹ OH) ₄ ⁻] for the above case × 10 ³ kJ mol ⁻¹ × 10 ³ kJ mol ⁻¹	$O + 4OH^- \longrightarrow 4Al(0)$ $H^- (\Delta G^{\circ}_{f}[OH^-]) = -15$ OH^{-1} then ΔG° for this reforms (B) -0.79 × 10 ³ kJ (D) 0.263 × 10 ³ kJ e is : (B) - 3.16 × 10 ³ kJ (D) 0	$OH)_4^-$; $E_{cell}^0 = 2.73 V$ 7 kJ mol^{-1} , & free energy of fraction is : 1 mol^{-1} 1 mol^{-1} 3 mol^{-1}
Q.28	Given that $E^{o} = 0$ $Fe^{3+} + 3e^{-}$ (A) 20.84 kJ	.036 V, the free energy \longrightarrow Fe(s) (B) 3.47 kJ	change ΔG° for the reats: (C) 5.21 kJ	(D) 10.42 kJ
Q.29	(i) The standa Cd(s) Cd (0) in which th is 0.6915 (A) - 176	ard emf of the cell, $Cl_2(aq) \parallel AgCl(s) \mid Ag(s)$ $AgCl(s) \mid Ag(s)$ Ag(s) Ag	(c) $f(x) = 1$ (c) $f(x) = 1$	Ag(s) + Cd ²⁺ (aq) + 2Cl ⁻ (aq) action at 25°C is : 26 kJ (D) -125.06 kJ
	(ii) In the above $(A) + 123$.	ve questions, ΔH of the 5 kJ (B) -167.2	e reaction at 25 °C is : 6 kJ (C) +64.8	kJ (D)–125.06kJ
Q.30	For the cell reacti	on, $Cu^{2+}(aq) + Zn(s) -$	\longrightarrow Zn ⁺² (aq) + Cu(s))
	of an electrochem of: $(A)^{2/2} n(C_1)$	(C_1) tical cell, the change in $(B)^{2}^{2}h(C_2/C_1)$	(C ₂) free energy ΔG at a gi (C) $2\overline{21}n(C_1 + C_2)$	ven temperature is a function $(D)^{2\overline{2}n}(C_2)$
0.31	The standard emf	of the cell reaction $\frac{1}{2}$	$Cu(s) + \frac{1}{2}Cl(\sigma) \longrightarrow$	$\frac{1}{2}$ Cu ²⁺ + Cl ⁻
~~~	is 1.02 V. The val (A) unpredictable	lue of $\Delta G^{\circ}$ will be : (B) - 98.43 kJ	(C) - 196.86  kJ	(D) – 188.43 kJ

# Answer Key

3.	Daily Pr	actice Problem	n Sheet			
1.	(a) Q	(b) P (c) Q	$Q \longrightarrow Q^{+n} + ne^{-}$ (	(d) $P^{+m} + me^{-4}$	$\longrightarrow P$	
	(e) mQ + nP	$m \longrightarrow mQ^{+n} + nP$	(	(f) $E_{cell} = E_{cell}^0$	$\frac{0.059}{mn} \log \frac{[Q^{+n}]^m}{[P^{+m}]^n}$	
2.	(a) 0.47 V (e) 0.34 V (i) 0.198 V	(b) 0.78 V (f) .44 V (j) -0.07V	(c) -0.3 (g) .268	3 V V	(d) 0.78 V (h) -0.737 V	
3.	$3 \times 10^{-2} \mathrm{M}$	<b>4.</b> 0.81V	5. 0.55	V		
6.	(i) 0.32 V (v) 0.114V	(ii) 0.46 V (vi) 1.1 V	(iii) 0.12 (vii) 0.9	2 V 26 V	(iv) 0.656 V (viii) 0.008 V	
7.	(i) 0.699 V	(ii) .463 V				
8.	(i) Anode–Cu	ı, Cathode–Ag (ii) 0	.46 V (iii) 0.342	V		
9.	(i) $Zn + Cu^+$ (iii) $[Cu^{+2}] >$		(ii) 1.1 V			
10. 12.	<ul><li>(a) 1.2 V</li><li>(i) standrad</li><li>(v) standrad</li></ul>	(b) More (+) (ii) -0.1475 (v) -0.59V	ve <b>11.</b> V (iii) stan (vii) -0.	1.07 V dard 755 V	(iv) 0.0855 V (viii) –0.234 V	
13.	$2 \times 10^{-7}$	<b>14.</b> pH = 4	<b>15.</b> pH	= 1.12	16. $\frac{[Pb^{+2}]}{[Sn^{+2}]} < 0.458 \text{ V}$	
17.	0.02	<b>18.</b> 0.31 M	<b>19.</b> 3.33	$3 \times 10^{-4}$	<b>20.</b> 10 ⁻⁴ M	
4.	Daily Pr	actice Probler	n Sheet			
3.	1.1 V	<b>4.</b> 1.411 V	<b>5.</b> 0.95	V	<b>6.</b> 1.327 V	
7.	6.6	<b>8.</b> 9.46, 0.6	55 V <b>9.</b> –0.29	95 V	<b>10.</b> 5.6 × 10 ⁻³ V	
11.	0.0295 V	<b>12.</b> 7.6	<b>13.</b> 0.42	25 V	<b>14.</b> $0.96 \times 10^{-7}$ m	
15.	(i) 4.74	(ii) 0.0V	(iii) (Aı	(iii) (Anode) _{pH} = 4.5752, (cathode) _{pH} = 4.90		
16.	-0.076 V					
5.	Daily Pr	actice Probler	n Sheet			
1. A	<b>2.</b> D	<b>3.</b> (i)A, (ii)-	A 4. A	<b>5.</b> A	<b>6.</b> A	
<b>7.</b> A	8. D	<b>9.</b> C	<b>10.</b> B	<b>11.</b> A	<b>12.</b> C,D	
<b>13.</b> B	14. A	15. A	<b>16.</b> (i) -	B (ii)–C,	<b>17.</b> C	
<b>18.</b> D	<b>19.</b> A	<b>20.</b> C	<b>21.</b> B	<b>22.</b> B	<b>23.</b> D	
<b>24.</b> A	<b>25.</b> A	<b>26.</b> C	<b>27.</b> (i)-A	A, (ii)-A	<b>28.</b> D	
<b>29.</b> (i)	-(B) (ii)-(B)	<b>30.</b> B	<b>31.</b> B			