



ENGINEERING CHEMISTRY

Department of Science and Humanities

ENGINEERING CHEMISTRY

Electrochemical equilibria



Class content:

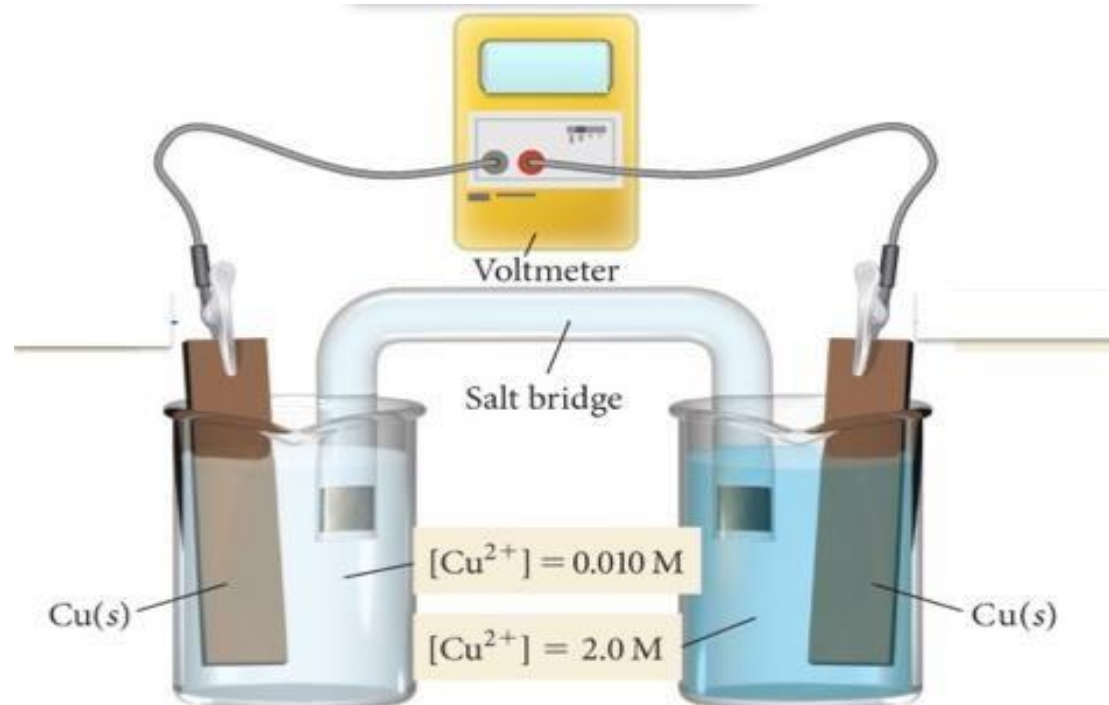
- ***Concentration cells***
 - ***Types of concentration cells***
 - ***Electrolyte concentration cells***
 - ***Electrode concentration cells***

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Electrochemical equilibria

Concentration cells:

- An electrochemical cell in which identical electrodes are in contact with a solution of identical species but of different concentration



<https://chemdemos.uoregon.edu/demos/Voltaic-Cell-CuCu-concentration-cell-Demonstration>

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Electrochemical equilibria

- In this cell 2 copper electrodes are immersed in copper sulphate solutions of concentration c_1 & c_2 , such that $c_2 > c_1$
- An electrolyte has spontaneous tendency to diffuse from a solution of higher concentration to a solution of lower concentration which is the **driving force** for development of potential
- Oxidation takes place at anode and reduction takes place at cathode
- e.g., **$\text{Cu}/\text{Cu}^{2+}(c_1)//\text{Cu}^{2+}(c_2)/\text{Cu}$**

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Electrochemical equilibria



Reactions :

At anode: $\text{Cu} \rightarrow \text{Cu}^{2+} (c_1) + 2e^-$

At cathode: $\text{Cu}^{2+} (c_2) + 2e^- \rightarrow \text{Cu}$

Expression for cell potential:

The emf of the cell = $E_{\text{cathode}} - E_{\text{anode}}$

$$E_{\text{cathode}} = E^{\circ} + \frac{2.303RT}{nF} \log c_2$$

$$E_{\text{anode}} = E^{\circ} + \frac{2.303RT}{nF} \log c_1$$

$$E_{\text{cell}} = \left(E^{\circ} + \frac{2.303RT}{nF} \log c_2 \right) - \left(E^{\circ} + \frac{2.303RT}{nF} \log c_1 \right)$$

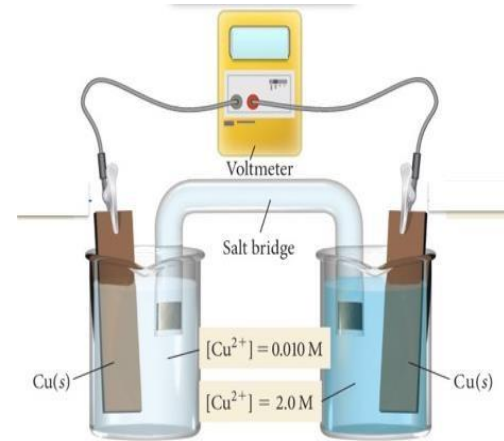
$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \left(\frac{c_2}{c_1} \right)$$

$$\text{At } 298\text{K, } E_{\text{cell}} = \frac{0.0591}{n} \log \left(\frac{c_2}{c_1} \right)$$

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Electrochemical equilibria

- The emf of the cell is positive only if $c_2 > c_1$
i.e., conc of metal ion at cathode > conc. of metal ion at anode
- The emf of the cell depends upon the ratio c_2/c_1
- When $c_2 = c_1$, the emf of the cell becomes zero
- During working of the cell, concentration of ions increases at anode decreases at cathode
- When current is drawn from the cell c_1 increases and c_2 decreases
- The cell can operate only as long as the concentration terms are different



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Electrochemical equilibria



Types of concentration cells:

- Electrolyte concentration cell
- Electrode concentration cell

Electrolyte concentration cell:

- Electrolyte concentration cell consists of two same electrodes that are dipped in the same electrolyte but with different concentrations of electrolytes
- $\text{Cu}/\text{Cu}^{2+}(c_1)//\text{Cu}^{2+}(c_2)/\text{Cu}$
- Cell potential is given by

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log\left(\frac{c_2}{c_1}\right)$$

Electrode concentration cell

- Electrode concentration cell consists of two identical electrodes of different activity which are dipped in the same solution of electrolyte
- $\text{Na-Hg}(c_1)/\text{Na}^+/\text{Na-Hg}(c_2)$
- Cell potential is given by

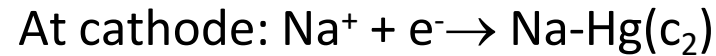
$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{\text{Na-Hg}(c_1)}{\text{Na-Hg}(c_2)}$$

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Electrochemical equilibria

- $\text{Na-Hg}(c_1)/\text{Na}^+/\text{Na-Hg}(c_2)$:

Reactions are :



$$\text{Cell potential} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cathode}} = E^0 - \frac{2.303RT}{nF} \log \frac{\text{Na-Hg}(c_2)}{\text{Na}^+}$$

$$E_{\text{anode}} = E^0 - \frac{2.303RT}{nF} \log \frac{\text{Na-Hg}(c_1)}{\text{Na}^+}$$

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{\text{Na-Hg}(c_1)}{\text{Na-Hg}(c_2)}$$

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Electrochemical equilibria

- $\text{Pt}/\text{H}_2(p_1 \text{ atm})/\text{H}^+/\text{H}_2(p_2 \text{ atm})/\text{Pt}$:

Nernst Equation:

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{p_1}{p_2}$$

- $\text{Pt}/\text{Cl}_2(p_1 \text{ atm})/\text{Cl}^-/\text{Cl}_2(p_2 \text{ atm})/\text{Pt}$:

Nernst Equation:

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{p_2}{p_1}$$



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THANK YOU

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