

Chapter 17 Electrochemistry

Framework of the Chapter

17.1 Introduction

I. Electrochemical Equilibria

17.2 Electromotive Force of Galvanic Cell and Interfacial Potential Difference

17.3 Thermodynamics of Electrochemical Systems

17.4 Potential and Standard Potential of Cell Reaction

17.5 Potential and Standard Potential of Electrode Reaction

17.6 Various Types of Electrodes and Standard Cell

17.7 Electrochemical-Equilibrium Calculations

17.8 Concentration Cell and Liquid-Junction Potential

II. Theories of Electrode-Solution Interface

17.9 Outer Potential, Surface Potential and Inner Potential

17.10 Surface Excess Charge and Double-Layer Capacitance

17.11 Electric Double-Layer Models and Outer Potential

17.12 Absolute Potential of Electrode Reaction

III. Electrochemical Kinetics

17.13 Relations among Reaction Rate, Current and Potential

17.14 Polarization Phenomena and Over-Potential

17.15 Examples of Application

17.16 Transition-State Theory of Electrode Reactions

Brief History, Concluding Remarks, General Problems, Numerical Problems

Framework of the Chapter

This chapter provides a comprehensive and multi-level discussion from macroscopic to microscopic for the general principles of the electrochemical reactions, as well as the equilibrium and rate properties and the experimental, semi-empirical and theoretical methods used for obtaining these properties. The peculiarities concerning the form of carrying out the reaction and the features of the corresponding thermodynamics and kinetics are briefly elucidated first. Then the Chapter is divided into three parts:

I. Electrochemical Equilibria As the general principles of equilibria at the macroscopic level, the electrochemical thermodynamics is introduced. The corresponding characteristic properties, the standard potentials of various electrode reactions provided mainly by experiment are discussed.

(1) **Conventions** To define the electromotive force and the interfacial potential difference, to write symbols for electric cells and electrodes, and for the corresponding electrode reactions, to fix the positive or negative sign of the electrodes in cells and of the electric current, various conventions commonly accepted should be paid attention to (17.2).

(2) **Electrochemical Thermodynamics** The electrochemical potential is introduced due to the presence of the interfacial potential difference. The thermodynamic fundamental equations, the equilibrium criterion, and the Nernst equation later for electrochemical systems are derived correspondingly (17.3).

(3) **Standard Potentials for Electrode Reactions** This section is the

focal point of the Chapter. Because of the difficulty in determination, the potentials are defined by adopting a standard hydrogen electrode as a reference. These standard potentials are the characteristic properties of electrochemical systems. Based on them, the potentials for cell reactions can be calculated and various applications can be carried out (17.4, 17.5, 17.6, and 17.7).

(4) **Concentration Cells** The peculiarities are briefly introduced (17.8).

II. Theories of Electrode-Solution Interfacial Layer To elucidate the essentials of the potentials of electrode reactions and to predict them, the transition level from microscopic to macroscopic and the deeper level should be involved. This part is a brief introduction.

(1) **Outer Potential, Surface Potential and Inner Potential** The interfacial potential difference is determined by the inner potential which is the sum of the outer potential and the surface potential (17.9).

(2) **Interfacial Electric Double-Layer Models** Based on experiments and the concept of the zero-charge potential, semi-empirical models concerning the interfacial electric double layer have been developed. Using the statistical mechanics, the outer potential can be well described and predicted (17.10, 17.11).

(3) **Absolute Potential of Electrode Reaction** Because of the progress on the surface potential, the absolute potential of the electrode reaction can be obtained in principle. However, the accuracy is not too high to replace the standard hydrogen-electrode as a reference (17.12).

III. Electrochemical Kinetics

(1) **Relation between Reaction Rate with Current and Potential** The concept of the over-potential is introduced which is a characteristic property measuring the deviation from equilibrium. It is distinguished by the activation over-potential and the mass-transfer over-potential. The former is described by the Tafel equation (17.13, 17.14).

(2) **Applications** Electrolysis, corrosion and anti-corrosion as examples are briefly introduced (17.15).

(3) **Transition-State Theory for Electrode Reactions** The theory involves the transition level from microscopic to macroscopic. The corresponding characteristic parameters such as the transport coefficient and the exchange current density are discussed (17.16).

17.1 Introduction

Electrochemistry and Electrochemical Reactions Electrochemistry studies the chemical reactions taking place mainly on the electrode-solution interface and the corresponding phenomena accompanied. The electrodes are usually metals or semiconductors. The solutions include aqueous solutions, non-aqueous solutions, molten salts and solid electrolytes. The reactions studied by the electrochemistry are generally called the electrochemical reactions. They are reactions with the following peculiarities different from the ordinary reactions:

(1) Electrochemical Reactions Are Carried Out in Electrochemical Cells Accompanied by Charge Flow The electrochemical cell is usually abbreviated as a **cell** composed of at least two electrode-solution interfaces.

Electrode Reaction The oxidation reaction or the reduction reaction taking place on the electrode-solution interface accompanied by the gain or loss of electrons is called an electrode reaction.

Cell Reaction The sum of various electrode reactions, changes on other interfaces and the transfer of ions in a cell is called a cell reaction. It is usually a redox reaction carried out in a cell but the reduction and the oxidation are performed separately on the electrode-solution interfaces of the cathode and the anode.

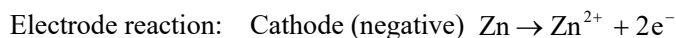
Cathode and Anode The electrode where the cations approach to or the anions leave from is called a cathode. On a cathode, the current (flow of positive charge) enters the electrode from the solution leading to a reduction reaction with electrons gained. The electrode where the anions approach to or the cations leave from is called an anode. On an anode, the current enters the solution from the electrode leading to an oxidation reaction with loss of electrons.

Positive Electrode and Negative Electrode The electrode with higher potential is called a positive electrode while that with lower potential is called a negative electrode.

Galvanic Cell It is a cell in running (discharging) of which the electrical work (electric energy) is exported toward outside.

Electrolytic Cell It is a cell in running (electrolysis) of which the electrical work from outside should be imported.

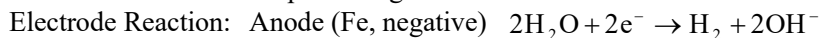
Example of Galvanic Cell Take the Daniel cell for example, in which the zinc electrode and the copper electrode are immersed in a zinc sulphate solution and a copper sulphate solution respectively. The two solutions are separated by a porous diaphragm which allows the passage of ions but prevents the solutions from mixing. A solution-solution interface is then formed. The electrochemical reaction during discharge can be written as:





The transfers of Zn^{2+} ions toward the cathode and SO_4^{2-} ions toward the anode through the solution-solution interface should be accounted also.

Example of Electrolytic Cell Take the electrolysis of water for example, the cell contains a KOH solution, an iron plate and a nickel plate served as electrodes are respectively immersed in the two compartments separated by a porous diaphragm and are respectively connected with the negative and the positive electrodes of a DC source. The electrochemical reaction when the circuit is put through can be written as:



The transfers of K^+ ions toward the cathode and OH^- ions toward the anode should be accounted also, referring to 16.5.

(2) Thermodynamic Characteristics of Electrochemical Reactions

In electrochemical reactions, the change of Gibbs function is less than the electrical work exchanging between the system and the surroundings. According to Eq.(2-36),

$$dG_{T,p} \leq dW' \quad , \quad \Delta G_{T,p} \leq W' \quad (17-3)$$

where W' is the electrical work. In terms of the positive or negative value of $\Delta G_{T,p}$, electrochemical reactions can be distinguished by two categories:

Reactions with Gibbs Function Depressed $\Delta G_{T,p} < 0$, this is the situation for a galvanic cell which produces electrical work during discharge, $W' < 0$. In the reversible condition, $\Delta G_{T,p} = W'_R$, the electrical work done is a maximum. In the irreversible condition, $-\Delta G_{T,p} = -W'_R > -W'$, the electrical work done is less than that in the reversible condition.

Reactions with Gibbs Function Enhanced $\Delta G_{T,p} > 0$, this is the situation for an electrolytic cell which gains electrical work during electrolysis, $W' > 0$. In the reversible condition, $\Delta G_{T,p} = W'_R$, the electrical work gained is a minimum. In the irreversible condition, $\Delta G_{T,p} = W'_R < W'$, the electrical work consumed is greater than that in the reversible condition.

(3) **Kinetic Characteristics of Electrochemical Reactions** The reaction rate of a chemical reaction in a cell can be expressed by the current I passed. If the rate of conversion ξ is adopted, ξ is the reaction extent, according to Eq.(7-11), $\xi = d\xi/dt$, and the Faraday's law Eq.(16-51), $\xi = Q/zF$, where z is the reaction charge number, F is the Faraday constant,

$$\xi = \frac{1}{zF} \frac{dQ}{dt} = \frac{I}{zF} \quad (17-4)$$

Reaction rates are strongly affected by the inner-potential difference in general or the terminal voltage for an electrolytic cell.

Inner-Potential Difference of Electrode-Solution Interface It occurs between the two sides of the electric double layer of the interface. The electrode reaction happens in this double layer and the reaction barrier just spans across this layer. The change of the inner-potential difference changes directly the height of the barrier and the activation energy then affects the reaction rate. For each 0.1V of depression, the rate increases about 7-fold. A depression of 0.6V will raise the rate to 10^5 -fold which corresponds to a notable extent of raising temperature (for each 10K of raising temperature, the rate will be increased by 2- to 4-fold of the original value), or the addition of an excellent catalyst. Different reactions have different inner-potential differences which can be used to improve the selectivity.

(4) **Applications of Electrochemistry** The applications extend all over the various fields including chemical engineering, materials, energy resources, life and environments. For examples: **Electro Synthesis**: the manufacture of chlorine and caustic soda by the electrolysis of salt, the manufacture of hexane dinitrile by the electro-reduction of acrylonitrile, the electro-fluorination of organic acids. **Electro Catalysis**: the manufacture of hydrogen, and the oxidation of hydrocarbons. **Electrolytic Formation**: the manufacture of aluminum and tantalum by electro-smelting, and the electroplating. **Chemical Electric Source**: the storage battery, the dry cell and the fuel cell. **Material Protection**: the electrochemical corrosion and corrosion protection. **Photo Electrochemistry**: the decomposition of water by absorption of light using semiconductors TiO_2 or Ge as electrodes. **Bio-Electrochemistry**: the potential of the cell membrane (an insulator), the

dependence of serum coagulation on the matrix potential, the cardiograph, the brain wave. **Electrochemical Analysis:** the polarograph, the Ampere titration, the Coulomb titration. And so on.

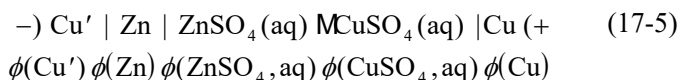
I. Electrochemical Equilibria

When the cell reaches electrochemical equilibrium, the current passed is zero. On this occasion, there is no difference between the galvanic cell and the electrolytic cell. The following discussions are all concerned about the galvanic cells.

17.2 Electromotive Force of Galvanic Cell and Interfacial Potential Difference

1. Conventions for Writing Galvanic Cell

Take the Daniel cell for example. Various phase boundaries occur in the cell. The conventions set that a stable boundary is represented by “|” and an unstable one between the mixable liquids by “ \parallel ”. The cell is expressed as:



where the negative electrode is represented by $-)$ and the positive electrode by $(+$. Cu' on the left is a copper lead connecting the Zn electrode. According to the conventions, the arranging sequence of various substances in a cell should be: The electric current flows from the left to the right passing through each phase boundary during discharge. This means that the negative electrode (anode) must be written on the left with a sequence of “electrode|solution”, it will lose electrons and leads to an oxidation reaction ($\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$), while the positive electrode (cathode) on the right written as “solution|electrode”, it will gain electrons and leads to a reduction reaction ($\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$). Strictly, the lead Cu' must be introduced but can be neglected for simplicity. Beneath the expression of the cell, the inner potentials of various phases are marked with a symbol of ϕ , which are the electrostatic potentials in the interior of various phases, referring to 17.9 later. Marking those ϕ s is for the convenience of discussion,

it is not a necessity for writing a cell.

2. Electromotive Force of Galvanic Cell

The inner-potential difference between the metal lead connecting the electrode (positive) on the right and the same metal lead connecting the electrode (negative) on the left is called the **cell potential**. The cell potential of a galvanic cell when the current is zero (reaches equilibrium) is called the **electromotive force** (abbreviated as EMF) with a symbol of E ,

$$E \stackrel{\text{def}}{=} \lim_{I \rightarrow 0} [\phi(\text{right lead}) - \phi(\text{left lead})] \quad (17-6)$$

For the above example, it is $\phi(\text{Cu}) - \phi(\text{Cu}')$. The same material should be used for the leads of the two electrodes. The copper lead connecting the Zn electrode in the above example is in accordance with this definition. If the sequence of the above cell is written oppositely, a negative value will be obtained by Eq.(17-6) for the electromotive force. Because of the existence of the electromotive force, the galvanic cell can produce electrical work.

3. Interfacial Inner-Potential Difference

Various Interfacial Inner-Potential Differences and Electromotive Force Take the Daniel cell for example. There are the following interfacial inner-potential differences:

$$\Delta_{\text{Cu}'}^{\text{Zn}} \phi = \phi(\text{Zn}) - \phi(\text{Cu}') \quad (17-7)$$

$$\Delta_{\text{ZnSO}_4, \text{aq}}^{\text{Zn}} \phi = \phi(\text{Zn}) - \phi(\text{ZnSO}_4, \text{aq}) \quad (17-8)$$

$$\Delta_{\text{ZnSO}_4, \text{aq}}^{\text{CuSO}_4, \text{aq}} \phi = \phi(\text{CuSO}_4, \text{aq}) - \phi(\text{ZnSO}_4, \text{aq}) \quad (17-9)$$

$$\Delta_{\text{CuSO}_4, \text{aq}}^{\text{Cu}} \phi = \phi(\text{Cu}) - \phi(\text{CuSO}_4, \text{aq}) \quad (17-10)$$

where Eqs.(17-8) and (17-10) are the interfacial inner-potential difference between an electrode and a solution **written customarily from solution to electrode**. Eq.(17-7) is the contact potential between two different metals. Eq.(17-9) is the liquid-junction potential between two different solutions. The electromotive force is the algebraic sum of various interfacial inner-potential differences when the current of the outer circuit is zero,

$$E = \lim_{I \rightarrow 0} \left(\Delta_{\text{Cu}'}^{\text{Zn}} \phi - \Delta_{\text{ZnSO}_4, \text{aq}}^{\text{Zn}} \phi + \Delta_{\text{ZnSO}_4, \text{aq}}^{\text{CuSO}_4, \text{aq}} \phi + \Delta_{\text{CuSO}_4, \text{aq}}^{\text{Cu}} \phi \right) \quad (17-11)$$

Obviously, the equation is in consistent with Eq.(17-6). The following is a further discussion for various interfacial inner-potential differences.

Interfacial Inner-Potential Difference between Electrode and

Solution Take a metal electrode for example.

The metal is composed of metal ions constructing a crystal lattice and free electrons moving in the lattice. When the metal (such as a piece of zinc) is immersed in water, the polar water molecules attract the metal ions, some ions are hydrated and enter the water, which makes the solution positively charged, and the metal negatively charged due to electro neutrality. The positively charged solution hinders the continuing dissolution of ions due to the repulsion while the hydrated ions can deposit back onto the metal surface. As a dynamic equilibrium is reached

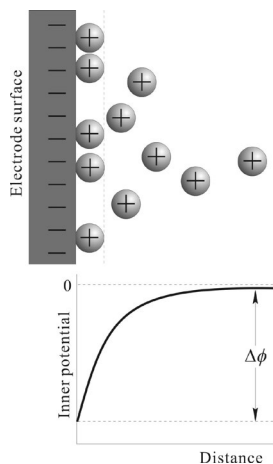


Figure 17-1 Electric double layer on the electrode and the inner potential across the layer

between the dissolution and the deposition, the excess metal ions in solution exhibit a certain distribution near the electrode surface forming a **diffusive electric double-layer** structure as shown in Figure 17-1. The layer is composed of a **compact layer** close to the interface with a thickness of an order of magnitude of 0.1nm and a **diffusive layer** dispersed toward the solution. Because of the potential distribution in the electric double layer as well as the surface potential distribution caused by the inhomogeneous structure on the surface, referring to 17.9 later, an inner-potential difference is formed between the electrode and the solution, as shown in the lower part of Figure 17-1. This is the most important component contributed to the electromotive force.

Contact Potential There is also an inner-potential difference existing on the interface of a contact between the electrode and the lead such as Cu'/Zn . This is because those different metals have different work functions. When two metals contact, the numbers of the electrons escaped from one to another are unequal for the two metals leading to an electric double-layer structure on the interface. The inner-potential difference formed is called the contact potential. It is usually small and can be neglected. However, it must be taken into account in accurate measurements.

Liquid-Junction Potential On the interface between two solutions

containing different solutes or the same solute but with different concentrations, a tiny inner-potential difference called the liquid-junction potential or the **diffusion potential** exists, referring to Figure 17-2. The dash line in the Figure

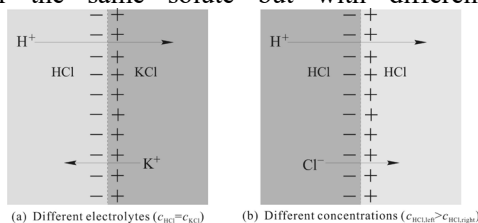


Figure 17-2 Liquid-junction potential

represents a porous diaphragm, in which a solution-solution interface forms. In the Figure: (a) On the left and right are HCl solution and KCl solution respectively with the same concentration. Through the interface, the H⁺ ions diffuse from the left to the right, while the K⁺ ions diffuse from the right to the left. As for the Cl⁻ ions, no diffusion happens due to the same concentration in both sides. It is known that the migration speed of H⁺ ions is much faster than that of K⁺ ions, referring to 16.6, the number of H⁺ ions from the left to the right is greater than that of K⁺ ions from the right to the left, which leads to an excess positive charges on the right side and an excess negative charges on the left side, the diffusion rate of the H⁺ ions is then retarded while that of the K⁺ ions accelerated. When the two rates are compatible, an electric double-layer structure forms on the interface, the corresponding inner-potential difference is the liquid-junction potential. (b) On the left and right are the same HCl solution but with different concentrations, $c_{\text{left}} > c_{\text{right}}$, the diffusion is carried out with a one-way direction. Because the much faster migration speed of H⁺ ions than that of Cl⁻ ions, the electric double-layer structure and the liquid-junction potential form as usual. Finally, the diffusion rates of the two ions are compatible.

Salt Bridge Although the liquid-junction potential is usually less than 0.03V, it can not be neglected in accurate measurements. On the other hand, due to the irreversibility of the diffusion, it is hard to obtain a stable electromotive force in practical measurements. Therefore, in experiments, the liquid-junction potential is always expected to be eliminated. There are two ways to eliminate: One is to avoid using a galvanic cell with liquid-liquid interface but can not assure to be realized in any case. The

other is the usage of a salt bridge which can avoid the direct contact of two solutions, referring to Figure 17-3 later. The salt bridge is usually a U-type glass tube filled with saturated KCl or NH_4NO_3 solution. To prevent the loss of solution, a gel such as the agar-agar is used to freeze the solution in the tube. Due to the high concentration of KCl, the diffusion of K^+ and Cl^- toward the solution is predominating when the salt bridge is inserted into a solution. As shown in Table 16-3, the mobilities of the two ions are close to each other, and the inner-potential difference between the salt bridge and the solution is then very small. What's more, the potential differences at the two terminals of the salt bridge have the opposite directions and compensate for each other. Therefore, the usage of the salt bridge can always diminish the liquid-junction potential to as low as several millivolts. The symbol of the salt bridge is "||". For example, after using the salt bridge, a Daniel cell can be written as:



Approximate Relation between Electromotive Force and Interfacial Inner-Potential Difference Because of the small contact potential that can be neglected generally and the usage of the salt bridge to eliminate the liquid-junction potential, Eq.(17-11) turns to:

$$E \approx \lim_{I \rightarrow 0} \left(\Delta_{\text{CuSO}_4, \text{aq}}^{\text{Cu}} \phi - \Delta_{\text{ZnSO}_4, \text{aq}}^{\text{Zn}} \phi \right) \quad (17-13)$$

The electromotive force approximately equals the interfacial inner-potential difference of the positive electrode (right) subtracted by that of the negative electrode (left).

17.3 Thermodynamics of Electrochemical Systems

1. Thermodynamic Fundamental Equations of Electrochemical Systems

An electrochemical system is a heterogeneous system with changeable compositions, each phase of it possesses a certain inner potential. Additional energy changes exist accompanying the increase or decrease of the charged particles due to the inner potentials. Besides, in certain cases such as a liquid mercury electrode, the surface area is changeable too. In terms of 3.3, the

thermodynamic fundamental equations for an electrochemical system with K components and π phases are as follows:

$$dU = TdS - pdV + \sum_{\alpha=1}^{\pi} \sum_{i=1}^K (\mu_i^{(\alpha)} dn_i^{(\alpha)} + z_i F \phi^{(\alpha)} dn_i^{(\alpha)}) + \sigma dA_s \quad (17-14)$$

$$dG = -SdT + Vdp + \sum_{\alpha=1}^{\pi} \sum_{i=1}^K (\mu_i^{(\alpha)} dn_i^{(\alpha)} + z_i F \phi^{(\alpha)} dn_i^{(\alpha)}) + \sigma dA_s \quad (17-15)$$

$$0 = SdT - Vdp + \sum_{\alpha=1}^{\pi} \sum_{i=1}^K (n_i^{(\alpha)} d\mu_i^{(\alpha)} + n_i^{(\alpha)} z_i F d\phi^{(\alpha)}) + A_s d\sigma \quad (17-16)$$

Comparing with Eqs.(3-42, 3-45, 3-46) for the ordinary cases and Eqs.(15-22, 15-25, 15-26) for systems including interfaces, the above equations have an extra term of $z_i F \phi^{(\alpha)} dn_i^{(\alpha)}$ accounting for the contribution of the inner potentials. Here z_i is the ionic charge number of the component (ion) i . For electro neutral substances, $z_i=0$. When the amount of the component i in the phase α changes $dn_i^{(\alpha)}$, the change of the charges is $z_i F dn_i^{(\alpha)}$, multiplied by the inner potential $\phi^{(\alpha)}$ gives the corresponding additional energy. Eq.(17-16) is the Gibbs-Duhem equation of an electrochemical system.

2. Electrochemical Potential

Similar to the interfacial chemical potential defined by Eq.(15-35), the electrochemical potential $\tilde{\mu}_i$ of a component i is defined as:

$$\tilde{\mu}_i \stackrel{\text{def}}{=} \mu_i + z_i F \phi \quad (17-17)$$

For electro neutral substances, $z_i=0$, $\tilde{\mu}_i=\mu_i$. By adopting $\tilde{\mu}_i$, neglecting the interface, Eqs.(17-14, 17-15, 17-16) turn to

$$dU = TdS - pdV + \sum_{\alpha=1}^{\pi} \sum_{i=1}^K \tilde{\mu}_i^{(\alpha)} dn_i^{(\alpha)} \quad (17-18)$$

$$dG = -SdT + Vdp + \sum_{\alpha=1}^{\pi} \sum_{i=1}^K \tilde{\mu}_i^{(\alpha)} dn_i^{(\alpha)} \quad (17-19)$$

$$0 = SdT - Vdp + \sum_{\alpha=1}^{\pi} \sum_{i=1}^K n_i^{(\alpha)} d\tilde{\mu}_i^{(\alpha)} \quad (17-20)$$

Obviously, $\tilde{\mu}_i = \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_{j \neq i}} = \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_{j \neq i}}$ (17-21)

The electrochemical potential is a partial molar Gibbs function. Eqs.(17-18, 17-19, 17-20) are the same in form with the ordinary fundamental equations. Notice that U, G contain the contribution of the charges of the components.

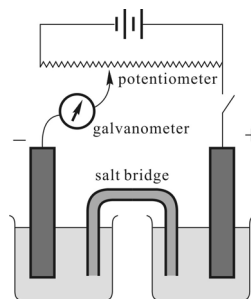


Figure 17-3 Compensation method determining electromotive force

3. Electrochemical Equilibria

Electrochemical Equilibrium State When connecting externally a load, a galvanic cell is in a closed-circuit condition and exports electrical work. If a potentiometer is used as the load, referring to Figure 17-3, its positive and negative terminals connect with the corresponding positive and the negative electrodes of the cell respectively; this is just the compensation method for determining the electromotive force. When the output voltage of the potentiometer is equal to the electromotive force of the cell but with the opposite direction, the pointer of the galvanometer is pointing zero, the state of the cell keeps unchanged for a long period that can be considered as in electrochemical equilibrium. At this moment, besides constant values for the temperature, pressure and concentrations of various components, a stable inner-potential difference, i.e., an electromotive force E exists between the two electrodes of the cell.

Electrochemical Equilibrium Criterion Derive in terms of a closed circuit. Suppose carrying out a perturbation, such as slightly lowering the output voltage of the potentiometer, the cell then discharges and exports electrical work. Because the perturbation is tiny, the cell is still in an equilibrium state and carries out a reversible process. The maximum work done should be the product of the amount of discharge $zF d\xi$ by the Faraday's law Eq.(16-51), and the electromotive force E , $dW'_{\text{electric,R}} = -zFE d\xi$, where z is the reaction charge number. It is the change of electrons in the cell reaction which can be shown intuitively in the corresponding positive or negative electrode reactions. Do not mix up z with the ionic charge number z_i . According to the first and the second laws of thermodynamics,

$$dU = dQ_R + dW_R = TdS - pdV + \sigma dA_s - zFE d\xi \quad (17-22)$$

Compared with Eq.(17-18), the electrochemical-equilibrium criterion in a condition of closed circuit and doing electrical work is obtained,

$$\sum_{\alpha=1}^{\pi} \sum_{i=1}^K \tilde{\mu}_i^{(\alpha)} dn_i^{(\alpha)} = dW'_{\text{electric,R}} = -zFE d\xi \quad (17-23)$$

or

$$\sum_{\alpha=1}^{\pi} \sum_B \nu_B \tilde{\mu}_B^{(\alpha)} = W'_{\text{electric,R}} = -zFE \quad (17-24)$$

Phase-Equilibrium Criterion If only examine the electrode-solution, the electrode-lead and the liquid junction interfaces, when a substances B is

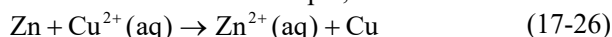
distributed between α and β two phases, the phase-equilibrium criterion is the same in form with the ordinary one,

$$\tilde{\mu}_B^{(\alpha)} = \tilde{\mu}_B^{(\beta)} \quad (17-25)$$

17.4 Potential and Standard Potential of Cell Reaction

1. Potential of Cell Reaction

Derivation Take the Daniel cell for example, the cell reaction is:



The number of electrons involved is 2 as shown in the corresponding positive or negative electrode reaction, $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ or $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$, the reaction charge number $z=2$. In terms of Eq.(17-24),

$$-2FE = \tilde{\mu}_{\text{Zn}^{2+}}^{(\text{aq})} + \tilde{\mu}_{\text{Cu}} - \tilde{\mu}_{\text{Zn}} - \tilde{\mu}_{\text{Cu}^{2+}}^{(\text{aq})} \quad (17-27)$$

For Zn and Cu, because they are electro neutral, the electrochemical potential is the same as the chemical potential,

$$\tilde{\mu}_{\text{Zn}} = \mu_{\text{Zn}}, \quad \tilde{\mu}_{\text{Cu}} = \mu_{\text{Cu}} \quad (17-28)$$

For Zn^{2+} and Cu^{2+} , the ionic charge number $z_i=2$, according to Eq.(17-17),

$$\tilde{\mu}_{\text{Zn}^{2+}}^{(\text{aq})} = \mu_{\text{Zn}^{2+}}^{(\text{aq})} + 2F\phi^{(\text{ZnSO}_4, \text{aq})}, \quad \tilde{\mu}_{\text{Cu}^{2+}}^{(\text{aq})} = \mu_{\text{Cu}^{2+}}^{(\text{aq})} + 2F\phi^{(\text{CuSO}_4, \text{aq})} \quad (17-29)$$

Suppose that a salt bridge is used, the liquid-junction potential is eliminated, $\phi^{(\text{ZnSO}_4, \text{aq})} = \phi^{(\text{CuSO}_4, \text{aq})}$, therefore,

$$\tilde{\mu}_{\text{Zn}^{2+}}^{(\text{aq})} - \tilde{\mu}_{\text{Cu}^{2+}}^{(\text{aq})} = \mu_{\text{Zn}^{2+}}^{(\text{aq})} - \mu_{\text{Cu}^{2+}}^{(\text{aq})} \quad (17-30)$$

The electrochemical potential difference is the same as the chemical potential difference. Substitution of Eqs.(17-28, 17-30) into Eq.(17-27) yields:

$$-2FE = \mu_{\text{Zn}^{2+}}^{(\text{aq})} + \mu_{\text{Cu}} - \mu_{\text{Zn}} - \mu_{\text{Cu}^{2+}}^{(\text{aq})} = \Delta_r G_m \quad (17-31)$$

where $\Delta_r G_m$ is the molar Gibbs function of reaction defined by Eq.(5-48). As is shown in this equation, although the electrochemical potentials are adopted in derivation, only the chemical potentials appear finally.

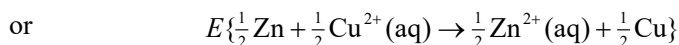
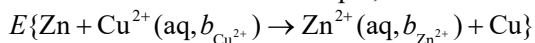
Definition The potential of cell reaction with a symbol of E the same as that of the electromotive force, is defined by generalizing Eq.(17-31),

$$E \stackrel{\text{def}}{=} -\frac{\Delta_r G_m}{zF} = -\frac{\sum_B \nu_B \mu_B}{zF} \quad (17-32)$$

Why don't call it the electromotive force of the cell? There is a subtle reason. The electromotive force is defined by Eq.(17-6) which includes the contact potential and the liquid-junction potential. However, in the derivation of Eq.(17-32), the liquid-junction potential is supposed to be eliminated completely and the contact potential is not considered, either. Even a salt bridge is used, or adopting other measures, these two potentials can not be neglected completely for a real cell. As is shown in Eq.(17-32), E is solely determined by the reaction, i.e., by the chemical potentials of various substances participating in the reaction, or by $\Delta_r G_m$ of the reaction. To distinguish from the electromotive force, the symbol E_{cell} should be adopted for the potential of cell reaction. However, E is still used traditionally. Only approximately, E_{cell} or E can be regarded as the electromotive force.

Notification When we talk about the **cell potential**, it is in a general sense for a potential in either equilibrium or non-equilibrium condition. As for the potential of cell reaction or the electromotive force of a cell, they are the potential in equilibrium condition when the current is zero.

Writing Conventions The potential of cell reaction E is defined by the reaction, a perfect writing should point out the reaction and the concentrations of various substances. E is an intensive property, $\Delta_r G_m$ depends on the writing of the cell reaction, and they are unified by the reaction charge number. For the above example, E is written as:



For the former, $z=2$. For the latter, $z=1$, $\Delta_r G_m$ is reduced by half, but E keeps unchanged.

2. Standard Potential of Cell Reaction

Definition The standard potential of cell reaction with a symbol of E° is defined in terms of Eq.(17-32) by:

$$E^\circ \stackrel{\text{def}}{=} -\frac{\Delta_r G_m^\circ}{zF} = -\frac{\sum_B \nu_B \mu_B^\circ}{zF} \quad (17-33)$$

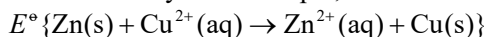
where $\Delta_r G_m^\circ$ is the standard molar Gibbs function of reaction, μ_B° is the standard chemical potential. For solid, liquid and gaseous electrode

materials, and the solvent water, the standard states selected are usually the solid, liquid pure substance and the gaseous pure substance in an ideal-gas state, and the pure water, at the system temperature and a pressure of p° (0.1 MPa). For ions, the solute ion in an ideal dilute solution of $b^\circ = 1 \text{ mol} \cdot \text{kg}^{-1}$ or $c^\circ = 1 \text{ mol} \cdot \text{dm}^{-3}$ is adopted. According to the above equation and Eq.(5-6),

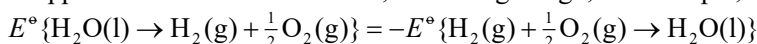
$$\Delta_r G_m^\circ = -zFE^\circ = -RT \ln K^\circ \quad (17-34)$$

$$E^\circ = \frac{RT}{zF} \ln K^\circ \quad (17-35)$$

The same as E , a perfect writing for E° should note the reaction but the concentrations are not necessary. For example,



The symbol (s) of Zn and Cu can be neglected because no misunderstanding could happen. For the reverse reaction, E° changes sign, for example,



3. Nernst Equation

According to Eq.(5-57), for a reaction $0 = \sum_B \nu_B B$, we have

$$\Delta_r G_m = \sum_B \nu_B \mu_B^\circ + RT \ln \prod_B a_B^{\nu_B} = \Delta_r G_m^\circ + RT \sum_B \nu_B \ln a_B \quad (17-36)$$

It is the so called the isothermal equation. Substituting into Eq.(17-32) and combining with Eq.(17-33), the Nernst equation is obtained,

$$E = E^\circ - \frac{RT}{zF} \sum_B \nu_B \ln a_B \quad (17-37)$$

The Nernst equation is virtually an electrochemical version of the isothermal equation. For the reaction of a Daniel cell, because Zn and Cu are pure substances, $a_{\text{Zn}} = a_{\text{Cu}} = 1$, Eq.(17-37) can be written as:

$$E = E^\circ - \frac{RT}{2F} \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} \quad (17-38)$$

For a gaseous component i , the corresponding activity in Eq.(7-37) is replaced by the reduced fugacity f_i/p° or reduced partial pressure p_i/p° .

Conditional Potential of Cell Reaction The activities in the Nernst equation are usually replaced by the molarities, correspondingly E° is replaced by $E^{\circ'}$ called the conditional potential of cell reaction. $E^{\circ'}$ contains the contribution of the activity factors. Therefore, it depends on the

concentrations of various components.

4. Temperature Dependence of Potential of Cell Reaction $(\partial E/\partial T)_p$

Take derivative for Eq.(17-32) with respect to temperature under constant pressure, also due to $(\partial \Delta G/\partial T)_p = -\Delta S$, the relation between $(\partial E/\partial T)_p$ and the molar entropy of reaction $\Delta_r S_m$ can be obtained,

$$\left(\frac{\partial E}{\partial T}\right)_p = -\frac{1}{zF} \left(\frac{\partial \Delta_r G_m}{\partial T}\right)_p = \frac{\Delta_r S_m}{zF} \quad (17-39)$$

Considering $\Delta G = \Delta H - T\Delta S$, the relation between $(\partial E/\partial T)_p$ and the molar enthalpy of reaction $\Delta_r H_m$ can also be obtained,

$$\Delta_r H_m = -zF \left[E - T \left(\frac{\partial E}{\partial T}\right)_p \right] \quad (17-40)$$

Applications Determine E and $(\partial E/\partial T)_p$ by experiment, variations of various thermodynamic functions for chemical reactions can be obtained by Eqs.(17-39) and (17-40). Table 17-1 lists the enthalpies of reaction for several chemical reactions by this EMF method compared with those by calorimetry measurements. Generally, the EMF method is more reliable.

Table 17-1 Molar enthalpies of reaction by EMF method compared with those by calorimetry

| Reaction | $\frac{E_{298K}}{V}$ | $\frac{10^4 \Delta E / \Delta T}{VK^{-1}}$ | $\Delta_r H_m / (kJ \cdot mol^{-1})$ | |
|--|----------------------|--|--------------------------------------|-------------|
| | | | EMF method | Calorimetry |
| $Ag + \frac{1}{2} Hg_2 Cl_2 \rightarrow AgCl + Hg$ | 0.0455 | +3.38 | +5.335 | +7.95 |
| $Pb + 2AgCl \rightarrow PbCl_2 + 2Ag$ | 0.4900 | -1.86 | -105.31 | -101.1 |
| $Pb + 2AgI \rightarrow PbI_2 + 2Ag$ | 0.2135 | -1.73 | -51.175 | -51.04 |
| $Pb + Hg_2 Cl_2 \rightarrow PbCl_2 + 2Hg$ | 0.5356 | +1.45 | -95.060 | -84.10 |
| $Tl + AgCl \rightarrow TlCl + Ag$ | 0.7790 | -0.47 | -76.567 | -76.15 |

Example 1 For a cell $-)Cd|CdCl_2 \cdot 2\frac{1}{2}H_2O \text{ saturated solution} | AgCl(s) | Ag (+$ at $25^\circ C$, the potential of cell reaction, $E=0.67533V$, the temperature dependence, $(\partial E/\partial T)_p = -6.5 \times 10^{-4} V \cdot K^{-1}$. Calculate $\Delta_r G_m$, $\Delta_r S_m$, $\Delta_r H_m$ at $25^\circ C$ for the reaction $Cd(s) + 2AgCl(s) + 2\frac{1}{2}H_2O(l) \rightarrow 2Ag(s) + CdCl_2 \cdot 2\frac{1}{2}H_2O(s)$.

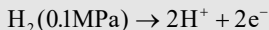
Solution: $\Delta_r G_m = -zFE = -(2 \times 96485 \times 0.67533) J \cdot mol^{-1} = -130.32 kJ \cdot mol^{-1}$

$\Delta_r S_m = zF(\partial E/\partial T)_p = [2 \times 96485 \times (-6.5 \times 10^{-4})] J \cdot K^{-1} \cdot mol^{-1} = -125 J \cdot K^{-1} \cdot mol^{-1}$

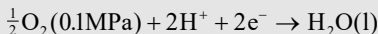
$\Delta_r H_m = \Delta_r G_m - T\Delta_r S_m = [-130.32 + 298.2 \times (-125) \times 10^{-3}] kJ \cdot mol^{-1} = -167.6 kJ \cdot mol^{-1}$

Calorimetry result: $\Delta_r H_m = -165.4 kJ \cdot mol^{-1}$

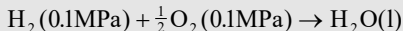
Example 2 Calculate the potential of cell reaction at $25^\circ C$ and its temperature coefficient for a cell: $Pt | H_2(0.1MPa) | H_2SO_4(0.01molkg^{-1}) | O_2(0.1MPa) | Pt$. For $H_2O(l)$, the standard molar enthalpy of formation is $-285.85 kJ \cdot mol^{-1}$, the standard molar Gibbs function of formation is $-237.14 kJ \cdot mol^{-1}$.

Solution: Negative electrode

Positive electrode



Cell reaction



Therefore,

$$\Delta_{\text{r}}G_{\text{m}} = \Delta_{\text{r}}G_{\text{m}}^{\circ}(\text{H}_2\text{O}) = -237.14\text{kJ} \cdot \text{mol}^{-1}$$

$$E = -\Delta_{\text{r}}G_{\text{m}} / zF = [-(-237.14) \times 10^3 / (2 \times 96485)] \text{V} = 1.229\text{V}$$

$$\left(\frac{\partial E}{\partial T} \right)_p = \frac{E}{T} + \frac{\Delta_{\text{r}}H_{\text{m}}}{zFT} = \left(\frac{1.229}{298.2} + \frac{-285.85 \times 10^3}{2 \times 96485 \times 298.2} \right) \text{V} \cdot \text{K}^{-1} = -0.85 \times 10^{-3} \text{V} \cdot \text{K}^{-1}$$

Note: If the formation reaction of H_2O carries out reversibly in a very large cell and $\Delta\xi=1\text{mol}$,

$\Delta_{\text{r}}H = \Delta_{\text{r}}H_{\text{m}} \times \Delta\xi = -285.85\text{kJ}$, $W'_{\text{r}} = \Delta_{\text{r}}G_{\text{m}} \times \Delta\xi = -237.14\text{kJ}$, $Q_{\text{r}} = \Delta_{\text{r}}H - W'_{\text{r}} = -48.71\text{kJ}$ The heat released is 48.71kJ . If H_2 and O_2 react directly,

$$W' = 0, \quad Q_p = \Delta_{\text{r}}H = -285.85\text{kJ}$$

No electrical work, the heat released is 285.85kJ .

Example 3 Calculate the potential of cell reaction of the above cell at 0°C .

Solution: $(\partial E / \partial T)_p = -0.85 \times 10^{-3} \text{V} \cdot \text{K}^{-1}$,

$$E_{298\text{K}} = 1.229\text{V}$$

$$\text{At } 0^\circ\text{C}, \quad E = [1.229 - 0.85 \times 10^{-3}(273 - 298)]\text{V} = 1.250\text{V}$$

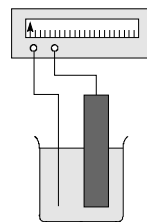


Figure 17-4
Determining inner-potential difference of a single electrode

17.5 Potential and Standard Potential of Electrode Reaction

As shown in Eq.(17-13), after eliminating the liquid-junction potential, the electromotive force equals the interfacial inner-potential difference of the positive electrode subtracted by that of the negative electrode. The electromotive force of a galvanic cell can be obtained if the interfacial inner-potential differences of various single electrodes are provided. Unfortunately, up to now, the absolute value of the inner-potential difference of a single electrode can not be determined accurately. For example, if an electronic voltmeter is used, one of its two leads connects the electrode; the other connects the solution, as shown in Figure 17-4. However, the lead connecting the solution forms another

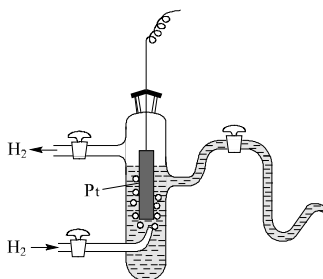
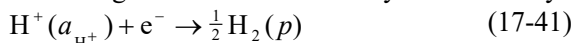


Figure 17-5 Hydrogen electrode

electrode; its inner-potential difference is unknown. Theoretically, the inner-potential difference can be calculated as will be introduced in the Part II of this Chapter. However, the accuracy is not high enough. Therefore, practically, we can only select a reference electrode. The inner-potential differences of various electrodes relative to this reference electrode are then used to replace the absolute values. The present used potentials and standard potentials of electrode reactions are all the relative values with respect to a standard hydrogen electrode which serves as a reference electrode.

1. Standard Hydrogen Electrode (SHE)

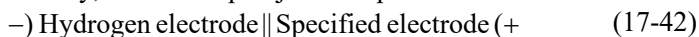
Figure 17-5 shows one type of a hydrogen electrode. A thin piece of platinum plated with platinum black is immersed in a solution containing hydrogen ions and is pounded continuously by a stream of pure hydrogen which escapes away from the upper space. The side siphon is used to compose a cell with the other electrode. The platinum black plated is a large amount of tiny platinum crystals deposited on the platinum piece to provide a great surface area. The incident light is absorbed nearly completely due to reflecting many times resulting in a black color for the platinum. The gaseous hydrogen contacting with the solution on the surface of the platinum black makes the following electrode reaction carry out reversibly:



The symbol of the hydrogen electrode is $\text{H}^+(\text{aq}) | \text{H}_2 | \text{Pt}$, also can be written as $\text{H}^+(\text{aq}) | \text{H}_2, \text{Pt}$. The electrode reaction Eq.(17-41) should always be written in terms of the reduction direction, the reversal form is inadvisable. If $p_{\text{H}_2} = p^\circ = 0.1\text{MPa}$ and $\text{a}_{\text{H}^+} = 1$, it is the standard hydrogen electrode with a symbol of SHE.

2. Standard Potential of Electrode Reaction

Definition Compose the following galvanic cell by a specified electrode as the positive electrode and a hydrogen electrode as the negative electrode respectively, with the liquid junction potential eliminated:



The standard potential of cell reaction of this cell is defined as the standard potential of electrode reaction of this specified electrode with a symbol of $E^\circ \{\text{solution} | \text{electrode}\}$ or $E^\circ \{\text{electrode reaction in reduction direction}\}$.

Example For the copper electrode $\text{Cu}^{2+}(\text{aq}) | \text{Cu}$, compose the following galvanic cell, referring to Figure 17-6,

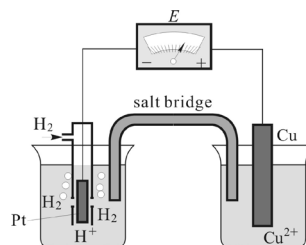
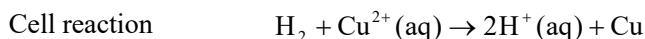
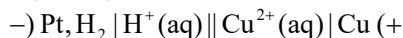
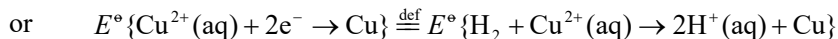
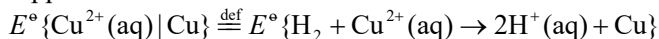


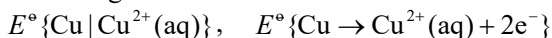
Figure 17-6 A galvanic cell composed by a hydrogen electrode



Written Conventions The standard potential of electrode reaction for the copper electrode should be written as:



Notice that in writing, the symbol of the electrode is always from solution to electrode, the electrode reaction should be written in reduction direction. The following written forms should be avoided:



Hydrogen Electrode According to the definition of the standard potential, naturally, the standard potential of electrode reaction of the hydrogen electrode is zero, that of any other electrode is a relative value with respect to it.

Data Table 17-2 lists standard potentials of electrode reaction and temperature coefficients for various electrodes at 25°C. They are the characteristic properties of substances needed in studying electrochemistry and are obtained mainly by experiment. As shown in the Table, the standard potential of various electrodes above the hydrogen electrode is negative indicating that when they compose a galvanic cell with the hydrogen electrode, the standard potential of cell reaction is negative. This is because that they are easier to carry out an oxidation reaction than the hydrogen electrode. During the process of discharge, they should be a negative

electrode. However, they artificially serve as a positive electrode according to the regulation and the negative potential is then obtained. The standard potential of various electrodes below the hydrogen electrode is positive indicating that they are easier to carry out a reduction reaction than the hydrogen electrode.

3. Potential of Electrode Reaction

Definition Compose the following galvanic cell by a specified electrode as the positive electrode and a standard hydrogen electrode as the negative electrode respectively, with the liquid junction potential eliminated:

–) Standard hydrogen electrode || Specified electrode (+ (17-43)

The potential of cell reaction of this cell is defined as the potential of electrode reaction of this specified electrode with a symbol of $E\{\dots\}$ similar to $E^\circ\{\dots\}$ but the concentrations and the partial pressures of various substances should be noted. The same as E° , E is also a relative value with respect to the standard hydrogen electrode which is served as a reference electrode.

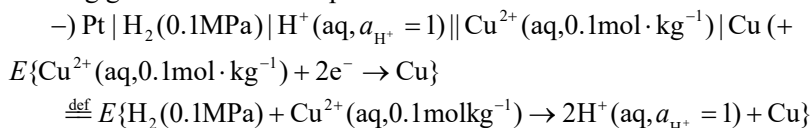
Notification When we talk about the **electrode potential**, it is in a general sense for a potential in either equilibrium or non-equilibrium condition. As for the potential of electrode reaction, it is the potential in equilibrium condition when the current is zero.

Table 17-2 Standard potentials of electrode reaction and temperature coefficients for various electrodes

| Electrode | Electrode reaction | E° / V (25°C) | dE° / dT $\text{mV} \cdot \text{K}^{-1}$ |
|--|---|--------------------------------|--|
| $\text{Na}^+ \text{Na}$ | $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$ | -2.71 | -0.772 |
| $\text{OH}^- \text{H}_2 \text{Pt}$ | $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ | -0.8277 | -0.80 |
| $\text{Zn}^{2+} \text{Zn}$ | $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$ | -0.7620 | 0.091 |
| $\text{Fe}^{2+} \text{Fe}$ | $\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$ | -0.447 | 0.052 |
| $\text{Cd}^{2+} \text{Cd}$ | $\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$ | -0.4032 | -0.093 |
| $\text{SO}_4^{2-} \text{PbSO}_4(\text{s}) \text{Pb}$ | $\text{PbSO}_4 + 2\text{e}^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$ | -0.3590 | -0.99 |
| $\text{Ni}^{2+} \text{Ni}$ | $\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$ | -0.257 | 0.060 |
| $\text{I}^- \text{AgI}(\text{s}) \text{Ag}$ | $\text{AgI} + \text{e}^- \rightarrow \text{Ag} + \text{I}^-$ | -0.15241 | 0.33 |
| $\text{Sn}^{2+} \text{Sn}$ | $\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$ | -0.1377 | 0.282 |
| $\text{Pb}^{2+} \text{Pb}$ | $\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$ | -0.1264 | 0.451 |
| $\text{H}^+ \text{H}_2 \text{Pt}$ | $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ | 0 | 0 |
| $\text{Br}^- \text{AgBr}(\text{s}) \text{Ag}$ | $\text{AgBr} + \text{e}^- \rightarrow \text{Ag} + \text{Br}^-$ | 0.07116 | -0.410 |
| $\text{Cl}^- \text{AgCl}(\text{s}) \text{Ag}$ | $\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$ | 0.22216 | -0.543 |
| $\text{Cl}^- \text{Hg}_2\text{Cl}_2(\text{s}) \text{Hg}$ | $\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Hg} + 2\text{Cl}^-$ | 0.26791 | -0.317 |
| $\text{Cu}^{2+} \text{Cu}$ | $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ | 0.3417 | 0.008 |
| $\text{OH}^- \text{Ag}_2\text{O}(\text{s}) \text{Ag}$ | $\text{Ag}_2\text{O} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + 2\text{Ag}$ | 0.342 | -2.000 |
| $\text{OH}^- \text{O}_2 \text{Pt}$ | $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$ | 0.401 | -0.44 |
| $\text{Cu}^+ \text{Cu}$ | $\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$ | 0.521 | -0.058 |
| $\text{I}^- \text{I}_2(\text{s}) \text{Pt}$ | $\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$ | 0.5353 | -0.148 |
| $\text{SO}_4^{2-} \text{Hg}_2\text{SO}_4(\text{s}) \text{Hg}$ | $\text{Hg}_2\text{SO}_4 + 2\text{e}^- \rightarrow 2\text{Hg} + \text{SO}_4^{2-}$ | 0.6123 | -0.850 |
| $\text{Fe}^{3+}, \text{Fe}^{2+} \text{Pt}$ | $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$ | 0.771 | 1.188 |
| $\text{Hg}_2^{2+} \text{Hg}$ | $\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow 2\text{Hg}$ | 0.7971 | -0.31 |
| $\text{Ag}^+ \text{Ag}$ | $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$ | 0.7994 | -1.000 |
| $\text{Br}^- \text{Br}_2(\text{l}) \text{Pt}$ | $\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$ | 1.066 | -0.629 |
| $\text{H}^+ \text{O}_2 \text{Pt}$ | $4\text{H}^+ + \text{O}_2 + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ | 1.229 | -0.85 |
| $\text{Cr}^{3+}, \text{Cr}_2\text{O}_7^{2-}, \text{H}^+ \text{Pt}$ | $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$ | 1.232 | -1.263 |
| $\text{Cl}^- \text{Cl}_2(\text{g}) \text{Pt}$ | $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$ | 1.35793 | -1.260 |
| $\text{MnO}_4^-, \text{H}^+ \text{MnO}_2 \text{Pt}$ | $\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$ | 1.679 | -0.666 |
| $\text{S}_2\text{O}_8^{2-}, \text{SO}_4^{2-} \text{Pt}$ | $\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \rightarrow 2\text{SO}_4^{2-}$ | 2.010 | -1.260 |

Cited from: Handbook of Chemistry and Physics, 77th ed. 1996–1997. Wu Weichang, etc. Handbook of Data of Standard Electrode Potential. Beijing: Science Press, 1991. Standard pressure has been converted from original 101325Pa to 0.1MPa.

Example For the electrode $\text{Cu}^{2+}(\text{aq}, 0.1\text{mol} \cdot \text{kg}^{-1}) | \text{Cu}$, the following galvanic cell is composed:

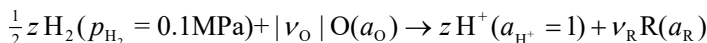


4. Nernst Equation for Electrode Reaction

Suppose an electrode reaction



where O and R are substances with oxidation and reduction states and ν_O , ν_R are the corresponding stoichiometry numbers respectively. For example, $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$, O is Cu^{2+} , R is Cu, $|\nu_O| = \nu_R = 1$, $z = 2$. Composing a galvanic cell with a standard hydrogen electrode in terms of Eq.(17-43), the cell reaction is



Due to $p_{\text{H}_2} = p^\circ$, $a_{\text{H}^+} = 1$, in terms of Eq.(17-37), the Nernst equation of the electrode reaction is

$$E = E^\circ - \frac{RT}{zF} \ln \frac{a_R^{\nu_R}}{a_O^{|\nu_O|}} = E^\circ + \frac{RT}{zF} \ln \frac{a_O^{|\nu_O|}}{a_R^{\nu_R}} \quad (17-45)$$

where E and E° are the potential and the standard potential of cell reaction of the galvanic cell Eq.(17-43), also are the potential and the standard potential of electrode reaction of Eq.(17-44) according to the definition.

The difference of Eq.(17-45) from Eq.(17-37) for a cell reaction lies in the fact that E and E° here are entirely the relative values with the standard hydrogen electrode as a reference electrode. The difference between E and E° is related with the activities of the substances of oxidation and reduction states in the electrode reaction.

Example Take $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ and $\text{H}^+ + e^- \rightarrow \frac{1}{2}\text{H}_2$ for example: For pure solids and liquids, such as Cu, $a_{\text{Cu}} = 1$. For gases, the relative fugacity or partial pressure is used to replace the activity, such as H_2 , f_{H_2}/p° or p_{H_2}/p° is adopted. Notice that $E^\circ\{\text{H}^+(\text{aq})|\text{H}_2|\text{Pt}\} = 0$. We can write

$$E\{\text{Cu}^{2+}(\text{aq}, a_{\text{Cu}^{2+}})|\text{Cu}\} = E^\circ\{\text{Cu}^{2+}(\text{aq})|\text{Cu}\} + \frac{RT}{2F} \ln a_{\text{Cu}^{2+}} \quad (17-46)$$

$$E\{\text{H}^+(\text{aq}, a_{\text{H}^+})|\text{H}_2(p_{\text{H}_2})|\text{Pt}\} = \frac{RT}{F} \ln \frac{a_{\text{H}^+}}{(p_{\text{H}_2}/p^\circ)^{1/2}} \quad (17-47)$$

Conditional Potential of Electrode Reaction It usually uses the molarity or the concentration to replace the activity in the Nernst equation of electrode reaction, correspondingly, E° is replaced by $E^{\circ'}$ called the conditional potential of electrode reaction. $E^{\circ'}$ includes the contribution of activity factors. Therefore, it depends on the concentrations of various

components.

5. Relation between Potential of Cell Reaction and Potentials of Electrode Reaction

Although the potential and the standard potential of electrode reaction are relative values with respect to the standard hydrogen electrode, because the cell reaction is the algebraic sum of the two electrode reactions, and the potential of cell reaction equals the interfacial inner-potential difference of the positive electrode subtracted by that of the negative electrode, therefore, we can write directly:

$$E(\text{Cell reaction}) = E(\text{Positive electrode}) - E(\text{Negative electrode}) \quad (17-48)$$

$$E^\circ(\text{Cell reaction}) = E^\circ(\text{Positive electrode}) - E^\circ(\text{Negative electrode}) \quad (17-49)$$

Example For the Daniel cell, the Nernst equations for the electrode reactions of the positive and the negative electrodes are respectively:

$$E\{\text{Zn}^{2+}(\text{aq}, a_{\text{Zn}^{2+}}) + 2\text{e}^- \rightarrow \text{Zn}\} = E^\circ\{\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}\} + (RT/2F) \ln a_{\text{Zn}^{2+}}$$

$$E\{\text{Cu}^{2+}(\text{aq}, a_{\text{Cu}^{2+}}) + 2\text{e}^- \rightarrow \text{Cu}\} = E^\circ\{\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}\} + (RT/2F) \ln a_{\text{Cu}^{2+}}$$

Substitution into Eqs.(17-48) and (17-49) yields the standard potential of cell reaction and the potential of cell reaction respectively,

$$E^\circ\{\text{Cell Reaction}\} = E^\circ\{\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}\} - E^\circ\{\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}\}$$

$$E\{\text{Zn} + \text{Cu}^{2+}(\text{aq}, a_{\text{Cu}^{2+}}) \rightarrow \text{Zn}^{2+}(\text{aq}, a_{\text{Zn}^{2+}}) + \text{Cu}\}$$

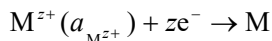
$$= E\{\text{Cu}^{2+}(\text{aq}, a_{\text{Cu}^{2+}}) + 2\text{e}^- \rightarrow \text{Cu}\} - E\{\text{Zn}^{2+}(\text{aq}, a_{\text{Zn}^{2+}}) + 2\text{e}^- \rightarrow \text{Zn}\}$$

$$= E^\circ\{\text{Zn} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}\} - \frac{RT}{2F} \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} \quad (17-50)$$

17.6 Various Types of Electrodes and Standard Cell

1. Metal-Metal Ion Electrodes

These electrodes are constructed by inserting a metal M into a solution of its salt. The above mentioned $\text{Zn}^{2+}|\text{Zn}$ and $\text{Cu}^{2+}|\text{Cu}$ are typical examples. The electrode reaction and the Nernst equation of them are:

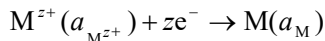


$$E\{\text{M}^{z+}(a_{\text{M}^{z+}})|\text{M}\} = E^\circ\{\text{M}^{z+}|\text{M}\} + \frac{RT}{zF} \ln a_{\text{M}^{z+}} \quad (17-51)$$

2. Metal Amalgam-Metal Ion Electrodes

These electrodes are composed of a metal amalgam and the solution of

the metal salt. For example: $\text{Na}^+|\text{Na}-\text{Hg}$ and $\text{Cd}^{2+}|\text{Cd}-\text{Hg}$. The peculiarities are basically the same as those of the metal-metal ion electrodes, the electrode reaction is also:

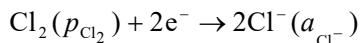


The difference is that the amalgam is an alloy of metal and mercury, the activity of the metal a_{M} in amalgam is no longer equal to 1. The corresponding Nernst equation is:

$$E\{\text{M}^{z+}(a_{\text{M}^{z+}})|\text{M}(a_{\text{M}})\} = E^\circ\{\text{M}^{z+}|\text{M}\} + \frac{RT}{zF} \ln \frac{a_{\text{M}^{z+}}}{a_{\text{M}}} \quad (17-52)$$

3. Platinum-Nonmetal-Nonmetal Ion Electrodes

These electrodes are composed of a gaseous, liquid or solid nonmetal and its ion with the platinum as a conducting terminal. For examples: $\text{H}^+|\text{H}_2(\text{g})|\text{Pt}$, $\text{Cl}^-|\text{Cl}_2(\text{g})|\text{Pt}$, $\text{Br}^-|\text{Br}_2(\text{l})|\text{Pt}$, $\text{I}^-|\text{I}_2(\text{s})|\text{Pt}$, etc. (or written as $\text{H}^+|\text{H}_2(\text{g}), \text{Pt}$, $\text{Cl}^-|\text{Cl}_2(\text{g}), \text{Pt}$, $\text{Br}^-|\text{Br}_2(\text{l}), \text{Pt}$, $\text{I}^-|\text{I}_2(\text{s}), \text{Pt}$). If the nonmetal is a gas, it is also called a **gaseous electrode**. Take the chlorine electrode for example, the electrode reaction and the Nernst equation are:

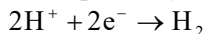


$$E\{\text{Cl}^-(a_{\text{Cl}^-})|\text{Cl}_2|(p_{\text{Cl}_2})\text{Pt}\} = E^\circ\{\text{Cl}^-|\text{Cl}_2|\text{Pt}\} + \frac{RT}{2F} \ln \frac{p_{\text{Cl}_2}/p^\circ}{a_{\text{Cl}^-}^2} \quad (17-53)$$

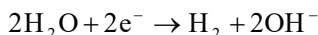
Because of the poor conductivity of nonmetals, the ability of transferring electrons is enhanced with the aid of an inert metal such as Pt.

Different Forms of Expression for Hydrogen Electrode and Oxygen

Electrode For example, the hydrogen electrode can be written either as $\text{H}^+|\text{H}_2|\text{Pt}$, or as $\text{OH}^-|\text{H}_2|\text{Pt}$. The former is usually used in the case of the acidic solution, the latter in the basic solution. Their electrode reactions are different in form expressed respectively as:



and

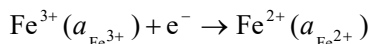


Although different in form, they are essentially the same with the same potential of electrode reaction. This is because the difference between them is: $2\text{H}_2\text{O} \rightleftharpoons 2\text{H}^+ + 2\text{OH}^-$, it is a reaction in chemical equilibrium, $\Delta_r G_m = 0$, therefore, no contribution to the potential of electrode reaction. However, the standard potentials of the two forms are different. When

$E^\circ\{\text{H}^+|\text{H}_2|\text{Pt}\}$ is used, it means $p_{\text{H}_2} = 0.1\text{MPa}$, $a_{\text{H}^+} = 1$, $E^\circ\{\text{H}^+|\text{H}_2|\text{Pt}\} = 0$ as mentioned before. When $E^\circ\{\text{OH}^-|\text{H}_2|\text{Pt}\}$ is used, it means $p_{\text{H}_2} = 0.1\text{MPa}$, $a_{\text{OH}^-} = 1$. Because the ionic product of water at 25°C , $a_{\text{H}^+}a_{\text{OH}^-} = K_w^\circ \approx 10^{-14}$, a_{H^+} is then equal to about 10^{-14} , obviously, this is a state completely different from that of $a_{\text{H}^+} = 1$. The difference between the two standard potentials can be calculated by the ionic product of water, referring to Example 5 in the next section. Similar to the hydrogen electrode, the oxygen electrode can also be written in two different forms: either $\text{H}^+|\text{O}_2|\text{Pt}$ or $\text{OH}^-|\text{O}_2|\text{Pt}$.

4. Oxidation-Reduction Electrodes

These electrodes are constructed by inserting the inert metal platinum into a solution containing ions of two different valence types. For example, $\text{Fe}^{3+}, \text{Fe}^{2+}|\text{Pt}$, the electrode reaction and the Nernst equation are:



$$E\{\text{Fe}^{3+}(a_{\text{Fe}^{3+}}), \text{Fe}^{2+}(a_{\text{Fe}^{2+}})|\text{Pt}\} = E^\circ\{\text{Fe}^{3+}, \text{Fe}^{2+}|\text{Pt}\} + \frac{RT}{F} \ln \frac{a_{\text{Fe}^{3+}}}{a_{\text{Fe}^{2+}}} \quad (17-54)$$

For other examples: $\text{Cr}^{3+}, \text{Cr}_2\text{O}_7^{2-}, \text{H}^+|\text{Pt}$, $\text{S}_2\text{O}_8^{2-}, \text{SO}_4^{2-}|\text{Pt}$.

5. Metal-Sparingly Soluble Salt-Anion of the Salt Electrodes

These electrodes are constructed by a metal, the sparingly soluble salt of the metal and a solution containing the anion of the sparingly soluble salt. For example: $\text{Cl}^-|\text{AgCl(s)}|\text{Ag}$ and $\text{SO}_4^{2-}|\text{PbSO}_4(\text{s})|\text{Pb}$. They can also be written as: $\text{Cl}^-|\text{AgCl(s)}, \text{Ag}$ and $\text{SO}_4^{2-}|\text{PbSO}_4(\text{s}), \text{Pb}$. This type of electrodes is very stable. Several of them are well recognized and are adopted as the secondary standard because of convenience in use, and are commonly called the **reference electrode**. The standard potentials of them have been measured accurately with respect to the standard hydrogen electrode. There are three phases in the electrode, the electrode reaction proceeds on the two solid-liquid interfaces. The mechanism of creating electrode potential is rather complex.

Calomel Electrode $\text{Cl}^-|\text{Hg}_2\text{Cl}_2(\text{s})|\text{Hg}$, also written as $\text{Cl}^-|\text{Hg}_2\text{Cl}_2(\text{s}), \text{Hg}$, referring

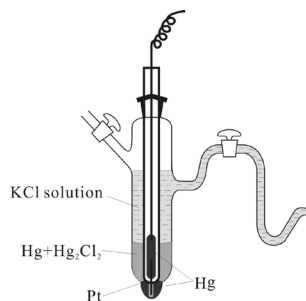
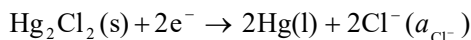


Figure 17-7 Calomel electrode

to Figure 17-7. A small amount of mercury is placed at the bottom of the instrument covered with a small amount of paste made of calomel, mercury and solution of potassium chloride, then the solution of potassium chloride saturated with calomel is added. The electrode reaction and the Nernst equation are:



$$E\{\text{Cl}^-(a_{\text{Cl}^-}) | \text{Hg}_2\text{Cl}_2(\text{s}) | \text{Hg}\} = E^\circ\{\text{Cl}^- | \text{Hg}_2\text{Cl}_2(\text{s}) | \text{Hg}\} + \frac{RT}{F} \ln \frac{1}{a_{\text{Cl}^-}} \quad (17-55)$$

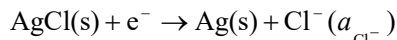
The standard potential of electrode reaction of the calomel electrode at 25°C is: $E^\circ\{\text{Cl}^- | \text{Hg}_2\text{Cl}_2(\text{s}) | \text{Hg}\} = 0.26791\text{V}$. Table 17-3 lists the potentials of electrode reaction and their temperature dependence within the range of 0°C~100°C for the calomel electrode with three different KCl concentrations.

Table 17-3 Potentials of electrode reaction for three different calomel electrodes

| $\frac{c_{\text{KCl}}}{\text{mol} \cdot \text{dm}^{-3}}$ | Temperature dependence of the potential of electrode reaction, E / V | $E_{298\text{K}} / \text{V}$ |
|--|--|------------------------------|
| 0.1 | $0.3335 - 8.75 \times 10^{-5}(t/^{\circ}\text{C} - 25) - 3 \times 10^{-6}(t/^{\circ}\text{C} - 25)^2$ | 0.3335 |
| 1 | $0.2799 - 2.75 \times 10^{-4}(t/^{\circ}\text{C} - 25) - 2.5 \times 10^{-6}(t/^{\circ}\text{C} - 25)^2$ $- 4 \times 10^{-9}(t/^{\circ}\text{C} - 25)^3$ | 0.2799 |
| Saturated | $0.2410 - 6.61 \times 10^{-4}(t/^{\circ}\text{C} - 25) - 1.75 \times 10^{-6}(t/^{\circ}\text{C} - 25)^2$ $- 9.0 \times 10^{-10}(t/^{\circ}\text{C} - 25)^3$ | 0.2410 |

Different Forms of Expression for Calomel Electrode Similar to the hydrogen electrode, because the tiny amount of Hg_2Cl_2 dissolved in solution can dissociate forming mercurous ion Hg_2^{2+} , the calomel electrode can also be expressed as $\text{Hg}_2^{2+} | \text{Hg}$, the corresponding electrode reaction is: $\text{Hg}_2^{2+}(a_{\text{Hg}_2^{2+}}) + 2\text{e}^- \rightarrow 2\text{Hg}(\text{l})$. Although different in form, the two expressions are essentially the same as usual with the same potential of electrode reaction but the standard potentials of the two forms are different. The difference between $E^\circ\{\text{Cl}^- | \text{Hg}_2\text{Cl}_2(\text{s}) | \text{Hg}\}$ and $E^\circ\{\text{Hg}_2^{2+} | \text{Hg}\}$ can be obtained by using the solubility product of calomel, $K_{\text{sp}}^\circ = a_{\text{Hg}_2^{2+}} a_{\text{Cl}^-}^2$, referring to Example 6 in 17-7.

Silver Chloride Electrode $\text{Cl}^- | \text{AgCl}(\text{s}) | \text{Ag}$, the electrode reaction is:



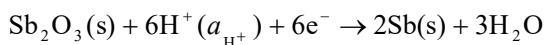
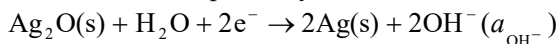
The standard potential of electrode reaction $E^\circ\{\text{Cl}^- | \text{AgCl}(\text{s}) | \text{Ag}\}$ is

0.22216V at 25°C. The Nernst equation is similar to Eq.(17-55). The merit of the silver chloride electrode lies in the fact that it is more stable than the calomel electrode at higher temperatures. Many ways can be used to prepare a silver chloride electrode. For example, a layer of silver is first plated on the platinum wire, and then electrolyzed as an anode in a chloride solution to convert part of silver to silver chloride, aged for a certain period, finally immersed in an aqueous solution of hydrochloric acid to complete the preparation. In accurate experiment, nitrogen gas is passing through to protect the electrode because a trace of oxygen in acidic solution will disturb the reaction. On the other hand, the electrode can not be used when the solution exists ions such as NO_3^- , Br^- , I^- , NH_4^+ , CN^- , etc. The silver chloride electrode is always used as an inner reference electrode for some electrodes such as the glass electrode and the ion-selective electrodes.

Different Forms of Expression for Silver Chloride Electrode The tiny amount of AgCl dissolved in solution can dissociate, forming Ag^+ ion, and the electrode can then be expressed as $\text{Ag}^+|\text{Ag}$. The difference between $E^\circ\{\text{Cl}^-|\text{AgCl(s)}|\text{Ag}\}$ and $E^\circ\{\text{Ag}^+|\text{Ag}\}$ can be estimated by using the solubility product of AgCl, $K_{\text{sp}}^\circ = a_{\text{Ag}^+} a_{\text{Cl}^-}$.

Other Examples For this type of electrodes, we also have electrodes constructed by a metal, the oxide of the metal and a solution containing OH^- or H^+ ions. For example: $\text{OH}^-|\text{Ag}_2\text{O(s)}|\text{Ag}$, $\text{H}^+|\text{Sb}_2\text{O}_3(\text{s})|\text{Sb}$, etc.

Their electrode reactions are respectively:



The latter one is called the **antimony electrode** which can be used for the pH determination for solutions because of the relation with a_{H^+} .

6. Ion-Selective Electrodes

Different from the ordinary oxidation-reduction mechanism, the electrode potential of ion-selective electrodes is a **membrane potential** originated from the ion-exchange equilibrium on the electrode membrane similar to the liquid-junction potential. Because of the convenience in use, the ion-selective electrodes have wide applications.

(1) **Glass Electrode** Refer to Figure 17-8. A solution with a certain pH is sealed in the glass membrane with an AgCl electrode as an inner reference electrode which connects the lead. When the electrode is immersed in a solution to be tested, the membrane responds to the H^+ ions in the solution, a membrane potential is created due to the H^+ ion exchange on the interface. A concentration potential is formed between the two sides of the glass membrane due to the different pH (the principle will be discussed in 17.8). The Nernst equation is:

$$E\{H^+(a_{H^+}) | \text{Glass electrode}\} = E^\circ\{H^+ | \text{Glass ele...}\} + (RT/F) \ln a_{H^+} \quad (17-56)$$

The contributions of the solution sealed, the inner reference electrode and the diffusion inside the membrane are all accounted in E° .

(2) **Solid Membrane Electrodes** These electrodes are constructed by solid membrane connecting with the lead.

The membrane is made of ionic crystal which is able to conduct electricity. Figure 17-9 shows an Ag_2S membrane electrode which can respond to S^{2-} and Ag^+ ions, a membrane potential is created due to the ion exchange. The ionic crystal is usually a semi-conductor, its conductive function and surface potential can be changed notably by creating defects or injecting ions. Besides

the Ag_2S membrane electrode, others such as $PbS(Pb^{2+})$, $CdS(Cd^{2+})$, $CuS(Cu^{2+})$, $LaF_3(F^-)$, $AgCl(Cl^-)$, $AgBr(Br^-)$ and $AgI(I^-)$, the responding ions are noted in the parenthesis.

(3) **Ion Exchange Membrane Electrodes** PVC or silicon rubber is usually used as a carrier with the solvent and chelating agent contained to form an ion exchange membrane. A membrane potential is formed between the membrane and the solution by the selective chelating of ions with various concentrations. The electrodes can be used to respond to the ions such as

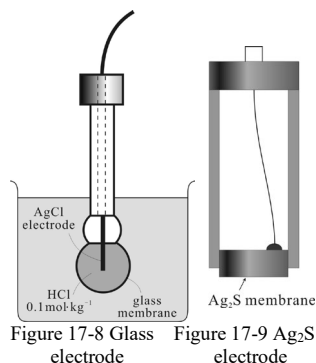


Figure 17-8 Glass electrode Figure 17-9 Ag_2S electrode

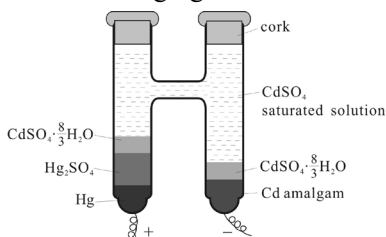


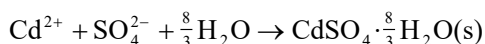
Figure 17-10 Standard cell

Ca^{2+} , NO_3^- , ClO_4^- , BF_4^- , CO_3^{2-} and Cl^- .

7. Standard Cell

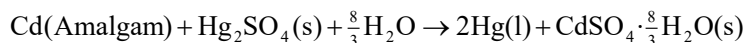
The standard cell is used for calibration in determinations because of its stable electromotive force and small temperature dependence. For example, the **Weston cell**, $E=1.018646\text{V}$ at 293K, $E=1.018421\text{V}$ at 198K. The structure is shown in Figure 17-10. The cadmium amalgam ($w_{\text{Cd}}=0.125$) is used as the negative electrode and a paste of mercury and mercurous sulfate as the positive electrode. Between the two electrodes, a saturated solution of cadmium sulfate hydrate crystals is filled. The reactions in discharge are:

Negative electrode $\text{Cd}(\text{Amalgam}) \rightarrow \text{Cd}^{2+} + 2\text{e}^-$



Positive electrode $\text{Hg}_2\text{SO}_4(\text{s}) + 2\text{e}^- \rightarrow \text{Hg}(\text{l}) + \text{SO}_4^{2-}$

Cell reaction



17.7 Electrochemical-Equilibrium Calculations

Now we have the general principles provided by the electrochemical thermodynamics, and the standard potentials of electrode reaction as the characteristic properties of substances involved in electrochemical systems, the practical applications can be discussed. This section is an epitome of many applications.

1. Basic Calculations for Potentials of Cell Reaction and Potentials of Electrode Reaction

Example 1 Calculate the standard potential of cell reaction E° at 25°C for the cell $\text{Sn}|\text{Sn}^{2+}(a_{\text{Sn}^{2+}})||\text{Pb}^{2+}(a_{\text{Pb}^{2+}})|\text{Pb}$ and write the corresponding cell reaction. Calculate the potential of cell reaction at 25°C if $a_{\text{Sn}^{2+}} = 0.1$ and $a_{\text{Pb}^{2+}} = 0.01$.

Solution: Table 17-2 gives

$$E^\circ\{\text{Pb}^{2+}|\text{Pb}\} = -0.1264\text{V}, \quad E^\circ\{\text{Sn}^{2+}|\text{Sn}\} = -0.1377\text{V},$$

$$E^\circ = E^\circ\{\text{Pb}^{2+}|\text{Pb}\} - E^\circ\{\text{Sn}^{2+}|\text{Sn}\} = 0.0113\text{V}$$

Negative electrode $\text{Sn} \rightarrow \text{Sn}^{2+} + 2\text{e}^-$

Positive electrode $\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$

Cell reaction $\text{Sn} + \text{Pb}^{2+} \rightarrow \text{Sn}^{2+} + \text{Pb}$

When $a_{\text{Sn}^{2+}} = 0.1$, $a_{\text{Pb}^{2+}} = 0.01$, the Nernst equation (17-37) gives

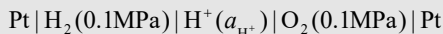
$$E = E^\ominus - \frac{RT}{2F} \ln \frac{a_{\text{Sn}^{2+}}}{a_{\text{Pb}^{2+}}} = \left[0.0113 - \frac{0.05916}{2} \lg \frac{0.1}{0.01} \right] \text{V} = -0.0183 \text{V}$$

Note: (1) The calculated electromotive force is negative indicating that Pb should be a negative electrode and Sn be a positive electrode. The cell should be written as:

–) Pb|Pb²⁺(*a*_{Pb²⁺})||Sn²⁺(*a*_{Sn²⁺})|Sn(+). It is shown that the redox ability of a substance can not be solely determined by the magnitude of *E*[°], the ionic concentration in solution should be considered simultaneously.

(2) When *T* = 298.15K, (*RT* / *F*) ln 10 = 0.05916V.

Example 2 Calculate the theoretical electromotive force of the following hydrogen-oxygen fuel cell at 25°C.



Solution: Table 17-2 gives *E*[°]{H⁺ | H₂} = 0, *E*[°]{H⁺ | O₂} = 1.229V

$$E^\ominus = E^\ominus \{ \text{H}^+ | \text{O}_2 \} - E^\ominus \{ \text{H}^+ | \text{H}_2 \} = 1.229 \text{V}$$

Negative electrode $2\text{H}_2 \rightarrow 4\text{H}^+(a_{\text{H}^+}) + 4\text{e}^-$,

Positive electrode $4\text{H}^+(a_{\text{H}^+}) + \text{O}_2 + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$

Cell reaction $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}(\text{l})$

Because *p*_{H₂} = *p*_{O₂} = *p*[°] = 0.1MPa, *a*_{H₂O} ≈ 1, the theoretical electromotive force is:

$$E = E^\ominus - \frac{RT}{4F} \ln \frac{a_{\text{H}_2\text{O}}^2}{(p_{\text{H}_2} / p^\ominus)^2 (p_{\text{O}_2} / p^\ominus)} = E^\ominus = 1.229 \text{V}$$

Note: (1) The electrode reactions of the positive and negative electrodes should be balanced, the electron gain and loss are compensated, and no electrons should appear in the cell reaction.

(2) The electromotive force is an intensive property irrelevant to the selection of the stoichiometry numbers in reaction.

Example 3 Design galvanic cells for the following reactions and write the corresponding expressions for the potentials of cell reaction.

(a) $\text{Sn} + 2\text{Fe}^{3+}(a_{\text{Fe}^{3+}}) \rightarrow \text{Sn}^{2+}(a_{\text{Sn}^{2+}}) + 2\text{Fe}^{2+}(a_{\text{Fe}^{2+}})$

(b) $\text{H}_2(p_{\text{H}_2}) + 2\text{AgCl}(\text{s}) \rightarrow 2\text{Ag} + 2\text{HCl}(a_{\pm})$, referring to Ex.8 for application.

Solution: First, decompose the total reaction into an oxidation reaction (negative electrode) and a reduction reaction (positive electrode).

(a) Oxidation $\text{Sn} \rightarrow \text{Sn}^{2+}(a_{\text{Sn}^{2+}}) + 2\text{e}^-$, electrode $\text{Sn}^{2+}(a_{\text{Sn}^{2+}})|\text{Sn}$

Reduction $2\text{Fe}^{3+}(a_{\text{Fe}^{3+}}) + 2\text{e}^- \rightarrow 2\text{Fe}^{2+}(a_{\text{Fe}^{2+}})$, electrode $\text{Fe}^{2+}(a_{\text{Fe}^{2+}}), \text{Fe}^{3+}(a_{\text{Fe}^{3+}})|\text{Pt}$

Galvanic cell –) Sn|Sn²⁺(*a*_{Sn²⁺})||Fe²⁺(*a*_{Fe²⁺}), Fe³⁺(*a*_{Fe³⁺})|Pt(+)

$$E = E^\ominus \{ \text{Fe}^{2+}, \text{Fe}^{3+} | \text{Pt} \} - E^\ominus \{ \text{Sn}^{2+} | \text{Sn} \} - \frac{RT}{2F} \ln \frac{a_{\text{Sn}^{2+}} a_{\text{Fe}^{2+}}^2}{a_{\text{Fe}^{3+}}^2}$$

Note: Sn²⁺ solution and Fe²⁺, Fe³⁺ solution must be separated by a salt bridge to avoid mixing.

(b) Oxidation $\text{H}_2(p_{\text{H}_2}) \rightarrow 2\text{H}^+(a_{\text{H}^+}) + 2\text{e}^-$, electrode $\text{H}^+(a_{\text{H}^+})|\text{H}_2(p_{\text{H}_2})|\text{Pt}$

Reduction $2\text{AgCl} + 2\text{e}^- \rightarrow 2\text{Ag} + 2\text{Cl}^-(a_{\text{Cl}^-})$, electrode $\text{Cl}^-(a_{\text{Cl}^-})|\text{AgCl}(\text{s})|\text{Ag}$

Galvanic cell $-) \text{Pt} | \text{H}_2(p_{\text{H}_2}) | \text{HCl}(a_{\pm}) | \text{AgCl(s)} | \text{Ag} (+$

$$E = E^\circ \{ \text{Cl}^- | \text{AgCl} | \text{Ag} \} - \frac{RT}{2F} \ln \frac{a_{\text{H}^+}^2 a_{\text{Cl}^-}^2}{(p_{\text{H}_2}/p^\circ)}$$

Note: (1) H^+ and Cl^- ions exist in the same HCl solution, the salt bridge is not necessary, $a_{\text{H}^+} a_{\text{Cl}^-} = a_{\pm}^2$.

(2) p_{H_2}/p° is the activity of H_2 in an ideal-gas state, referring to 17.4.3.

Example 4 Calculate the standard potential of electrode reaction of $\text{Fe}^{3+} | \text{Fe}$ using the data of $\text{Fe}^{2+} | \text{Fe}$ and $\text{Fe}^{3+}, \text{Fe}^{2+} | \text{Pt}$ given in Table 17-2.

Solution: According to the definition of the standard potential of electrode reaction, the cell reactions corresponding to the three electrodes are respectively:

- (a) $\text{H}_2(p^\circ) + \text{Fe}^{2+}(a_{\text{Fe}^{2+}} = 1) \rightarrow 2\text{H}^+(a_{\text{H}^+} = 1) + \text{Fe}$
- (b) $\frac{1}{2}\text{H}_2(p^\circ) + \text{Fe}^{3+}(a_{\text{Fe}^{3+}} = 1) \rightarrow \text{H}^+(a_{\text{H}^+} = 1) + \text{Fe}^{2+}(a_{\text{Fe}^{2+}} = 1)$
- (c) $\frac{3}{2}\text{H}_2(p^\circ) + \text{Fe}^{3+}(a_{\text{Fe}^{3+}} = 1) \rightarrow 3\text{H}^+(a_{\text{H}^+} = 1) + \text{Fe}$

Also we have $\Delta_r G_m^\circ(\text{a}) = -2FE^\circ\{\text{Fe}^{2+} | \text{Fe}\}$, $\Delta_r G_m^\circ(\text{b}) = -FE^\circ\{\text{Fe}^{2+}, \text{Fe}^{3+} | \text{Pt}\}$,
 $\Delta_r G_m^\circ(\text{c}) = -3FE^\circ\{\text{Fe}^{3+} | \text{Fe}\}$

Obviously, (a) + (b) = (c), $\Delta_r G_m^\circ(\text{a}) + \Delta_r G_m^\circ(\text{b}) = \Delta_r G_m^\circ(\text{c})$

Therefore, $2E^\circ\{\text{Fe}^{2+} | \text{Fe}\} + E^\circ\{\text{Fe}^{2+}, \text{Fe}^{3+} | \text{Pt}\} = 3E^\circ\{\text{Fe}^{3+} | \text{Fe}\}$

Substitution of $E^\circ\{\text{Fe}^{2+} | \text{Fe}\} = -0.447\text{V}$ and $E^\circ\{\text{Fe}^{2+}, \text{Fe}^{3+} | \text{Pt}\} = 0.771\text{V}$ yields

$$E^\circ\{\text{Fe}^{3+} | \text{Fe}\} = \frac{1}{3}[2 \times (-0.447) + 0.771]\text{V} = -0.041\text{V}$$

2. Calculations of Thermodynamic Functions and Standard Equilibrium Constant of Chemical Reactions Examples refer to 17.3.

3. Calculations of Ionic Product of Water, Solubility Product of Sparingly Soluble Salts and Instability Constant of Complex Ions

Example 5 Given the ionic product of H_2O , K_w° , at a temperature of T , calculate the standard potential $E^\circ\{\text{OH}^- | \text{H}_2\}$.

Solution: According to 17.6.5, for $E^\circ\{\text{OH}^- | \text{H}_2\}$, $a_{\text{OH}^-} = 1$,

$$\begin{aligned} a_{\text{H}^+} &= K_w^\circ / a_{\text{OH}^-} = K_w^\circ \\ E^\circ\{\text{OH}^- | \text{H}_2\} &= E\{\text{H}^+(a_{\text{H}^+} = K_w^\circ) | \text{H}_2(0.1\text{MPa})\} \\ &= E^\circ\{\text{H}^+ | \text{H}_2\} + (RT/F) \ln a_{\text{H}^+} = (RT/F) \ln K_w^\circ \end{aligned}$$

Substitution of $T=298.15\text{K}$ and $K_w^\circ = 1.008 \times 10^{-14}$ yields

$$E^\circ\{\text{OH}^- | \text{H}_2\} = -0.8280\text{V}$$

Example 6 Calculate the solubility product of calomel in water at 25°C using E° s of the calomel electrode and the mercury-mercurous ion electrode.

Solution: According to 17.6.4, for $E^\circ\{\text{Cl}^- | \text{Hg}_2\text{Cl}_2 | \text{Hg}\}$, $a_{\text{Cl}^-} = 1$,

$$a_{\text{Hg}_2^{2+}} = K_{\text{sp}}^{\circ} / a_{\text{Cl}^-}^2 = K_{\text{sp}}^{\circ},$$

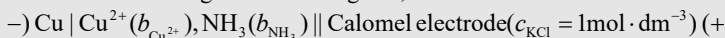
$$\begin{aligned} E^{\circ} \{ \text{Cl}^- | \text{Hg}_2\text{Cl}_2 | \text{Hg} \} &= E \{ \text{Hg}_2^{2+} (a_{\text{Hg}_2^{2+}} = K_{\text{sp}}^{\circ}) | \text{Hg} \} \\ &= E^{\circ} \{ \text{Hg}_2^{2+} | \text{Hg} \} + (RT/2F) \ln a_{\text{Hg}_2^{2+}} = E^{\circ} \{ \text{Hg}_2^{2+} | \text{Hg} \} + (RT/2F) \ln K_{\text{sp}}^{\circ} \end{aligned}$$

Substitution of $E^{\circ} \{ \text{Cl}^- | \text{Hg}_2\text{Cl}_2 | \text{Hg} \} = 0.26791\text{V}$ and $E^{\circ} \{ \text{Hg}_2^{2+} | \text{Hg} \} = 0.7971\text{V}$ yields

$$\begin{aligned} \ln K_{\text{sp}}^{\circ} &= 2F [E^{\circ} \{ \text{Cl}^- | \text{Hg}_2\text{Cl}_2 | \text{Hg} \} - E^{\circ} \{ \text{Hg}_2^{2+} | \text{Hg} \}] / RT \\ &= 2 \times 96485 \times (0.26791 - 0.7971) / (8.3145 \times 298.15) = -41.194 \\ K_{\text{sp}}^{\circ} &= 1.29 \times 10^{-18} \end{aligned}$$

Example 7 Cu^{2+} ion and NH_3 in aqueous solution can form a complex ion $\text{Cu}(\text{NH}_3)_4^{2+}$ in terms of $\text{Cu}^{2+} + 4\text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}$. Design a cell to calculate the instability constant $K_{\text{instab.}}^{\circ}$ of this complex ion.

Solution: To sum up, the problem is how to obtain the concentration of Cu^{2+} remained in solution. Design the following cell,



According to Eq.(17-48), $E(\text{Positive electrode}) - E(\text{Cell}) = E(\text{Negative electrode})$

$$\begin{aligned} E \{ \text{Calomel electrode}, c_{\text{KCl}} = 1 \text{mol} \cdot \text{dm}^{-3} \} - E &= E \{ \text{Cu}^{2+} (b_{\text{Cu}^{2+}}), \text{NH}_3 (b_{\text{NH}_3}) | \text{Cu} \} \\ &= E^{\circ} \{ \text{Cu}^{2+} | \text{Cu} \} + (RT/2F) \ln a_{\text{Cu}^{2+}} \end{aligned}$$

Determining E experimentally, obtaining $E^{\circ} \{ \text{Cu}^{2+} | \text{Cu} \}$ from Table 17-2, $a_{\text{Cu}^{2+}}$ can be calculated. Set $\gamma=1$ approximately,

$$\begin{aligned} a_{\text{Cu}^{2+}} &\approx (b_{\text{remaining Cu}^{2+}} / b^{\circ}), \quad a_{\text{Cu}(\text{NH}_3)_4^{2+}} \approx b_{\text{Cu}(\text{NH}_3)_4^{2+}} / b^{\circ} = (b_{\text{Cu}^{2+}} - b_{\text{remaining Cu}^{2+}}) / b^{\circ} \\ a_{\text{NH}_3} &\approx b_{\text{remaining NH}_3} / b^{\circ} = (b_{\text{NH}_3} - 4b_{\text{Cu}(\text{NH}_3)_4^{2+}}) / b^{\circ} \end{aligned}$$

Therefore, $K_{\text{instab.}}^{\circ} = a_{\text{Cu}^{2+}} a_{\text{NH}_3}^4 / a_{\text{Cu}(\text{NH}_3)_4^{2+}}$

At 25°C , a typical determination gives:

$$b_{\text{Cu}^{2+}} = 0.020 \text{mol} \cdot \text{kg}^{-1}, \quad b_{\text{NH}_3} = 0.50 \text{mol} \cdot \text{kg}^{-1}, \quad E = 0.260\text{V},$$

$$E \{ \text{Calomel electrode}, c_{\text{KCl}} = 1 \text{mol} \cdot \text{dm}^{-3} \} = 0.2799\text{V}, \quad E^{\circ} \{ \text{Cu}^{2+} | \text{Cu} \} = 0.3417\text{V},$$

Calculation gives $a_{\text{Cu}^{2+}} = 1.3 \times 10^{-11}$, indicating the most of Cu^{2+} are complex ions.

$$K_{\text{instab.}}^{\circ} = 1.3 \times 10^{-11} \times (0.50 - 4 \times 0.020)^4 / 0.020 = 2.0 \times 10^{-11}$$

4. Calculations of Mean Ionic Activity Factors

Example 8 Calculate the mean ionic activity factors of HCl solutions with different concentrations.

Solution: Design a cell: $-) \text{Pt} | \text{H}_2 (p^{\circ}) | \text{HCl} (b) | \text{AgCl} (s) | \text{Ag} (+$

The potential of cell reaction $\text{H}_2 (p^{\circ}) + 2\text{AgCl} (s) \rightarrow 2\text{Ag} (s) + 2\text{H}^+ (a_{\text{H}^+}) + 2\text{Cl}^- (a_{\text{Cl}^-})$ is:

$$E = E^{\circ} \{ \text{Cl}^- | \text{AgCl} | \text{Ag} \} - \frac{RT}{2F} \ln (a_{\text{H}^+} a_{\text{Cl}^-})^2 = E^{\circ} \{ \text{Cl}^- | \text{AgCl} | \text{Ag} \} - \frac{RT}{F} \ln (b_{\pm} \gamma_{\pm} / b^{\circ})^2$$

Determining E , obtaining $E^{\circ} \{ \text{Cl}^- | \text{AgCl}, \text{Ag} \}$ from Table 17-2, γ_{\pm} of various concentrations b can be calculated.

At 25°C, a typical determination gives: $b = 0.0134 \text{ mol} \cdot \text{kg}^{-1}$, $E = 0.4495 \text{ V}$, substitution of $E^\ominus \{\text{Cl}^- | \text{AgCl} | \text{Ag}\} = 0.22216 \text{ V}$ into the above expression for the potential of cell reaction yields

$$\lg \gamma_{\pm} = \frac{E^\ominus \{\text{Cl}^- | \text{AgCl} | \text{Ag}\} - E}{2RT \ln 10 / F} - \lg \frac{b}{b^\ominus} = \frac{0.22216 - 0.4495}{2 \times 0.05916} - \lg 0.01341 = -0.0488$$

$$\gamma_{\pm} = 0.894$$

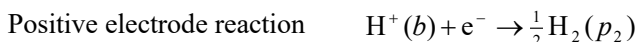
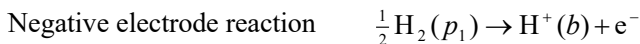
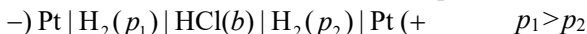
Note: $E^\ominus \{\text{Cl}^- | \text{AgCl} | \text{Ag}\}$ can also be obtained experimentally by the data of b - E of dilute solutions using a graphical method.

17.8 Concentration Cell and Liquid-Junction Potential

Concentration Cells The feature of concentration cells is that their cell reaction is a transfer of substance from a higher concentration region to a lower one. Here the cell reaction is not a redox reaction.

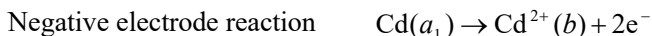
Electrode Concentration Cells They are galvanic cells with a single solution but the electrode materials have different concentrations.

(1) **Gas-Electrode Concentration Cell** For example,



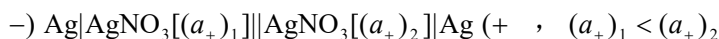
$$E = -\frac{\Delta_r G_m}{F} = -\frac{RT}{F} \ln \left(\frac{p_2}{p_1} \right)^{1/2} = \frac{RT}{2F} \ln \frac{p_1}{p_2} \quad (17-57)$$

(2) **Amalgam-Electrode Concentration Cell** For example,



$$E = -\frac{\Delta_r G_m}{2F} = -\frac{RT}{2F} \ln \frac{a_2}{a_1} = \frac{RT}{2F} \ln \frac{a_1}{a_2} \quad (17-58)$$

Solution Concentration Cells They are galvanic cells with the same electrode but the solutions have different ionic concentrations. For example,



Negative electrode reaction $\text{Ag} \rightarrow \text{Ag}^+[(a_+) _1] + \text{e}^-$

Positive electrode reaction $\text{Ag}^+[(a_+) _2] + \text{e}^- \rightarrow \text{Ag}$

Cell reaction $\text{Ag}^+[(a_+) _2] \rightarrow \text{Ag}^+[(a_+) _1]$

$$E = -\frac{\Delta_r G_m}{F} = \frac{RT}{F} \ln \frac{(a_+) _2}{(a_+) _1} \quad (17-59)$$

Because the activity of a single ion can't be determined, it should be replaced by the mean ionic activity approximately, $(a_+) _2 / (a_+) _1 \approx (a_{\pm}) _2 / (a_{\pm}) _1$. Substituting into Eq.(17-59), the approximate expression for the electromotive force is obtained,

$$E = -\frac{\Delta_r G_m}{F} = \frac{RT}{F} \ln \frac{(a_{\pm}) _2}{(a_{\pm}) _1} \quad (17-60)$$

Solution Concentration Cells with Liquid-Junction Potential

Avoided In the above solution concentration cell, a liquid-junction potential exists on the interface between two solutions. The following special arrangement of the two same cells with different electrolyte concentrations results in a concentration cell with the liquid-junction potential avoided:

→ $\text{Pt} | \text{H}_2(p) | \text{HCl}(b_1) | \text{AgCl} | \text{Ag} - \text{Ag} | \text{AgCl} | \text{HCl}(b_2) | \text{H}_2(p) | \text{Pt}$ (+
 $b_1 < b_2$). The total reaction of this cell is the sum of the two simple cells.

Left cell $\frac{1}{2} \text{H}_2(p) + \text{AgCl} \rightarrow \text{Ag} + \text{H}^+(b_1) + \text{Cl}^-(b_1)$

Right cell $\text{Ag} + \text{H}^+(b_2) + \text{Cl}^-(b_2) \rightarrow \frac{1}{2} \text{H}_2(p) + \text{AgCl}$

Total reaction $\text{H}^+(b_2) + \text{Cl}^-(b_2) \rightarrow \text{H}^+(b_1) + \text{Cl}^-(b_1)$

Obviously, in the case of the same hydrogen pressure for the two electrodes, the total reaction of the cell is a transfer of HCl from a higher concentration b_2 to a lower b_1 .

$$E = -\frac{\Delta_r G_m}{F} = -\frac{RT}{F} \ln \frac{(a_{\text{H}^+}) _1 (a_{\text{Cl}^-}) _1}{(a_{\text{H}^+}) _2 (a_{\text{Cl}^-}) _2} = -\frac{2RT}{F} \ln \frac{(a_{\pm}) _1}{(a_{\pm}) _2} \quad (17-61)$$

As is shown by this equation, the electrolyte activity of a solution with a certain concentration can be calculated by the known electrolyte activity of another solution. Also, if the vapor pressure of a concentrate solution of HCl is known, that of a dilute solution can be estimated.

Example Calculate the potential of cell reaction at 25°C of the following cell.

$\text{Ag} | \text{AgNO}_3(b = 0.01 \text{mol} \cdot \text{kg}^{-1}, \gamma_{\pm} = 0.900) || \text{AgNO}_3(b = 0.1 \text{mol} \cdot \text{kg}^{-1}, \gamma_{\pm} = 0.720) | \text{Ag}$

Solution: This is a concentration cell with the liquid-junction potential eliminated. In terms of Eq.(17-60),

$$E = \frac{RT}{F} \ln \frac{a_{\pm,2}}{a_{\pm,1}} = \frac{RT}{F} \ln \frac{b_2 \gamma_{\pm,2}}{b_1 \gamma_{\pm,1}} = \left(\frac{8.3145 \times 298.15}{96485} \ln \frac{0.1 \times 0.720}{0.01 \times 0.900} \right) \text{V} = 0.0534 \text{V}$$

Calculation of Liquid-Junction Potential Comparing the potentials of the solution concentration cells with and without liquid-junction potential, the liquid-junction potential can be estimated in principle.

II. Theories of Electrode-Solution Interface

17.9 Outer Potential, Surface Potential and Inner Potential

The potential and the standard potential of electrode reaction on the electrode-solution interface are the most basic equilibrium characteristic properties of the electrochemical systems. They are mainly obtained by experiment at present. To

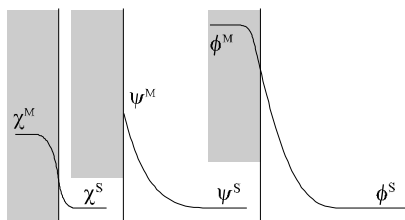


Figure 17-11 Inner potential ϕ , outer potential ψ and surface potential χ

elucidate the essentials of the formation of potentials theoretically and finally to predict the potentials from the structural properties of molecules and solids, it is necessary to have a deep understanding toward the structure of the electrode-solution interfacial layer. This is also important in studying the electrochemical kinetics. Three kinds of potential difference can be distinguished due to their different formation mechanisms, referring to Figure 17-11.

Outer Potential The symbol used is ψ . It is the electrostatic potential formed due to the excess charge. The ions in the electrode enter the solution due to the hydration leading to the electrons remained, or the ions in the solution dehydrate and deposit on the electrode, both processes result in the formation of the excess charge on the surface layer of the electrode and the excess charge of opposite sign on the surface layer of the solution. Correspondingly, the electrode and the solution exhibit different outer potentials ψ^M and ψ^S respectively, the order of magnitude of the distance

across from ψ^S to ψ^M is about 0.1nm. The theory of outer potential is nearly complete and will be introduced first.

Surface Potential The symbol used is χ . Because of the discontinuous change of structure, even without excess charge, the potential difference still exists on the electrode-solution interface called the surface potential. For a metal surface, because the electrons can escape, a density distribution of electrons exhibits in this region which can even extend to outside the surface. For a solution, the water molecule dipoles on the surface form a certain extent of oriented arrangement. Correspondingly, a surface potential χ^M exists slightly inside the electrode surface and a surface potential χ^S inside the solution surface. The distance across from χ^S to χ^M is about 0.1nm. The theory of the surface potential is immature and will be mentioned briefly.

Inner Potential Symbol used is ϕ . The sum of the outer potential and the surface potential is called the inner potential,

$$\phi = \psi + \chi \quad (17-62)$$

The potential of electrode reaction is determined by the inner potential difference $\Delta_s^M \phi$ on the electrode-solution interface,

$$\Delta_s^M \phi = \phi^M - \phi^S = \psi^M - \psi^S + \chi^M - \chi^S = \Delta_s^M \psi + \Delta_s^M \chi \quad (17-63)$$

17.10 Surface Excess Charge and Double-Layer Capacitance

Surface Excess Charge The outer potential ψ is determined by the surface excess charge Q . The fundamental equations of thermodynamics provide ways of studying. For an electrode surface with a surface area of A_s and a charge of Q , in the condition of isothermal, isobaric and iso-chemical potential, the Gibbs-Duhem equation, Eq.(17-16) gives

$$Qd\phi + A_s d\sigma = 0 \quad , \quad Q = -A_s \left(\frac{\partial \sigma}{\partial \phi} \right)_{T, p, \mu} \quad (17-64)$$

where $Q = nzF$, σ is the interfacial tension, ϕ is the inner potential. It is shown in this equation that the surface charge Q can be obtained by determining the variation of σ with the change of ϕ , the information of ψ is

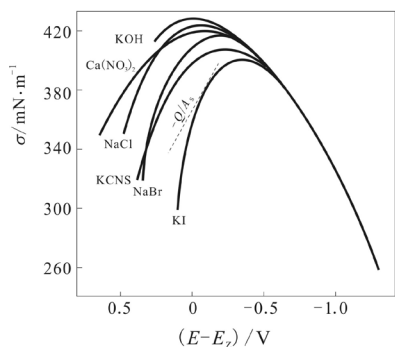


Figure 17-12 Variation of Hg-solution interfacial tension with potential for various solutions. E_z is

then provided.

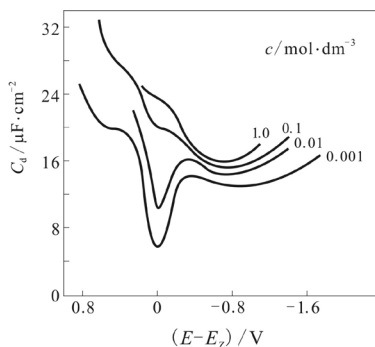


Figure 17-13 Variation of differential capacitance of Hg-NaF solution interface with potential.

Electro-Capillary Phenomenon and Zero-Charge Potential As early as 1873, Lippmann G built a galvanic cell composed of a capillary Hg electrode and a reference electrode, obtained the variation of interfacial tension σ between Hg and the solution by measuring the height h and the contact angle θ of the Hg column in capillary, with respect to the change of the potential of electrode reaction E by using a potentiometer to adjust and determine E , referring to Figure 17-12. It is called the electro-capillary phenomenon. Because the variation of E is equivalent to that of ϕ , the slope of the $\sigma \sim E$ curve, $\partial\sigma/\partial E$ is the same as $\partial\sigma/\partial\phi$, according to Eq.(17-64), it is $-Q/A_s$. As is shown in the Figure, the $\sigma \sim E$ curves of different electrolyte solutions all exhibit a parabola type. On the left side with higher potential, Q is positive, while on the right side with lower potential, Q is negative. At the extremum, $Q=0$, the corresponding potential of electrode reaction is called the zero-charge potential with a symbol of E_z . Different Hg-solution interfaces have different zero-charge potentials. For the solid electrodes, in the 70s of the 20th century, using the principle of contraction of the metal sheet with the reduction of charge, the interfacial tensions are also measured and the similar $\sigma \sim E$ curves are obtained. The zero-charge potential E_z has an important significance because on this occasion $\Delta_s^M \psi = 0$, we then have an absolute standard for the outer-potential difference, by which the absolute value of $\Delta_s^M \psi$ at other potential E can be obtained.

Double-Layer Capacitance The electrode-solution interfacial layer can be regarded as a capacitance and a resistance in parallel connection. The differential capacitance is defined by $C_d = (\partial Q / \partial \phi) / A_s$. Notice that $d\phi = dE$, substitution of Eq.(17-64) yields

$$C_d = - \left(\frac{\partial^2 \sigma}{\partial \phi^2} \right)_{T, p, \mu} \quad (17-65)$$

By using this equation, C_d can be obtained by the $\sigma \sim E$ relation in principle. However, because of the worse accuracy of the second order derivatives, C_d is usually determined directly by using the impedance method. As is shown in Eq.(17-65), the differential capacitance is directly connected with the excess charge and the potential. Practice shows that it reflects the structural change of the interfacial layer more sensitively. Figure 17-13 plots the variation of the differential capacitance of the Hg-NaF solution interface with the potential. When the concentration is not too high, a minimum appears at the zero-charge potential ($E_z = -0.19V$), however, the curves in both sides are not symmetry. When the concentration is higher, the minimum disappears.

17.11 Electric Double-Layer Models and Outer Potential

Electric Double-Layer Models The earliest one is the Helmholtz model established in 1879 which proposed that the hydrated ions form an electric double layer on the electrode surface similar to a planar condenser. The plane where the hydrated ions are located is called the Helmholtz plane (HP). The next one is the diffusive electric double-layer model developed by Gouy G in 1910 and Chapman D L in 1913. It is similar to an ionic atmosphere. Therefore, the Debye-Hückel theory can be applied. Later, Stern O developed a new model which is the combination of the above two models, as shown in Figure 17-1, part of the hydrated ions assemble at the HP in a tightly adsorbed form. The others compose the diffusive electric double layer.

Stern-Grahame Model In 1947, Grahame D C improved the Stern model. He considered that the chemisorption of ions exists on the electrode

surface accompanied by the dehydration resulting in two Helmholtz planes near the surface, referring to Figure 17-14. As is shown in the Figure, the position of the chemisorbed dehydrated anions close to the surface is called the **inner Helmholtz plane (IHP)**, and that of the adsorbed cations due to the electrostatic interactions near the surface is called the **outer Helmholtz plane (OHP)**. Outside these planes is the diffusive electric double layer. The variation of the potential with distance inside

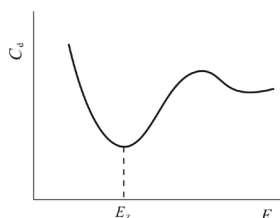


Figure 17-15 Model predicted variation of differential capacitance with potential

the IHP and in between the IHP and OHP is linear, and

gradually tends to be gently outside the OHP as shown in the lower part of the Figure. In theoretical treatment, an isotherm of chemisorption is needed. Figure 17-15 shows the predicted variation of the differential capacitance with

potential. The trend is in consistent with the experimental results in Figure 17-13. At present, the Stern- Grahame model is commonly recognized as a comparatively more accurate model.

It should be pointed out that the double-layer models concern only the outer potential difference. For the inner potential difference, the surface potential difference should be further studied.

17.12 Absolute Potential of Electrode Reaction

Surface Potential The further development of the double-layer models mainly focuses on the studies of the surface potential.

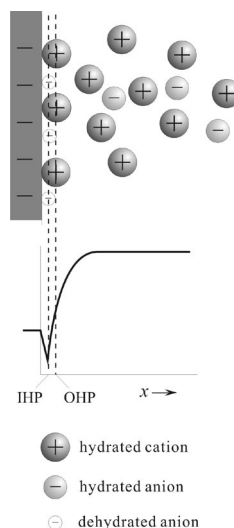


Figure 17-14 Stern-Grahame model

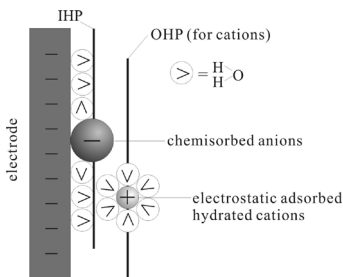


Figure 17-16 Orientation of water molecules on the electrode surface

(1) **BDM Model** In 1963, Bockris J O' M, Devanathan M A V and Müller K considered the dipole feature of the water molecules that they form a layer near the electrode surface with an oriented arrangement and construct a surface potential of the solution surface, referring to Figure 17-16. The surface potential can be estimated theoretically by the structural model of water molecules in the interfacial layer.

(2) **Solid Surface** An idea has been developed since 1980s that the potential of a metal surface starts to change from only about 0.1nm inside the surface and can extend to the vacuum outside the surface. This is also an important contribution to the surface potential and can be estimated by the work function.

Absolute Potential of Standard Hydrogen Electrode By discussion of the surface potential in this section and that of the outer potential in 17.10 and 17.11, the problem of obtaining the inner potential theoretically has been solved in principle. The aim of the theory is the absolute potential of electrode reaction which is related with the potential of electrode reaction by a constant of difference, this constant is the absolute potential of electrode reaction of the standard hydrogen electrode, $E_{\text{abs}}(\text{SHE})$. If $E_{\text{abs}}(\text{SHE})$ is given exactly, all the absolute potentials of electrode reaction are known naturally. At present, as a notable achievement reached by the theory of electrode-solution interface, $E_{\text{abs}}(\text{SHE})$ is determined roughly as:

$$E_{\text{abs}}(\text{SHE}) = 4.62\text{V}$$

However, $E_{\text{abs}}(\text{SHE})$ can not be used to replace the potential of electrode reaction yet at present because on the one side, the model estimation is involved in the process. On the other side, the measurement of the work function is not as accurate as that of the potential. As for the prediction of the potentials on the molecular and electronic level, because the movement of electrons and protons (H^+) observes the quantum mechanical rules, the Schrödinger equation of the electrode-solution interface should be solved. This kind of studies is rare because of the extreme difficulties.

III Electrochemical Kinetics

17.13 Relations among Reaction Rate, Current and Potential

1. Rate and Current of Electrode Reaction

Rate of Electrode Reaction The rate of an electrode reaction v is defined as the variation rate of the reaction extent with time in a unit electrode-solution interface with a unit of $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$,

$$v \stackrel{\text{def}}{=} \frac{1}{A_s} \frac{d\xi}{dt} \quad (17-66)$$

Rate of Cell Reaction Because of the different areas for the cathode and the anode, the rate of conversion $d\xi/dt$ is adopted.

Positive or Negative Sign of Current Electrochemical reaction rate is proportional to the current. In terms of the concept of the opposite reactions, the directions of reduction and oxidation always exist simultaneously for an electrode reaction. According to the conventions, **the current entering the solution from the electrode is positive, and the contrary is negative**. For an arbitrary electrode, the reaction is expressed as:



The reduction rate and the oxidation rate are v_{red} and v_{ox} respectively; they have their own contribution to the current.

Partial Cathodic Current The symbol used is I_c . It is the current accompanying the reduction reaction. It flows from the solution to the electrode (electrons flow from the electrode to the solution). Therefore, it takes the negative value. Its relation with the reduction reaction rate is:

$$I_c = -zFA_s v_{\text{red}} \quad (17-68)$$

Partial Anodic Current The symbol used is I_a . It is the current accompanying the oxidation reaction. It flows from the electrode to the solution (electrons flow from the solution to the electrode). Therefore, it takes the positive value. Its relation with the oxidation reaction rate is:

$$I_a = zFA_s v_{\text{ox}} \quad (17-69)$$

Current The symbol used is I . It is the sum of the partial cathodic current and the partial anodic current,

$$I = I_c + I_a = zFA_s(v_{ox} - v_{red}) \quad (17-70)$$

If the electrode is a cathode, reduction is predominating, $v_{red} > v_{ox}$, the current is negative. If the electrode is an anode, oxidation is predominating, $v_{ox} > v_{red}$, the current is positive.

Current Density The symbol used is j . It is the current in unit electrode-solution interface,

$$j \stackrel{\text{def}}{=} I/A_s = j_a + j_c = zF(v_{ox} - v_{red}) \quad (17-71)$$

where j_c and j_a are called the **partial cathodic current density** and the **partial anodic current density** respectively.

Rate Equation of Electrode Reaction For the directions of reduction and oxidation, we can write respectively:

$$v_{red} = k_{red} c_O^{n(O)} \quad (17-72)$$

$$v_{ox} = k_{ox} c_R^{n(R)} \quad (17-73)$$

where k_{red} and k_{ox} are the rate coefficients (constants) of the direction of reduction and oxidation, $n(O)$ and $n(R)$ are the reaction orders of substances of oxidation form and reduction form, respectively. Substitution of Eqs.(17-68) and (17-69) yields

$$k_{red} = -\frac{I_c}{zFA_s c_O^{n(O)}} = -\frac{j_c}{zFc_O^{n(O)}} \quad (17-74)$$

$$k_{ox} = \frac{I_a}{zFA_s c_R^{n(R)}} = \frac{j_a}{zFc_R^{n(R)}} \quad (17-75)$$

Rate of Electrode Reaction For the cathode and the anode, we can write respectively:

$$v(\text{Cathode}) = v_{red} - v_{ox} = -\frac{I}{zFA_s} = -\frac{j}{zF} \quad (17-76)$$

$$v(\text{Anode}) = v_{ox} - v_{red} = \frac{I}{zFA_s} = \frac{j}{zF} \quad (17-77)$$

As is shown above, the electrochemical kinetics is the same in principle as the ordinary chemical kinetics except that the reaction rate is proportional to the current density. The characteristic properties of substances needed are also the reaction orders, the rate coefficient (constant) or the pre-exponential factor and the activation energy. More relevant are the exchange current density and the transfer coefficient, referring to 17.16 later.

2. Current-Potential Relation

Current-Potential Diagram

A dilute solution of KI of $0.01\text{mol}\cdot\text{dm}^{-3}$ with H_2SO_4 added is placed in a cell using two Pt electrodes to electrolyze. H_2 and I_2 are separated out on the cathode and the anode respectively. Figure 17-17 shows the corresponding current-potential diagram, the upper left is a partly magnified picture.

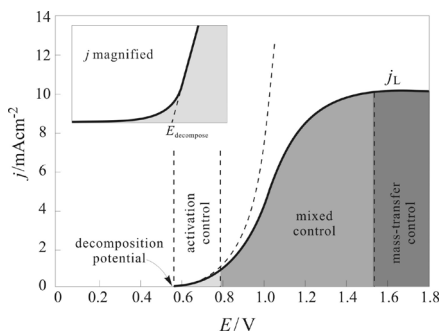


Figure 17-17 Current-potential diagram of the electrolysis of an acidic solution of KI

Initial Stage When the voltage, the potential E of the cell, starts to increase, the current increases very slowly with no electrolysis observed. At this moment, tiny amounts of hydrogen and iodine in an adsorbed state create on the two electrodes composing a galvanic cell with an electromotive force opposite to the external voltage exerted. The electrolysis is therefore retarded, the current should be zero. However, because of the diffusion of the products, to compensate for the diffusion loss, a tiny current is getting through called the **residue current**. With the increase of E , the extent of saturation of the products on the electrodes enhances, H_2 and I_2 are finally separated out, and the electrolysis starts. After then, the reaction rate or the current rises notably with the increase of the voltage. Extrapolate this $j\sim E$ line, referring to the upper left of the Figure, the potential at the intersection with the abscissa E is the minimum voltage to electrolyze the $\text{KI}/\text{H}_2\text{SO}_4$ solution called the **decomposition potential**.

Middle and Later Stages As E further increases, the $j\sim E$ curve first rises exponentially, then gradually develops gently, and finally approaches a limiting value j_L called the **limiting current**. The latter phenomenon is because of the extremely high rate of electrode reaction, the concentration of the reactant on the electrode surface approaches zero. At this moment, the whole reaction is determined by the migration of reactant from the bulk solution toward the electrode surface, i.e., the **mass-transfer control**. The above part rising exponentially is caused by the depression of the activation

barrier by the interfacial potential, i.e., the **activation control**. In the intermediate part, the activation and the mass transfer contribute simultaneously, i.e., the **mixed control**.

17.14 Polarization Phenomena and Over-Potential

Irreversible Processes Whatever in a galvanic cell or an electrolytic cell, there is a certain current passing through during working, therefore, the processes are all irreversible. The galvanic cell proceeded in a reversible condition is an ideal standard for realizing an electrochemical process. For example, as shown in Example 2 in 17.7, the potential of cell reaction of a hydrogen-oxygen galvanic cell is 1.229V. While working as a hydrogen-oxygen fuel cell, the real potential is much lower, less than 0.9V. On the other hand, during the electrolysis of water, the voltage used is generally greater than 2V. Even for the decomposition potential, although the current is nearly zero, it is not necessarily equal to the potential of cell reaction in equilibrium. For the electrolysis of water, the theoretical decomposition potential should be 1.229V. However, if the Pt electrodes are adopted, the decomposition potential is about 1.68V. If Fe is used to replace the cathode, it is 0.2V higher. If Cd is used, 0.46V more is observed.

Polarization Phenomena They are the phenomena concerning notable difference between the real electrode potential and the potential of electrode reaction.

Polarizable Electrodes They are the electrodes with polarization phenomena accompanied. Most real electrodes belong to this category.

Non-Polarizable Electrodes They are the electrodes with negligible polarization phenomena. For examples, the hydrogen electrode, the calomel electrode, the silver chloride electrode. When the current passed is not large, the electrode potential is basically the same as the equilibrium potential of electrode reaction. When the current passed is large, the non-polarizable electrode turns to a polarizable electrode.

Over-Potential The symbol used is η . It is the difference between the real electrode potential and the potential of electrode reaction,

$$\eta = E(j) - E(0)$$

where $E(j)$ is the potential at a current density of j , $E(0)$ is the potential at $j=0$ and in equilibrium. η is a characteristic parameter expressing the deviation from equilibrium for an electrochemical system. It has an important effect on the reaction rate.

1. Determination of Over-Potential

Typical determination equipment for the over-potential in an electrolysis process is shown in Figure 17-18. A reference electrode such as the calomel electrode is installed aside the electrode to be determined to form a galvanic cell. During the electrolysis or discharge process, the current density of the process is determined with an ammeter, and the electromotive force of the galvanic cell is measured by a potentiometer. With the potential of electrode reaction of the calomel electrode deducted from the electromotive force, the electrode potential of the determined electrode is obtained. Figures 17-19 and 17-20 show the results of determination during the electrolysis and the discharge respectively. The variations of the cathode potential and the anode potential with the current density are plotted respectively, the cathode over-potential η_c and the anode over-potential η_a are then obtained correspondingly,

$$\eta_c = E_c(j) - E_c(0) \quad (17-79)$$

$$\eta_a = E_a(j) - E_a(0) \quad (17-80)$$

where $E_c(0)$ and $E_a(0)$ are the equilibrium potentials of electrode reaction for the cathode and the anode respectively.

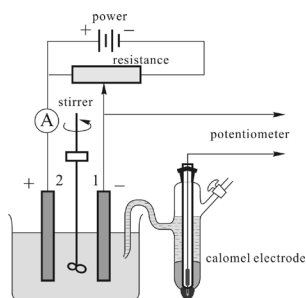


Figure 17-18 Determination of over-potential

Over-Potentials in Electrolysis As is shown in Figure 17-19, the cathode is the negative electrode in electrolysis with lower potential while the anode is positive electrode with higher potential. The electrode potential of the cathode, $E_c(j)$, depresses with the increasing j , $\eta_c < 0$, indicating a higher energy for electrons favoring the reduction reaction with electrons gained. The electrode potential of the anode, $E_a(j)$, enhances with the increasing j , $\eta_a > 0$, indicating a lower energy for electrons favoring the oxidation reaction with electrons lost. The potential of the whole electrolytic cell, $E_{\text{electrolytic cell}}(j)$, is expressed by the following equation:

$$\begin{aligned} E_{\text{electrolytic cell}}(j) &= E_a(j) - E_c(j) + IR \\ &= E_a(0) + \eta_a - E_c(0) - \eta_c + IR \end{aligned} \quad (17-81)$$

where IR is the potential drop caused by the resistance of solution in cell. The equation indicates that $E_{\text{electrolytic cell}}(j)$ rises with the increase of current density. To accelerate the electrolysis, the voltage of the electrolytic cell should be increased.

Over-Potentials during Discharge As is shown in Figure 17-20, the cathode is the positive electrode during discharge with higher potential while the anode is negative electrode with lower potential. The variations of

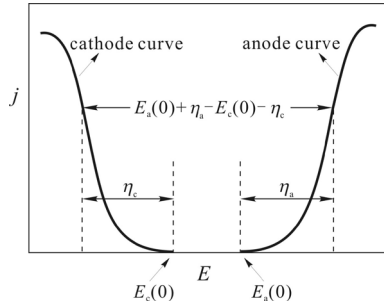


Figure 17-19 Relation between over-potential and current density

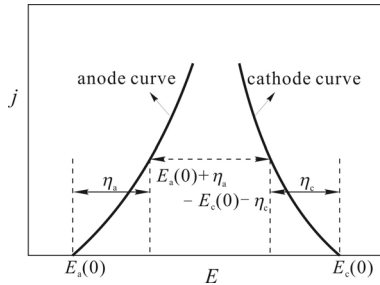


Figure 17-20 Relation between over-potential and current density

$E_c(j)$ of cathode and $E_a(j)$ of anode are the same as those in electrolysis, $\eta_c < 0$, $\eta_a > 0$. The potential of the whole cell, $E_{\text{galvanic cell}}(j)$, is expressed by the following equation:

$$\begin{aligned}
 E_{\text{galvanic cell}}(j) &= E_c(j) - E_a(j) - IR \\
 &= E_c(0) + \eta_c - E_a(0) - \eta_a - IR
 \end{aligned}
 \quad (17-82)$$

where IR is the internal consumption, because it should be deducted, the negative sign is added. The equation indicates that $E_{\text{galvanic cell}}(j)$ diminishes with the increase of current density. Accompanying accelerating the discharge, the potential of the galvanic cell will decrease.

Examples Tables 17-4, 17-5 and 17-6 list respectively the over-potentials of hydrogen η_c in a H_2SO_4 solution of $1\text{mol}\cdot\text{dm}^{-3}$, those of oxygen η_a in a KOH solution of $1\text{mol}\cdot\text{dm}^{-3}$, and those of chlorine η_a in a solution of KCl or NaCl pre-saturated with Cl_2 , at 25°C on various metal electrodes. For metal-metal ion electrodes, the over-potential is usually so small that it can be neglected.

2. Activation Over-Potential

Definition The over-potential which affects the activation-energy barrier of the electrode reaction directly is called the activation over-potential. Those over-potentials at lower current density are primarily the activation over-potential.

Table 17-4 Over-potentials of hydrogen at 25°C , $-\eta_c/\text{V}$

| $\frac{j}{\text{mA}\cdot\text{cm}^{-2}}$ | Cd | Cu | Pt black | Pt | Graphite | Ag | Fe | Zn | Ni | Pb | $\frac{j}{\text{mA}\cdot\text{cm}^{-2}}$ | Hg |
|--|-------|-------|----------|-------|----------|--------|--------|-------|-------|-------|--|--------|
| 0 | 0.466 | | 0.000 | | 0.0022 | | 0.2026 | | | | 0 | 0.2805 |
| 0.1 | 0.651 | 0.351 | 0.0034 | | 0.3166 | 0.2981 | 0.2183 | | | | 0.0769 | 0.5562 |
| 1 | 0.981 | 0.479 | 0.0154 | 0.024 | 0.5995 | 0.4751 | 0.4036 | 0.716 | 0.563 | 0.52 | 0.769 | 0.8488 |
| 10 | 1.134 | 0.584 | 0.0300 | 0.068 | 0.7788 | 0.7618 | 0.5571 | 0.746 | 0.747 | 1.090 | 7.69 | 1.0361 |
| 1000 | 1.254 | 1.254 | 0.0483 | 0.676 | 1.2200 | 1.0890 | 1.2915 | 1.229 | 1.241 | 1.262 | 769 | 1.108 |

Source: Creighton H J. Principle and Application of Electrochemistry. John Wiley & Sons.1997. p.248.

Table 17-5 Over-potentials of oxygen at 25°C , $-\eta_a/\text{V}$

| $\frac{j}{\text{mA}\cdot\text{cm}^{-2}}$ | Graphite | Au | Cu | Ag | Pt | Pt black | Ni |
|--|----------|-------|-------|-------|-------|----------|-------|
| 1 | 0.525 | 0.673 | 0.422 | 0.580 | 0.721 | 0.398 | 0.353 |
| 10 | 0.896 | 0.963 | 0.580 | 0.729 | 0.85 | 0.521 | 0.519 |
| 100 | 1.091 | 1.224 | 0.660 | 0.984 | 1.28 | 0.638 | 0.726 |
| 1000 | 1.240 | 1.63 | 0.793 | 1.131 | 1.49 | 0.766 | 0.853 |

Source: The same as Table 17-4, p.251.

Table 17-6 Over-potentials of chlorine at 25°C , $-\eta_a/\text{V}$

| $\frac{j}{\text{mA}\cdot\text{cm}^{-2}}$ | Pt black | $\frac{j}{\text{mA}\cdot\text{cm}^{-2}}$ | Pt | $\frac{j}{\text{mA}\cdot\text{cm}^{-2}}$ | Graphite |
|--|----------|--|--------|--|----------|
| 1.1 | 0.0060 | 1.1 | 0.008 | 40 | 0.186 |
| 14.5 | 0.0180 | 11.4 | 0.0299 | 100 | 0.251 |
| 100 | 0.026 | 100 | 0.0540 | 740 | 0.466 |
| 1340 | 0.089 | 1000 | 0.236 | 1131 | 0.535 |

Source: The same as Table 17-4, p.250.

Tafel Equation In 1905, Tafel J studied comprehensively the relation between the activation over-potential of hydrogen separated out on the metal electrode with the current density, and obtained:

$$|\eta| = a + b \ln \{j\} \quad (17-83)$$

It is called the Tafel equation where a and b are two empirical constants. For the clean surface of most metal electrodes, the constant b is about the same value in between 0.10V and 0.14V. The constant a is different for different electrode materials. The Tafel equation gives that the constant a is the over-potential at a unit current density. The larger a is, the higher over-potential of hydrogen will be. As is shown in Table 17-4, the over-potentials of hydrogen on Pt are the smallest, those on Ag, Cu, Fe, Ni and graphite are higher, and those on Zn, Cd and Hg are very large. The value of $-\eta_c$ at $j=1\text{mA}\cdot\text{cm}^{-2}$ can be considered approximately as the value of a for these metals. As for the over-potentials of oxygen, as shown in Table 17-5, those on platinum black and Ni are the smallest, those on Cu and graphite are higher, and those on Pt, Au and Ag are large. Notice that the value of a depends on the selection of the unit of current density. Because η and $\ln\{j\}$ has a linear relation, η affects j exponentially. According to Eqs.(17-76) and (17-77), j is directly proportional to the reaction rate, and according to the Arrhenius equation, Eq.(7-82), the activation energy affects the rate coefficient exponentially. Therefore, it is speculated that the over-potential is mainly through the activation energy to affect the electrode reaction rate.

3. Mass Transfer Over-Potential

The effect of mass transfer to the rate of electrochemical reactions is more prominent than that of the ordinary reactions. As is shown in Figure 17-17, the mass transfer plays important role in quite a wide range of current density, even a decisive role at high current densities. For the transport phenomena in electrolyte solutions, refer to 16.6 to 16.9.

Ionic Diffusion Suppose in an electrode process, the concentration of the ion B in bulk phase is $c_{B\infty}$, that on the electrode surface is c_{B0} , the diffusion flux j_B can be written in terms of the Fick's first law as:

$$j_B = -D \left(\frac{dc_B}{dx} \right)_{x=0} \quad (17-84)$$

Usually it can be approximately suggested that there is a linear diffusion layer near the interface, called the **Nernst diffusion layer** with a thickness of δ . Eq.(17-84) turns to:

$$j_B = -D(c_{B\infty} - c_{B0})/\delta = -k_d(c_{B\infty} - c_{B0}), \quad k_d = D/\delta \quad (17-85)$$

where k_d is the **diffusion rate coefficient**, or the **mass transfer coefficient**. Take anions for example. Oxidation reaction carries out on the anode with the negative charges flowing from the solution to the electrode, the corresponding anode current density is:

$$j = j_B zF = k_d |z| F(c_{B\infty} - c_{B0}) \quad (17-86)$$

Concentration Polarization Now we discuss the over-potential caused by the ionic diffusion. For simplicity, the electrode is supposed to be a non-polarizable electrode without the activation over-potential. On this occasion, the formation of the over-potential is solely determined by the change of ionic concentration on the electrode surface from the original $c_{B\infty}$ to c_{B0} due to diffusion resulting in a change of the potential. For example for anions with oxidation reaction on the anode, the over-potential obtained is η_a , which can be estimated by Eq.(17-59) of a solution concentration cell,

$$\eta_a = \frac{RT}{zF} \ln \frac{c_{B0}}{c_{B\infty}} = \frac{RT}{|z|F} \ln \frac{c_{B\infty}}{c_{B0}}, \quad z < 0 \quad (17-87)$$

Combining Eq.(17-86) with Eq.(17-87) and eliminating c_{B0} , a relation between j and η_a is obtained. As j increases, c_{B0} diminishes, and η_a enhances. This phenomenon of electrode potential change is originated from the concentration difference. Therefore, it is called the concentration polarization.

Limiting Current Density As η_a continuously enhances, c_{B0} will approach zero. Eq.(17-86) turns to

$$j_L = k_d |z| F c_{B\infty} \quad (17-88)$$

where j_L is the limiting current density of the anode dependent on the bulk concentration only. In practice, for reaching this limiting current, the **minisize electrode** is adopted. For example, the mercury drop electrode in polarographic analysis. Because of the very small surface area, a very high

current density is attained at a very small current and the limiting value is reached.

Example 1 Using Pt electrodes to electrolyze an aqueous H_2SO_4 solution at 25°C , the decomposition potential is 1.67V . Calculate the over-potential of oxygen at zero current density.

Solution: Water decomposes to H_2 and O_2 , the theoretical decomposition potential is the electromotive force of a hydrogen-oxygen cell, 1.229V .

At zero current density, the over-potential of hydrogen on the Pt electrode, $\eta_c=0$. Substituting into Eq.(17-81),

$$\eta_a = E_{\text{decompose}} - E(0) = (1.67 - 1.229)\text{V} = 0.44\text{V}$$

Example 2 Calculate the over-potential of hydrogen on graphite electrode at a current density of $0.5\text{mA}\cdot\text{cm}^{-2}$ and 25°C using Table 17-4.

Solution: Take $j=0.1\text{mA}\cdot\text{cm}^{-2}$, $\eta_c=-0.3166\text{V}$ and $j=1\text{mA}\cdot\text{cm}^{-2}$, $\eta_c=-0.5995\text{V}$, substituting into the Tafel equation,

$$0.3166\text{V} = a + b \ln 0.1, \quad 0.5995\text{V} = a + b \ln 1 = a$$

$$b = [(0.5995 - 0.3166) / 2.303]\text{V} = 0.1228\text{V}$$

$$|\eta_c| = a + b \ln\{j\} = (0.5995 + 0.1228 \times \ln 0.5)\text{V} = 0.5144\text{V}, \quad \eta_c = -0.5144\text{V}$$

17.15 Examples of Application

1. Electrolysis

Example Mercury is used as the cathode for the electrolysis of aqueous salt solution. The cathode reaction is $\text{Na}^+ + \text{e}^- \rightarrow \text{Na-Hg}$. The metal sodium created by the reduction of Na^+ ions forms sodium amalgam with mercury, then enters the mercury separation chamber and reacts with water to produce H_2 and highly pure caustic soda with almost no NaCl mixed. The reason why the cathode reaction is not the reduction of H^+ ions on the mercury anode is due to the high over-potential of hydrogen on the mercury.

Adjusting Over-Potential The reduction or oxidation of various substances has their own corresponding potential of electrode reaction. In principle, we can select a suitable electrode with certain over-potential of hydrogen or oxygen to extend the voltage used without the formation of hydrogen or oxygen in the corresponding limit. For examples, using PbO_2 as the anode, the electrode potential extends to $+2\text{V}$, using Hg as the cathode, the electrode potential extends to -1V . If the non-aqueous solvents are selected, for example, pyridine and formamide, because they do not contain H^+ and OH^- ions, the problem of creating hydrogen and oxygen does not

exist. With the well-selected solvent, the limit of the oxidation reaction can be extended to +3V, that of the reduction reaction to -2V. By adjusting the over-potential, different extent of reduction or oxidation can be achieved for a same substance. For example, in the electrolytic reduction of nitrobenzene, if using electrode of higher over-potential of hydrogen such as lead or zinc, the reduction product is aniline. If an electrode of silver, platinum or nickel is used, in neutral solution, the products are mainly phenyl hydroxylamine ($\text{C}_6\text{H}_5\text{NHOH}$), in acidic solution, the products are p-aminophenol ($\text{H}_2\text{NC}_6\text{H}_4\text{OH}$), benzidine ($\text{H}_2\text{NC}_6\text{H}_4\text{-C}_6\text{H}_4\text{NH}_2$) and aniline, in basic solution, the final product is azoxybenzene ($\text{C}_6\text{H}_5\text{-}\overset{\text{N}}{\underset{\text{O}}{\text{N}}}\text{-C}_6\text{H}_5$). For another example, using Pt electrode for the oxidation of ethanol, when the anode potential is controlled at 0.37V~0.9V, almost hundred percent of acetaldehyde is formed. At 1.5V~1.7V, the yield of acetaldehyde lowers to 39%, the rest 61% is acetic acid.

Example Using Zn as the cathode to electrolyze a neutral aqueous solution of ZnSO_4 with a concentration of $0.1\text{mol}\cdot\text{kg}^{-1}$, the current density is $10\text{mA}\cdot\text{cm}^{-2}$. What substance will be separated out, Zn or H_2 ? If it is Zn, what is the concentration H_2 starts to form? If it is H_2 , what is the concentration Zn starts to form? Because O_2 and H^+ are formed on anode during electrolysis, alkaline solution is added continuously to keep the solution neutral.

Solution: The potential of electrode reaction of $\text{Zn}^{2+}(b=0.1\text{mol}\cdot\text{kg}^{-1})|\text{Zn}$ is:

$$E = E^*\{\text{Zn}^{2+}|\text{Zn}\} - (RT/2F)\ln(1/a_{\text{Zn}^{2+}}) = (-0.762 + \frac{1}{2} \cdot 0.05916 \lg 0.1)\text{V} = -0.792\text{V}$$

where $\gamma_{\pm}=1$ is supposed. Because the over-potential of the metal-metal ion electrode is very small that can be neglected, this E is the electrode potential of $\text{Zn}^{2+}|\text{Zn}$.

If H_2 is formed, the electrode is $\text{H}^+(a_{\text{H}^+}=10^{-7})|\text{H}_2|\text{Zn}$, the potential of electrode reaction is:

$$E = E^*\{\text{H}^+|\text{H}_2\} - (RT/F)\ln(1/a_{\text{H}^+}) = (-0.05916 \lg 10^{-7})\text{V} = -0.414\text{V}$$

The potential is higher that H^+ seems to be easier than Zn^{2+} to be reduced. However, as shown in Table 17-4, when $j=10\text{mA}\cdot\text{cm}^{-2}$, the over-potential of H_2 on Zn electrode is: $\eta_c=-0.746\text{V}$. Therefore, the electrode potential is:

$$E = -0.414\text{V} - 0.746\text{V} = -1.160\text{V}$$

The potential is lower than the electrode potential of $\text{Zn}^{2+}|\text{Zn}$, H^+ is harder than Zn^{2+} to be reduced. In the condition of the example, Zn should be separated out.

With the proceeding of electrolysis, the concentration of Zn^{2+} depresses continuously, the electrode potential of $\text{Zn}^{2+}|\text{Zn}$ drops as well. When it reaches -1.160V, H_2 will be separated out simultaneously with Zn. The concentration of Zn^{2+} in solution at this time can be calculated as:

$$-1.160 = -0.762 + (0.05916/2)\lg a_{\text{Zn}^{2+}}, \quad a_{\text{Zn}^{2+}} = 3.5 \times 10^{-14}$$

The concentration of Zn^{2+} should be depressed to less than $4 \times 10^{-14}\text{mol}\cdot\text{kg}^{-1}$, H_2

can then be separated out. This indicates that the electrolysis of ZnSO_4 solution to produce Zn is very safe.

2. Electrochemical Corrosion and Protection

Electrochemical Corrosion The basic process is forming a micro cell, the anode (negative electrode) part oxidizes and be corroded. For example, copper and zinc are connected and immersed in an electrolyte solution, as shown in Figure 17-21, zinc playing the role of an anode is then corroded. For another example, if only the zinc is immersed but contains a few impurity of iron, as shown in Figure 17-22, zinc is corroded due to the low electrode potential.

Electrochemical Protection Usually adding the corrosion inhibitor to increase the over-potential, the formation of hydrogen can then be retarded or the dissolution of the metal can be postponed. An alternative is adopting the **anodic protection** method by connecting the protected metal with the positive electrode of a DC source and an auxiliary electrode with the negative electrode. Figure 17-23 shows an anodic passivity curve. The segment AB represents the normal anodic dissolution of the metal. When the point B is reached, because a passive film (oxidized film or oxygen-adsorbed layer) starts to form, the rate of dissolution of metal quickly depresses, as

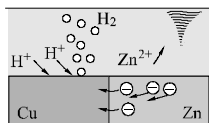


Figure 17-21 Corrosion of Zn and Cu in electrolyte solution.

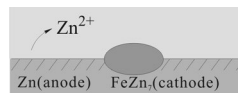


Figure 17-22 Micro cell

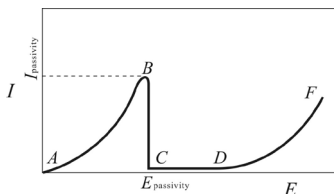


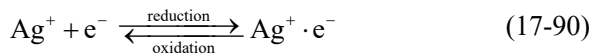
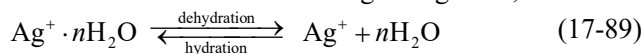
Figure 17-23 Anodic passivity curve of a metal

shown by the BC segment, called the **anodic passivity**. In the CD segment, the electrode is in a stable passive state, the metal is effectively protected. In the DF segment, the current enhances again indicating a new oxidation process starting, called the **super passivity phenomenon**.

17.16 Transition-State Theory of Electrode Reactions

1. Potential Energy Curve

The electrode reaction happens in between the outer Helmholtz plane (OHP) of the electric double layer and the electrode surface. Take the electrode $\text{Ag}^+(\text{aq})|\text{Ag}$ for example, the hydrated Ag^+ ion in solution reached the OHP through the diffusion layer should first be dehydrated then combines with the electron of the electrode forming an Ag atom,



The two processes have their own potential energy curves. The variation of potential energy with the distance between an Ag^+ ion and a H_2O molecule relevant to Eq.(17-89) is shown on the right of Figure 17-24. The dehydration and the hydration can be regarded as a vibration between the Ag^+ ion and the H_2O molecule. The variation of potential energy in the combination process of an Ag^+ ion and an electron e^- relevant to Eq.(17-90) is shown on the left of Figure 17-24. The oxidation and the reduction can also be regarded as a vibration between the Ag^+ ion and the electron e^- . The sum of the two potential energy curves forms a potential barrier of the electrode reaction. When the vibration of the hydrated Ag^+ ion reaches the intersection of the two curves, the connection between the Ag^+ ion and the H_2O molecules is very relaxed and a dehydrated Ag^+ ion is formed. On this occasion, the Ag^+ ion enters another vibration state with respect to the electrode, i.e., the coupling vibration with the electron. After releasing the energy, the Ag^+ ion combines with the electron forming an Ag atom. The result is the dehydration of the hydrated Ag^+ ion followed by a reduction forming an Ag atom. The result of the opposite process is the oxidation of an Ag atom followed by a hydration forming a hydrated Ag^+ ion.

2. Transition-State Theory

The intersection of the above two curves, the dehydrated Ag^+ ion, can be regarded as the transition state activated complex of the electrode reaction.

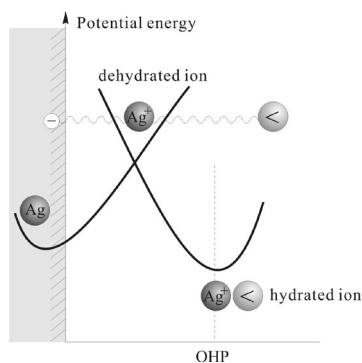
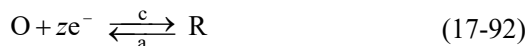


Figure 17-24 Potential energy curve of the electrode reaction of $\text{Ag}^+|\text{Ag}$

According to Eq.(14-50) of the transition-state theory, the rate constant has the following relation with the standard Gibbs function of activation, $\Delta^\ddagger G_m^\ominus$,

$$k = \frac{k_B T}{hc^\ominus} \exp - \frac{\Delta^\ddagger G_m^\ominus}{RT} \quad (17-91)$$

(1) Effect of Electrode Potential on Standard Gibbs Function of Activation Suppose an electrode reaction:



The absolute potential E_{abs} should be used in discussion. Figure 17-25 shows the variation of Gibbs function during the electrode reaction process. It is similar to the potential energy curve in Figure 17-24 but including the contributions of pV and TS .

Without Interfacial Potential Difference On the occasion of without interfacial potential difference, the Gibbs function change for the hydration and the dehydration expressed by Eq.(17-89) is represented by the dash line on the right of the Figure, while that of the oxidation and the reduction expressed by Eq.(17-90) is by the solid line on the left. For the cathodic reduction reaction (c), there is the standard Gibbs function of activation $\Delta^\ddagger G_m^\ominus(c, 0)$, while for the anodic oxidation reaction (a), there is $\Delta^\ddagger G_m^\ominus(a, 0)$, correspondingly.

Existing Electrode Potential On the occasion of the existing of a potential difference from solution to electrode, i.e., an electrode potential, the Gibbs function curve will change. If $E_{\text{abs}} < 0$, the electrode surface possesses negative charge, with the surface as a reference, this corresponds to the rise of the potential of the solution. Different effects will be exerted on the two processes. For the hydration or the dehydration process, because both Ag^+ and $\text{Ag}^+ \cdot n\text{H}_2\text{O}$ are cations, the rise of potential makes the

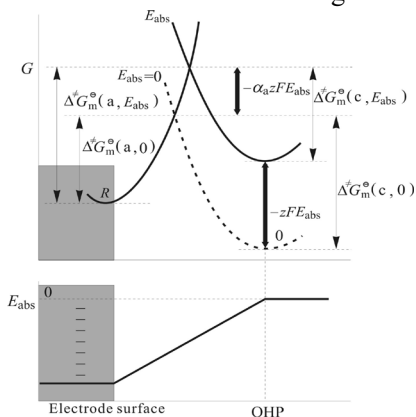


Figure 17-25 Relation between the electrode potential and the standard Gibbs function of activation.

whole Gibbs function curve elevate a value of $-zFE_{\text{abs}}$, E_{abs} is negative, referring to the solid line on the right of the Figure. For the reaction of electron gain or loss, because $\text{Ag}^+ \cdot \text{e}^-$ is neutral in total, the Gibbs function curve keeps unchanged.

Change of $\Delta^\ddagger G_m^\circ$ The displacement of the Gibbs function curve will lead to the change of the standard Gibbs function of activation. As is shown in the Figure, the rise at OHP (the minimum of the curve) is $-zFE_{\text{abs}}$, the rise at the intersection with the other curve will have a discount, be $-\alpha_a zFE_{\text{abs}}$. The latter makes the $\Delta^\ddagger G_m^\circ$ of the cathodic reduction and the anodic oxidation reactions at an absolute potential E_{abs} turn respectively to:

$$\Delta^\ddagger G_m^\circ(\text{a}, E_{\text{abs}}) = \Delta^\ddagger G_m^\circ(\text{a}, 0) - \alpha_a zFE_{\text{abs}} \quad (17-93)$$

$$\Delta^\ddagger G_m^\circ(\text{c}, E_{\text{abs}}) = \Delta^\ddagger G_m^\circ(\text{c}, 0) + \alpha_c zFE_{\text{abs}} \quad (17-94)$$

where α_a and α_c are called the **transfer coefficient** with $\alpha_a + \alpha_c = 1$. They reflect the extent of sensitivity of the potential affecting the reaction rates. The transfer coefficient is an important characteristic parameter or characteristic property of substances in electrochemical systems. The situation of Figure 17-25 is $E_{\text{abs}} < 0$. If $E_{\text{abs}} > 0$, the above equations do not change in form.

(2) Effect of Electrode Potential on Reaction Rate Constant

Substituting Eqs.(17-93) and (17-94) into Eq.(17-91), the reaction rate constants k_{ox} and k_{red} are obtained for the cathodic reduction and the anodic oxidation reactions respectively. However, the E_{abs} in equations is the absolute potential that is not convenient for use. On the other hand, the concentration instead of the activity is generally adopted in kinetics. Therefore, the conditional potential of electrode reaction $E^{\circ'}$ mentioned in 17.5.4 is better to be adopted in derivation, which contains the contribution of the activity factors, correspondingly, Eq.(17-46) of the Nernst equation of electrode reactions turns to:

$$E = E^{\circ'} + \frac{RT}{zF} \ln \frac{c_{\text{O}}}{c_{\text{R}}} \quad (17-95)$$

Butler-Volmer Equation Butler J A V in 1924 and Volmer M in 1930 derived respectively the relations between k_{ox} , k_{red} and $E^{\circ'}$:

$$k_{\text{ox}} = k^{\circ'} \exp \frac{\alpha_a z F (E - E^{\circ'})}{RT} \quad (17-96)$$

$$k_{\text{red}} = k^{\circ'} \exp - \frac{\alpha_c z F (E - E^{\circ'})}{RT} \quad (17-97)$$

where $k^{\circ'}$ is called the **conditional rate constant of electrode reaction**, which can be considered as the rate constant (coefficient) at the conditional potential $E^{\circ'}$ of electrode reaction, and is the same for both the oxidation and the reduction reactions. E in the equations is the electrode potential with SHE as a reference. As is shown in the equations, $k^{\circ'}$ corresponds to the pre-exponential factor, α , $E^{\circ'}$ and the electrode potential E jointly compose the activation energy.

(3) Effect of Electrode Potential on Current or Reaction Rate Substituting Eqs.(17-96) and (17-97) into Eqs.(17-74) and (17-75), suppose both the oxidation and the reduction are first-order reactions, we have

$$j_a = z F c_R k_{\text{ox}} = z F c_R k^{\circ'} \exp \frac{\alpha_a z F (E - E^{\circ'})}{RT}$$

$$j_c = -z F c_O k_{\text{red}} = -z F c_O k^{\circ'} \exp - \frac{\alpha_c z F (E - E^{\circ'})}{RT} \quad (17-99)$$

Exchange Current Density When the electrode reaction reaches equilibrium, $j_a = -j_c$, on this occasion, the electrode potential is the potential of electrode reaction in equilibrium, $E(0)$. Define j_a or $-j_c$ in equilibrium as j_0 called the exchange current density. It is a characteristic property of substance. By Eqs.(17-98) and (17-99), we have

$$\begin{aligned} j_0 &= z F c_R k^{\circ'} \exp \frac{\alpha_a z F [E(0) - E^{\circ'}]}{RT} \\ &= z F c_O k^{\circ'} \exp - \frac{\alpha_c z F [E(0) - E^{\circ'}]}{RT} \end{aligned} \quad (17-100)$$

As is shown in this equation, the exchange current density j_0 integrates the

Table 17-7 Exchange current densities of various metals at 20°C

| Metal | $\log(j_0/\text{A}\cdot\text{m}^{-2})$ |
|-------|--|
| Pt | 1.0 |
| Pd | 0.3 |
| Ni | -1.4 |
| Au | -2.0 |
| Fe | -2.0 |
| Mo | -2.0 |
| W | -2.0 |
| Cu | -2.7 |
| Cd | -3.0 |
| Sn | -4.0 |
| Hg | -7.7 |
| Pb | -8.7 |

Note: Contact with HCl solution of 1.0mol·dm⁻³ and H₂.

contributions of the concentration of reactant (including the reaction order in principle), $k^{\circ'}$ (corresponding to the pre-exponential factor), as well as α and $E^{\circ'}$ (the components of the activation energy). It is a comprehensive characteristic property of substance which is determined not only by the electrode reaction but also relies on the electrode material. Table 17-7 lists the exchange current densities of various metals in contact with an HCl solution of $1.0\text{mol}\cdot\text{dm}^{-3}$ and H_2 at 20°C . As is shown in the Table, those metals such as Pt, Pd with lower over-potential of hydrogen have very large j_0 while those such as Hg, Pb with higher one have very small j_0 . The exchange current density is a characteristic parameter relevant to the electrode reaction rate which indicates that when the rate is higher, the over-potential is lower, and on the contrary, when the rate is lower, the over-potential is higher.

Expressing Current by Exchange Current Density Substituting Eq.(17-100) back to Eqs.(17-98) and (17-99), we have

$$j_a = j_0 \exp \frac{\alpha_a z F [E - E(0)]}{RT} = j_0 \exp \frac{\alpha_a z F \eta}{RT} \quad (17-101)$$

$$j_c = -j_0 \exp -\frac{\alpha_c z F [E - E(0)]}{RT} = -j_0 \exp -\frac{\alpha_c z F \eta}{RT} \quad (17-102)$$

where the over-potential $\eta = E - E(0)$, it is η_a or η_c for the anode or the cathode respectively.

(4) Derive Tafel Equation Theoretically

For an anode, if neglecting the partial cathodic current, according to Eq.(17-101),

$$\eta_a = -\frac{RT}{\alpha_a z F} \ln\{j_0\} + \frac{RT}{\alpha_a z F} \ln\{j\} \quad (17-103)$$

Comparing with Eq.(17-83) of the Tafel equation, $\eta = a + b \ln\{j\}$, we have

$$a = -\frac{RT}{\alpha_a z F} \ln\{j_0\}, \quad b = \frac{RT}{\alpha_a z F} \quad (17-104)$$

For a cathode, if neglecting the partial anodic current, according to Eq.(17-102),

$$-\eta_c = |\eta_c| = -\frac{RT}{\alpha_c z F} \ln\{j_0\} + \frac{RT}{\alpha_c z F} \ln\{-j\} \quad (17-105)$$

Notice that $j < 0$, $\eta_c < 0$. Comparing with Eq.(17-83) of the Tafel equation,

$|\eta| = a + b \ln\{-j\}$, we have

$$a = -\frac{RT}{\alpha_c zF} \ln\{j_0\}, \quad b = \frac{RT}{\alpha_c zF} \quad (17-106)$$

3. Characteristic Properties of Substance Determining the Rate

As is shown in Eqs.(17-96) and (17-97) of the Butler-Volmer equation, the characteristic properties of substance determining the rate constant (coefficient) of electrode reaction are mainly $k^{\circ'}$ and α . They affect the pre-exponential factor and the activation energy, not only determined by the electrode reaction but also strongly relied on the electrode material used. More comprehensively, as is shown in Eqs.(17-101) and (17-102), the characteristic properties of substance determining the rate of electrode reaction or the current density are j_0 and α . They integrate the contributions of the reactant concentration, the reaction order, as well as the pre-exponential factor and the activation energy. At present situation of the electrochemistry, these parameters are obtained primarily by experiment. However, the development of electrochemical theory is also striving to predict those parameters. The approaches are nothing more than using the quantum mechanics and the statistical mechanics.

Brief History

The earliest record of electrochemical studies is in about 80s of the 18th century, an Italian physician Galvani L started from an accidental discovery in anatomizing a frog then carried out many similar experiments. For example, using two metal conductors (copper and iron) to build a circuit loop between the muscle and the nerve of a frog, the muscle will be tremble and shrink. Galvani regarded this as a bioelectric phenomenon. After getting acquainted with this result, his compatriot, a physicist Volta A studied from the view of physics. He thought that the phenomenon is caused by contacting the material with two different metals, and the muscle of the frog plays the role of an electric conductor. In 1800, he invented a Volta cell assembly formed by separating copper plates and zinc plates with pasteboard which had immersed by salt water. In the same year, Nicholson W and Carlisle A of England (referring also to Chapter 16) adopted this assembly to electrolyze the water and obtained hydrogen and oxygen. As a successor, using the Volta cell, Davy H of England in 1807 electrolyzed the potash and obtained the metal potassium. In 1808, by using the mercury as a cathode, he further obtained magnesium, calcium, strontium and barium. In 1834, Faraday M, a British chemist and physicist (referring also to Chapter 18) delivered the well-known equivalent law of electrolysis. In 1839, Sir Grove W of England invented the fuel cell to obtain the electric energy by using

hydrogen and oxygen. In 1889, Nernst W of Germany (referring also to Chapters 2, 4, 5) proposed a thermodynamic equation named after him to calculate the electrode potential. In 1905, Tafel J, who was born in Swiss, discovered that the over-potential has a linear relation with the current density, i.e., the Tafel equation. The Nernst equation and the Tafel equation laid a solid foundation for the electrochemical studies in the thermodynamics side and the kinetics side respectively. However, in the first half of the 20th century, the thermodynamic studies are predominating and the kinetic studies are comparatively retarded. Except the kinetic studies of the electrode processes by Фрумкин А Н of the former Soviet Union, almost all the progresses are founded on the Nernst equation. After 1950s, the over-potential was further affirmed. People started to recognize that the real electrochemical processes deviate from equilibrium pretty far, and the studies of electrochemical kinetics were activated again.

Now back to Galvani L, to mark his discovery, those cells are named after him and are called the Galvanic cell. The device detecting the small current is called the galvanometer. On the other hand, his studies turned on the development of electric physiology after 19th century. The bioelectric phenomena have been confirmed. At present, a series of diagnosis techniques in medicine field such as the electroencephalogram, electrocardiogram, electro myograph, electro retina-graph and electro enteric-stomach graph have been successfully developed.

Besides the thermodynamic and kinetic studies on the macroscopic level, studies on the molecular level have also been developing. On the double-layer structure of the electrode-solution interface, since the determination of surface charge by Lippmann G of France in 1873 through the variation of surface tension with electrode potential, and the establishment of the first planar-condenser model by Helmholtz H of Germany in 1879, the studies have spanned a long period more than hundred years. Especially the diffusive double-layer model developed by Gouy G of France and Chapman D L of England, the improvement by Stern O (referring also to Chapter 9) of Germany and Grahame D C of the US, and the important contributions of Bockris J O' M, Devanathan M A V and Müller K of the US, the essential illustration and prediction of the electrode potential theoretically to obtain the absolute potential have been realized. Theoretical studies of the electrode-solution interface using quantum mechanics and solid-state physics have also achieved new progress. The other category of studies on the molecular level concerns the mechanism of electrode reaction and the rate theories. Started from the studies concerning the potential barrier from metal to solution and the rate of the charge transfer using Schrödinger equation in the early stage, many new theories and models have appeared especially in the latter half of the 20th century.

Concluding Remarks

Real electrochemical processes are all very complex. Generally, a change on the electrode-solution interface is composed of the following steps, referring to Figure 17-26, in which the electrode $\text{Cl}^-|\text{Cl}_2$ is taken for example:

(1) **Mass-transfer step in liquid phase** Reaction ions or reactants diffuse toward the electrode surface.

(2) **Prepossessed surface transform step** Reaction ions or reactants adsorb on the electrode surface, or carry out chemical reaction in the liquid layer

near the surface. For example, Cl^- adsorbs on the electrode surface.

(3) **Electrochemical reaction step** Gaining or losing electrons, the products are formed. For example, $\text{Cl}^- \rightarrow \text{Cl} + \text{e}^-$.

(4) **Thereafter surface transform step** Reaction products desorb from the electrode surface, or carry out chemical reaction in the liquid layer near the surface. For example, the desorption of Cl , followed by $2\text{Cl} \rightarrow \text{Cl}_2$.

(5a) **New phase forming step** Reaction products form bubbles or precipitates. For example, Cl_2 bubbles release.

(5b) **Mass-transfer step in liquid phase** Reaction products diffuse from the electrode surface toward the bulk solution.

Among these steps, the step (3), the electrochemical reaction, is the content of this Chapter which involves both the equilibrium and the rate. Steps (1) and (5) are mass-transfer processes which have been introduced in Chapter 6, 17.14.3 of this Chapter also has a further illustration. Steps (2) and (4) are the adsorption and desorption which have been discussed in Chapter 15.

Electrochemistry is a science which develops very fast. On the experimental techniques, besides the traditional conductance, electromotive force and over-potential, techniques of the potentiostat, the galvanostat, the potential sweep and the electrical impedance analysis have also been developed which can more effectively determine both the equilibrium and the rate of the electrochemical reactions. Especially the *in situ* and *ex situ* techniques using spectrograph, they can study the structural change of the interface directly during or before and after the process which provide new impetus for the theoretical studies of electrochemistry based on quantum mechanics and statistical mechanics.

The applications of electrochemistry are extending continuously especially in the field of environmental science. The prominent features of the electrochemical processes can be listed as: Besides the temperature and pressure, there is an additional adjustable factor, the interfacial potential. The electrochemical processes usually carry out in lower temperature. The electrochemical processes usually carry out in solution with far less amount of pollutants such as NO_x , SO_x , CO_x discharged into the atmosphere. Because of these features, the electrochemical methods have wide prospect in the green technology. As a clean energy resource, hydrogen not only can comply with the standard of zero contamination, it is even cheaper than the electricity in the long distance transportation. The manufacture of hydrogen from water by the electro catalysis has been developed rapidly. Using the electrochemical methods, the conversion of N_2O into N_2 , the removal of SO_2 and Cl_2 from waste water, the reduction of CO_2 into CH_3OH , the manufacture of O_3 as oxidizers of organics, all of them have played a vital role in improving the environment. Another field is the life science. The earliest discovery concerning the galvanic cell by Galvani was really a bio-electrochemical phenomenon. Potential widely exists in the interface of various cell membranes and the nerve systems. The transport of ions and

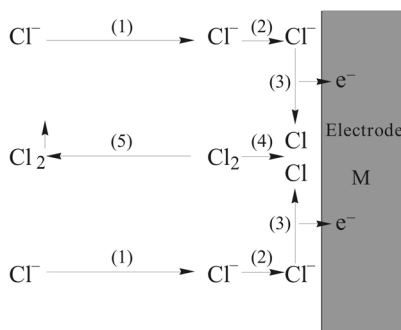


Figure 17-26 Composing steps of the electrode reaction of $\text{Cl}^- \rightarrow \frac{1}{2}\text{Cl}_2 + \text{e}^-$

other substances between the two sides of the membrane, the transport of the nerve signals, the metabolism of energy, as well as the enzyme electrodes, the electrochemical fuel cells, are all the hot studying objects of the electrochemistry.

The regret for the electrochemistry is the notation which is still unsatisfactory up to the present. The symbols for the potential of cell reaction and the potential of electrode reaction defined in the equilibrium condition, and the symbols of the cell potential and the electrode potential defined in the non-equilibrium condition, are all the same one, E . For the symbol of electrodes, take the hydrogen electrode for example, most books adopt $\text{H}^+|\text{H}_2|\text{Pt}$ which is always being misunderstood that the electrode potential is the sum of the two interfaces, $\text{H}^+|\text{H}_2$ and $\text{H}_2|\text{Pt}$. The real mechanism is quite complicated. If written as $\text{H}^+|\text{H}_2, \text{Pt}$, the trouble is avoided. The symbol of calomel electrode, $\text{Cl}^-|\text{Hg}_2\text{Cl}_2(\text{s})|\text{Pt}$, has the same problem, if written as $\text{Cl}^-|\text{Hg}_2\text{Cl}_2(\text{s}), \text{Pt}$, it will be much better. Besides, the current and the potential are all defined in terms of the positive charge. However, the real charge flow is the electron flow. We have to pay more attention to the above problems.

General Problems

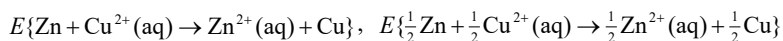
1. Is it true that the anode is a positive electrode while the cathode is a negative electrode?

2. For the expression of a galvanic cell, why must the lead Cu' be written in strictly?

3. For an open circuit, what change in form will it have for the electrochemical equilibrium criterion, Eq.(17-24)?

4. If in non-equilibrium condition, what change in form will it have for Eq.(17-24), $\sum_{\alpha=1}^n \sum_B \nu_B \tilde{\mu}_B^{(\alpha)} = W'_{\text{electric}} = -zFE$?

5. For the following two written forms of a zinc-copper cell, why $\Delta_r G_{\text{ms}}$ of them are different but E is the same?



6. What are the differences and connections among the following terminologies: the cell potential, the electromotive force, the potential of cell reaction, the standard potential of cell reaction and the conditional potential of cell reaction?

7. Why should the standard hydrogen electrode be used in Eq.(14-73) for the potential of electrode reaction while the hydrogen electrode should be used in Eq.(14-72) for the standard potential of electrode reaction?

8. What are the differences and connections among the following terminologies: the electrode potential, the potential of electrode reaction, the standard potential of electrode reaction and the conditional potential of electrode reaction?

9. According to the conventions, how do we write a galvanic cell, an electrode, an electrode reaction, an interfacial potential difference, a potential of cell reaction and a standard potential of electrode reaction?

10. The calomel electrode can be expressed as $\text{Hg}_2^{2+}(\text{aq})|\text{Hg}$. Can the oxygen electrode and the hydrogen electrode be expressed respectively as $\text{OH}^-(\text{aq})|\text{H}_2|\text{Pt}$ and $\text{H}^+(\text{aq})|\text{O}_2|\text{Pt}$? From this question, what rules can be summed up?

11. What is the relation between $E^\circ\{\text{SO}_4^{2-}|\text{PbSO}_4|\text{Pb}\}$ and $E^\circ\{\text{Pb}^{2+}|\text{Pb}\}$?

12. Using the cell $-\text{Pt}|\text{H}_2(p^\circ)|\text{HCl}(b)|\text{AgCl}(\text{s})|\text{Ag}(+)$, design a method to determine the vapor pressure of HCl on a dilute HCl solution.

13. In the following galvanic cells, which of them is the potential of cell reaction dependent on the concentration of chloride ions?

- ① $\text{Zn} | \text{ZnCl}_2 \text{ solution} | \text{Cl}_2(p) | \text{Pt}$,
 ② $\text{Zn} | \text{ZnCl}_2 \text{ solution} || \text{KCl solution} | \text{Hg}_2\text{Cl}_2 | \text{Hg}$,
 ③ $\text{Pt} | \text{H}_2(p) | \text{HCl solution} | \text{Cl}_2(p) | \text{Pt}$, ④ $\text{Ag} | \text{AgCl} | \text{KCl solution} | \text{Cl}_2(p) | \text{Pt}$.

14. Make a comparison between the double-layer model and the concept of ionic atmosphere.

15. Estimate the standard absolute potentials of electrode reaction respectively for the electrodes $\text{Na}^+ | \text{Na}$ and $\text{Ag}^+ | \text{Ag}$.

16. Compare the similarity and dissimilarity between Figure 17-19 of electrolysis and Figure 17-20 of discharge.

17. For the Example in 17.15, what would be the result if the measure of keeping solution neutral is not taken?

18. Figure 17-25 depicts the situation when $E_{\text{abs}} < 0$. If $E_{\text{abs}} > 0$, those expressions in the Figure keep unchanged, why?

19. Discuss the relation between the Tafel equation and the Arrhenius equation in chemical kinetics.

20. In 17.14.3 of the concentration polarization, we have mentioned that combining Eq.(17-86) with Eq.(17-87) and eliminating $c_{\text{B}0}$, a relation between j and η_a is obtained. Derive this relation.

21. Substituting Eqs.(17-93) and (17-94) into Eq.(17-91), combining with the conditional potential of electrode reaction E^{*} and the conditional rate constant of the electrode reaction k^{*} derived from it, derive the Butler-Volmer equation, Eqs.(17-96) and (17-97).

Numerical Problems

1. The potential of cell reaction of $\text{Ag} | \text{AgCl(s)} | \text{HCl(aq)} | \text{Cl}_2(0.1 \text{ MPa}) | \text{Pt}$ at 25°C is 1.1362V, its temperature coefficient is $-5.95 \times 10^{-4} \text{ V} \cdot \text{K}^{-1}$. Calculate $\Delta_r G_m$, $\Delta_r S_m$ and $\Delta_r H_m$ for the cell reaction $\text{Ag(s)} + (1/2)\text{Cl}_2(0.1 \text{ MPa}) \rightarrow \text{AgCl(s)}$ at 25°C .

2. Calculate the potential of cell reaction and its temperature coefficient at 25°C for the cell $\text{Ag} | \text{AgCl(s)} | \text{KCl(aq)} | \text{Hg}_2\text{Cl}_2(\text{s}) | \text{Hg}$. It is known that at 25°C for the reaction $\text{Ag} + (1/2)\text{Hg}_2\text{Cl}_2 \rightarrow \text{AgCl} + \text{Hg}$, $\Delta_r H_m^\circ = 5.54 \text{ kJ} \cdot \text{mol}^{-1}$, the standard molar entropy for various substances are: Ag, $42.55 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, AgCl, $96.2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, Hg, $76.02 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, Hg_2Cl_2 , $192.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

3. Write the electrode reaction and the cell reaction for the following cells:

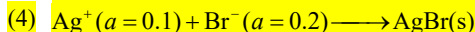
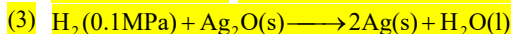
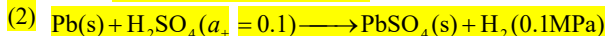
- (1) $\text{Pt} | \text{H}_2(0.1 \text{ MPa}) | \text{HCl}(0.1 \text{ mol} \cdot \text{kg}^{-1}) | \text{Cl}_2(0.1 \text{ MPa}) | \text{Pt}$
 (2) $\text{Pt} | \text{H}_2(0.1 \text{ MPa}) | \text{KOH}(0.1 \text{ mol} \cdot \text{kg}^{-1}) | \text{O}_2(0.1 \text{ MPa}) | \text{Pt}$
 (3) $\text{Zn} | \text{ZnCl}_2(0.1 \text{ mol} \cdot \text{kg}^{-1}) | \text{Hg}_2\text{Cl}_2 | \text{Hg}$
 (4) $\text{Zn} | \text{ZnO(s)} | \text{KOH}(0.5 \text{ mol} \cdot \text{kg}^{-1}) | \text{HgO(s)} | \text{Hg}$

4. Calculate the potential of cell reaction at 25°C for the cell:



5. The potential of cell reaction of $\text{Zn} | \text{ZnCl}_2(0.005 \text{ mol} \cdot \text{kg}^{-1}) | \text{Hg}_2\text{Cl}_2(\text{s}) | \text{Hg}$ at 25°C is 1.227V. The mean activity factor of the ZnCl_2 solution of $0.005 \text{ mol} \cdot \text{kg}^{-1}$ is: $\gamma_{\pm} = 0.789$. Calculate the standard potential of cell reaction at 25°C for this cell.

6. Design cells for the following reactions and calculate the potentials of cell reaction at 25°C. Data can be found in Table 17-2, $E^\circ\{\text{Cr}^{3+}, \text{Cr}^{2+} | \text{Pt}\} = -0.407 \text{ V}$.



7. Design a cell for the reaction $\text{H}_2(0.1\text{MPa}) + \text{I}_2(\text{s}) \rightarrow 2\text{HI}(a=1)$ and calculate:

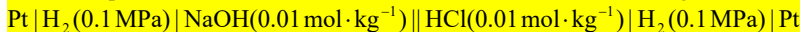
(1) The standard potential of cell reaction E° . (2) The standard molar Gibbs function of reaction $\Delta_r G_m^\circ$. (3) The standard equilibrium constant K° . (4) If the reaction is written as $(1/2)\text{H}_2(0.1\text{MPa}) + (1/2)\text{I}_2(\text{s}) \rightarrow \text{HI}(a=1)$, are there any changes for the results?

8. Using the data of $E^\circ\{\text{Cu}^{2+} | \text{Cu}\}$ and $E^\circ\{\text{Cu}^+ | \text{Cu}\}$ in Table 17-2, calculate $E^\circ\{\text{Cu}^{2+}, \text{Cu}^+ | \text{Pt}\}$ at 25°C and the standard equilibrium constant at 25°C for the reaction $\text{Cu} + \text{Cu}^{2+} \longrightarrow 2\text{Cu}^+$.

9. Using the data in Table 17-2, calculate the standard equilibrium constant at 25°C for the reaction $2\text{Hg} + 2\text{Fe}^{3+} \longrightarrow \text{Hg}_2^{2+} + 2\text{Fe}^{2+}$. If all the substances are in the standard state, point out the direction of the reaction.

10. For a cell $\text{Pt} | \text{H}_2(0.1\text{MPa}) | \text{HCl}(0.1\text{mol}\cdot\text{kg}^{-1}) | \text{AgCl}(\text{s}) | \text{Ag}$, the potential of cell reaction at 25°C is 0.3522V. (1) Calculate the standard equilibrium constant at 25°C for the reaction $\text{H}_2(\text{g}) + 2\text{AgCl}(\text{s}) \rightarrow 2\text{H}^+ + 2\text{Cl}^- + 2\text{Ag}$. (2) Calculate the equilibrium pressure of H_2 formed by the metal Ag in a solution of HCl of $0.1\text{mol}\cdot\text{kg}^{-1}$ with a mean ionic activity factor of $\gamma_\pm=0.798$.

11. The potential of cell reaction at 25°C is 0.587V for the following cell:



The mean ionic activity factors of the solutions of NaOH and HCl at the same concentration of $0.01\text{mol}\cdot\text{kg}^{-1}$ and at the same temperature are the same, $\gamma_\pm=0.798$. Calculate K_w° of water.

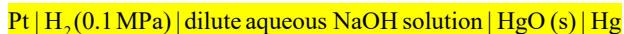
12. The potential of cell reaction of $\text{Cd} | \text{CdI}_2(\text{aq}) | \text{AgI}(\text{s}) | \text{Ag}$ at 25°C is 0.2860V. Calculate the mean ionic activity a_\pm , and the activity a_B of the electrolyte as a whole for the CdI_2 solution.

13. The potential of cell reaction of $\text{Zn} | \text{ZnCl}_2(0.01\text{mol}\cdot\text{kg}^{-1}) | \text{AgCl}(\text{s}) | \text{Ag}$ at 25°C is 1.1566V. Calculate the mean ionic activity, the mean ionic activity factor and the activity of ZnCl_2 for the ZnCl_2 solution of $0.01\text{mol}\cdot\text{kg}^{-1}$. Other data needed can be found in Table 17-2.

14. The potentials of cell reaction of $\text{Cu} | \text{CuCl}_2(\text{aq}) | \text{AgCl}(\text{s}) | \text{Ag}$ at 25°C with different CuCl_2 concentrations are: $b=0.0001\text{mol}\cdot\text{kg}^{-1}$, $E=0.191\text{V}$, $b=0.2\text{mol}\cdot\text{kg}^{-1}$, $E=-0.074\text{V}$. The mean ionic activity factor of the CuCl_2 solution of $0.0001\text{mol}\cdot\text{kg}^{-1}$ is: $\gamma_\pm=0.960$. Calculate γ_\pm of the CuCl_2 solution of $0.2\text{mol}\cdot\text{kg}^{-1}$.

15. In a cell $\text{Pt} | \text{H}_2(0.1\text{MPa}) | \text{S} || \text{KCl}(0.1\text{mol}\cdot\text{dm}^{-3}) | \text{Hg}_2\text{Cl}_2(\text{s}) | \text{Hg}$, when S is a buffer solution with $\text{pH}=6.86$, the potentials of cell reaction at 25°C is determined as 0.7409V. Now S is replaced by an unknown solution, the potential of cell reaction at the same temperature is determined as 0.6097V. What is the pH of this solution?

16. The potential of cell reaction at 25°C is 0.9265V for the following cell:

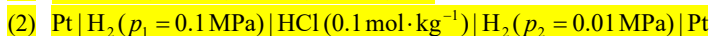
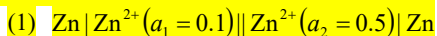


The standard molar enthalpy of formation of $\text{H}_2\text{O(l)}$ is $-285.830 \text{ kJ}\cdot\text{mol}^{-1}$. The standard molar entropies of various substances are: HgO , $70.29 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, Hg(l) , $76.02 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, $\text{O}_2(\text{g})$, $205.138 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, $\text{H}_2(\text{g})$, $130.684 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, $\text{H}_2\text{O(l)}$, $69.91 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. Calculate the decomposition pressure of HgO at 25°C .

17. Calculate the temperature at which $\text{Ag}_2\text{O(s)}$ starts to decompose in air in terms of the reaction $\text{Ag}_2\text{O(s)} \rightarrow 2\text{Ag(s)} + (1/2)\text{O}_2(\text{g})$. The pressure of air is 101.3 kPa . The mole fraction of O_2 in air is 0.21 . The standard molar enthalpy of formation of $\text{Ag}_2\text{O(s)}$ is $-31.05 \text{ kJ}\cdot\text{mol}^{-1}$. The standard molar enthalpy of reaction for the decompose reaction is independent of temperature.

18. For the cell $\text{Pt} | \text{H}_2(p) | \text{HCl}(0.1 \text{ mol}\cdot\text{kg}^{-1}) | \text{Hg}_2\text{Cl}_2(\text{s}) | \text{Hg}$ at 25°C , it is determined at different pressures that: $p=0.1013 \text{ MPa}$, $E=0.3990 \text{ V}$, $p=11.16 \text{ MPa}$, $E=0.4596 \text{ V}$. H_2 at 0.1013 MPa can be regarded as an ideal gas. Calculate the fugacity factor of H_2 at 25°C and 11.16 MPa .

19. Calculate the potentials of the cell reaction at 18°C for the following concentration cells:



20. The potential of the cell reaction at 18°C of the cell $\text{Hg} | \text{S}_1 || \text{S}_2 | \text{Hg}$ is 0.029 V . 1 dm^3 of S_1 contains 6.30 g of nitric acid and 0.263 g of mercurous nitrate. 1 dm^3 of S_2 contains 6.30 g of nitric acid and 2.63 g of mercurous nitrate. Make a judgment whether the mercurous ion in solution is Hg^+ or Hg_2^{2+} ?

21. Using lead as electrodes to electrolyze a sulfuric acid solution with $\text{pH}=4.76$, when the cathodic current densities are $1 \text{ A}\cdot\text{cm}^{-2}$ and $0.01 \text{ A}\cdot\text{cm}^{-2}$, the electrode potentials of lead cathode are determined as -1.8416 V and -1.6216 V respectively. Calculate the over-potential of hydrogen on cathode when the cathodic current densities is $0.1 \text{ A}\cdot\text{cm}^{-2}$.

22. A solution containing $\text{NiCl}_2(0.01 \text{ mol}\cdot\text{kg}^{-1})$ and $\text{CuCl}_2(0.02 \text{ mol}\cdot\text{kg}^{-1})$ is electrolyzed at 25°C using platinum as electrodes. The solution is stirred continuously during the electrolysis. If the over-potential of metals on the platinum electrode can be neglected and the activity can be replaced by the concentration, ask: (1) What metal is deposited first on the cathode? (2) When the second metal starts to deposit, what is the concentration of the first metal in solution? The data of the standard potentials of electrode reaction needed can be found in Table 17-2.

23. A solution of ZnCl_2 of $0.1 \text{ mol}\cdot\text{kg}^{-1}$ is electrolyzed using copper sheet as cathode and graphite as anode. If the current density is $10 \text{ mA}\cdot\text{cm}^{-2}$, what substance is first deposited on the cathode? What substance is deposited on the anode? The over-potential of H_2 on the copper electrode at this current density is -0.584 V and that of O_2 on the graphite electrode is 0.896 V . The over-potential of Cl_2 on the graphite electrode can be neglected. The activities can be replaced by the concentration.

24. A solution containing CuSO_4 of $0.5 \text{ mol}\cdot\text{kg}^{-1}$ and H_2SO_4 of $0.01 \text{ mol}\cdot\text{kg}^{-1}$ is electrolyzed at 25°C by using platinum sheet as electrodes. The over-potential of H_2 on copper is -0.23 V . If the activity can be replaced by the concentration, what is the concentration of Cu^{2+} remained in solution when H_2 starts to separate out on the cathode? Note that because of O_2 formed in anodic reaction, the concentration of H^+ is continuously enhanced during the deposition of Cu .