

Numericals on Electrode Potential



Do you know all equations and terms used for solving the problems



Do you know what all important to write or solve the problems ?

$$E_{\text{cell}} = \frac{n E^0}{[M^{n+}]} = E_{M^{n+}/M} - E^0_{M^{n+}/M} \quad \Delta G = -nFE$$

$$E^0_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \quad E^0_G$$

anode / anode electrolyte // cathode electrolyte / **cathode**

↑
Less reduction
potential

↑
More reduction
potential

For concentration cell

anode / anode electrolyte // cathode electrolyte / **cathode**

↑
Less concentration

↑
More concentration

For complete cell

$$E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$$

Anodic ion

$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{0.0591}{n} \log \frac{[P]}{[R]} \quad \text{Or} \quad E_{\text{cell}} = E^0_{\text{cell}} + \frac{0.0591}{n} \log \frac{[R]}{[P]}$$

For half cell

Cathodic ion

$$E_{\text{Mn}^+/M} = E^0_{\text{Mn}^+/M} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]} \quad \text{Or} \quad E_{\text{Mn}^+/M} = E^0_{\text{Mn}^+/M} + \frac{0.0591}{n} \log [M^{n+}]$$

For concentration cell

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{[M_2]}{[M_1]} \quad M_2 > M_1$$

Determination of pH

$$\text{pH} = \frac{E^0_G - E_{\text{cal}} - E_{\text{cell}}}{0.0591}$$

Numerical for Electrode Potential

1. Calculate the electrode potential of Zinc electrode when the standard potential of Zinc electrode is -0.76 V and concentration of Zn^{2+} ion is 0.1M.

$$E^0_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V},$$

$$[\text{Zn}^{2+}] = 0.1\text{M}$$

$$E_{\text{Zn}^{2+}/\text{Zn}} = ?$$

$$E_{\text{Mn}^{n+}/\text{M}} = E^0_{\text{Mn}^{n+}/\text{M}} + \frac{0.0591}{n} \log [\text{M}^{n+}]$$

$$E_{\text{Mn}^{n+}/\text{M}} = E^0_{\text{Mn}^{n+}/\text{M}} - \frac{0.0591}{n} \log \frac{1}{[\text{M}^{n+}]}$$

$$E_{\text{Zn}^{2+}/\text{Zn}} = E^0_{\text{Zn}^{2+}/\text{Zn}} + \frac{0.0591}{n} \log [\text{Zn}^{2+}]$$

$$= -0.76\text{V} + \frac{0.0591}{2} \log (0.1)$$

$$= -0.7895 \text{ V}$$

2. Calculate at 25°C the electrode potential of Fe²⁺(0.1M)/ Fe given E⁰_{Fe2+/Fe} = -0.44 V.

$$E^0_{\text{Fe}^{2+}/\text{Fe}} = -0.76\text{V},$$

$$[\text{Fe}^{2+}] = 0.1\text{M}$$

$$E_{\text{Fe}^{2+}/\text{Fe}} = ?$$

$$E_{\text{M}^{n+}/\text{M}} = E^0_{\text{M}^{n+}/\text{M}} + \frac{0.0591}{n} \log [\text{M}^{n+}]$$

$$E_{\text{Fe}^{2+}/\text{Fe}} = E^0_{\text{Fe}^{2+}/\text{Fe}} + \frac{0.0591}{n} \log [\text{Fe}^{2+}]$$

$$= -0.44 + \frac{0.0591}{2} \log [0.1]$$

$$= -0.44 + \frac{0.0591}{2} \log [10]$$

$$= -44 - \frac{0.0591 (1)}{2}$$

$$= -0.4695 \text{ V}$$

3. Calculate the reduction potential of copper when it is in contact with 5M CuSO₄ solution at 298K. The E⁰ value of copper electrode is 0.34 V.

$$E^0_{\text{Cu}^{2+}/\text{Cu}} = 0.34$$

$$[\text{Cu}^{2+}] = 5\text{M}$$

$$E_{\text{Cu}^{2+}/\text{Cu}} = ?$$

$$E_{\text{M}^{n+}/\text{M}} = E^0_{\text{M}^{n+}/\text{M}} + \frac{0.0591}{n} \log [\text{M}^{n+}]$$

$$E_{\text{Cu}^{2+}/\text{Cu}} = E^0_{\text{Cu}^{2+}/\text{Cu}} + \frac{0.0591}{n} \log [\text{Cu}^{2+}]$$

$$E_{\text{Cu}^{2+}/\text{Cu}} = 0.34 + \frac{0.0591}{2} \log [5]$$

$$E_{\text{Cu}^{2+}/\text{Cu}} = 0.36 \text{ Volts}$$

4. Calculate the electrode potential of copper its electrode potential at 25 °C is 0.292V when $[\text{Cu}^{2+}] = 0.015\text{M}$.

$$E^0_{\text{Cu}^{2+}/\text{Cu}} = 0.292$$

$$[\text{Cu}^{2+}] = 0.015\text{M}$$

$$E_{\text{Cu}^{2+}/\text{Cu}} = ?$$

$$E_{\text{Mn}^{n+}/\text{M}} = E^0_{\text{Mn}^{n+}/\text{M}} + \frac{0.0591}{n} \log [\text{M}^{n+}]$$

$$E_{\text{Cu}^{2+}/\text{Cu}} = E^0_{\text{Cu}^{2+}/\text{Cu}} + \frac{0.0591}{n} \log [\text{Cu}^{2+}]$$

$$E_{\text{Cu}^{2+}/\text{Cu}} = 0.292 + \frac{0.0591}{2} \log [0.015]$$

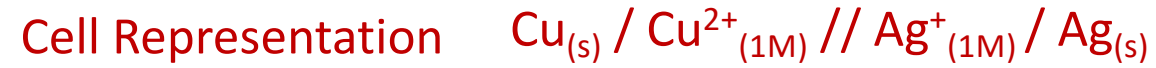
$$E_{\text{Cu}^{2+}/\text{Cu}} = 0.23810 \text{ V}$$

5. Write the cell representation and calculate the emf of a cell containing Copper and Silver electrode given that the electrode potentials of copper and silver are 0.34 V and 0.8 V respectively.

$$E_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$$

$$E_{\text{Ag}^{+}/\text{Ag}} = 0.8 \text{ V}$$

$$E_{\text{cell}} = ?$$



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

$$E_{\text{cell}} = 0.8 - 0.34$$

$$E_{\text{cell}} = 0.46\text{V}$$

6. A galvanic cell formed by immersing Cd rod in 1M CdSO₄ and Cu rod in 1M CuSO₄ solution. The standard E⁰ values of Cu and Cd electrodes are +0.34V and -0.40V respectively.

- How the cell is represented?
- Write the electrode reactions and cell reaction
- Calculate the standard emf of the cell at 298K.

$$E_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$$

$$E_{\text{Cd}^{2+}/\text{Cd}} = -0.40 \text{ V}$$

$$[\text{Cu}^{2+}] = 1\text{M}$$

$$[\text{Cd}^{2+}] = 1\text{M}$$

a. Cell representation $\text{Cd}_{(\text{s})} / \text{Cd}^{2+}_{(1\text{M})} // \text{Cu}^{2+}_{(1\text{M})} / \text{Cu}_{(\text{s})}$

b. Electrode reactions



c. EMF of cell.

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

$$= E_{\text{Cu}} - E_{\text{Cd}}$$

$$= 0.34 - (-0.4)$$

$$E_{\text{cell}} = 0.74 \text{ Volts}$$

7. Write the cell representation, electrode reactions, cell reaction and calculate the emf of the cell at 298K for the cell formed by Fe^{2+}/Fe , $E^0 = -0.44$ and Zn^{2+}/Zn $E^0 = -0.76\text{V}$ respectively.

$$E^0_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$$

$$E^0_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$$

a. Cell representation $\text{Zn} / \text{Zn}^{2+} // \text{Fe}^{2+} / \text{Fe}$

b. Electrode reactions are



c. EMF of cell.

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

$$= -0.44 - (-0.76)$$

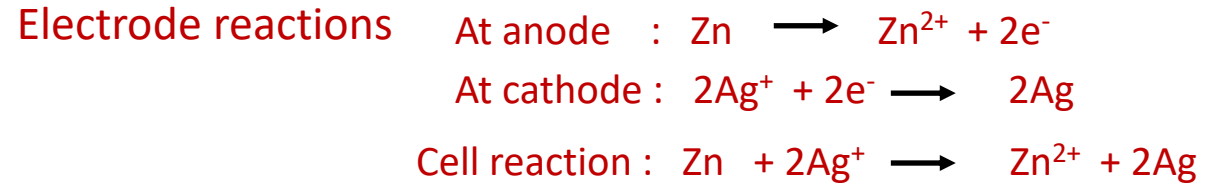
$$= 0.32 \text{ V}$$

8. Calculate the potential of Ag-Zn cell at 298K if the concentration of Ag^+ and Zn^{2+} are $5.2 \times 10^{-6}\text{M}$ and $1.3 \times 10^{-3}\text{M}$ respectively E^0 of the cell at 298K is 1.5V. Calculate the change in free energy ΔG for the reduction of 1 mole of Ag^+ . Given that 1 Faraday = $96.5\text{kJ V}^{-1}\text{mol}^{-1}$ (KJ per volt gram equivalent)

$$E^0_{\text{cell}} = 1.5 \text{ V}$$

$$[\text{Ag}^+] = 5.2 \times 10^{-6}\text{M}$$

$$[\text{Zn}^{2+}] = 1.3 \times 10^{-3}\text{M}$$



$$E_{\text{Cell}}$$

$$E_{\text{Cell}} = E^0_{\text{Cell}} - \frac{0.0591}{n} \log \frac{[\text{P}]}{[\text{R}]}$$

$$E_{\text{Cell}} = E^0_{\text{Cell}} - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$$

$$E_{\text{Cell}} = 1.5 - \frac{0.0591 \log [1.3 \times 10^{-3}]}{[5.2 \times 10^{-6}]^2}$$

$$E_{\text{Cell}} = 1.5 - \frac{0.0591 \log 0.048 \times 10^9}{2}$$

$$E_{\text{Cell}} = 1.5 - \frac{0.0591 \times 7.68}{2}$$

$$= 1.5 - 0.226944$$

$$= 1.27 \text{ V.}$$

Change in free energy for the reduction 1 mole of Ag^+

$$\Delta G = -nFE$$

$$= -1 \times 96.5 \times 1.27$$

$$\Delta G = -122 \text{ KJ}$$

9. An electrochemical cell consists of iron electrode dipped in 0.1M FeSO₄ and Silver electrode dipped in 0.05M AgNO₃. Write the cell representation, cell reaction and calculate the electrode potential of the cell at 298 K. Given that the standard reduction potential of iron and silver electrodes are -0.44 and +0.80V respectively.

$$E^0_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$$

$$E^0_{\text{Ag}^+/\text{Ag}} = 0.80 \text{ V}$$

$$[\text{Fe}^{2+}] = 0.1\text{M}$$

$$[\text{Ag}^+] = 0.05\text{M}$$

Cell representation $\text{Fe}_{(\text{s})} / \text{Fe}^{2+}_{(0.1\text{M})} // \text{Ag}^+_{(0.05\text{M})} / \text{Ag}_{(\text{s})}$

Electrode reactions are



EMF of cell.

$$\begin{aligned} E^0_{\text{cell}} &= E^0_{\text{Ag}^+/\text{Ag}} - E^0_{\text{Fe}/\text{Fe}^{2+}} \\ &= 0.80 - (-0.44) \end{aligned}$$

$$E^0_{\text{cell}} = 1.24 \text{ V}$$

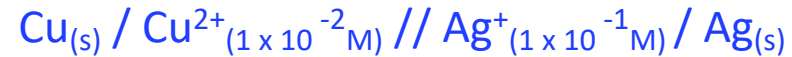
E_{cell}

$$E_{\text{Cell}} = E^0_{\text{Cell}} - \frac{0.0591}{n} \log \frac{[\text{Fe}^{2+}]}{[\text{Ag}^+]^2}$$

$$E_{\text{Cell}} = 1.24 - \frac{0.0591}{2} \log \frac{[0.1]}{[0.05]^2}$$

$$E_{\text{cell}} = 1.1927 \text{ V}$$

10. Write the electrode reaction and calculate the electrode potential of the following cell at 298K.
Given $E^0_{\text{cell}}=1.3\text{V}$.



$$E^0_{\text{cell}}=1.3\text{V}.$$

Electrode reactions are

Electrode reactions

$$E_{\text{cell}}$$



$$E_{\text{cell}}$$

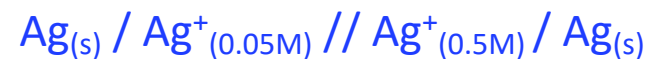
$$E_{\text{Cell}} = E^0_{\text{Cell}} - \frac{0.0591}{n} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^{+}]^2}$$

$$E_{\text{Cell}} = 1.3 - \frac{0.0591}{2} \log \frac{[1 \times 10^{-2}]}{[1 \times 10^{-1}]^2}$$

$$E_{\text{cell}} = 1.3 - 0.0591/2 \{\log 10^{-2} - \log 10^{-2}\}$$

$$E_{\text{cell}} = 1.3\text{V}$$

11. Calculate the electrode potential of the following concentration cell at 298k.



Electrode reactions are



$$E_{\text{Cell}} = \frac{0.0591}{n} \log \frac{[M_2]}{[M_1]} \quad \text{Where } M_2 > M_1$$

$$E_{\text{Cell}} = 0.0591 \log \frac{[0.5]}{[0.05]}$$

$$E_{\text{cell}} = 0.0591 \text{ V}$$

12. Calculate the pH of a solution in which a glass electrode is placed and connected with a standard calomel electrode. The emf of the cell is found to be 0.034V. Standard calomel electrode potential is 0.2422V and $E^0_G = 0.8304V$.

$$E^0_G = 0.8304 \text{ V}$$

$$E_{\text{cal}} = 0.2422 \text{ V}$$

$$E_{\text{cell}} = 0.034 \text{ V}$$

$$p^H = \frac{E^0_G - E_{\text{cal}} - E_{\text{cell}}}{0.0591}$$

$$p^H = \frac{0.8304 - 0.2422 - 0.034}{0.0591}$$

$$p^H = 9.3$$

13. Two silver electrodes containing 0.0012M and 0.0137M AgNO_3 solution respectively are coupled by salt bridge. Formulate the concentration cell. Calculate the valency of silver ions if the emf of the cell is 0.0627 V at 298 K

$$[\text{Ag}^+] = 0.0012\text{M}$$

$$[\text{Ag}^+] = 0.0137\text{M}$$

$$E_{\text{cell}} = 0.0627 \text{ V}$$

$$n = ?$$

Representation of the cell $\text{Ag}_{(\text{s})} / \text{AgNO}_3 (0.0012\text{M}) // \text{AgNO}_3 (0.0137\text{M}) / \text{Ag}_{(\text{s})}$

E_{cell}

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{[M_2]}{[M_1]} \quad \text{Where } M_2 > M_1$$

Here, $M_2=0.0137 \text{ M}$; $M_1=0.0012 \text{ M}$; $T=298 \text{ K}$; $R=8.314\text{J/K}$; $F=96500$; $E_{\text{cell}} = 0.0627\text{V}$

$$n = \frac{2.303 \times 8.31 \times 298}{0.0627 \times 96500} \log \frac{[0.0137]}{[0.0012]}$$

$$= 0.9972$$

$$= 1 \quad \text{Silver in } \text{AgNO}_3 \text{ is univalent.}$$

14. Calculate the electrode potential when copper electrode is dipped in a 0.125 M CuSO_4 solution which is 80% dissociated into copper ions

$$[\text{Cu}^{2+}] = 0.125 \text{ M}$$

$$\begin{aligned} 100 &= 0.125 \\ 80 &= ? \end{aligned}$$

Which is 80% dissociated

$$E^0_{\text{Cu}^{2+}/\text{Cu}} = 0.34\text{V}$$

$$\begin{aligned} [\text{M}^{n+}] &= \frac{0.125 \times 80}{100} \\ &= 0.1 \end{aligned}$$

$$E_{\text{Cu}^{2+}/\text{Cu}} = E^0_{\text{Cu}^{2+}/\text{Cu}} + \frac{0.0591}{n} \log [\text{Cu}^{2+}]$$

$$\begin{aligned} E_{\text{Cu}^{2+}/\text{Cu}} &= 0.34 + \frac{0.0591}{2} \log [0.1] \\ &= 0.31\text{V} \end{aligned}$$

15. Two copper electrodes placed in copper sulphate solutions of equal concentration are connected to form a concentration cell. What is the cell voltage if one of the solution is diluted until the concentration of Cu^{2+} ions is $1/5^{\text{th}}$ of its original value. What is the cell voltage after dilution?

$$[\text{Cu}^{2+}] = 1 \text{ M}$$

$$[\text{Cu}^{2+}] = 1/5 \text{ M}$$

$$E_{\text{Cell}} = \frac{0.0591}{n} \log \frac{[M_2]}{[M_1]} \quad \text{Where } M_2 > M_1$$

$$E_{\text{Cell}} = \frac{0.0591}{2} \log \frac{[1]}{[1/5]}$$

$$E_{\text{Cell}} = \frac{0.0591}{2} \log 5$$

$$= 0.0206\text{V}$$

16. Calculate the cell potential of Ag/Ag⁺ coupled with Cu/Cu²⁺ if the concentration of Ag⁺ and Cu²⁺ are 4.2x10⁻⁶ M and 1.3x 10⁻³M respectively. E⁰_{Cell} = 0.46 V . what is the value of delta G for the reduction of 1 mole Ag⁺. Given F=96.5k JV⁻¹mol⁻¹ (KJ per volt gram equivalent)

$$E^0_{\text{cell}} = 0.46 \text{ V}$$

$$[\text{Ag}^+] = 4.2 \times 10^{-6} \text{ M}$$

$$[\text{Cu}^{2+}] = 1.3 \times 10^{-3} \text{ M}$$

$$E_{\text{Cell}} = E^0_{\text{Cell}} - \frac{0.0591}{n} \log \frac{[\text{Reduced form}]}{[\text{Oxidized form}]}$$

$$E_{\text{Cell}} = E^0_{\text{Cell}} - \frac{0.0591}{n} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$$

$$E_{\text{Cell}} = 0.46 - \frac{0.0591}{2} \log \frac{[1.3 \times 10^{-3}]}{[4.2 \times 10^{-6}]^2}$$

$$E_{\text{Cell}} = 0.46 - \frac{0.0591}{2} \log 0.0736 \times 10^9$$

$$\begin{aligned} E_{\text{Cell}} &= 0.46 - \frac{0.0591}{2} \times 7.86 \\ &= 0.23 \text{ V.} \end{aligned}$$

For the reduction of 2 mole of Ag⁺ ions 2 equivalent required

For the reduction of 1 mole of Ag⁺ ions 1 equivalent required

Change in free energy for the reduction 1 mole of Ag⁺

$$\Delta G = -nFE$$

$$= -1 \times 96.5 \times 0.23$$

$$\Delta G = -22 \text{ KJ}$$