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Solution of Tutorial I, Engineering Chemistry, Electrochemical Cells

1. Write cell notation, electrode reaction and E_{cell} for a cell at 25°C having following electrodes: $E_{\text{Zn}^{++}/\text{Zn}}^{\circ} = -0.76 \text{ V}$, $[\text{Zn}^{++}] = 1.2\text{M}$, $E_{\text{Cu}^{++}/\text{Cu}}^{\circ} = -0.34 \text{ V}$, $[\text{Cu}^{++}] = 0.01\text{M}$.

Solution: $E_{\text{Cu}^{++}/\text{Cu}}^{\circ} = 0.34 \text{ V}$

Cell Notation $\text{Zn} / \text{Zn}^{++} (1.2 \text{ M}) // \text{Cu}^{++} (0.01\text{M}) / \text{Cu}$

Cell Reaction Anode: $\text{Zn} \longrightarrow \text{Zn}^{++} + 2\text{e}^-$ (oxidation)
Cathode: $\text{Cu}^{++} + 2\text{e}^- \longrightarrow \text{Cu}$ (reduction)

Net Reaction: $\text{Zn} + \text{Cu}^{++} \longrightarrow \text{Zn}^{++} + \text{Cu}$ (redox reaction)

Now, $E_{\text{cell}} = E^{\circ}_{\text{cell}} - 2.303 \frac{RT}{nF} \log Q$

Since, $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = 0.34 - (-0.76) = 1.1 \text{ Volt}$

And, $Q = \frac{[\text{Zn}^{++}][\text{Cu}]}{[\text{Cu}^{++}][\text{Zn}]} = \frac{[\text{Zn}^{++}]}{[\text{Cu}^{++}]} = \frac{1.2}{0.01}$

Therefore, $E_{\text{cell}} = 1.1 - 2.303 \frac{8.314 \times 298}{2 \times 96500} \log \frac{1.2}{0.01} = \mathbf{1.038 \text{ V Answer}}$

2. From the given electrode couple $E_{\text{Fe}^{++}/\text{Fe}}^{\circ} = 0.44 \text{ volt}$, $[\text{Fe}^{++}] = 0.5\text{M}$ and $E_{\text{Ag}^{+}/\text{Ag}}^{\circ} = -0.80\text{volt}$, $[\text{Ag}^{+}] = 0.2\text{M}$. Write the (i) electrode reaction (ii) net cell reaction (iii) cell notation (iv) E_{cell} and (v) spontaneity of the cell.

Solution: Cell Notation $\text{Fe} / \text{Fe}^{++} (0.5 \text{ M}) // \text{Ag}^{+} (0.2\text{M}) / \text{Ag}$

Cell Reaction Anode: $\text{Fe} \longrightarrow \text{Fe}^{++} + 2\text{e}^-$ (oxidation)
Cathode: $2\text{Ag}^{+} + 2\text{e}^- \longrightarrow 2\text{Ag}$ (reduction)

Net Reaction: $\text{Fe} + 2\text{Ag}^{+} \longrightarrow \text{Fe}^{++} + 2\text{Ag}$ (redox reaction)

Now, $E_{\text{cell}} = E^{\circ}_{\text{cell}} - 2.303 \frac{RT}{nF} \log Q$

Since, $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = 0.80 - (-0.44) = 1.24 \text{ Volt}$

And, $Q = \frac{[\text{Fe}^{++}][\text{Ag}]^2}{[\text{Ag}^{+}]^2[\text{Fe}]} = \frac{[\text{Fe}^{++}]}{[\text{Ag}^{+}]^2} = \frac{0.5}{0.2^2}$

Therefore, $E_{\text{cell}} = 1.24 - 2.303 \frac{8.314 \times 298}{2 \times 96500} \log \frac{0.5}{0.2^2} = \mathbf{1.207\text{V Answer}}$

3. Find the Emf of the cell at 25°C in which silver electrodes are dipped in 0.1 M and 0.5 M silver nitrate solution respectively. $E_{\text{Ag}^{+}/\text{Ag}}^{\circ} = -0.80\text{volt}$

Solution: $E_{\text{Ag}^{+}/\text{Ag}}^{\circ} = 0.80\text{volt}$ (standard reduction potential)

Reduction rxn: $\text{Ag}^{+} + \text{e}^- \longrightarrow \text{Ag}$

$\therefore Q = \frac{[\text{Ag}]}{[\text{Ag}^{+}]} = \frac{1}{[\text{Ag}^{+}]}$

For first electrode (silver dipped in 0.1M silver nitrate) at 25°C;

$E_{1\text{red}} = E^{\circ}_{\text{red}} - \frac{0.0591}{n} \log \frac{1}{[\text{Ag}^{+}]} = 0.80 - \frac{0.0591}{1} \log \frac{1}{0.1} = 0.7409 \text{ V}$

For second electrode (silver dipped in 0.5M silver nitrate) at 25°C;

$$E_{2\text{red}} = E^{\circ}_{\text{red}} - \frac{0.0591}{n} \log \frac{1}{[Ag^+]} = 0.80 - \frac{0.0591}{1} \log \frac{1}{0.5} = 0.7822 \text{ V}$$

Since the reduction potential of second electrode is greater it functions as cathode.

$$\therefore E_{\text{cell}} = E_{2\text{red}} - E_{1\text{red}} = 0.7822 - 0.7409 = \mathbf{0.413 \text{ V Answer}}$$

4. The Emf of a cell consisting of standard AgCl/Ag, Cl⁻ electrode and copper electrode dipped in CuSO₄ is found to be 0.06V. What is the molar concentration of Cu⁺⁺ ions in the cell?



Solution: Looking at the reduction potential value, the system of Cu function as cathode and AgCl/Ag, Cl⁻ function as anode.

$$\therefore E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$\text{Or, } E_{\text{cathode}} = E_{\text{cell}} + E_{\text{anode}} = 0.06 - 0.22 = -0.16 \text{ V [anode is in standard state]}$$

$$\text{Now, } E_{\text{cathode}} = E^{\circ}_{\text{cathode}} - \frac{0.0591}{n} \log \frac{1}{[Cu^{++}]}$$

$$\text{Or, } -0.16 = 0.34 - \frac{0.0591}{2} \log \frac{1}{[Cu^{++}]}$$

$$\therefore [Cu^{++}] = \mathbf{0.01 \text{ M Answer}}$$

5. The Emf of a following cell of the following cell at 25°C is 1.12 volt. Find the concentration of CuSO₄? Zn/ Zn⁺⁺ (0.1M) // Cu⁺⁺ (xM)/ Cu. Standard electrode potential provided in the previous questions.

Solution: Cell reaction from question 1 (same)



$$\therefore Q \frac{[Zn^{++}]}{[Cu^{++}]} = \frac{0.1}{[Cu^{++}]}$$

$$\text{Since, } E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = 0.34 - (-0.76) = 1.1 \text{ Volt}$$

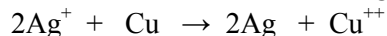
$$\text{And, } Q = \frac{[Zn^{++}][Cu]}{[Cu^{++}][Zn]} = \frac{[Zn^{++}]}{[Cu^{++}]} = \frac{0.1}{x}$$

$$\text{Therefore, } E_{\text{cell}} = 1.1 - 2.303 \frac{8.314 \times 298}{2 \times 96500} \log \frac{0.1}{x}$$

$$\text{Or, } 1.12 = 1.1 - 2.303 \frac{8.314 \times 298}{2 \times 96500} \log \frac{0.1}{x}$$

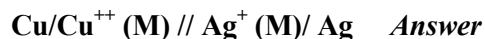
$$\text{Therefore, } x = [Cu^{++}] = \mathbf{0.5 \text{ M Answer}}$$

6. Formulate a cell with the following cell reaction: (standard electrode potential provided in question 1 and 2)



Solution: Here copper is oxidized and silver is reduced. Hence, copper functions as anode and silver as cathode.

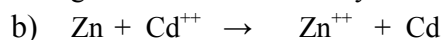
The cell notation for the cell is:



7. Predict which one of the following reactions is feasible. Given $E^{\circ}_{Zn^{++}/Zn} = -0.76 \text{ volt}$ and $E^{\circ}_{Cd^{++}/Cd} = -0.40 \text{ volt}$.



Solution: This reaction is not possible because zinc has tendency to oxidize and cadmium has tendency to get reduced. Zinc already is oxidized form and cadmium in reduced form.



Solution: This reaction takes place because cadmium has higher reduction potential than zinc, hence Cd⁺⁺ gets reduced to Cd by oxidizing Zn to Zn⁺⁺.

Electrochemical Cells Tutorial contd..

8. By how much will the potential of half cell Cu^{++}/Cu change if the solution is diluted 10 times at 25°C ?

Solution: Here, $E^\circ\text{Cu}^{++}/\text{Cu} = 0.34 \text{ V}$

Let the concentration of CuSO_4 before dilution is 1 M and after dilution is 0.1 M.

Electrode reaction: $\text{Cu}^{++} + 2\text{e}^- \longrightarrow \text{Cu}$ Therefore, $Q=1/[\text{Cu}^{++}]$ and $n=2$

Before dilution: $E_{\text{red}1} = E^\circ_{\text{red}} - \frac{0.0591}{2} \log \frac{1}{1} = 0.34 - 0 = 0.34 \text{ V}$

After dilution (ten times): $E_{\text{red}2} = E^\circ_{\text{red}} - \frac{0.0591}{2} \log \frac{1}{0.1} = 0.34 - 0.030 = 0.310 \text{ V}$

There change in potential: $E_{\text{red}1} - E_{\text{red}2} = 0.34 - 0.310 = 0.030 \text{ V}$ **Answer**

9. Calculate the electrode potential for $\text{Fe}^{3+}/\text{Fe}^{2+}$ electrode at 25°C when the concentration of Fe^{2+} is exactly five times that of Fe^{3+} . Given $E^\circ\text{Fe}^{3+}/\text{Fe}^{2+} = +0.77 \text{ V}$.

Solution: Electrode reaction: $\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+}$; Therefore, $Q = [\text{Fe}^{2+}]/[\text{Fe}^{3+}]$ and $n = 1$

Given: Let, $[\text{Fe}^{2+}] = 5x$ and $[\text{Fe}^{3+}] = x$; Therefore $Q = [\text{Fe}^{2+}]/[\text{Fe}^{3+}] = 5x/x = 5$

Now: $E_{\text{red}} = E^\circ_{\text{red}} - \frac{0.0591}{1} \log 5 = 0.77 - 0.041 = 0.729 \text{ V}$ **Answer**