

# **BSK1133 PHYSICAL CHEMISTRY**

# CHAPTER 8 ELECTROCHEMISTRY

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### Description

#### Aims

- To learn the way in balancing equation of chemical processes.
- ➤ To study the relationship between a cell's emf, the change in the standard Gibbs free energy and the equilibrium constant for the cell reaction.
- To study the mean activity coefficient and Debye-Hückel limiting law



### Description

#### **Expected Outcomes**

- Able to learn the way in balancing equation of chemical processes.
- Able to study the relationship between a cell's emf, the change in the standard Gibbs free energy and the equilibrium constant for the cell reaction.
- Able to study the mean activity coefficient and Debye-Hückel limiting law.

#### References

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- Conclusion







# **8.1 Introduction**



# Introduction

- Electrolysis is a process where a substance (electrolyte) undergo decomposition (dissociate to ions) when electric current is passed through.
- Example for electrolytes: acidic solution, basic solution and salts solution.
- ✓ **Voltameter** is a device in which the process of electrolysis is carried out.
- ✓ In voltameter, electrons flow from anode to cathode and current flow from cathode to anode.
- **Anode electrode:** oxidation takes place (positive pole) **Cathode electrode:** reduction takes place (negative pole)

At cathode:  $B^+ + e^- \longrightarrow B$  (Reduction)

At anode :  $A^- \longrightarrow A + e^-$  (Oxidation)





# 8.2 Balancing Equation



# **Balancing Redox Equations**

**Step 1: Write unbalanced equation:** 

$$\mathrm{Fe}^{2+} + \mathrm{Cr}_2\mathrm{O}_7^{2-} \longrightarrow \mathrm{Fe}^{3+} + \mathrm{Cr}^{3+}$$

#### **Step 2: Write two half-reactions:**



**Step 3: Balance two half-reaction:** 

$$\mathrm{Fe}^{2+} \longrightarrow \mathrm{Fe}^{3+} + e^{-} \qquad 14\mathrm{H}^{+} + \mathrm{Cr}_{2}\mathrm{O}_{7}^{2-} + 6e^{-} \longrightarrow 2\mathrm{Cr}^{3+} + 7\mathrm{H}_{2}\mathrm{O}_{7}^{2-}$$

**Step 4: Balance equation:** 

$$6Fe^{2+} + 14H^+ + Cr_2O_7^{2-} \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$







# **8.3 Electromotive Force (emf)**



### **Electromotive Force (emf)**



Electromotive Force (emf) - of the cell is the difference in potentials of the two half – cells which attributed to the flow of electrons from anode to cathode and flow of current from cathode to anode.

### Method of calculation:

- i. oxidation potential of anode and reduction potential of cathode
- ii. reduction potentials of both electrodes
- iii. oxidation potentials of both electrodes

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





# 8.4 Thermodynamics of Redox Reactions



**Thermodynamics of Redox Reactions** 



#### **Spontaneous Reactions:**

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

## Relate $E_{cell}^{\circ}$ to the equilibrium constant, K:

$$E_{\text{cell}}^{\circ} = \frac{0.0592 \text{ V}}{n} \log K$$





# **8.5 Ostwald Dilution Law**



## **Ostwald Dilution Law**



- $AB (aq) \rightleftharpoons A^{+} (aq) + B^{-} (aq)$ Initial/mol dm<sup>-3</sup>: C 0 0 Equilibrium/mol dm<sup>-3</sup>: C(1 - \alpha) C \alpha C \alpha
- The equilibrium constant, K<sub>c</sub>:

$$K_{C} = \frac{[A^{+}B^{+}]}{[AB]}$$
$$K_{C} = \frac{(C\alpha)(C\alpha)}{C(1-\alpha)}$$
$$K_{C} = \frac{C\alpha^{2}}{C(1-\alpha)}$$





# 8.6 Activity and Debye-Hückel Limiting Law







- Interaction between ions are STRONG
  - ✓ therefore, replacing activities by molalities is only
     VALID in a very dilute solution (less than 10<sup>-3</sup> mol kg<sup>-1</sup> in total ion concentration).
- a. Mean activity coefficients
- b. The Debye-Hückel limiting law



#### a. Mean activity coefficients

Total molar Gibbs energy, *Gm*, of the ions in the electrically neutral solution is the sum of partial molar quantities  $(\mu_+ + \mu_-)$ .

Chemical potential of a **univalent cation**,  $M^+ = \mu_+$ 

Chemical potential of a **univalent anion**,  $X^- = \mu_-$ 

➤ Ideal solution:

Molar Gibbs energy, 
$$G_m^{ideal} = \mu_+^{ideal} + \mu_-^{ideal}$$

**Real solution** ( $M^+$  and  $X^-$  of the same molality):

$$G_{m} = \mu_{+} + \mu_{-}$$

$$= \mu_{+}^{ideal} + RT \ln \gamma_{+} + \mu_{-}^{ideal} + RT \ln \gamma_{-}$$

$$= \mu_{+}^{ideal} + \mu_{-}^{ideal} + RT \ln \gamma_{+} + RT \ln \gamma_{-}$$

$$G_{m} = G_{m}^{ideal} + RT \ln \gamma_{+} \gamma_{-}$$
(deviations from ideality)

- ✓ cannot separate the product of **activity coefficients**,  $\gamma_+ \gamma_-$ , into contributions from cations and anions via experimentally
- ✓ Solve: use mean activity coefficient,  $\gamma_{\pm} = (\gamma_{\pm} \gamma_{\pm})^{1/2}$ cation:  $\mu_{\pm} = \mu_{\pm}^{\text{ideal}} + \text{RT ln } \gamma_{\pm}$  anion:  $\mu_{\pm}$

anion:  $\mu = \mu^{\text{ideal}} + RT \ln \gamma_+$ 

imilar



- A compound M<sub>p</sub>X<sub>q</sub> dissolves to give a solution of *p* cation and *q* anion from each formula unit.
- ✓ Introduce the **mean activity coefficient**:

$$\gamma_{\pm} = (\gamma_{+}^{p} \gamma_{-}^{q})^{1/s}$$
 where  $s = p + q$ 

 $\checkmark$  The chemical potential of each ion as:

 $\mu_{+} = \mu_{+}^{ideal} + RT \ln \gamma_{\pm}$ 

$$\mu_{-} = \mu_{-}^{\text{ideal}} + \mathbf{RT} \ln \gamma_{\pm}$$

Total molar Gibbs energy, *Gm*, of the ions is the sum of their partial molar Gibbs energy

$$G_{m} = p\mu_{+} + q\mu_{-}$$

$$= \mu_{+}^{ideal} + pRT \ln \gamma_{+} + \mu_{-}^{ideal} + qRT \ln \gamma_{-}$$

$$= \mu_{+}^{ideal} + \mu_{-}^{ideal} + pRT \ln \gamma_{+} + qRT \ln \gamma_{-}$$

$$G_{m} = G_{m}^{ideal} + pRT \ln \gamma_{+} + qRT \ln \gamma_{-}$$
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# **b.** The Debye-Hückel limiting law



At very low concentrations the activity coefficient can be calculated from the Debye-Huckel limiting law:

 $\log \gamma_{\pm} = \text{-} |z_{+}z_{-}|AI^{1/2}$ 

where A = 0.509 for an aqueous solution at 25°C and I is dimensionless ionic strength:

$$\mathbf{I} = \frac{1}{2} \sum_{i} z_i^2 (\mathbf{b}/\mathbf{b}^\theta)$$

➢ For two types of ions at molalities b+ and b-:

$$I = \frac{1}{2} (b_{+}z_{+}^{2} + b_{-}z_{-}^{2})/b^{\theta}$$



### Conclusion

Redox reactions are electrochemical reactions that involve the transfer of electrons.



- Electrons flow through an external circuit, oxidation process takes place at the anode and reduction process takes place at cathode.
- The electromotive force (emf) of a cell is the potential difference between the two electrodes.



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