Battery - 1

Electrochemical Fundamentals

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CHEG 3128
Redox Processes

Always written in the reduction form

\[ R \xleftrightarrow{\text{O + ne}} O + ne \]

Equilibrium

Oxidation

\[ R \xleftrightarrow{\text{O + ne}} O + ne \]

Electron Donating

\[ O + ne \xrightarrow{\text{R}} \]

Electron Accepting

\[ \text{R} \xrightarrow{\text{O + ne}} \]
All Electrochemical Processes Occur on a Surface
1. Electrodeposition (Reduction)

Types of Reactions

\[ \text{Ag}^+ + e^- \leftrightarrow \text{Ag(s)} \]

\[ \text{Al}^3+ + 3e^- \leftrightarrow \text{Al(s)} \]

\[ \text{Cl}^2+ + 2e^- \leftrightarrow \text{Cl}_2(s) \]
2. Corrosion (oxidation)

Types of Reactions

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

$\text{Li(s)} \rightleftharpoons \text{Li}^+ + e^-$

$\text{Fe(s)} \rightleftharpoons \text{Fe}^{3+} + 3e^-$
Types of Reactions

$\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$

$2\text{Cl}^- + 2\text{H}_2\text{O} \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^- + 2\text{H}^+$

(i) Traditional Catalysis

$\text{Fe(CN)}_6^{3-} + 3\text{e}^- \rightarrow \text{Fe(CN)}_4^{4-}$

$\text{Cu}^2+ + 2\text{e}^- \rightarrow \text{Cu}^{+}$

(ii) Pure Redox

(iii) Electrochemical

Chemical Engineering Junior Lab (CHEG 3128)
Spring 2017
Membrane Fuel Cell

Example Cell: Proton Exchange
pure Ohmic resistance

Ionic movement through electrolyte is akin to a

Minimize distance between them

Must be electrically conducting

(in detail next time)

Layer charging/discharging (we'll discuss this).

Non-Faradic – adsorption/desorption, double

Non-Faradic and non-Faradic processes have both

Faradic – electrochemical reactions

Faradic and non-Faradic processes

Anode and Cathode
This leads to the so-called electrochemical "Three Phase Boundary". Since the electrolyte solvates the ions (which complete the electrochemical circuit), the reactant must also be solvated in the electrolyte to react.

Liquids: Dissolved salts in a solvent

Solids: Ion conducting groups

Provides a media for ion transport

Mostly discuss aqueous in this class
Three Phase boundary

For an electrochemical reaction to occur, we

MUST have three things present

Reactant

Electrolyte

Catalyst/Electrode

Designing this interface is critical for device

performance

Void Space

Reactant mass transport

Maximize interface between catalyst and

electrolyte
\[ \text{Ag}_2\text{SO}_4 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{Ag}_2\text{O} + 2\text{H}_2\text{SO}_4 \]
\[ \text{O}_2 + 2\text{H}_2 \rightarrow \text{H}_2\text{O}_2 + 2\text{H}^+ \]
$2H_2 + O_2 \rightarrow 2H_2O$

for $H(T)$ and $AG(T)$.
Extra Resources

and Larry R. Faulkner.

and Applications; 2nd Edition. Allen J. Bard

Electrochemical Methods: Fundamentals

Chemical Engineering Junior Lab (CHEG 3128)
Spring 2017
All reactions are electron transfer processes. What I mean is that every reacting system is a combination of complementary redox reactions.

For instance, take the combustion of H₂

\[ 2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(l) \]

→ Is this spontaneous? Exo/Endo thermoic?

→ How do we capture energy?
    → As heat \( \Delta H(t) \)

→ In this reaction, what is oxidized?
    → what is reduced?

What if I write it like this:

\[
\begin{align*}
(\text{H}_2 & \rightarrow 2\text{H}^+ + 2\text{e}^-) \times 2 \\
2\text{H}_2 & \rightarrow 4\text{H}^+ + 4\text{e}^- \\
\text{O}_2 + 4\text{H}^+ + 4\text{e}^- & \rightarrow 2\text{H}_2\text{O} \\
\text{total} & \quad 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}
\end{align*}
\]
Reductions are e\(^-\) accepting reactions
Oxidations are e\(^-\) donating reactions

- H is oxidized from \(\text{H}(0) \rightarrow \text{H}(\text{O}1\text{t})\)
- O is reduced from \(\text{O}(0) \rightarrow \text{O}(\text{2}^-)\)

In a chemical system, we recover the energy from this reaction as heat. \(\text{H}_2\) combustion is used in combined cycle power plants. The combustion heat creates steam, which turns a turbine, spinning a shaft between 2 magnets. A looped Cu wire \(\rightarrow\) the rotation of the shaft in the magnetic field (Physics 2!) produces a current.

What if we didn't need to do that? What if we could directly use the electrons from the \(\text{H}_2\) reactions? \(\Rightarrow\) This is electrochemical engineering. One such system is a proton exchange membrane fuel cell.

\(\Rightarrow\) Diagram on next page

- Oxidations happen @ the anode
  - (-) "negative" electrode

- Reduction happen @ the cathode
  - (+) "positive" electrode

How much energy can we get from electrochemical processes?
H₂ → 2H⁺ + 2e⁻

O₂ + 4H⁺ + 4e⁻ → 2H₂O
Let's do an energy/entropy balance on one electrode:

\[ O + ne^- \rightarrow R \]

**Generalized Energy Balance**

\[ U_E = U_B + \sum H_{in}^\text{mass} - \sum H_{out}^\text{mass} + Q + W \]

- Break up work term:
  \[ W = -(P\Delta V + W_{elec}) \]

\[ U_E = U_B + \sum H_{in}^\text{mass} - \sum H_{out}^\text{mass} + Q - P\Delta V - W_{elec} \]

**Assumptions:**
1. Closed System
2. All electrochemical reactions are reversible

\[ U_E = U_B + Q - P\Delta V - W_{elec} \]

\[ U_E - U_B + P\Delta V = Q - W_{elec} \]

\[ \Delta U + P\Delta V = T\Delta S - W_{elec} \]

\[ \Delta H - T\Delta S = -W_{elec} \]

\[ \Delta G = -W_{elec} \]

\[ W_{elec} = -\Delta G \]

**Entropy Balance**

\[ S_E = S_B + \sum S_{in}^\text{mass} - \sum S_{out}^\text{mass} + \frac{Q}{T} \]

\[ Q = T\Delta S \]

**Units:**
- \[ W = J/mol \]
- \[ Q = \text{charge, potential} \]
- \[ n = \text{number of moles, mol} \]
- \[ F = \text{Faraday constant, C/mole} \]

\[ W = -\Delta G = nFE \]

\[ \Delta G = -nFE \]
@ STP, 25°C, 1 bar (a 1M)

\[ \Delta G^0 = -nFE^0 \]

Where \( E^0 \) is called the "Standard Potential."

How to find the standard potential for an individual reaction?

First, know that it is impossible to know how much energy we have in a system, which is why we always report them as \( \Delta G, \Delta H \), etc.

Therefore, we need an internal standard

\[ \Delta G \text{ for } 2H^+ + 2e^- \rightarrow H_2 (g) \text{ at } 25°C, 1 \text{ bar} = 0 \]

\[ E^0_{H^+/H_2} = 0.0 \text{ V} \]
Oxygen Reduction in acid media

\[ O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O (\text{aq}) \quad ① \]

\[ 2H_2 \rightleftharpoons 4H^+ + 4e^- \quad ② \Rightarrow 2x \text{ reference!} \]

\[ O_2 + 2H_2 \rightleftharpoons 2H_2O \]

\[ \Delta G^{\circ}_{f, H_2O} = -237,200 \text{ J/mol} \]

\[ \Delta G^{\circ}_{f, O_2} = 0 \text{ J/mol} \]

\[ \Delta G^{\circ}_{f, H_2} = 0 \text{ J/mol} \]

\[ \Delta G^\circ = 2(-237,200 \text{ J/mol}) - [0 \text{ J/mol} + 2(0 \text{ J/mol})] \]

\[ \Delta G^\circ = -474,400 \text{ J/mol} \]

\[ \Delta G_{\text{Rxn}} = -nFV_{\text{Th}} \]

\[ V_{\text{Th}} = \frac{-\Delta G_{\text{Rxn}}}{nF} = \frac{-(-474,400 \text{ J/mol})}{4 \text{ mol}_2 \text{ mol}_1^{-1} \times 96,485.3 \text{ C mol}_1^{-1}} = 1.229 \text{ V} \]

\[ 1.229 = E^{\circ}_{\text{Cathode}} - E^{\circ}_{\text{Anode}} \]

\[ E^{\circ}_{O_2} = 1.229 \text{ V} \]
Do we need to do that work every time?

No → most electrochemical redox couples are tabulated

Some can be found in Appendix C
- Page 808 in B&F, Ed 2
→ Also attached to next page

How does our ORR calculated \( E^\circ \) compare with the Table? They are EXACTLY THE SAME!

Now, let's answer our question about the Daniell cell...

What if we attached the Cu foil to the \( \oplus \) terminal

- Cathode
  \[ \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu(s)} \]

- Zn foil to the \( \ominus \) terminal

- Anode
  \[ \text{Zn} \rightarrow \text{Zn}^{+2} + 2e^- \]
$E_{\text{Cu}^{2+}/\text{Cu}}^\circ = 0.34 \text{ V}$

$E_{\text{Zn}^{2+}/\text{Zn}}^\circ = -0.76 \text{ V}$

\[
V_{\text{th}} = E_c^\circ - E_A^\circ = 0.34 \text{ V} - (-0.76 \text{ V}) = 1.1 \text{ V}
\]

\[\downarrow\]

galvanic! will occur spontaneously

What if we connected this the other way?

Cathode: $\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn(s)}$  

Anode: $\text{Cu(s)} \rightarrow \text{Cu}^{2+} + 2e^-$

\[
V_{\text{th}} = E_c^\circ - E_A^\circ = -0.76 - 0.34 = -1.1 \text{ V}
\]

\[\downarrow\]

nonspontaneous!  

$\downarrow$ Electrolytic cell

How would we "recharge" this cell?

Make $\Delta G < 0$, so, we have to apply a voltage $> 1.1 \text{ V}$ on the cell to make it go!  

$\rightarrow$ That's why you plug your phone in!
**APPENDIX**

**C**

REFERENCE TABLES

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Potential, V</th>
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<td>Ag⁺ + e ⇌ Ag</td>
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<td>$2\text{H}^+ + 2e \rightleftharpoons \text{H}_2$</td>
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<td>$2\text{H}_2\text{O} + 2e \rightleftharpoons \text{H}_2 + 2\text{OH}^-$</td>
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<td>$\text{Hg}_2^{2+} + 2e \rightleftharpoons 2\text{Hg}$</td>
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<td>$\text{Hg}_2\text{Cl}_2 + 2e \rightleftharpoons 2\text{Hg} + 2\text{Cl}^-$ (sat'd. KCl)</td>
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<td>$\text{I}_3^- + 2e \rightleftharpoons 3\text{I}^-$</td>
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<td>$\text{Mn}_2\text{O}_7 + 8\text{H}^+ + 5e \rightleftharpoons 2\text{Mn}^{2+} + 4\text{H}_2\text{O}$</td>
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<td>$\text{O}_3 + 2\text{H}^+ + 2e \rightleftharpoons \text{H}_2\text{O}_2$</td>
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(continued)
### TABLE C.1 (continued)

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<td>$\text{V}^{3+} + e \rightarrow \text{V}^{2+}$</td>
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### Table C.2 Selected Formal Potentials in Aqueous Solution at 25°C in V vs. NHE

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<th>Potential, V</th>
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<td>Cu(II) + $e \rightarrow \text{Cu}$</td>
<td>$1 M \text{NH}_3 + 1 M \text{NH}_4^+$</td>
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<td>&amp;</td>
<td>$1 M \text{KBr}$</td>
<td>0.52</td>
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<td>Ce(IV) + $e \rightarrow \text{Ce(III)}$</td>
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<td>&amp;</td>
<td>$1 M \text{HCl}$</td>
<td>1.28</td>
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<tr>
<td>&amp;</td>
<td>$1 M \text{H}_2\text{SO}_4$</td>
<td>1.44</td>
</tr>
<tr>
<td>Fe(III) + $e \rightarrow \text{Fe(II)}$</td>
<td>$1 M \text{HCl}$</td>
<td>0.70</td>
</tr>
<tr>
<td>&amp;</td>
<td>$10 M \text{HCl}$</td>
<td>0.53</td>
</tr>
<tr>
<td>&amp;</td>
<td>$1 M \text{HClO}_4$</td>
<td>0.735</td>
</tr>
<tr>
<td>&amp;</td>
<td>$1 M \text{H}_2\text{SO}_4$</td>
<td>0.68</td>
</tr>
<tr>
<td>&amp;</td>
<td>$2 M \text{H}_3\text{PO}_4$</td>
<td>0.46</td>
</tr>
<tr>
<td>Fe(CN)$_6^{3-}$ + $e \rightarrow \text{Fe(CN)}_6^{4-}$</td>
<td>$0.1 M \text{HCl}$</td>
<td>0.56</td>
</tr>
<tr>
<td>&amp;</td>
<td>$1 M \text{HCl}$</td>
<td>0.71</td>
</tr>
<tr>
<td>&amp;</td>
<td>$1 M \text{HClO}_4$</td>
<td>0.72</td>
</tr>
<tr>
<td>Sn(IV) + 2$e \rightarrow \text{Sn(II)}$</td>
<td>$1 M \text{HCl}$</td>
<td>0.14</td>
</tr>
</tbody>
</table>

In class: Cu/2n demo

Al/"Cu" demo

What is the reaction that is really happening?
How do we know?

"Scale-up" to "practical" solution

What happens when we don't have infinite resistance and current is allowed to flow?
Is this enough energy/power to run anything?

Discuss assignment 1 for Battery lab

What if our device is not at STP?

$\Delta g = \Delta g(T, P, N)$
Remember: \( \Delta G = \Delta G(T, P, N) \)

How does impact cell voltage?

\( 2H_2 + O_2 \rightarrow 2H_2O \)

2 ways to find \( \Delta G(T) \)

1. Method in SUN (attached) \( \rightarrow \Delta G_p \) method

2. Use webbook.nist.gov/chemistry
   \( \rightarrow \) NIST chemistry Webbook
   to find \( \Delta G_f(T) \) \( \rightarrow \) Then do \( \Delta G = \) Products - Reactants

This is my preferred method, but either will work

\( \Delta G \) vs T + V vs T

Excel spreadsheet attached

Also what is efficiency?

\( \eta = \frac{\Delta G}{\Delta H} \)

\( \rightarrow \) Voltage eff = \( \frac{V}{V_{in}} \)

\( \rightarrow \) Total \( \eta = \left( \frac{\Delta G}{\Delta H} \right) \left( \frac{V}{V_{in}} \right) \)

Importance? \( \rightarrow \) Later!
4.6 TEMPERATURE DEPENDENCE OF $\Delta H^\circ$

In the foregoing sections, standard heats of reaction are discussed for a reference temperature of 298.15 K. In this section we treat the calculation of standard heats of reaction at other temperatures from knowledge of the value at the reference temperature.

The general chemical reaction may be written:

$$|\nu_1|A_1 + |\nu_2|A_2 + \cdots \rightarrow |\nu_3|A_3 + |\nu_4|A_4 + \cdots$$

where $|\nu_i|$ is a stoichiometric coefficient and $A_i$ stands for a chemical formula. The species on the left are reactants; those on the right, products. The sign convention for $\nu_i$ is as follows:

positive (+) for products and negative (−) for reactants

The $\nu_i$ with their accompanying signs are called stoichiometric numbers. For example, when the ammonia synthesis reaction is written:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

then

$$\nu_{N_2} = -1 \quad \nu_{H_2} = -3 \quad \nu_{NH_3} = 2$$

This sign convention allows the definition of a standard heat of reaction to be expressed mathematically by the equation:

$$\Delta H^\circ = \sum_i \nu_i H_i^\circ$$  \hspace{1cm} (4.14)

where $H_i^\circ$ is the enthalpy of species $i$ in its standard state and the summation is over all products and reactants. The standard-state enthalpy of a chemical compound is equal to its heat of formation plus the standard-state enthalpies of its constituent elements. If the standard-state enthalpies of all elements are arbitrarily set equal to zero as the basis of calculation, then the standard-state enthalpy of each compound is its heat of formation. In this event, $H_i^\circ = \Delta H_f^\circ$ and Eq. (4.14) becomes:

$$\Delta H^\circ = \sum_i \nu_i \Delta H_f^\circ$$  \hspace{1cm} (4.15)

where the summation is over all products and reactants. This formalizes the procedure described in the preceding section for calculation of standard heats of other reactions from standard heats of formation. Applied to the reaction,

$$4HCl(g) + O_2(g) \rightarrow 2H_2O(g) + 2Cl_2(g)$$

Eq. (4.15) is written:

$$\Delta H^\circ = 2\Delta H_{H_2O}^\circ - 4\Delta H_{HCl}^\circ$$

With data from Table C.4 for 298.15 K, this becomes:

$$\Delta H_{298}^\circ = (2)(-241,818) - (4)(-92,307) = -114,408 \text{ J}$$

in agreement with the result of Ex. 4.5.
For standard reactions, products and reactants are always at the standard-state pressure of 1 bar. Standard-state enthalpies are therefore functions of temperature only, and by Eq. (2.21),

\[ dH_f^0 = C_p^0 \, dT \]

where subscript \( i \) identifies a particular product or reactant. Multiplying by \( v_i \) and summing over all products and reactants gives:

\[ \sum_i v_i \, dH_f^0 = \sum_i v_i C_p^0 \, dT \]

Since \( v_i \) is a constant, it may be placed inside the differential:

\[ \sum_i \, d(v_i H_f^0) = d \, \sum_i v_i H_f^0 = \sum_i v_i C_p^0 \, dT \]

The term \( \sum_i v_i H_f^0 \) is the standard heat of reaction, defined by Eq. (4.14) as \( \Delta H^\circ \). The standard heat-capacity change of reaction is defined similarly:

\[ \Delta C_p^\circ \equiv \sum_i v_i C_p^0 \]

As a result of these definitions, the preceding equation becomes:

\[ d \, \Delta H^\circ = \Delta C_p^\circ \, dT \]

This is the fundamental equation relating heats of reaction to temperature. Integration gives:

\[ \Delta H^\circ = \Delta H_0^\circ + R \int_{T_0}^{T} \frac{\Delta C_p^\circ}{R} \, dT \]

where \( \Delta H^\circ \) and \( \Delta H_0^\circ \) are heats of reaction at temperature \( T \) and at reference temperature \( T_0 \) respectively. If the temperature dependence of the heat capacity of each product and reactant is given by Eq. (4.4), then the integral is given by the analog of Eq. (4.7) \( (\tau \equiv T/T_0) \):

\[ \int_{T_0}^{T} \frac{\Delta C_p^\circ}{R} \, dT = (\Delta A)T_0(\tau - 1) + \frac{\Delta B}{2} T_0^2(\tau^2 - 1) + \frac{\Delta C}{3} T_0^3(\tau^3 - 1) + \frac{\Delta D}{T_0} \left( \frac{\tau - 1}{\tau} \right) \]

where by definition,

\[ \Delta A = \sum_i v_i A_i \]

with analogous definitions for \( \Delta B, \Delta C, \) and \( \Delta D. \)

An alternative formulation results when a mean heat capacity change of reaction is defined in analogy to Eq. (4.8):

\[ \frac{\langle \Delta C_p^\circ \rangle_H}{R} = \Delta A + \frac{\Delta B}{2} T_0(\tau + 1) + \frac{\Delta C}{3} T_0^2(\tau^2 + \tau + 1) + \frac{\Delta D}{\tau T_0^2} \]

Equation (4.18) then becomes:

\[ \Delta H^\circ = \Delta H_0^\circ + \langle \Delta C_p^\circ \rangle_H (T - T_0) \]
13.4 EFFECT OF TEMPERATURE ON THE EQUILIBRIUM CONSTANT

Since the standard-state temperature is that of the equilibrium mixture, the standard property changes of reaction, such as $\Delta G^\circ$ and $\Delta H^\circ$, vary with the equilibrium temperature. The dependence of $\Delta G^\circ$ on $T$ is given by Eq. (13.13), which may be rewritten:

$$\frac{d(\Delta G^\circ / RT)}{dT} = -\frac{\Delta H^\circ}{RT^2}$$

In view of Eq. (13.11b), this becomes:

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2}$$

Equation (13.14) gives the effect of temperature on the equilibrium constant, and hence on the equilibrium conversion. If $\Delta H^\circ$ is negative, i.e., if the reaction is exothermic, the equilibrium constant decreases as the temperature increases. Conversely, $K$ increases with $T$ for an endothermic reaction.

If $\Delta H^\circ$, the standard enthalpy change (heat) of reaction, is assumed independent of $T$, integration of Eq. (13.14) from a particular temperature $T'$ to an arbitrary temperature $T$ leads to the simple result:

$$\ln \frac{K}{K'} = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T} - \frac{1}{T'} \right)$$

(13.15)

This approximate equation implies that a plot of $\ln K$ vs. the reciprocal of absolute temperature is a straight line. Figure 13.2, a plot of $\ln K$ vs. $1/T$ for a number of common reactions, illustrates this near linearity. Thus, Eq. (13.15) provides a reasonably accurate relation for the interpolation and extrapolation of equilibrium-constant data.

The rigorous development of the effect of temperature on the equilibrium constant is based on the definition of the Gibbs energy, written for a chemical species in its standard state:

$$G_i^\circ = H_i^\circ - TS_i^\circ$$

Multiplication by $v_i$ and summation over all species gives:

$$\sum_i v_i G_i^\circ = \sum_i v_i H_i^\circ - T \sum_i v_i S_i^\circ$$

As a result of the definition of a standard property change of reaction, this reduces to:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

(13.16)

The standard heat of reaction is related to temperature:

$$\Delta H^\circ = \Delta H_0^\circ + R \int_{T_0}^{T} \frac{\Delta C_v^\circ}{R} dT$$

(4.18)
The temperature dependence of the standard entropy change of reaction is developed similarly. Equation (6.21) is written for the standard-state entropy of species $i$ at the constant standard-state pressure $P^*:\$

$$dS_i^o = C_i^o \frac{dT}{T}$$

Multiplying by $v_i$, summing over all species, and invoking the definition of a standard property change of reaction yields:

$$d\Delta S^o = \Delta C_P^o \frac{dT}{T}$$

Integration gives:

$$\Delta S^o = \Delta S_0^o + R \int_{T_0}^{T} \frac{\Delta C_P^o}{R} \frac{dT}{T}$$  \hspace{1cm} (13.17)

where $\Delta S^o$ and $\Delta S_0^o$ are standard entropy changes of reaction at temperature $T$ and at reference temperature $T_0$ respectively. Equations (13.16), (4.18), and (13.17) are combined to yield:

$$\Delta G^o = \Delta H_0^o + R \int_{T_0}^{T} \frac{\Delta C_P^o}{R} \frac{dT}{dT} - RT \Delta S_0^o - RT \int_{T_0}^{T} \frac{\Delta C_P^o}{R} \frac{dT}{T}$$

However,

$$\Delta S_0^o = \frac{\Delta H_0^o - \Delta G_0^o}{T_0}$$

Whence,

$$\Delta G^o = \Delta H_0^o - \frac{T}{T_0} (\Delta H_0^o - \Delta G_0^o) + R \int_{T_0}^{T} \frac{\Delta C_P^o}{R} \frac{dT}{dT} - RT \int_{T_0}^{T} \frac{\Delta C_P^o}{R} \frac{dT}{T}$$

Finally, division by $RT$ yields:

$$\frac{\Delta G^o}{RT} = \frac{\Delta G_0^o - \Delta H_0^o}{RT_0} + \frac{\Delta H_0^o}{RT} + \frac{1}{T} \int_{T_0}^{T} \frac{\Delta C_P^o}{R} \frac{dT}{dT} - \int_{T_0}^{T} \frac{\Delta C_P^o}{R} \frac{dT}{T}$$  \hspace{1cm} (13.18)

Recall that by Eq. (13.11b), $\ln K = -\Delta G^o/RT$.

When the temperature dependence of the heat capacity of each species is given by Eq. (4.4), the first integral on the right side of Eq. (13.18) is given by Eq. (4.19), represented for computational purposes by:

$$\int_{T_0}^{T} \frac{\Delta C_P^o}{R} \frac{dT}{dT} = IDCH(T_0, T; DA, DB, DC, DD)$$

where "D" denotes "Δ". Similarly, the second integral is given by the analog of Eq. (5.15):

$$\int_{T_0}^{T} \frac{\Delta C_P^o}{R} \frac{dT}{T} = \Delta A \ln \tau + \left[ \Delta B T_0 + \left( \Delta C T_0^2 + \frac{\Delta D}{\tau^2 T_0^2} \right) \left( \frac{\tau + 1}{2} \right) \right] (\tau - 1)$$  \hspace{1cm} (13.19)

where

$$\tau \equiv \frac{T}{T_0}$$
<table>
<thead>
<tr>
<th>$S$</th>
<th>$H$</th>
<th>$C$</th>
<th>$SO_2$</th>
<th>$S\text{CO}_2$</th>
<th>$H\text{CO}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Equations:**

- $S = S_{\text{standard}} - S_{\text{reaction}}$ (1)
- $H = H_{\text{standard}} - H_{\text{reaction}}$ (2)
- $C = C_{\text{initial}} - C_{\text{final}}$ (3)
- $G = G_{\text{initial}} - G_{\text{final}}$ (4)

**Notes:**

- $S_{\text{standard}}$ is the standard entropy of formation in J/K/mol.
- $H_{\text{standard}}$ is the standard enthalpy of formation in J/mol.
- $G_{\text{standard}}$ is the standard Gibbs free energy of formation in J/mol.
- $C_{\text{initial}}$ is the initial concentration in mol/L.
- $C_{\text{final}}$ is the final concentration in mol/L.

What if our reaction is not at STP?

\[ V_0 + ne^- \rightarrow V_2 R \]

\[ \Delta G = \Delta G^\circ + RT \ln \left( \frac{Q_0^{V_2}}{Q_0^{V_0}} \right) \]

\[ -nF E_{eq} = -nF E^\circ + RT \ln \left( \frac{Q_0^{V_2}}{Q_0^{V_0}} \right) \]

\[ E_{eq} = E^\circ - \frac{RT}{nF} \ln \left( \frac{Q_0^{V_2}}{Q_0^{V_0}} \right) \]

\[ E_{eq} = E^\circ + \frac{RT}{nF} \ln \left( \frac{Q_0^{V_2}}{Q_0^{V_0}} \right) \]

\[ \Rightarrow \text{Nernst Equation} \]

for liquid: \[ Q_i = Y_i C_i \]

for vapor: \[ Q_i = Y_i P_i \]

for solid: \[ Q_i = 1 \]
For liquids:

\[ E_{eq} = E^o + \frac{RT}{nF} \ln \left( \frac{y_0^v y_0^c}{y_2^v y_2^c} \right) \]

\[ E_{eq} = E^o + \frac{RT}{nF} \ln \left( \frac{y_0^v y_0^c}{y_2^v y_2^c} \right) + \frac{RT}{nF} \ln \left( \frac{c_0^v c_0^c}{c_2^v c_2^c} \right) \]

\[ E^{0i} \equiv \text{Formal Potential} \]

\[ E^{0i} = E^o + \frac{RT}{nF} \ln \left( \frac{y_0^v y_0^c}{y_2^v y_2^c} \right) \]

When \( y_0 = y_2 = 1 \):

\[ E^{0i} = E^o \Rightarrow \text{Common Assumption!} \]

\[ E_{eq} = E^{0i} + \frac{RT}{nF} \ln \left( \frac{c_0^v c_0^c}{c_2^v c_2^c} \right) \]

Most Common Form of the Nernst Equation!

[relate to Al/Air cell] \[ [\text{O}_2] \approx 2 \times 10^{-4} \text{ M} \]

[Al(III)] \approx \text{very low} \text{ (initially ~0)}
Example:

\[
Fe^{3+} + e^- \rightleftharpoons Fe^{2+}
\]

\[
V_{eq} \quad 0 \to Fe^{3+}, \quad V_0 = 1
\]
\[
R \to Fe^{2+}, \quad V_R = 1
\]

\[
E_{eq} = E^o + \frac{RT}{nF} \ln \left( \frac{[Fe^{3+}]}{[Fe^{2+}]} \right)
\]

If we assume: \( V_0 = V_R = 1 \)

\[
E_{eq} = E^o
\]

\[
E_{eq} = 0.77V + \frac{RT}{nF} \ln \left( \frac{[Fe^{3+}]}{[Fe^{2+}]} \right)
\]

Example 2: \( Fe^{2+} + 2e^- \rightleftharpoons Fe(s) \)

Assume \( \delta_s = 1 \)

\[
E_{eq} = \boxed{E^o + \frac{RT}{nF} \ln \left( \frac{Q_{Fe^{2+}}}{Q_{Fe}} \right)}
\]

\[
E_{eq} = E^o + \frac{RT}{nF} \ln Q_{Fe^{2+}} = E^o + \frac{RT}{nF} \ln (\Delta _{Fe^{2+}} C_{Fe^{2+}})
\]

\[
E_{eq} = E^o + \frac{RT}{nF} \ln \left[ Fe^{2+} \right]
\]

\[
E_{eq} = -0.44 + \frac{RT}{nF} \ln \left[ Fe^{2+} \right]
\]