Type I: **Problems based on electrode reactions**:

1) Write the anode and cathode reactions for a galvanic cell that utilizes the reaction:

$$Ni_{(s)} + 2Fe^{2+} \rightarrow Ni^{2+} + 2Fe^{2+}$$

2) Write the electrode reactions, the overall reactions and the expression for emf for each of the following reversible cells.

1. Pt, $H_{2(atom)}$ | $HCl_{(aq)}$ | Pt, $Cl_{2(1\ atm)}$
2. Hg – $Hg_2C1_{2(s)}$ | $HCl_{(aq)}$ | Pt, $H_{2(1\ atm)}$
3. $Ag_{(s)}$ – $AgCl_{(s)}$ | $KCl_{(aq)}$ | $Hg_2Cl_{2(s)}$ – $Hg_{(s)}$
4. Ag – $AgCl_{(s)}$ | — | $KCl_{(s)}$ | $AgC1_{(s)}$ – $Ag_{(s)}$

3)Write the individual electrode reactions and the total cell reaction for the following cells:

a) $Ag_{(s)}$ – $AgCl_{(s)}$ | Cl^- | | I^- | $AgI_{(s)}$ = $Ag_{(s)}$
b) Pt | Fe^{2+} , Fe^{3+} | | MnO_4^{-1} , Mn^{2+} | Pt
c) Pt| $H_{2(g)}$ | HCl | $Cl_{2(g)}$, Pt
d) Ag | Ag^+ | | Fe^{2+} | | Fe

Type II : **Problems based on construction of cells**

1) Construct the cells in which the following reactions occur. Which of the electrode cell acts as anode and which one is cathode?

(i) **$Zn + CuSO_4$ $ZnSO_4 + Cu$**
(ii) $Fe + SnCl_2$ $FeCl_3 + Sn$
(iii) $Cu + 2AgNO_3$ $Cu(NO_3)_2 + 2Ag$
(iv) $Zn + H_2SO_4$ $ZnSO_4 + H_2$(Pt)

2) Set up the cell corresponding to each of the following cell react ions:

(i)$Sn(s) + Sn^{4+} \rightarrow 2Sn^{2+}$
(ii)$Cd(s) + Hg_2^{2+} \rightarrow Cd^{2+} + 2Hg_{(l)}$
(iii) $Zn(s) + 2AgC1(s) \rightarrow ZnC1_2\ (aq) + 2Ag(s)$

3) Construct the cell, showing the polarities of the electrodes to produce current from the reaction,

(i) $Zn_{(s)} + Cu^{2+}{}_{(aq)}$ $Zn^{2+}{}_{(aq)} + Cu_{(s)}$
(ii) $Cu_{(s)} + 2Ag^{+}{}_{(aq)}$ $Cu^{2+}{}_{(aq)} + 2Ag_{(s)}$

(iii) $2Cu^{2+}_{(aq)} \quad Cu_{(s)} + Cu^{2+}_{(s)}$
(iv) $2Al_{(s)} + 3Zn^{2+}_{(aq)} \quad 2Al^{3+}_{(aq)} + 3Zn_{(s)}$

4) Represent the Galvanic cells using line notations for the following cell reactions:
(i) $S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$
(ii) $Pb + 2Ag^+ \rightarrow Pb^{2+} + 2Ag$
(iii) $Cd + 2H^+ \rightarrow Cd^{2+} + H_2$
(iv) $Zn + 2AgCl \rightarrow ZnCl_2 + 2Ag$

Type III: **Problems based on calculation of single electrode potential**

1) Calculate standard potentials of the following electrodes at 298K
(i) $Zn \mid Zn^{2+}$ (a = 1)
(ii) $Pt|Fe^{3+}(a=0.01),Fe^{2+}(a=0.1)$
(iii) $Ag \mid AgNO_3$ (0.02m)
(iv) $Fe|FeSO_4(a=0.1)$ m)
(v) $Pt|FeCl_3(a=0.05m)FeCl_2(a=0.0001)$ m)
(Ans.: , (i) – 0.763 V (ii) + 0.712 V, (iii) 0.09004 V (iv) – 0.410 V (v) – 0.87 V)

2) Calculate the electrode potential of the following electrodes at 298K:
(i) $Pt \mid Fe^{2+}$ (a = 1) , Fe^{3+} (a = 0.1) ii) $Pt \mid I_{2(s)}$, I^- (a =0.03)
(Ans (i) 0.7118 V , (ii) +0.6257 V)

3) Calculate the potential of the following electrodes:
(i) $Co \mid Co^{2+}$ (a = 0.025)
(ii) $Ag \mid AgBr_{(s)}$, Br^- (a = 0.02)
(iii) $Pt \mid Sn^{2+}$ (a = 0.03), Sn^{4+} (a = 0.02)
(iv) $Al \mid Al^{3+}$ (a = 0.025)
(Ans. (i) E = – 0.3244 V, (ii) E = 0.1716 V, (iii) E = 0.1448 V , (iv) E = 1.6935V)

4) Calculate the potential of the electrode, $Ag \mid AgCl_{(s)}$, Cl^- (a = 0.01)
(Ans. E = 0.3407 V)

5) For the galvanic cell, $Zn \mid Zn^{2+}(1M) \mid \mid Ag^+(1M) \mid Ag$, Calculate the cell potential when the standard reduction electrode potentials of Zn and Ag electrodes are – 0.763 V and +0.8 V respectively.
(Ans. Cell potential = 1.563 V)

6) What is the potential of the following electrode at 298K:
Zn^{2+} (2.0×10^{-3}M) | Zn (s) , E^0 = – 0.76 V
(Ans.E = – 0.84 volts)

7) Calculate the electrode potential if the following half cells at 298K
(i) $Zn \mid Zn^{+2}$ (a = 0.15M)
(ii) $Ag_{(s)} – AgBr_{(s)} \mid Br^-$ (a = 0.2)

(Ans : (i) = – 0.7548V , (ii) = 0.112V)

Type IV:**Problems based on Nernst equation and spontaneity of a process**

1) Write the Nernst equation for the following processes at some temperature T.
a) $Mg_{(s)} + Sn^{2+}{}_{(aq.)} \rightarrow Mg^{2+}{}_{(aq)} + Sn_{(s)}$
b) $2Cr_{(s)} + 3Pb^{2+}{}_{(aq)} \rightarrow 2\ Cr^{3+}{}_{(aq)} + 3Pb_{(s)}$
c) $Sr_{(s)} + Mg^{2+}{}_{(aq)} \rightarrow Sr^{2+}{}_{(aq)} + Mg_{(s)}$

2) Construct the cell with Zn | Zn^{2+} and Cd^{2+} | Cd electrode. Write the cell reactions. Also indicate the polarities and determine the standard e.m.f. of the cell. Given that SRP of Zn^{2+} | Zn = – 0.763 volt and of Cd^{2+} | Cd = – 0.403V.

(Ans. = +0.360 volt)

3) Construct the cell with Zn | Zn^{2+} and Ag | Ag^{+} electrode. Write the cell reactions. Also indicate the polarities and determine the standard e.m.f. of the cell.
Given Zn^{2+} | Zn = – 0.763 volt and of Ag^{+} | Ag = + 0.799V.

(Ans. = 1.562 volts)

4) Construct the cell indicating the polarities of the electrodes to produce current from the reaction: $Cu_{(s)} + 2Ag^{+}{}_{(aq)}$ $Cu^{2+}{}_{(aq)} + 2Ag_{(s)}$.
Calculate the std. emf of the cell.
Given Cu^{2+} | Cu = +0.337 volt and of Ag^{+} | Ag = + 0.799 volt

(Ans. = 0.462 volts)

5) The following reaction takes place in a cell: $Zn(s) + Co^{2+}$ $Co(s) + Zn^{2+}$ Write down the electrode reactions and calculate the standard e.m.f. of cell.
Given that E^0 of Zn| Zn^{2+} = 0.76 volt and of Co | Co^{2+} = 0.28V.

(Ans. = 0.48 volts)

6) Calculate the e.m.f. of the cell at 298K : Fe | $FeSO_4$(0.1M) | | $CuSO_4$ (0.1M) |Cu .
Given that E^0 of Fe| Fe^{2+} = 0.44 volt and of Cu^{2+} | Cu= 0.337V.

(Ans.E = 0.75 volts)

7) Calculate the e.m.f. of the following cell at 298 K
Sn | Sn^{2+} (a=1) | | Pb^{2+} (a = 1)| Pb
Standard potential of Sn^{2+} | Sn = – 0.14 V
Standard potential of Pb^{2+} | Pb = – 0.126V

8) Calculate the e.m.f. of the following cell at 298K:
Sn(s) | Sn^{2+} (0.05m) | |H^{+}(0.02M) | H_2(l atm)Pt

(Ans. 0.08V)

9) Predict whether the following reaction would proceed spontaneously at 298 K.
$Co_{(s)} + Fe^{2+}{}_{(aq)} \rightarrow Co^{2+}{}_{(aq)} + Fe_{(s),}$
given that $[Co^{2+}]$ = 0.15m and $[Fe^{2+}]$ =0.68 m

(Ans $E^0 = -0.14V$, therefore the reaction is non-spontaneous)

10) Calculate the e.m.f. of the following cells at 298 K.

(i)**$Zn_{(s)}|ZnCl_2,(0.0102m),AgCl_{(s)}|Ag$**

(ii) **Pt , H_2 (1 atm) | H_2S0_4 (0.05m), $Hg_2SO_{4(s)}$ | Hg**

(Ans. (i) 0.717 V, (ii) 0.7353 V)

11) The e.m.f. of the cell : Cd | CdI_2 (m = ?), $AgI_{(s)}$ | Ag
is 0.286 V at 298K. Calculate the concentration of CdI_2 solution.

(Ans. Molarity of CdI_2 = 0.4002)

12) For the reaction $Fe^{3+} + 3e^-$ Fe , $E^0 = -0.04V$ and for reaction $Fe^{3+} | Fe^{2+}$, E^0 = +0.77V – 0.04V. Calculate E° for Fe | Fe^{2+} reaction.
Is the reaction $Fe + 2Fe^{3+}$ $3Fe^{2+}$ spontaneous or non-spontaneous.

(Ans. $E^0 = -0.44$ V, spontaneous)

13) The e.m.f. of the following cell at 298 K is 0.3991 V
$^-$Ag | $AgCl_{(s)}$, Cl^- (a = 0.1) | | Ag^+ (a = 0.01) Ag^+
If the standard potential of silver-silver chloride electrode is + 0.2224. Calculate
The standard potential of Ag^+/Ag electrode.

(Ans. 0.7991)

14) Set up the cell in which the following reaction takes place and calculate the e.m.f. of the cell.
$2Al_{(s)} + 3I_2$ $2Al^{+3}(0.lm) + 6I^-$ (0.01m)

(Ans. 2.20 V)

15) The standard potentials of Pb $|Pb^{2+}$ and Sn $| Sn^{2+}$ electrodes are – 0.126 V and – 0.14 V respectively .Construct the galvanic cell, write the cell reaction and calculate the standard e.m.f. of the cell. (Ans. E^0_{cell} = 0.014V)

16) The standard potentials of Zn $|Zn^{2+}$ and Ag $| Ag^+$ electrodes are – 0.763 V and + 0.799 V respectively. Construct the galvanic cell , mention the polarities, write the cell reaction and calculate the standard e.m.f. of the cell . (Ans. E^0_{cell} = 1.562V)

17)Calculate the emf of the following cell at 298K:
Pt | $I_{2(s)}$, I^- (a = 0.03) | | Fe^{3+} (a = 0.1) , Fe^{2+} (a =1) | Pt

(Ans**. E = 0.0861 V**)

18) Find the emf of the following cell at 298K:
Ag | $AgCl_{(s)}$, Cl^- (a = 0.1) | | Ag^+ (a = 0.01) | Ag

(Ans. **E_{cell} = 0.3991 V)**

19) The emf of the following cell:
Pt | Sn^{2+} (a = 0.1) , Sn^{4+} (a = 0.1) | | Cl^- (a = 0.01) , Cl_2 (g, 1 atm) | Pt

(Ans. **= 1.3595 V)**

20) The emf of the cell : Ag | $AgCl_{(s)}$, Cl^- (a = ?) | | Fe^{2+} (a = 0.1) , Fe^{3+} (a = 0.01) | Pt is 0.4303 V. calculate the activity of chloride ions.

(Ans. **= 0.1)**

21) Find the emf of the following cells:
(i) Cu^+ | Cu^{2+} (a = 0.1) | | Ag^+ (a = 0.01) | Ag
(ii) Al | Al^{3+} (a = 0.01)| | Cl^- (a = 0.02) , Cl_2 (g , 1 atm) | Pt

(iii) Ag | $AgBr_{(s)}$, Br^- (a = 0.01)| | Cl^- (a = 0.02) , Cl_2 (g , 1 atm) | Pt
(iv) Pt | $I_{2(s)}$, I^- (a = 0.03)| | Ag^+ (a = 0.02) | Ag
(Ans. (i) E_{cell} = 0.4325V , (ii) E_{cell} = 3.0335 V , (iii) E_{cell} = 1.2707V , (iv) E_{cell} = 0.0729 V)

22)What is the standard emf of a galvanic cell made of a Cd electrode dipped in 1.0M $Cd(NO_3)_2$ solution and a Cr electrode dipped in a 1.0M $Cr(NO_3)_3$ solution at 25^0C.
Given ,

(Ans. = 0.34V)

23) A galvanic cell consists of a Mg electrode in a 1.0M $Mg(NO_3)_2$ solution and a Ag electrode in a 1.0M $AgNO_3$ solution. Calculate the standard e.m.f. of the cell at 25^0C.
Given the standard reduction potential of ,

(Ans. = 3.17V)

24) Predict whether the following reaction will occur spontaneously at 298K:
$Co_{(s)}$ + → + $Fe_{(s)}$, Given that $[Co^{2+}]$ = 9.15M and $[Fe^{2+}]$ = 0.68M
(Ans : E_{cell} = – 0.14 V , since it is negative the reaction is non-spontaneous)

25) Calculate the emf of the following cell:

$^-Fe_{(s)}$ | Fe^{2+} (a = 0.1) | | Cd^{2+} (a = 0.05) | Cd^+ ,
Given = – 0.441V, = – 0.403V , will the cell reaction is spontaneous?
(Ans : E_{cell} = 0.0291 , since it is positive the cell reaction is spontaneous)

26)Calculate the emf of the following cells at 298K:
(a) $Hg_{(l)}$ – $Hg_2Cl_{2(s)}$ | $KCl_{(sat)}$ | | Co^{+2}, Co^{+3} | Pt
= 0.242 V 0.242V = = 1.82V
The ratio of [Co+3]/[Co+2] = 3

(Ans : E_{cell} = 1.606 V)

(b) _ +
Pt | Sn^{+2} , Sn^{+4} | | $KCl_{(sat)}$ | $Hg_2Cl_{2(s)}$ – $Hg_{(l)}$, —— = 2
= – 0.140 V , $E_{calomel}$ = 0.242 V

(Ans : E_{cell} = 0.3909 V)

27) Calculate the emf of the following concentration of cell:
$Mg_{(s)}$ | | | | $Mg_{(s)}$

(Ans : E_{cell} = 0.3909 V)

28)Calculate the standard emf of a cell that uses Mg/Mg^{2+} and Cu/Cu^{2+} half cell at 25^0C. Write the cell representation Write the equations for the cell reaction that occurs under standard state conditions.

29)Calculate the standard emf of a cell that uses Ag/Ag^+ and Al/Al^{3+} half cell reactions. Represent the cell using line notations and write the overall cell reaction under standard

state conditions.

30) Calculate the em.f. of the cell:
$Zn \mid Zn^{2+}$ (0.001m) $\mid\mid Ag^{+}$ (0.1m) $\mid Ag$.
The standard potentials of $Ag \mid Ag^{+}$ and $Zn \mid Zn^{2+}$ electrodes are + 0799 V and – 0.763V respectively.

(Ans. E_{cell} = 1.5916 V)

Type V:**Problems based on calculation of equilibrium constant**

1)Calculate the equilibrium constant for the reaction taking place in the cell:
$Zn \mid Zn^{2+}$ (a = 1) $\mid\mid Sn^{2+}$ (a = 1) Sn

(Ans. $K = 1.122 \times 10^{21}$)

2) An excess of metallic zinc is added to 0.1M solution of $AgNO_3$. Calculate the (i) equilibrium constant and (ii) concentration of Ag^{+} ions at equilibrium.

(Ans. (i) $K = 5.888 \times 10^{52}$, (ii) = 9.215×10^{-28})

3) At 298K, an excess of finely divided aluminium is added to a solution 0.3M in cupric ions. Calculate the concentration of Cu^{2+} when equilibrium is reached. Assume activity and concentration to be equal. Experimentally it has been found that the reaction goes practically to completion.

(Ans. = 1.175×10^{-68})

4) The equilibrium constant for the reaction: ½ H_2 (g , 1 atm) + $AgI_{(s)}$ = H^{+} + I^{-} +$Ag_{(s)}$ is 2.68×10^{-3} at 298K. Devise a cell in which this reaction takes place and calculate the standard potential of the $Ag \mid AgI_{(s)}, I^{-}$ electrode.

(Ans. = – 0.1523 V)

5) For the following cell, $Pt \mid H_2$ (g, 1 atm) | HI solution (a = 1) $\mid I_{2(s)}$ Pt calculate (i) the emf ,(ii) ΔG^0 and (iii) equilibrium constant for the cell reaction at 298 K.

(Ans. (i) = 0.5355 V , ΔG^0 = – 51.68 kJ , (iii) $K = 1.111 \times 10^{9}$)

6) Calculate the standard free energy change for the following reaction at 298K:
2Au(s) + $\rightarrow 2Au^{3+} + 3Ca_{(s)}$, state whether this reaction is spontaneous or not.

(Ans. $\Delta G^0 = 2.53 \times 10^{3}$ kJ/mol , spontaneous)

7) Calculate the equilibrium constant for the following reaction at 298K:
Sn(s) + (Ans : $K = 6.367 \times 10^{9}$)

8)What is the equilibrium constant for the following reactions at 25°C.
$Mg + Zn^{2+}_{(aq)}$ $Mg^{2+}_{(aq)} + Zn$

(Ans. $K = 1.536 \times 10^{51}$)

9) The equilibrium constant for the reaction:
$Sr + Mg^{2+}_{(aq)}$ $Sr^{2+}_{(aq)} + Mg$ is 2.69×10^{12} at 25°C. Calculate

(Ans. = 0.368 V)

Type VI: **Problems based on calculation of ΔG, ΔH and ΔS**

1) The emf of the cell, Pb | $PbCl_{2(s)}$, KCl(soln), $Hg_2Cl_{2(s)}$ |Hg is 0.5356 V at 298K. The temperature coefficient is 1.45 x $10^{-4}VK^{-1}$. Calculate the ΔG , ΔH and ΔS for the cell reaction at 298K.

(Ans.ΔG = –103.4kJ , ΔH =–95.03 kJ ,ΔS = 27.99 JK^{-1})

2) For the cell, Zn | $ZnCl_{2(aq)}$ | $AgCl_{(s)}$ Ag the emf is 1.02 V at 273K and 1.0196 at 274K. Write the cell reaction and calculate ΔH , ΔS and ΔG for the cell reaction at 273K.

(Ans.ΔH = –217.9kJ , ΔS =–77.2 J , ΔG = – 196.9 kJ)

3) The emf of the cadmium – calomel cell in which the reaction Cd + = Cd^{2+}+ 2Hg, takes place is, represented by E = 0.6705 – 1.02 x 10^{-4}(T – 298) – 2.40 x 10^{-6} (T – 198)^2 volt. Set up the cell and calculate ΔH , ΔS and ΔG for the cell reaction at 298K.

(Ans.ΔH = –135.27kJ , ΔS =–19.69 J , ΔG = – 129.41 kJ)

4)The emf of a Clark cell is 1.4209 V at 298 K and 1.391 V at 318 K. The cell reaction is $Zn + Hg_2 SO_4 \rightarrow ZnSO_4 + 2 Hg$, Calculate ΔG, ΔH and ΔS at 298 K.

(Ans. : ΔG = – 274233 J, ΔS = – 288.53 $J.K^{-1}$ and ΔH = – 360215.6 J)

5)The emf of the cell

$Zn_{(s)}$ | $ZnCl_{2(aq)}$. $AgCl_{(s)}$ /$Ag_{(s)}$

is 0.20 at 275 K and 1.011 V at 285K.

Write the cell reaction, calculate temperature coefficient of cell emf and ΔS , ΔG , and ΔH at 285 K for the cell reaction.

(Ans. = — = 0.811 V K^{-1}. ΔS = 156523J K^{-1}, ΔH =ΔG_{285K}= 195123J. mol^{-1}

ΔH = 4.449 x 10^7J mol^{-1})

----------X----------