

K. J. Somaiya College of Engineering, Vidyavihar, Mumbai 400077.

(A Constituent College of Somaiya Vidyavihar University.)

Department of Science and Humanities
Applied Chemistry Laboratory

Subject: Engineering Chemistry

Therefore, EMF of the cell = 3.354 V

The Gibb's free energy change of the cell reaction, ΔG = Negative

The Equilibrium constant of the cell reaction, $K = > 1$

The spontaneity of the cell reaction = Spontaneous

Anode : $\text{Ba(s)} \rightarrow \text{Ba}^{2+}(\text{aq}) + 2\text{e}^-$

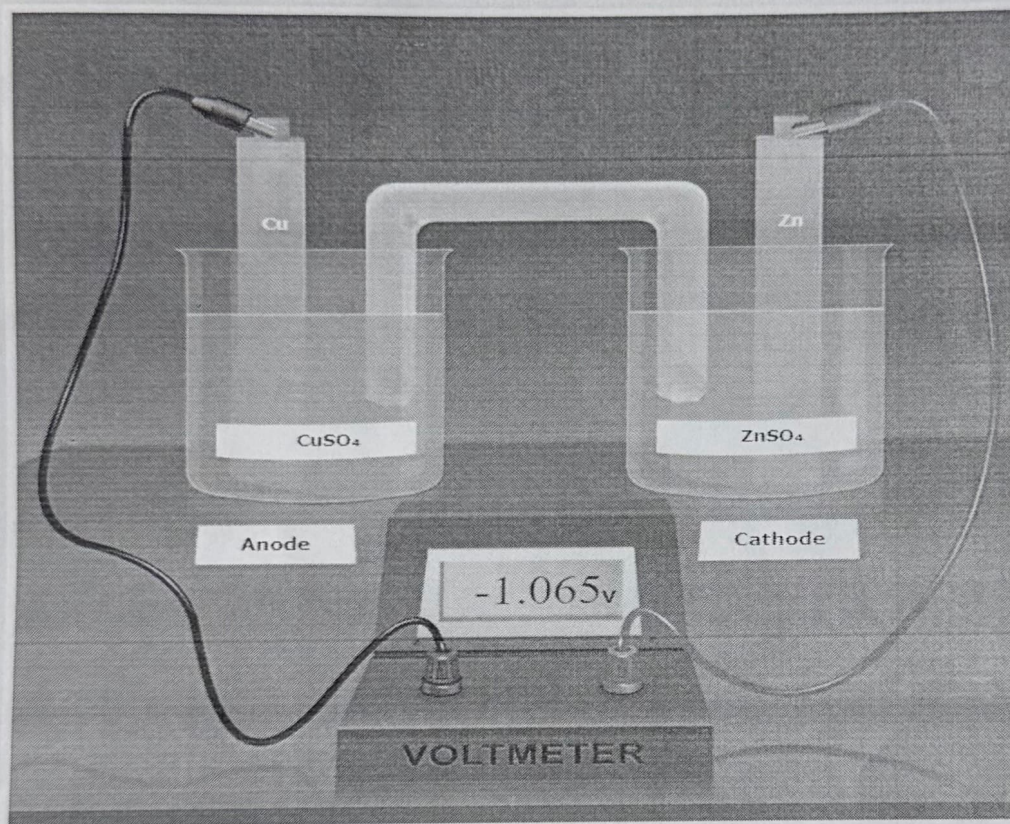
Cathode : $2\text{Ag}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Ag(s)}$

Overall Reaction: $\text{Ba(s)} + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Ba}^{2+}(\text{aq}) + 2\text{Ag(s)}$

Cell Reaction:

$\text{Ba}_{(\text{s})} \mid \text{BaCl}_{2(\text{aq})} \parallel \text{AgNO}_{3(\text{aq})} \mid \text{Ag}_{(\text{s})}$

2)



Temperature = 20° C

Cathode used = Zinc

Concentration of electrolyte = 10 M

Anode used = Copper

Concentration of electrolyte = 3 M

Therefore, EMF of the cell = -1.065 V

The Gibb's free energy change of the cell reaction, ΔG = Positive

The Equilibrium constant of the cell reaction, K = >1

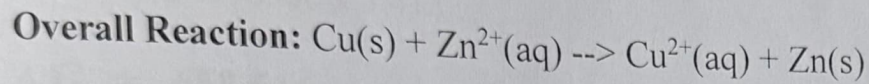
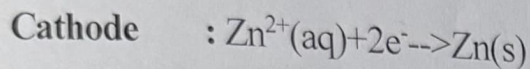
The spontaneity of the cell reaction = Non-Spontaneous

Anode : $\text{Cu(s)} \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$

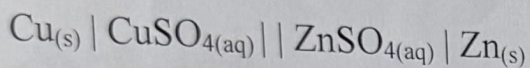


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Cell Representation:



Calculations:

1)

$$E^\circ_{\text{Cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$E^\circ_{\text{Cell}} = (0.80) - (-2.90)$$

$$E^\circ_{\text{Cell}} = 3.7$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{RT}{nF} \right) \ln \left(\frac{[\text{Ba}^{2+}]}{[\text{Ag}^+]^2} \right)$$

$$E_{\text{cell}} = 3.7 - \frac{2.303 \times 8.314 \times 303.15}{2 \times 96500} \log \frac{0.01^2}{10^2}$$

$$E_{\text{cell}} = 3.7 - 0.288$$

$$\underline{E_{\text{cell}} = 3.412}$$

$$\text{Electric work done} = nFE_{\text{cell}}$$

$$-\Delta G = nFE_{\text{cell}}$$

Therefore,

$$\Delta G = -nFE_{\text{cell}}$$

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$$= -2 \times 96500 \times 3.412$$

$$\Delta G = -658.516$$

$$-\Delta G^0 = nFE_{\text{cell}}^0$$

$$\Delta G^0 = -nFE_{\text{cell}}^0$$

$$= -2 \times 96500 \times 3.7$$

$$\Delta G^0 = -714.100 \text{ kJ}$$

$$\Delta G^0 = -RT \ln K$$

$$-714.100 = -8.314 \times 303.15 \ln K$$

$$\ln K = -714.100 / -2520.38$$

$$\ln K = 0.28$$

$$\underline{K = 1.32}$$

2)

$$E_{\text{Cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$$

$$E_{\text{Cell}}^0 = (-0.76) - (0.34)$$

$$E_{\text{Cell}}^0 = -1.1$$

$$E_{\text{cell}} = E_{\text{cell}}^0 - (RT/nF) \ln ([\text{Cu}^{2+}]/[\text{Zn}^{2+}])$$

$$E_{\text{cell}} = -1.1 - \frac{2.303 \times 8.314 \times 293.15}{2 \times 96500} \log \frac{3^2}{10^2}$$

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$$E_{\text{cell}} = -1.1 - (-0.069)$$

$$E_{\text{cell}} = -1.1 + 0.069$$

$$\underline{E_{\text{cell}} = -1.031}$$

$$\text{Electric work done} = nFE_{\text{cell}}$$

$$-\Delta G = nFE_{\text{cell}}$$

Therefore,

$$\Delta G = -nFE_{\text{cell}}$$

$$= -2 \times 96500 \times -1.031$$

$$\underline{\Delta G = 198.983 \text{ kJ}}$$

$$-\Delta G^0 = nFE_{\text{cell}}^0$$

$$\Delta G^0 = -nFE_{\text{cell}}^0$$

$$= -2 \times 96500 \times -1.1$$

$$\underline{\Delta G^0 = 212.3 \text{ kJ}}$$

$$\Delta G^0 = -RT \ln K$$

$$212.3 = -8.314 \times 293.15 \ln K$$

$$\ln K = 212.3 / -2437.24$$

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$$\ln K = -0.08$$

$$K = 0.92$$

Assignment:

1. What is the electrode potential of electrode in which conc. of Mg^{2+} is 0.01 M? =- 2.36 V.

Ans: $E_{Mg^{2+}/Mg} = E^{\circ}_{Mg^{2+}/Mg} + 0.0591/n \times \log [Mg^{2+}]/[Mg]$

$$E_{Mg^{2+}/Mg} = -2.36 + 0.0591/2 \times \log (0.01/1)$$

$$E_{Mg^{2+}/Mg} = -2.42 \text{ V}$$

2. 100 mL of a neutral solution containing 0.2 g of copper was electrolysed till the whole of copper was deposited. The current strength was maintained at 1.2 and the volume of solution was maintained at 100 mL. Assuming 100% efficiency, find out the time taken for deposition of copper. [At.wt of copper = 63.58]

Ans: The quantity of electricity passed (100% efficiency) = $Q(C)$
 $= I(A) \times t(s)$
 $= 1.2 \text{ A} \times t(s)$
 $= \underline{1.2t \text{ C.}}$

The atomic weight of copper = 63.58 g/mol.

$$\text{Moles of electrons passed} = Q / 96500 = 1.2t / 96500$$

The mass of copper deposited = 0.2 g.

Hence,

$$0.2 \text{ g} = \text{atomic weight of copper} \times \text{mole ratio} \times \text{moles of electrons passed}$$

$$0.2 \text{ g} = 63.58 \times 1/2 \times 1.2t / 96500$$

$$t = 506s.$$

3. The reduction potentials of and electrode are 0.34 V and 0.80 V respectively. Construct a galvanic cell using these values. For what concentration of Ag^+ ions will e.m.f of the cell at 25 °C be zero if conc. of Cu^{2+} is 0.01 M. Given, $E_{Cu^{2+}/Cu} = 0.34$ volt and $E_{Ag^+/Ag} = 0.80$ volt.

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Ans: Given, $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$ and $E^{\circ}_{\text{Ag}^{+}/\text{Ag}} = 0.80 \text{ V}$.
The standard emf will be positive if Cu/Cu^{2+} is anode and Ag^{+}/Ag is cathode. The cell can be represented as:
 $\text{Cu} \mid \text{Cu}^{2+} \parallel \text{Ag}^{+} \mid \text{Ag}$

The cell reaction is,
 $\text{Cu} + 2\text{Ag}^{+} \rightarrow \text{Cu}^{2+} + 2\text{Ag}$

$$\begin{aligned} E^{\circ}_{\text{cell}} &= \text{Oxid. potential of anode} + \text{Red. potential of cathode} \\ &= -0.34 + 0.80 \\ &= 0.46 \text{ volt} \end{aligned}$$

Applying the Nernst equation,
 $E_{\text{cell}} = E^{\circ}_{\text{cell}} - 0.0591/2 \times \log [\text{Cu}^{2+}] / [\text{Ag}^{+}]^2$

When, $E_{\text{cell}} = 0$
 $E^{\circ}_{\text{cell}} = 0.0591/2 \times \log [\text{Cu}^{2+}] / [\text{Ag}^{+}]^2$
or $\log [\text{Cu}^{2+}] / [\text{Ag}^{+}]^2 = 0.462 \times 2 / 0.0591 = 15.6345$

$$\begin{aligned} [\text{Cu}^{2+}] / [\text{Ag}^{+}]^2 &= 4.3102 \times 10^{15} \\ [\text{Ag}^{+}]^2 &= 0.01 / 4.3102 \times 10^{15} \\ &= 0.2320 \times 10^{-17} \\ &= 2.320 \times 10^{-18} \\ [\text{Ag}^{+}] &= \underline{\underline{1.523 \times 10^{-9} \text{ M}}} \end{aligned}$$

4. Calculate the maximum work that can be obtained from the Daniel cell. Given that $E^{\circ}_{\text{anode}} = -0.76 \text{ V}$ and $E^{\circ}_{\text{cathode}} = +0.34 \text{ V}$ respectively.

Ans: According to given cell reaction
 $E^{\circ}_{\text{anode}}(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$
 $E^{\circ}_{\text{cathode}}(\text{Cu}^{2+}/\text{Cu}) = +0.34 \text{ V}$
 $n = 2$

$$\begin{aligned} \text{Now, } W_{\text{electrical}} &= -nF E^{\circ}_{\text{cell}} \\ &= -2 \times 96500 \times [0.34 - (-0.76)] \\ &= -2 \times 96599 \times 1.1 \\ &= \underline{\underline{-212.3 \text{ K Joule}}} \end{aligned}$$

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5. For Daniel Cell involving the cell reaction, the standard free energies of Zn (s), Cu (s), Cu^{2+} (aq) and Zn^{2+} (aq) are 0, 0, 64.4 KJmol^{-1} and -154.0 KJmol^{-1} respectively. Calculate the standard EMF of the cell.

Ans.: $\Delta G^0 = (G_{\text{Zn}^{2+}}^0 - G_{\text{Cu}^{2+}}^0) = (-154 - 64.4) \text{KJ/Mole}$

$$\therefore (-2 \times E^0 \times F) = (-218.4 \times 103)$$

$$\therefore E^0 = 1.1316 \text{volt}$$

Result:

1)

1. The EMF of the cell is 3.412V

2. The Gibb's free energy change of the cell reaction, $\Delta G = \underline{-658.516 \text{ kJ}}$

3. The Equilibrium constant of the cell reaction, $K = \underline{1.32}$

4. The spontaneity of the cell reaction = Spontaneous

2)

1. The EMF of the cell is -1.031V

2. The Gibb's free energy change of the cell reaction, $\Delta G = \underline{198.983 \text{ kJ}}$

3. The Equilibrium constant of the cell reaction, $K = \underline{0.92}$

4. The spontaneity of the cell reaction = Non-Spontaneous

Conclusion:

Thus, we have measured the EMF of a cell and predicted the spontaneity of the cell reaction.