6.5 Half-reactions and electrodes

Key points

1. A redox reaction is expressed as the difference of two reduction half-reactions
2. Each reduction half-reaction defines a redox couple
6.5 Half-reactions and electrodes

- The electrochemical methods can be used to determine thermodynamic properties of reactions that may be inaccessible by other methods.
- Electrochemical cell consist of two electrodes (metallic conductors) in contact with an electrolyte (an ionic conductor).
- An electrode and its electrolyte comprise an electrode compartment.
- Any ‘inert metal’ shown in the following table is present to act as a source or sink of electrons.
- If the electrolytes are different, the two compartments may be joined by a salt bridge.

- A galvanic cell: a spontaneous reaction.
- An electrolytic cell: a non-spontaneous reaction driven by an external source of current.

### Table 6.1 Varieties of Electrode

<table>
<thead>
<tr>
<th>Electrode type</th>
<th>Designation</th>
<th>Redox couple</th>
<th>Half-reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal/metal ion</td>
<td>M(s)</td>
<td>M⁺(aq)</td>
<td>M⁺/M</td>
</tr>
<tr>
<td>Gas</td>
<td>Pt(s)</td>
<td>X₂(g)</td>
<td>X⁺(aq)</td>
</tr>
<tr>
<td></td>
<td>Pt(s)</td>
<td>X₂(g)</td>
<td>X⁻(aq)</td>
</tr>
<tr>
<td>Metal/insoluble salt</td>
<td>M(s)</td>
<td>MX(s)</td>
<td>X⁻(aq)</td>
</tr>
<tr>
<td>Redox</td>
<td>Pt(s)</td>
<td>M⁺(aq)</td>
<td>M²⁺(aq)</td>
</tr>
</tbody>
</table>
6.5 Half-reactions and electrodes

- Oxidation is the removal of electrons from a species
- Reduction is the addition of electrons to a species
- A redox reaction is a reaction in which there is a transfer of electrons from one species to another
- The reducing agent is the electron donor
- The oxidizing agent is the electron acceptor
- Any redox reaction may be expressed as the difference of two reduction half-reactions
- The reduced and oxidized species in a half-reaction form a redox couple

\[ \text{Ox} + \nu e^- \rightarrow \text{Red} \]
As the reaction proceeds, the electrons released in the oxidation \( \text{Red}_1 \rightarrow \text{Ox}_1 + \nu e^- \) at one electrode travel through the external circuit and re-enter the cell through the other electrode, where they bring about the reduction \( \text{Red}_2 \rightarrow \text{Ox}_2 + \nu e^- \).

- **Anode**: the electrode at which oxidation occurs
- **Cathode**: the electrode at which reduction occurs
Key points

1. Galvanic cells are classified as electrolyte concentration and electrode concentration cells
2. A liquid junction potential arises at the junction of two electrolyte solutions
3. The cell notation specifies the structure of a cell
6.6 Varieties of cells

(a) Liquid junction potentials

- **Daniell Cell**: Cells where the electrodes are immersed in different electrolytes.
- **Electrolyte concentration cell**: the electrode compartments are identical except for the concentrations of the electrolyte.
- **Electrode concentration cell**: the electrodes themselves have different concentrations, either because they are gas electrodes operating at different pressures or because they are amalgams (solutions in mercury) with different concentrations.
(a) Liquid junction potentials

- In a cell with two different electrolyte solutions in contact, there is an additional source of potential difference across the interface: the liquid junction potential ($E_{lj}$).

- Between different concentrations of hydrochloric acid, the mobile H+ ions diffuse into the more dilute solution. The bulkier Cl- ions follow but more slowly, which results in a potential difference. The potential then settles down to a value such that the ions diffuse at the same rates.

- The liquid junction potential can be reduced by using a salt bridge (about 1 to 2mV).
6.6 Varieties of cells

(b) Notation

- A liquid junction is denoted by \( \vdots \).
- \( || \) denotes an interface for which it is assumed that the junction potential is eliminated.

\[
\text{Pt}(s) | \text{H}_2(g) | \text{AgCl}(s) | \text{Ag}(s)
\]

\[
\text{Zn}(s) | \text{ZnSO}_4(aq) | \vdots | \text{CuSO}_4(aq) | \text{Cu}(s)
\]

\[
\text{Zn}(s) | \text{ZnSO}_4(aq) || \text{CuSO}_4(aq) | \text{Cu}(s)
\]

- An example of an electrolyte concentration cell

\[
\text{Pt}(s) | \text{H}_2(g) | \text{HCl}(aq, b_1) || \text{HCl}(aq, b_2) | \text{H}_2(g) | \text{Pt}(s)
\]
6.7 The cell potential

Key points

1. The Nernst equation relates the cell potential to the composition of the reaction mixture

2. The standard cell potential may be used to calculate the equilibrium constant of the cell reaction
6.7 The cell potential

(a) The Nernst equation

- Cell reactions: the reactions in the cell written on the assumption that the right-hand electrode is the cathode, and hence that the spontaneous reaction is one in which reduction is taking place in the right-hand compartment

\[
\text{Zn(s)}|\text{ZnSO}_4(\text{aq})||\text{CuSO}_4(\text{aq})|\text{Cu(s)}
\]

Right-hand electrode: \( \text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)} \)

Left-hand electrode: \( \text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn(s)} \)

\( \text{Cu}^{2+}(\text{aq}) + \text{Zn(s)} \rightarrow \text{Cu(s)} + \text{Zn}^{2+}(\text{aq}) \)
6.7 The cell potential

(a) The Nernst equation

- A cell in which the overall cell reaction has not reached chemical equilibrium can do electrical work as the reaction drives electrons through an external circuit.
- With a large potential difference, a given number of electrons travelling can do a larger amount of electrical work.
- A cell in which the overall reaction is at equilibrium can do no work with zero potential difference.
- The maximum non-expansion work a system can do is $w_{\text{add, max}} = \Delta G$.
- Maximum work is produced when a change occurs reversibly.
- The reaction Gibbs energy is actually relating a specified composition, which means we need ensure that the cell is operating reversibly at a specific, constant composition.
- The above condition is achieved by measuring the cell potential when it is balanced by an exactly opposing source of potential so that the cell reaction reversibly, the composition is constant, and no current flows.
6.7 The cell potential

(a) The Nernst equation

- Cell potential, $E_{\text{cell}}$: the resulting potential difference measured when the previous condition is achieved

$$-\nu F E_{\text{cell}} = \Delta_r G$$

- $F = eN_A$: Faraday’s constant
- $\nu$ is the stoichiometric coefficient of the electrons in the half-reactions
- Negative $\Delta_r G$: a positive cell potential
- Positive $\Delta_r G$: a negative cell potential
- The driving power of a cell is proportional to the slope of the Gibbs energy with respect to the extent of reaction
6.7 The cell potential

(a) The Nernst equation

- $\Delta_r G = \Delta_r G^\Theta + RT \ln Q$

\[
E_{\text{cell}} = - \frac{\Delta_r G^\Theta}{\nu F} - \frac{RT}{\nu F} \ln Q
\]

- Standard potential

\[
E^\Theta_{\text{cell}} = - \frac{\Delta_r G^\Theta}{\nu F}
\]

- Nernst equation

\[
E_{\text{cell}} = E^\Theta_{\text{cell}} - \frac{RT}{\nu F} \ln Q
\]
6.7 The cell potential

(b) Cells at equilibrium

- Suppose the reaction has reached equilibrium; \( Q = K \)
- A chemical reaction at equilibrium cannot do work and \( E_{\text{cell}} = 0 \)

\[
\ln K = \frac{\nu F E^\Theta_{\text{cell}}}{RT}
\]

- The above equation lets us predict equilibrium constants from measured standard cell potentials
Key points

1. The standard potential of a couple is the cell potential in which it forms the right-handed electrode and the left-handed electrode is a standard hydrogen electrode.
We can define the potential of one of the electrodes as zero and then assign values to others on that basis, although it is not possible to measure the contribution of a single electrode.

The standard hydrogen electrode (SHE)

At all temperatures,

\[
\text{Pt}(s)\mid \text{H}_2(g)\mid \text{H}^+(aq) \quad E^\Theta = 0
\]

The activity of the hydrogen ions must be 1 (pH = 0) and the pressure of the hydrogen gas must be 1 bar.

For silver chloride electrode as an example,

\[
\text{Pt}(s)\mid \text{H}_2(g)\mid \text{HCl}(aq)\mid \text{AgCl}(s)\mid \text{Ag}(s)
\]

\[
\frac{1}{2} \text{H}_2(g) + \text{AgCl}(s) \rightarrow \text{HCl}(aq) + \text{Ag}(s)
\]

\[
E^\Theta_{\text{cell}} = E^\Theta(\text{AgCl}/\text{Ag},\text{Cl}^-) - E^\Theta(\text{SHE}) = E^\Theta(\text{AgCl}/\text{Ag},\text{Cl}^-)
\]
For silver chloride electrode as an example,

\[
E_{\text{cell}} = E^\Theta(\text{AgCl}/\text{Ag}, \text{Cl}^-) - \frac{RT}{F} \ln \frac{a_{\text{H}^+}a_{\text{Cl}^-}}{a_{\text{H}_2}}
\]

\[
E_{\text{cell}} = E^\Theta - \frac{RT}{F} \ln a_{\text{H}^+}a_{\text{Cl}^-}
\]

\[
a_{\text{H}^+} = \gamma_\pm \frac{b}{b^\Theta} \quad a_{\text{Cl}^-} = \gamma_\pm \frac{b}{b^\Theta}
\]

\[
E_{\text{cell}} = E^\Theta - \frac{RT}{F} \ln b^2 - \frac{RT}{F} \ln \gamma_\pm^2
\]

\[
E_{\text{cell}} + \frac{2RT}{F} \ln b = E^\Theta - \frac{2RT}{F} \ln \gamma_\pm
\]

Apply the Debye-Hückel theory

\[
E_{\text{cell}} + \frac{2RT}{F} \ln b = E^\Theta + Cb^{1/2}
\]

The standard potential of cells is an intensive property
6.9 Applications of standard potentials

Key points

1. The electrochemical series
2. The cell potential is used to measure the activity coefficient of electroactive ions
3. The standard cell potential is used to infer the equilibrium constant of the cell reaction
4. Species-selective electrodes contribute a potential that is characteristic of certain ions in solution
5. The temperature coefficient of the cell potential is used to determine the standard entropy and enthalpy of reaction
6.9 Applications of standard potentials

(a) Electrochemical series

- If $E_{\text{cell}}^\Theta > 0$, $K > 1$

$$\text{Red}_1, \text{Ox}_1 \parallel \text{Red}_2, \text{Ox}_2$$

$$\Delta E_{\text{cell}}^\Theta = E_{2}^\Theta - E_{1}^\Theta$$

$$\text{Red}_1 + \text{Ox}_2 \rightarrow \text{Ox}_1 + \text{Red}_2$$

- Red$_1$ has a thermodynamic tendency to reduce Ox$_2$
- Electrochemical series: The metallic elements arrange in the order of their reducing power as measured by their standard potentials in aqueous solution

<table>
<thead>
<tr>
<th>Table 6.3</th>
<th>The electrochemical series of the metals$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Least strongly reducing</td>
<td></td>
</tr>
<tr>
<td>Gold</td>
<td></td>
</tr>
<tr>
<td>Platinum</td>
<td></td>
</tr>
<tr>
<td>Silver</td>
<td></td>
</tr>
<tr>
<td>Mercury</td>
<td></td>
</tr>
<tr>
<td>Copper (Hydrogen)</td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td></td>
</tr>
<tr>
<td>Tin</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td></td>
</tr>
<tr>
<td>Iron</td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td></td>
</tr>
<tr>
<td>Chromium</td>
<td></td>
</tr>
<tr>
<td>Aluminium</td>
<td></td>
</tr>
<tr>
<td>Magnesium</td>
<td></td>
</tr>
<tr>
<td>Sodium</td>
<td></td>
</tr>
<tr>
<td>Calcium</td>
<td></td>
</tr>
<tr>
<td>Potassium</td>
<td></td>
</tr>
<tr>
<td>Most strongly reducing</td>
<td></td>
</tr>
</tbody>
</table>

$^*$ The complete series can be inferred from Table 6.2.
(b) The determination of activity coefficients

- We can use the standard potential of an electrode to determine mean activity coefficients.
- The mean activity coefficient of the ions in hydrochloric acid of molality $b$ is obtained from

$$\ln \gamma_{\pm} = \frac{E^\Theta - E_{\text{cell}}}{2RT/F} - \ln b$$
6.9 Applications of standard potentials

(c) The determination of equilibrium constant

- The principal use for standard potentials is to calculate the standard potential of a cell formed from any two electrodes.
- We subtract the standard potential of the left-hand electrode from the standard potential of the right-hand electrode.

\[ E_{cell}^{\Theta} = E^{\Theta}(\text{right}) - E^{\Theta}(\text{left}) \]

- Because \( \Delta_r G^{\Theta} = -\nu F E_{cell}^{\Theta} \),

\[ \ln K = \frac{\nu F E_{cell}^{\Theta}}{RT} \]
(d) The determination of thermodynamic functions

- The standard potential of a cell is related to the standard reaction Gibbs energy, i.e.,

\[ \Delta_r G^\Theta = -\nu F E_{\text{cell}}^\Theta \]

- Because of the thermodynamic relation \((\partial G/\partial T)_p = -S\),

\[ \frac{dE_{\text{cell}}^\Theta}{dT} = \frac{\Delta_r S^\Theta}{\nu F} \]

- The derivative is complete (not partial) because \(E^\Theta\) (and \(G^\Theta\)) is independent of the pressure

\[ \Delta_r H^\Theta = \Delta_r G^\Theta + T \Delta_r S^\Theta = -\nu F \left( E_{\text{cell}}^\Theta - T \frac{dE_{\text{cell}}^\Theta}{dT} \right) \]