13-1. Basic Concepts of electrochemistry

redox reaction: reactions with electron transfer
- oxidized: loses electrons
- reduced: gains electrons

Fe$^{3+}$ + V$^{2+}$ → Fe$^{2+}$ + V$^{3+}$

oxidizing agent (oxidant): takes electrons from others and reduces
reducing agent (reductant): oxidizes itself

1. Electric charge (q)
   - $q: [\text{coulomb}]$ or [C] = $1.602 \times 10^{-19}$ C for a single electron
     for 1 mole of e
   - $q = n \times F$
     - $1.602 \times 10^{-19}$ C x $6.02 \times 10^{23}$ /mol
     - 9.649 x $10^4$ C/mol Faraday constant [F]

ex) If 5.585 g of Fe$^{2+}$ was reduced in the reaction above, how many coulombs of charge must have been transferred from V$^{2+}$ to Fe$^{3+}$?

9.649 x $10^3$ C
13.1 Basic Concepts of electrochemistry

2. Electric Current: quantity of charge per second [A], ampere

<example of a charge of one coulomb per second>

Ex) Suppose that electrons are forced into a platinum wire immersed in a solution containing Sn^{4+}, which is reduced to Sn^{2+} at a constant rate of 4.24 mmol/h. How much current flows into the solution?

\[ 0.227 \text{ C/s} = 0.227 \text{A} \]

3. Voltage, work, free energy

- difference in electrical potential (E) between two points

\[ E = \text{potential difference} \quad [\text{V}, \text{volts}] \]

- work: energy in joules [J]

\[ J = E \cdot q \]

one joule of energy = one coulomb of charge is moved between points whose potential differ by one volt.

Ex) How much work is required to move 2.36 mmol of electrons through a potential difference of 1.05 V?

\[ 2.39 \times 10^2 \text{ J} \]
13.5

13-1. Basic Concepts of electrochemistry

The free energy change: $\Delta G$
work done on surrounding: $-\Delta G$

$$\Delta G = -E \ q = -n \ F \ E$$

4) Ohm's law  
Current, I, flowing through a circuit

$$I = \frac{E}{R} \quad [\Omega]$$

Electric current is analogous to volume of water per second flowing out of a hose.

13-1. Basic Concepts of electrochemistry

5) Power: $p$  
work done per unit time, $J/s$ or watt

$$p = \frac{\text{work}}{s} = \frac{E q}{s} = \frac{E}{s}$$

$$= E \ I$$
13-1. Basic Concepts of electrochemistry

Type of Electrochemical cells

Galvanic Cells
: A cell generates electric energy from where a chemical reaction. = spontaneous reaction

Electrolytic Cells
: requires an external source of E.E.

one reagent must be oxidized, the other reduced.

13-2. A galvanic cell in Action

reduction: $2\text{AgCl (s)} + 2 \text{e}^- \leftrightarrow 2 \text{Ag(s)} + 2 \text{Cl}^- (\text{aq})$

oxidation: $\text{Cd(s)} \rightarrow \text{Cd}^{2+} (\text{aq}) + 2 \text{e}^-$

Net: $\text{Cd(s)} + 2\text{AgCl (s)} \leftrightarrow \text{Cd}^{2+} (\text{aq}) + 2 \text{Cl}^- (\text{aq}) + \text{Ag(s)}$

$\Delta G = -150 \text{ KJ/mol of Cd}$
13.2. A galvanic cell in Action

2. Salt Bridge

KCl contained gel agar with KCl

\[ \text{Net: } \text{Cd(s)} + 2\text{Ag}^+(aq) \rightarrow \text{Cd}^{2+} + 2\text{Ag(s)} \]

3) Line notation

\[ \text{Cd(s)} | \text{Cd(NO}_3\text{)}_2(aq) \ || \text{AgNO}_3(aq) | \text{Ag(s)} \]


measured voltage → potential difference between Ag and Cd electrodes

- Positive voltage when e- flows from anode into neg terminal.
- Opposite connection: negative

- Standard reduction potential \( (E^0) \):
  activities of all species are unity

- Left half cell:
  standard hydrogen electrode (SHE)

\[ E_{H_2,H^+} = 0, \text{ definition} \]

By convention, it is written as

SHE || Ag\(^+\) | Ag(s)
13.3. Standard Potentials

**Standard Reduction Potentials**

- **std. Reduction potential** = potential difference between the std potential of the reduction of interest and the potential of SHE
- **positive**: electrons move from SHE to Ag⁺
- **negative**: electrons move in reverse direction

<table>
<thead>
<tr>
<th>Oxidizing agent</th>
<th>Reducing agent</th>
<th>( E^0 ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{F}_2(g) + 2e^- \rightleftharpoons 2\text{F}^- )</td>
<td></td>
<td>2.890</td>
</tr>
<tr>
<td>( \text{O}_2(g) + 2\text{H}^+ + 2e^- \rightleftharpoons \text{O}_2(g) + \text{H}_2\text{O} )</td>
<td></td>
<td>2.075</td>
</tr>
<tr>
<td>( \text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O} )</td>
<td></td>
<td>1.507</td>
</tr>
<tr>
<td>( \text{Ag}^+ + e^- \rightleftharpoons \text{Ag(s)} )</td>
<td></td>
<td>0.799</td>
</tr>
<tr>
<td>( \text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu(s)} )</td>
<td></td>
<td>0.339</td>
</tr>
<tr>
<td>( 2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2(g) )</td>
<td></td>
<td>0.000</td>
</tr>
<tr>
<td>( \text{Cd}^{2+} + 2e^- \rightleftharpoons \text{Cd(s)} )</td>
<td></td>
<td>-0.402</td>
</tr>
<tr>
<td>( \text{K}^+ + e^- \rightleftharpoons \text{K(s)} )</td>
<td></td>
<td>-2.936</td>
</tr>
<tr>
<td>( \text{Li}^+ + e^- \rightleftharpoons \text{Li(s)} )</td>
<td></td>
<td>-3.040</td>
</tr>
</tbody>
</table>

13.4. Nernst eq : net driving force

1) Nernst eq. for a half reaction,
\[ a \text{ A} \ + \ n \text{ e}^- \underset{b \text{ B}}{\rightarrow} \]

\[ E = E^0 - \frac{RT}{nF} \log \frac{A_b^b}{A_a^a} \]

\( E^0 \) : std. reduction potential
\( R \): gas constant \( 8.314 \text{ J/mol-K} \)
\( n \): number of moles

It shows two terms.

1. **driving force under std. condition** = \( E^0 \)
2. **concentration dependence (activity term)**

concentration term in Nernst Eq.
\[ \frac{A_b^b}{A_a^a} = Q \]

reaction quotient
pure solids, pure liquids, solvent not included

At 25°C Nernst equation simplifies to
\[ E = E^0 - \frac{0.05916}{n} \log \frac{A_b^b}{A_a^a} \]

59.16mV change per 10 fold change
13-4. Nernst eq : net driving force

2) Nernst equation for a complete reaction

voltage difference (E) for the two electrodes.
\[ E = E_+ - E_- \]

\( E_+ \): potential of electrode at positive input terminal of potentiometer
\[ = E_{\text{cathode}} \]

Procedure:
1. write half reactions with S.R.P.
2. write Nernst equation for half reaction
3. The more positive \( E^0 \) reduction predominantly happen
4. calculate net cell voltage
\[ E = E_+ - E_- \]
5. write balanced reaction by subtracting the half reaction

---

ex) Find the voltage of the cell in Figure 14-5 if the right half cell contains 0.50 M AgNO\(_3\) (aq) and the left half cell contains 0.010 M CdCl\(_2\) (aq). Write the net cell reaction and state whether it is spontaneous in the forward or reverse direction.

right: \[ 2 \text{Ag}^+ (aq) + 2 \text{e}^- \rightleftharpoons 2 \text{Ag(s)} \] \[ 0.799\text{V} \]
left: \[ \text{Cd}^{2+} (aq) + 2 \text{e}^- \rightleftharpoons \text{Cd (s)} \] \[ -0.402\text{V} \]

net: \[ \text{Cd(s)} + 2 \text{Ag}^+(aq) \rightleftharpoons \text{Cd}^{2+} + 2 \text{Ag(s)} \]

\[ E^+ = 0.781\text{V}, \ E^-=-0.461\text{V}, \ E = E^+ - E^- = 1.242\text{V} \]
13.4. Nernst eq : net driving force

* Advice for finding relevant half-cell reactions

\[ \text{Pb(s)} \mid \text{PbF}_2 (s) \mid \text{F}^- (aq) \parallel \text{Cu}^{+2} (aq) \mid \text{Cu(s)} \]

anode oxidation

right : \( \text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu (s)} \)

left : \( \text{PbF}_2 (s) + 2e^- \rightleftharpoons 2\text{F}^- + \text{Pb (s)} \)

in fact, \( 2\text{F}^- + \text{Pb (s)} \rightleftharpoons \text{PbF}_2 (s) + 2e^- \)

13.5. \( E^0 \) and the equilibrium constant

\( E^0 \) and the equilibrium constant

: galvanic cell produces electricity until the cell reaches eq.

At eq. \( E=0 \)

right electrode : \( a\text{ A} + n\text{ e}^- \rightleftharpoons c\text{ C} \quad E_{+}^0 \)

left electrode : \( d\text{ D} + n\text{ e}^- \rightleftharpoons b\text{ B} \quad E_{-}^0 \)

\[
E = E_{+} - E_{-} = (E_+^0 - E_-^0) - \frac{0.05916}{n} \left( \log \frac{A_c^e}{A_a^a} - \log \frac{A_b^b}{A_d^d} \right)
\]

\[
= E^0 - \frac{0.05916}{n} \left( \log \frac{A_c^e}{A_a^a} + \log \frac{A_d^d}{A_b^b} \right)
\]

\( Q : \) reaction quotient

at eq. \( E=0 \) as \( Q=K \)

\[
E^0 = \frac{0.05916}{n} \log k \quad (\text{at } 25^\circ C)
\]

\[
K = 10^{\frac{nE^0}{0.05916}}
\]
13-6. Cells as chemical probes

Right half cell: \( \text{AgCl(s)} \rightleftharpoons \text{Ag}^+ (aq) + \text{Cl}^- (aq) \)

Left half cell: \( \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- (aq) + \text{H}^+ (aq) \)

They come to equilibrium without other half-cell

--- chemical reaction

With cell assembled,

\[
\text{AgCl(s)} + e^- \rightleftharpoons \text{Ag} (s) + \text{Cl}^-(aq, 0.10M) \quad E^0 = 0.222V
\]

In left: the only element -- hydrogen gas bubbles out

\[
2 \text{H}^+ (aq, ?M) + 2 e^- \rightleftharpoons \text{H}_2 (g, 1.0\text{atm}) \quad E^0 = 0
\]

\[
E = E^+ - E^- = (0.222 - \frac{0.05916}{2} \log[\text{Cl}^+]^2) - (0 - \frac{0.05916}{2} \log \frac{P_{H_2}}{[H^+]^2})
\]

In order to have same electrons

\[
= 0.222 - \log \frac{[H^+]^2[Cl^-]^2}{P_{H_2}} = 0.503 \text{ V}
\]

Thus, \([H^+] = 1.8 \times 10^{-4} \text{ M}\)

We can calculate \(K_a\) for this case \(K_a\)

\[
K_a = \frac{P_{H_2}}{[H^+]^2[Cl^-]^2}
\]

Cell \(\rightarrow\) probe to measure the unknown \(H^+\) conc.
ex) The cell in the following figure measures the formation constant ($K_f$) of Hg(EDTA)$^{2-}$. The solution in the right hand compartment contains 0.500 mmol of Hg$^{2+}$ and 2.00 mmol of EDTA in a volume of 0.100 L buffered to pH 6.00. If the voltage is 0.331V, find the value of $K_f$ for Hg(EDTA)$^{2-}$.

Selected Problem No.
14-4, -5, -10, -17, -35, -38,