2. Principles determining the voltages and capacities of electrochemical cells (Huggins, ch. 2)

1. Thermodynamic properties of individual species
2. A simple example: lithium/iodide cell
3. The shape of discharge curves and Gibbs phase rule
4. The coulometric titration technique
1. Thermodynamic Properties of Individual Species

- If there is no current flowing, this chemical driving force is balanced by an electrical driving force in the opposite direction.

- Chemical potential of species i in a phase j

\[ \mu_i = \frac{\partial G_j}{\partial n_i} \]

- Integral form,

\[ \Delta \mu_i = \Delta G_i \]

\[ \Delta \mu_i = -z_iFE \]

- Chemical potential of a given species is related to another thermodynamic quantity, its activity, \( a_i \).
\[ \mu_i = \mu_i^\circ + RT \ln a_i \]

where \( \mu_i^\circ \): a constant, in its standard state

\( R \): gas constant (8.315 J/mol K), \( T(K) \)

- **Activity**: effective concentration
  
  \( a_i = 1 \) for pure \( i \),
  
  \( a_i = 0.5 \) for half species \( i \) (half chemically inert)

- **Electrochemical cell**

  \( a_i(+) \) in the negative electrode, \( a_i(-) \) in the positive electrode

\[ \mu_i(+) - \mu_i(-) = RT[\ln a_i(+)-\ln a_i(-)] = RT \ln[a_i(+)/a_i(-)] \]

\[ E = -(RT/zF) \ln[a_i(+)/a_i(-)] \]  
Nernst equation
2. A Simple Example: The Lithium/Iodine Cell

- A lithium/iodine (Li/I$_2$) cell
- Currently widely used in cardiac pacemakers (primary battery)
- Metallic lithium as the negative electrode
- A composite of iodine with about 10 wt% of poly-2-vinylpyridine (P2VP) as positive $\rightarrow$ P2VP acting as an electron donor, and iodine as an acceptor
- Solid LiI as a solid electrolyte

\[
(-) \text{Li/electrolyte}/I_2(+) \]

Virtual reaction (가상반응), \( \text{Li} + \frac{1}{2}I_2 \rightarrow \text{LiI} \)

\[
E = -\Delta G_r/z_i F \\
\text{where} \\
\Delta G_r = \Delta G_r(\text{LiI}) \text{ and } z_i \text{ is } +1 \text{ for Li}^+ 
\]
Fig. 2.1 Schematic representation of the microstructure of a Li/I₂ cell at several stages of discharge
\[ \Delta G_f(LiI) = -269.67 \text{ kJ/mol at } 25^\circ C \rightarrow 2.795 \text{ V} \]

- Reaction $\uparrow \rightarrow$ Lil thickness (solid electrolyte)$\uparrow$
- "positive-electrode limited": positive electrode capacity is less than negative electrode capacity; this is the part of the cell that determines overall capacity
2.1 Calculation of the maximum theoretical specific energy

MTSE (Wh/kg) = 26805(xE/Wt) = 559.77 Wh/kg  

cf. 15 times Pb-acid cell  
disadvantages: rechargeability, cost, discharge rate

2.2 Temperature dependence of the cell voltage

\[ \Delta G_r = \Delta H_r - T\Delta S_r \]
\[ d(\Delta G_r)/dT = -\Delta S_r \quad \text{and} \quad dE/dT = \Delta S_r/z_i F \]

\[ \Delta S \] for the formation of LiI is given by

\[ \Delta S_r(\text{LiI}) = S(\text{LiI}) - S(\text{Li}) - 1/2 S(I_2) \]
\[ = -1.38 \text{ J/K} \cdot \text{mol} \]

→ cell voltage varies only slightly: -1.43 x 10^{-5} V/K
Table 2.1  Entropy data for some species at 25 and 225°C [3]

<table>
<thead>
<tr>
<th>Species</th>
<th>$S$ (25°C) J/K mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>29.08</td>
</tr>
<tr>
<td>Zn</td>
<td>41.63</td>
</tr>
<tr>
<td>$\text{H}_2$</td>
<td>130.68</td>
</tr>
<tr>
<td>$\text{O}_2$</td>
<td>205.15</td>
</tr>
<tr>
<td>$\text{Cl}_2$</td>
<td>304.32</td>
</tr>
<tr>
<td>$\text{I}_2$</td>
<td>116.14</td>
</tr>
<tr>
<td>LiF</td>
<td>35.66</td>
</tr>
<tr>
<td>LiCl</td>
<td>59.30</td>
</tr>
<tr>
<td>LiBr</td>
<td>74.06</td>
</tr>
<tr>
<td>LiI</td>
<td>85.77</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$ (liquid)</td>
<td>69.95</td>
</tr>
<tr>
<td>ZnO</td>
<td>43.64</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>$S$ (225°C) J/K mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2$</td>
<td>145.74</td>
</tr>
<tr>
<td>$\text{O}_2$</td>
<td>220.69</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$ (gas)</td>
<td>206.66</td>
</tr>
</tbody>
</table>
- Zn/O₂ battery that is commonly used in hearing aids, where it is $-5.2 \times 10^{-4} \text{ V/K}$

- H₂/O₂ fuel cell where the voltage varies $-1.7 \times 10^{-3} \text{ V/K}$
3. The shape of discharge curves and the Gibbs phase rule

- 3 types of discharge curves: flat, one-flat portion, S-shape (large slope)
  
  e.g. Li/I₂ cell (Fig.2.2): 1st type

- Why is flat in Li/I₂ cell? To understand the types → Gibbs phase rule

  \[ F = C - P + 2 \]

  C: the number of components (e.g. elements) present,
  P: the number of phases present in this materials system
  F: the number of degrees of freedom; i.e., the number of intensive thermodynamic parameters (pressure, temp, chemical potential or chemical composition)

- Li/I₂ cell: (-)electrode: only one phase Li, P = 1, C = 1, F = 2
  
  F = 2 (temp, pressure) → no other freedom left → chemical as well as electrical potential have fixed value
The amount of Li in (-) electrode↓ as cell discharged and Lil produced → since $F = 2$, if $T \& P$ are constant → $F = 0$ → electrical potential of lithium electrode is independent of the state of charge of the cell

**Fig. 2.4** Potential of a pure lithium electrode does not vary with the state of charge of the LiI cell.
If some iodide could dissolve in lithium, forming a solid solution, which it does not (actually not happened) → C = 2, P = 1, F = 3 → if T, P const, F = 1 → electrical potential varies

Fig. 2.5 Schematic representation of the variation of the electrical potential of an electrode as a function of its composition for the case in which the residual value of $F$ is not zero.
-positive electrode, one component, iodide $C = 1, P = 1, F = 2$
(same as negative electrode) $\rightarrow F = 0$ for $T \& P$ const

(-), (+) both same: full cell (Fig. 2.2)

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**Fig. 2.2** Output voltage and internal resistance of a typical Li/I$_2$ battery of the type used in cardiac pacemakers
- chemical potential of the iodine electrode

\[ \mu(l_2) = \mu^o(l_2) + RT \ln a(l_2) \]

for pure \( l_2 \),

\[ \mu(l_2) = \mu^o(l_2) \]

- Now consider the voltage of the \( \text{Li}/l_2 \) cell

\[ E = -\Delta \mu(l_2)/z_iF \]

\( z_i \) is \(-2\). Activity of iodine at the positive side is unity

For \( \text{Li} \),

\[ E = -\Delta \mu(\text{Li})/z_iF \]

\( z_i \) is \(+1\). Activity of lithium at the negative side is unity

- The shape of discharge curve is the result of the charge of both electrodes
e.g. multi-phase reactions in which residual $F = 0 \rightarrow$ set of constant voltage plateaus

**Fig. 2.6** Schematic equilibrium discharge curve of an electrode that undergoes a series of multi-phase reactions in which the residual value of $F$ is zero
e.g. sequential reactions that are not similar Li with Li-Ti-O spinel systems → 1 Li/mol inserted in the host spinel phase as a solid solution rxn → the potential varies continuously as a function of composition, $F = 2 - 1 + 2 = 3$ → additional Li causes nucleation, subsequent growth of a second phase with rocksalt structure, 2 Li/mol composition, $F = 2 - 2 + 2 = 2$

Fig. 2.7 Equilibrium discharge curve of a material in the Li–Ti–O system that initially had a composition with a spinel type of crystal structure
Insertion reaction up to 1 Li/mol $\rightarrow$ reconstitution reaction (formation or displacement) takes place when more than one lithium is added $\rightarrow$ two regions within the material with different Li contents

$\text{Li} \uparrow \rightarrow$ interface movement

![Diagram](image-url)
Example of a series of reactions: Li-Mn-O system → three different reactions, two phase plateau, a single-phase solid solution region followed another two phase plateau.

Fig. 2.9 Equilibrium discharge curve for $\text{Li}_x\text{Mn}_2\text{O}_4$
Experimentally confirmed by XRD

lattice parameters remain constant within two-phase regions, and vary with the composition within the single-phase solid solution region.
4. The Coulometric titration technique
- Electrochemical measurement to obtain thermodynamic information
- Consider electrochemical cell to investigate phase $A_yB$
  $A / \text{electrolyte}(A^+ \text{ion}) / A_yB$

Assume pure $A$ ($a(A) = 1$), isobaric(const P), isothermal(const T) condition
$\rightarrow$ OCV $E$ is a direct measure of chemical potential and activity $A$ in phase $A_yB$ according to

$$E = -\Delta \mu_A/z_{A^+}F = -(RT/z_{A^+}F) \ln a(A)$$

where $z_{A^+} = 1$

- If a positive current is passed through the cell using an electronic source, $A^+$ ions are transported through the electrolyte from the left electrode to the right electrode $\rightarrow y$ in the $A_yB$ phase is increased.
-When a steady value of current $I$ is applied for a fixed time $t$, the amount of charge $Q$ that is passed across the cell is

$$Q = It$$

-Number of moles of species A which is transported during this current pulse is

$$\Delta m(A) = \frac{Q}{z_A F}$$

so that change in the value of $y$, the mole fraction of species A, is

$$\Delta y = \frac{\Delta m(A)}{m(B)} = \frac{Q}{z_A F m(B)}$$

where $m(B)$ is the number of moles of B present in the electrode

e.g.