

Ch 18 Electrochemistry 電化學

Electrochemistry is the study of the interconversion of electrical and chemical energy.

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This conversion takes place in an electrochemical cell.

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1. Voltaic cell. (伏打電池)
2. Electrolytic cell. (電解電池)

§ Redox reaction:

contains reduction and oxidation reaction.

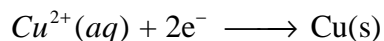
Reduction: electrons are consumed.

Oxidation: electrons are produced.

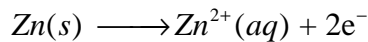
The number of electrons consumed in reduction must be exactly equal to the number (of electrons) produced in oxidation half-reaction.

§ Electrochemical cell:

Cathode 陰極: reduction reaction.



Anode 陽極: oxidation reaction.



Anions (陰離子) moves to anode, cations (陽離子) moves to cathode.

Cathode 陰極: 發生還原反應, 氧化數減少, 被氧化.

Anode 陽極: 發生氧化反應, 氧化數增加, 被還原.

Voltage (電壓、電位): is a measure of reaction spontaneity. Cell voltages depend on the nature of the half-reactions occurring at the electrodes and on

the concentrations of species involved. $E = E^{\circ} - \frac{RT}{nF} \ln Q$

From the voltage measured at standard concentrations, it is possible to calculate the standard free energy change ($\Delta G^\circ = -nFE^\circ$) and the equilibrium constant ($\Delta G^\circ = -RT \ln K$) of the reaction involved.

Content:

18-1 Voltaic cells

18-2 Standard voltages

18-3 Relations between E° , ΔG° , and K

18-4 Effect of concentration on voltage

18-5 Electrolytic cells

18-6 Commercial cells

§ 18-1 Voltaic Cell (伏打電池)

Any spontaneous redox reaction can serve as a source of energy in a voltaic cell.

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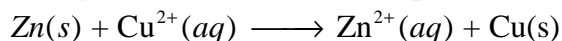
The cell must be designed that oxidation occurs at anode with reduction at cathode.

↓

The electrons produced at the anode must be transferred to the cathode, where they are consumed.

§ The $Zn - Cu^{2+}$ cell:

When a piece of zinc is added to a water solution containing Cu^{2+} ions, the following redox reaction takes place:



Cu metal plates out on the surface of the zinc. The blue color of the aqueous Cu^{2+} ions fades as it is replaced by the colorless aqueous Zn^{2+} ion.

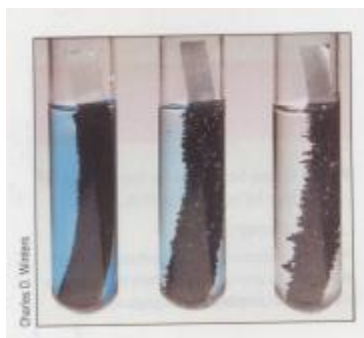


Fig. 18.1: $Zn - Cu^{2+}$ spontaneous redox reaction.

Using the $Zn-Cu^{2+}$ reaction as a source of electrical energy, the electron transfer must occur indirectly; that is the electrons given off by zinc atoms must be made to pass through an external circuit before they reduce Cu^{2+} to copper atoms.

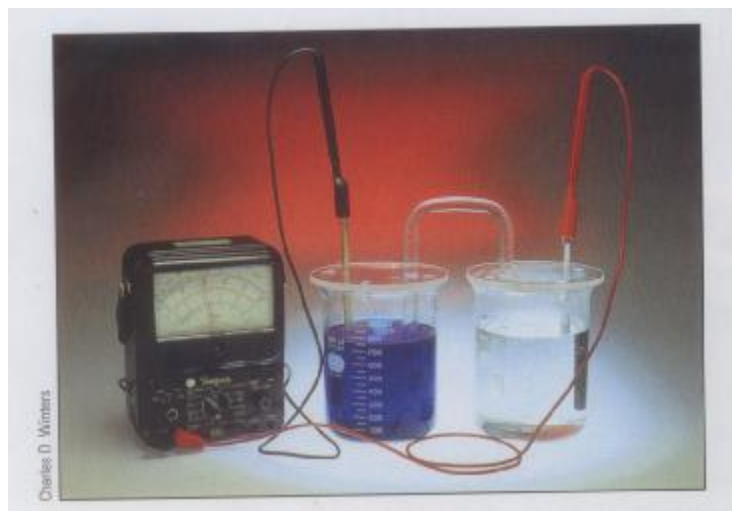


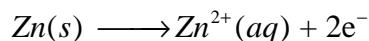
Fig. 18.2: A $Zn-Cu^{2+}$ voltaic cell.

The voltaic cell consists two half-cells:

- g a zinc anode dipping into a solution containing Zn^{2+} ions. (on the right of Fig. 18.2)
- g a Cu cathode dipping into a solution containing Cu^{2+} ions. (on the left of Fig. 18.2)
- g The “external circuit” consist of a voltmeter with leads to the anode and cathode.

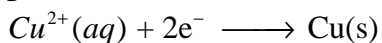
§ The $Zn | Zn^{2+} || Cu^{2+} | Cu$ voltaic cell:

1. At the Zn anode: electrons are produced by the oxidation half-reaction.



“pumps” electrons into the external circuit, is ordinarily marked as the “negative pole” of the cell.

2. Electrons generated at the anode move through the external circuit to the copper cathode. At the cathode, the electrons are consumed, reducing Cu^{2+} ions present in the solution around the electrode.



The electrode, which “pull” electrons from the external circuit, is considered to be the “positive pole” of the cell.

3. A surplus of positive ions (Zn^{2+}) tends to build up around the zinc electrode. The region around the copper electrode tends to become deficient in positive ions as (Cu^{2+}) are consumed.

↓

To maintain electrical neutrality, cations must move toward the copper cathode or, alternatively, anions must move toward zinc anode. In practice, both migrations occur.

§ Salt bridge:

The movement of ions occurs through a salt bridge connecting the two beakers.

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An inverted glass U-tube, plugged with glass wool at each end.

↓

The tube is filled with a solution of that takes no part in the electrode reactions; potassium nitrate KNO_3 , is frequently used.

↓

K^+ ions move from the salt bridge into the cathode half-cell. NO_3^- ions move into the anode half-cell.

↓

Electrical neutrality is maintained without Cu^{2+} ions coming in contact with the zinc electrode, which would short-circuit the cell.

↓

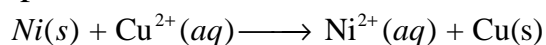
Fig. 18.2 is often abbreviated as: $Zn \mid Zn^{2+} \mathbf{P} Cu^{2+} \mid Cu$

In this notation:

- g The anode reaction (oxidation) is shown at the left. Zn atoms oxidized to Zn^{2+} ions.
- g The salt bridge is indicated by the symbol **P**.
- g The cathode reaction (reduction) is shown at the right. Cu^{2+} ions are reduced to Cu atoms.
- g A single vertical line indicates a phase boundary, such as that between a solid cathode and an aqueous solution.

§ Other salt bridge cells:

Example 1:



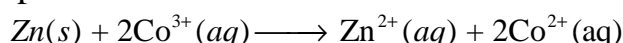
Anode: Ni; solution: NiCl_2 or NiSO_4

Cathode: Cu; solution: CuSO_4

↓

The cell notation: $\text{Ni} \mid \text{Ni}^{2+} \text{ P } \text{Cu}^{2+} \mid \text{Cu}$

Example 2:



Anode: Zn; solution: ZnSO_4

Cathode: **because no metal involved in the cathode half-reaction, an inert electrode** that conducts an electric current is used.

↓

“platinum”

Solution: $\text{Co}(\text{NO}_3)_3$

∴ anode: $\text{Zn}(s) \longrightarrow \text{Zn}^{2+}(aq) + 2e^-$

Cathode: $\text{Co}^{3+}(aq) + e^- \longrightarrow \text{Co}^{2+}(aq)$

The cell notation: $\text{Zn} \mid \text{Zn}^{2+} \text{ P } \text{Co}^{3+}, \text{Co}^{2+} \mid \text{Pt}$

] indicate the presence of an inert electrode as cathode.

Ex 18.1: When chlorine gas is bubbled through an aqueous solution of NaBr, chloride ions and liquid bromine are the products of the spontaneous reaction. For the cell,

- Draw a sketch of the cell, labeling the anode, the cathode, and the direction of electron flow.
- Write the half-reaction that takes place at the anode and at the cathode.
- Write a balanced equation for the cell reaction.
- Write an abbreviated notation for the cell.

Ans:

a).

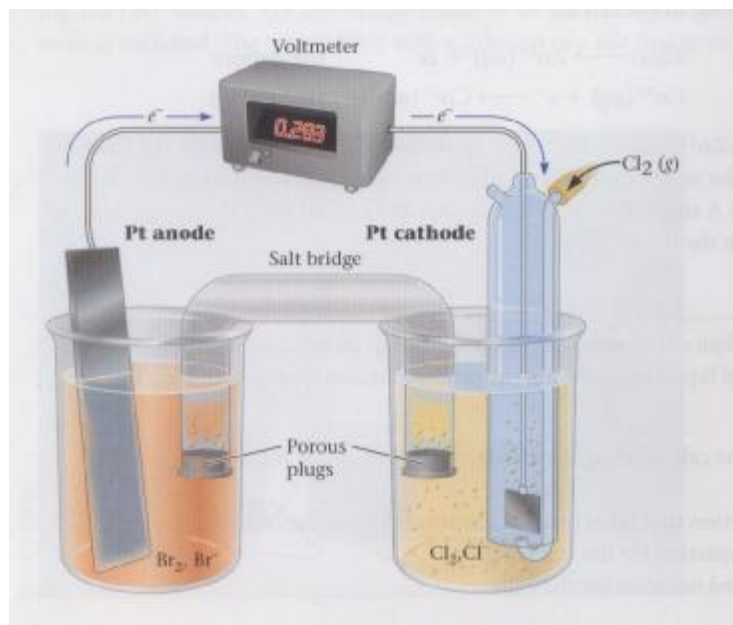
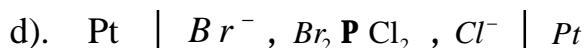
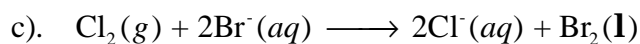
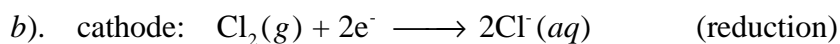


Fig. 18.4: A $\text{Cl}_2 - \text{Br}_2$ voltaic cell.



§ Summarization:

g a voltaic cell consists of two half-cells. They are joined by an external electrical circuit through which electrons move and a salt bridge through which ions move.

g each half-cell consists of an electrode dipping into a water solution.

g in one half-cell, oxidation occurs at the anode, in another, reduction takes place at the cathode.

§ 18-2 Standard Voltages, E° . 標準電位

The driving force behind the spontaneous reaction in a voltaic cell is measured by the cell voltage.

↓

An **intensive property**.

↓

Independent of the number of electrons passing through the cell. **Cell voltage depends on the nature of the redox reaction and the concentrations of the species involved.**

The standard voltage for a given cell is that measured when the current flow is essentially zero, all ions and molecules in solution are at a concentration of 1 M, and all gases are at a pressure of 1 atm.

Ex: $Zn - H^+$ cell; $Zn \mid Zn^{2+} \parallel H^+, H_2 \mid Pt$

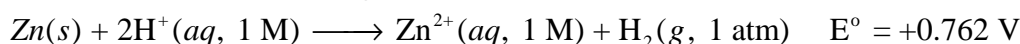
Zn^{2+} and H^+ are both 1 M, and the pressure of $H_2(g)$ is 1 atm.

↓

The cell voltage at very low current flow is +0.762 V.

↓

The standard voltage, E° .



§ E_{red}° and E_{ox}° :

E_{red}° : standard reduction voltage.

E_{ox}° : standard oxidation voltage.

$$E^\circ = E_{red}^\circ + E_{ox}^\circ \quad (18-1)$$

For $Zn \mid Zn^{2+} \parallel H^+, H_2 \mid Pt$ cell:

$$+0.762 V = E_{red}^\circ (H^+ \rightarrow H_2) + E_{ox}^\circ (Zn \rightarrow Zn^{2+})$$

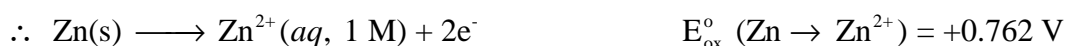
There is “no way” to measure the standard voltage for a half-reaction, only E° can be measured directly.

↓

To obtain values for E_{ox}° and E_{red}° , the value zero is arbitrarily assigned to the standard voltage for reduction of H^+ ions to H_2 gas:



$$\text{Q } E^\circ = E_{red}^\circ + E_{ox}^\circ$$



↓

As soon as one half-reaction voltage is established, others can be calculated.

Ex: $Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$ cell:

$$E^\circ = +1.101 \text{ V}; \quad E_{\text{ox}}^\circ (Zn \rightarrow Zn^{2+}) = +0.762 \text{ V}$$

$$Q \quad E^\circ = E_{\text{red}}^\circ (Cu^{2+} \rightarrow Cu) + E_{\text{ox}}^\circ (Zn \rightarrow Zn^{2+})$$

$$+1.101 \text{ V} = E_{\text{red}}^\circ (Cu^{2+} \rightarrow Cu) + (+0.762 \text{ V})$$

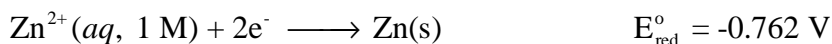
$$\therefore E_{\text{red}}^\circ (Cu^{2+} \rightarrow Cu) = +0.339 \text{ V}$$

↓

Standard E_{red}° is given in Table 18.1.

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Standard potential = $E_{\text{red}}^\circ \Rightarrow$ 獲得電子之能力

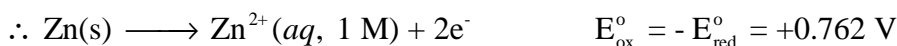


§ E_{ox}° : standard oxidation voltage

To obtain the standard voltage for an oxidation half-reaction, all you have to do is “change the sign of the standard potential listed in Table 18.1”

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$$E_{\text{ox}} = -E_{\text{red}}$$



↓

Standard voltages for forward and reverse half-reaction are equal in magnitude but opposite in sign.

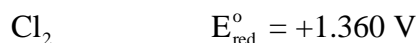
§ Strength of Oxidizing and Reducing agents

The strength of an oxidizing agent is directly related to the standard voltage for its reduction, E_{red}° .

$$\downarrow E_{\text{red}} \uparrow \Rightarrow \text{oxidizing agent strength} \uparrow$$

The more positive E_{red}° is, the stronger the oxidizing agent. The

strongest oxidizing agents are those at the bottom of the left column.



\therefore The strongest reducing agents are listed in the top of the right column.



The more positive E_{ox}° is, the stronger the reducing agent.

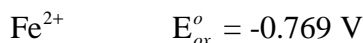
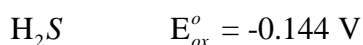
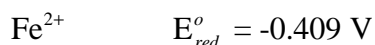
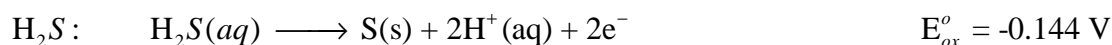
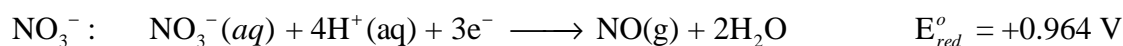
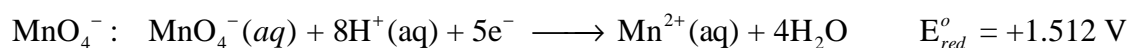
Reducing agent: K, Ba, Sr, Ca, Na, Mg, Al, Mn, Zn, Cr, Fe, Co, Ni, Sn, Pb, H, Cu, Hg, Ag, Pt, Au.

Ex. 18.2: Consider the following species in acidic solution: MnO_4^- , I^- , NO_3^- , H_2S and Fe^{2+} , Using Table 18.1.

- classify each of those as an oxidizing agent and/or reducing agent ?
- arranging the oxidizing agents in order of increasing strength ?
- do the same with the reducing agents ?

Ans:

From Table 18.1:



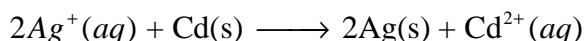
b). the strength of oxidizing agents: $\text{Fe}^{2+} < \text{NO}_3^- < \text{MnO}_4^-$

c). the strength of reducing agents: $\text{Fe}^{2+} < \text{I}^- < \text{H}_2\text{S}$

§ Calculation of E° from E_{red}° and E_{ox}°

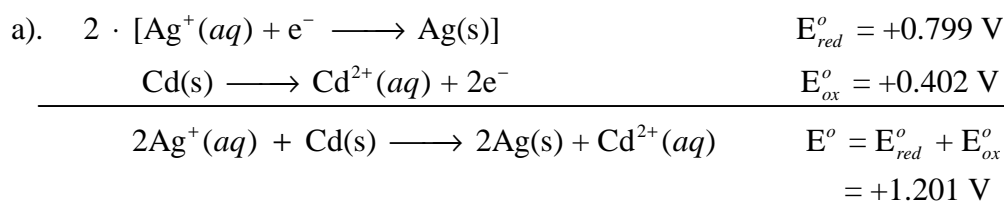
$$E^\circ = E_{red}^\circ + E_{ox}^\circ$$

Ex. 18.3: Consider the voltaic cell in which the reaction is



- Use Table 18.1 to calculate E° for the voltaic cell.
- If the value zero is arbitrarily assigned to the standard voltage for the reduction of Ag^+ ions to Ag, what is E_{red}° for the reduction of Cd ions to Cd?

Ans:



b). $E^\circ = E_{red}^\circ + E_{ox}^\circ$; if $E_{red}^\circ = 0 \text{ V}$
 $\Rightarrow E^\circ = 0 + E_{ox}^\circ$
 $E_{ox}^\circ = +1.201 \text{ V}$
 $E_{red}^\circ = -1.201 \text{ V}$

Conclusions:

- The calculated voltage, E° , is always a positive quantity for a reaction taking place in a voltaic cell.
- The quantities E° , E_{ox}° and E_{red}° are “independent” of how the equation for the cell reaction is written.



Intensive property.

§ Spontaneity of redox reactions

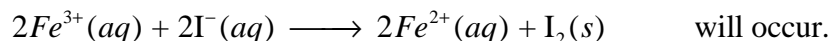
If the calculated voltage for a redox reaction is a positive quantity, the reaction will be spontaneous.

$$E^\circ > 0 \Rightarrow \text{spontaneous reaction}$$

Ex. 18.4: Using standard potentials listed in Table 18.1, decide whether at

standard concentrations

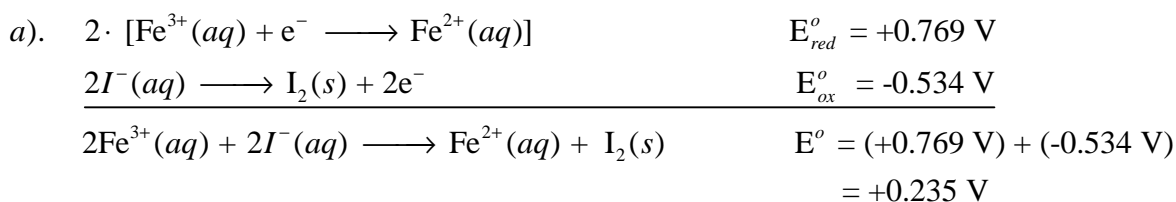
a). the reaction



b). Fe(s) will be oxidized to Fe^{2+} by treatment with hydrochloric acid.

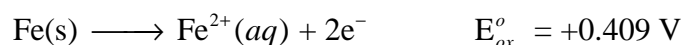
c). a redox reaction will occur when the following species are mixed in acidic solution: Cl^{-} , Fe^{2+} , Cr^{2+} , I_2 .

Ans:

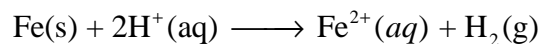
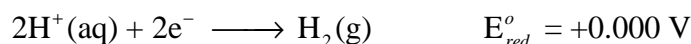


Q $E^{\circ} > 0 \Rightarrow \therefore$ spontaneous

b). oxidation half-reaction of Fe(s):

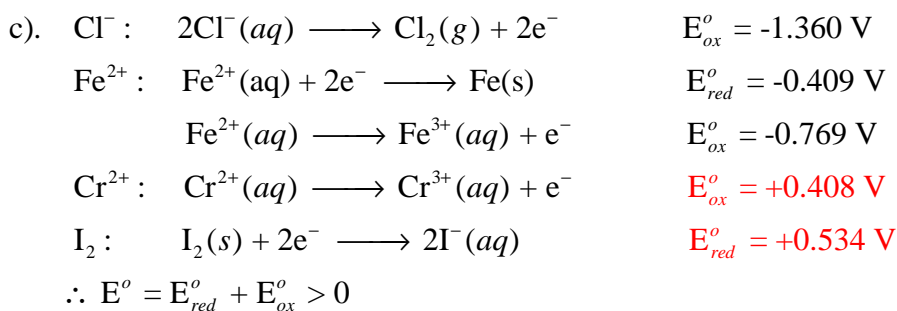


hydrochloric acid: reduction reaction:



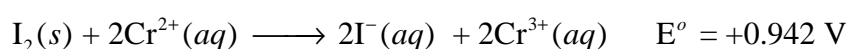
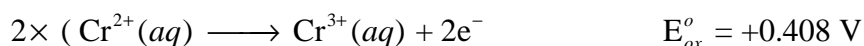
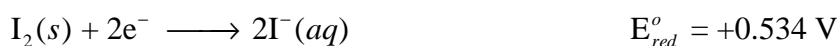
$$E^{\circ} = E_{\text{red}}^{\circ} + E_{\text{ox}}^{\circ} = (+0.000 \text{ V}) + (+0.409 \text{ V})$$

$$= +0.409 \text{ V} \Rightarrow \therefore \text{spontaneous}$$



↓

The only combination reaction is: I_2 react with Cr^{2+} :



§ 18-3 Relations Between E° , ΔG° , and K

ΔG° : the standard free energy change.

K: equilibrium constant.

§ E° and ΔG° :

From thermodynamics:

$$\Delta G^\circ = -n F E^\circ \quad (18-2)$$

n: the number of moles of electrons transferred in the reaction.

F: Faraday constant; 9.648×10^4 J/mol·V

$$\Delta G^\circ < 0 \Rightarrow \text{spontaneous reaction}$$

§ E° and K :

From thermodynamics (Ch. 17):

$$\Delta G^\circ = -RT \ln K$$

$$\Delta G^\circ = -n F E^\circ \quad (18-2)$$

$$\therefore -RT \ln K = -n F E^\circ$$

$$E^\circ = \frac{RT}{nF} \ln K$$

if $T = 25^\circ\text{C} = 298\text{ K}$

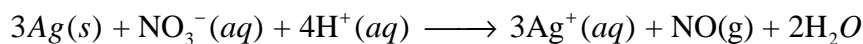
$$\frac{RT}{F} = \frac{8.31 \text{ J/mol} \cdot \text{K} \cdot 298 \text{ K}}{9.648 \times 10^4 \text{ J/mol} \cdot \text{V}} = 0.0257 \text{ V}$$

$$\therefore E^\circ = \frac{0.0257}{n} \ln K \quad (T = 298 \text{ K}) \quad (18-3)$$

$$\text{if } E^\circ > 0 \Rightarrow K > 1$$

$$E^\circ < 0 \Rightarrow K < 1$$

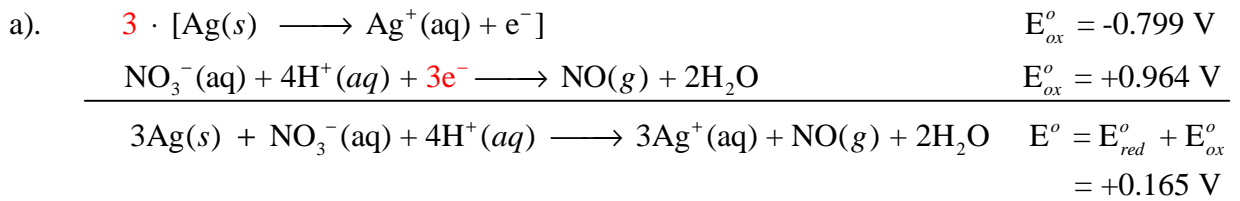
Ex. 18.5: For the reaction:



Use Table 18.1 to calculate, at 25°C

a). ΔG° b). K

Ans:



$$\begin{aligned}
 \Delta G^\circ &= -nFE^\circ \\
 &= -3 \cdot 9.468 \times 10^4 \cdot 0.165 \\
 &= -4.78 \times 10^4 \text{ J} = -47.8 \text{ kJ}
 \end{aligned}$$

$$\begin{aligned}
 \text{b).} \quad \Delta G^\circ &= -RT \ln K \\
 -4.78 \times 10^4 \text{ J} &= -8.314 \cdot 298 \cdot \ln K \\
 \ln K &= 19.3 \\
 K &= 2.39 \times 10^8 \\
 \text{or} \quad E^\circ &= \frac{0.0257}{n} \ln K \\
 0.165 &= \frac{0.0257}{3} \ln K \\
 K &= 2.39 \times 10^8
 \end{aligned}$$

§ 18-4 Effect of Concentration on voltage

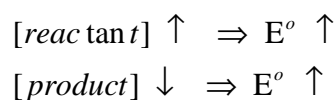
Standard voltage: gas: 1 atm

Aqueous solution: 1 M

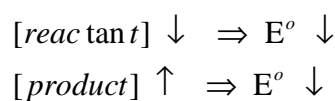
↓

When the concentration of a reactant or product changes, the voltage changes as well.

1. Voltage will increase if the concentration of a reactant is increased or that of a product is decreased.



2. Voltage will decrease if the concentration of a reactant is decreased or that of a product is increased.



When a voltaic cell operates, supplying electrical energy, the

concentration of reactants decreases and that of the products increases.

↓

As time passes, the voltage drops steadily. Eventually it becomes zero.

↓

The redox reaction taking place within the cell is at equilibrium.

§ Nernst equation

From Ch. 17:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\Delta G^\circ = -nFE^\circ; \Delta G = -nFE \text{ 代入:}$$

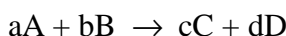
$$-nFE = -nFE^\circ + RT \ln Q$$

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

T = 298K; Nernst equation:

$$E = E^\circ - \frac{0.0257}{n} \ln Q \quad (18-4)$$

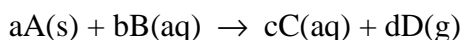
Q: reaction quotient



$$Q = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$$

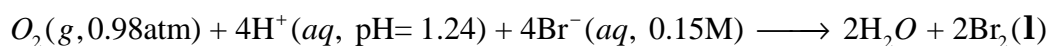
Discussion:

1. If $Q > 1$, which means that the concentrations of products are high relative to those of reactants, $\ln Q$ is positive and $E < E^\circ$.
2. If $Q < 1$ (concentrations of product low relative to reactants), $\ln Q$ is negative and $E > E^\circ$.
3. If $Q = 1$, $\Rightarrow \ln Q = 0 \Rightarrow E = E^\circ$.



$$Q = \frac{[C]^c \cdot (P_d)^d}{[B]^b}$$

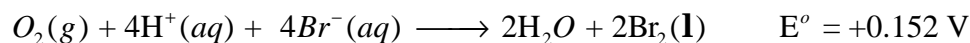
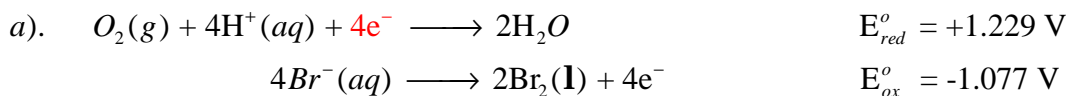
Ex. 18.6: Consider a voltaic cell in which the following reaction occurs



- a). Calculate E for the cell at 25°C.
- b). When the voltaic cell is at 35°C, E is measured to be 0.039 V.

What is E° at 35°C .

Ans:



$$\begin{aligned} E^\circ &= E_{red}^\circ + E_{ox}^\circ \\ &= (+1.229) + (-1.077) = +0.152 \text{ V} \end{aligned}$$

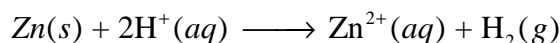
$$\begin{aligned} E &= E^\circ - \frac{0.0257}{n} \ln Q \\ &= (+0.152) - \frac{0.0257}{4} \ln \frac{1}{P_{O_2} \cdot [H^+]^4 \cdot [Br^-]^4} \\ &= (+0.152) - 0.0643 \ln \frac{1}{(0.98)^1 \cdot (0.58)^4 \cdot (0.15)^4} \\ &= (+0.152) - 0.0643 \cdot \ln(1.8 \times 10^8) \\ &= (+0.152) - 0.122 = +0.030 \text{ V} \end{aligned}$$

$$\begin{aligned} b). \quad E &= E^\circ - \frac{0.0257}{n} \ln Q \\ E^\circ &= E + \frac{0.0257}{n} \ln Q = 0.039 + \frac{8.31 \cdot 308}{4 \cdot 9.648 \times 10^4} \ln(1.8 \times 10^8) \\ &= +0.165 \text{ V} \end{aligned}$$

The Nernst equation can be also used to determine the effect of change in concentration on the voltage of an individual half-cell, E_{red}° or E_{ox}° .

§ Use of the Nernst equation to determine ion concentration

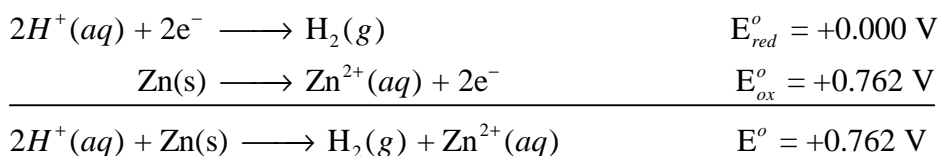
Ex: 18.7: Consider a voltaic cell at 25°C in which the reaction is



It is found that the voltage is $+0.560 \text{ V}$ when $[Zn^{2+}] = 0.85 \text{ M}$,

$P_{H_2} = 0.988 \text{ atm}$. What is the pH in the $H^+ - H_2$ half-cell?

Ans:



$$E = E^{\circ} - \frac{0.0257}{n} \ln Q$$

$$(+0.560) = (+0.762) - \frac{0.0257}{2} \ln \frac{[Zn^{2+}]^1 \cdot (P_{H_2})^1}{[H^+]^2}$$

$$-0.202 = - \frac{0.0257}{2} \ln \frac{(0.85) \cdot (0.988)}{[H^+]^2}$$

$$\ln \frac{0.84}{[H^+]^2} = \frac{(0.202) \cdot 2}{0.0257} = 15.7$$

$$\frac{0.84}{[H^+]^2} = 6.72 \times 10^6$$

$$[H^+] = 3.53 \times 10^{-4}$$

$$pH = 3.45$$

Usage: pH meter.

§ 18-5 Electrolytic Cells 電解電池

A spontaneous redox reaction is made to occur by pumping electrical energy into the system.

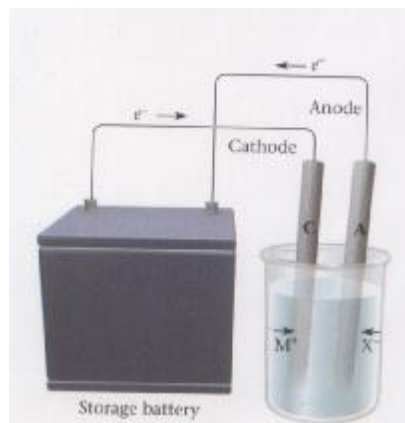


Fig. 18.8: Diagram of an electrolytic cell.

Oxidation occurs at the anode, reduction at the cathode, in both voltaic and electrolytic cells.

§ Quantitative relationships

Quantity of electrical charge:

$$1 \text{ mole electrons} = 9.648 \times 10^4 \text{ C.}$$

Rate of current flow: Ampere, A.

$$1 \text{ A} = 1 \text{ C/s}$$

Amount of electrical energy: J

When a charge of one coulomb (C) moves through a potential difference of one volt (V), it acquires an energy of 1 J.

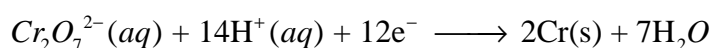
$$1 \text{ J} = 1 \text{ C} \cdot \text{V}$$

Electrical energy: kWh

$$1 \text{ kWh} = 3.600 \times 10^6 \text{ J} = 3.600 \times 10^3 \text{ kJ}$$

Table 18.3 Electrical Units			
Quantity	Unit	Defining Relation	Conversion Factors
Charge	coulomb (C)	$1 \text{ C} = 1 \text{ A} \cdot \text{s} = 1 \text{ J/V}$	$1 \text{ mol } e^- = 9.648 \times 10^4 \text{ C}$
Current	ampere (A)	$1 \text{ A} = 1 \text{ C/s}$	
Potential	volt (V)	$1 \text{ V} = 1 \text{ J/C}$	
Power	watt (W)	$1 \text{ W} = 1 \text{ J/s}$	
Energy	joule (J)	$1 \text{ J} = 1 \text{ V} \cdot \text{C}$	$1 \text{ kWh} = 3.600 \times 10^6 \text{ J}$

Ex 18.8: Chromium metal can be electroplated from a water solution of potassium dichromate. The reduction half-reaction is:



A current of 6.00 A and a voltage of 4.5 V are used in the electroplating.

- How many grams of chromium can be plated by if the current is run for 48 minutes ?
- How long will it take to completely convert 215 mL of 1.25 M $\text{K}_2\text{Cr}_2\text{O}_7$ to elemental chromium ?
- How many kilowatt hours (kWh) of electrical energy are required to plate 1.00 g of chromium ?

Ans:

$$\begin{aligned}
 a). & \frac{6.00 \text{ A} \cdot (48 \cdot 60) \text{ s}}{9.648 \times 10^4 \text{ C/mol}} \cdot \frac{2}{12} \cdot (52.00 \text{ g/mol}) = 1.55 \text{ g} \\
 b). & 0.215 \text{ L} \cdot 1.25 \text{ M/L} \cdot \frac{12}{1} \cdot 9.648 \times 10^4 \text{ C/mol} = 3.11 \times 10^5 \text{ C} \\
 & t = \frac{\text{charge}}{\text{current}} = \frac{3.11 \times 10^5 \text{ C}}{6.00 \text{ A}} = 5.19 \times 10^4 \text{ s} = 14.4 \text{ h} \\
 c). & \frac{1.00}{52.00} \text{ mol} \cdot \frac{12}{2} \cdot 9.648 \times 10^4 \text{ C/mol} \cdot 4.5 \text{ V} = 5.01 \times 10^4 \text{ C} \cdot \text{V} = 5.01 \times 10^4 \text{ J} \\
 & \frac{5.01 \times 10^4 \text{ J}}{3.600 \times 10^4 \text{ J/kWh}} = 0.014 \text{ kWh}
 \end{aligned}$$

Some electrical energy is wasted in side reactions at the electrodes and in the forming of heat.

⇓

The actual yield of products is less than the theoretical yield.

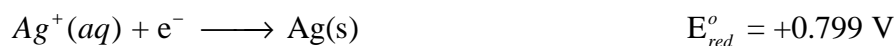
§ Cell reactions (water solution) ⇒ Electrolysis of water solution

Solution	Cathode Product	Anode Product
CuBr ₂ (aq)	Cu(s)	Br ₂ (l)
AgNO ₃ (aq)	Ag(s)	O ₂ (g)
KI(aq)	H ₂ (g)	I ₂ (s)
Na ₂ SO ₄ (aq)	H ₂ (g)	O ₂ (g)

A reduction half-reaction occurs at the cathode of an electrolytic cell. This half-reaction will be:

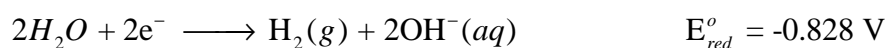
Cathode:

g the reduction of a cation to the corresponding metal.



This is an electroplating processes, in which a metal object serve as the cathode.

g the reduction of a water molecule to hydrogen gas.



This half-reaction occurs when the cation in the solution is very difficult to reduce.

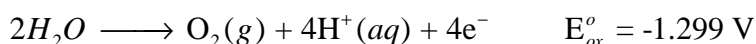
Ex. K^+ ions $E_{red}^{\circ} = -2.936 \text{ V}$ or Na^+ ions $E_{red}^{\circ} = -2.714 \text{ V}$.

Anode:

g the oxidation of an anion to the corresponding nonmetal.



g the oxidation of a water molecule to oxygen gas.



This half-reaction occurs when the anion cannot be oxidized.

Ex. NO_3^{-} , SO_4^{2-} : the nonmetal present is already in its highest oxidation state. (+5 for N, +6 for S)

§ 18-6 Commercial Cells

Applications of electrolytic cells in electroplating and electrosynthesis are of particular importance.

§ Electrolysis of aqueous NaCl

The most important electrolysis carried out in water solution is that of sodium chloride.

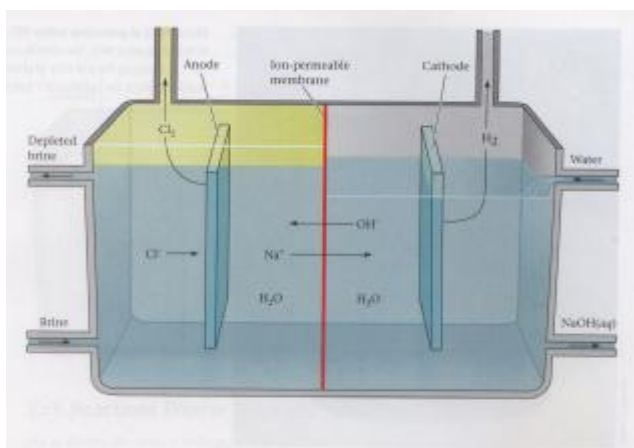
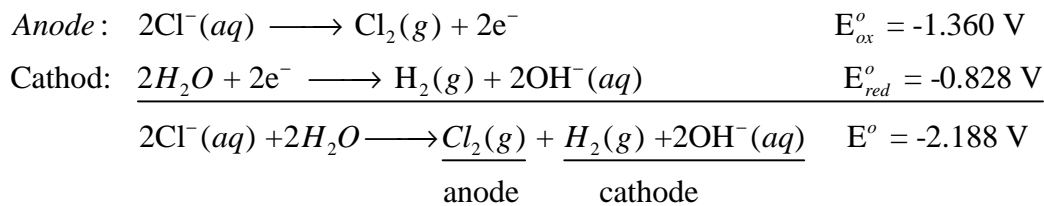


Fig. 18.10: Electrolysis of aqueous NaCl.



Usage:

Cl₂: 1). is used to purify drinking water.

2). raw material for PVC.

H₂: synthesis of ammonia.

NaOH: 1). processing pulp and paper.

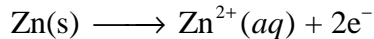
2). purification of aluminum ore.

3). manufacture of glass and textiles.

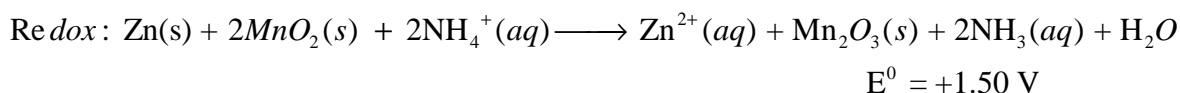
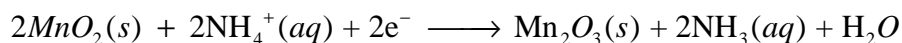
§ Primary (nonrechargeable) voltaic cells

⇒ Dry cell. (Leclanche' cell)

Anode: zinc wall of the cell.



Cathode: graphite rod.

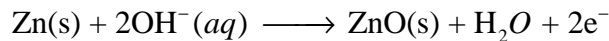


If too large a current is drawn from a Leclanche' cell, the ammonia forms a gaseous insulating layer around the carbon cathode. When this happens, the voltage drops sharply and then returns slowly to its normal of 1.50 V.

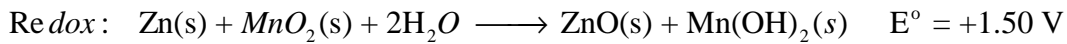
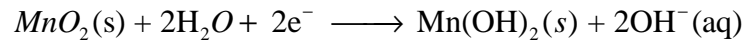
§ Alkaline dry cell:

The paste between the electrodes contains KOH rather than NH₄Cl.

Anode: Zn + KOH



Cathode: MnO₂

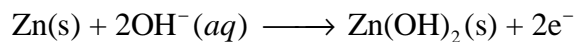


優點: longer shelf life and provide more current.

缺點: more expensive.

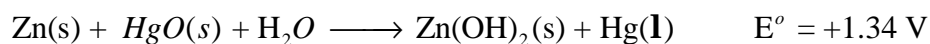
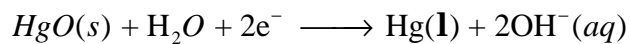
§ Mercury cell:

Anode: Zinc-mercury amalgam



Cathode: a plate made up of mercury(II) oxide, HgO

Electrolyte: a paste containing HgO and sodium or potassium hydroxide.



優點:

1. small size.
2. the overall reaction does not involve any ions in solution, so there are no concentration changes when current is drawn.

↓

∴ the battery maintains a constant voltage of 1.34 V throughout its life.

缺點:

1. Expensive.
2. not environmental friendly.

§ Storage (rechargeable) voltaic cells

⇒ can be recharged repeatedly.

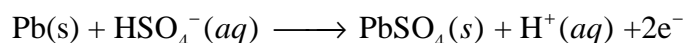
↓

This can be accomplished because the products of the reaction are deposited directly on the electrodes. By passing through a storage cell, it is possible to reverse the electrode reactions and restore the cell to its original

condition.

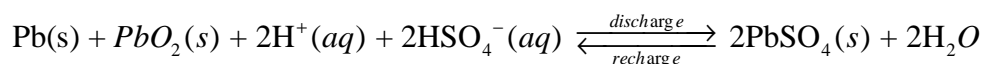
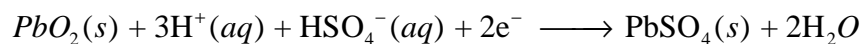
§ Lead storage battery

Anode: Pb plates.



Cathode: lead oxide PbO_2 .

Electrolyte: H_2SO_4 .



$$\Delta G^\circ = -371.4 \text{ kJ}$$

$$E^\circ = +2.10 \text{ V}$$

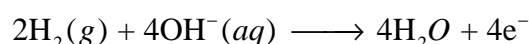
Recharge: a direct current is passed through it in the proper direction so as to reverse the above reaction.

何時 recharge: $\text{H}_2\text{SO}_4(aq)$ 之比重 < 1.05 時.

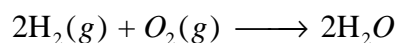
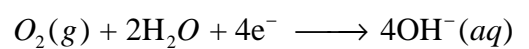
§ Fuel cells 燃料電池

A fuel, usually hydrogen, is oxidized at the anode.

Anode: Graphite.



Cathode: 碳棒.



$$\Delta G^\circ = -474.4 \text{ kJ}$$

$$E^\circ = +0.75 \text{ V}$$

The deterrents to the use of fuel cells:

1. The cost per kilojoule of energy is ten times that with a gasoline or diesel powered engine.
2. The storage of hydrogen in a vehicle is a serious problem.