Thermodynamics of electrochemical systems

Thermodynamics, the science of possibilities is of general utility. The well established methods of thermodynamics may be readily applied to electrochemical cells. We can readily compute thermodynamic state functions such as $\Delta G$, $\Delta H$ and $\Delta S$ for a chemical reaction by determining how the open circuit cell potential $E_{\text{cell}}$ varies with solution temperature.

We can compute the thermodynamic efficiency of a fuel cell provided that $\Delta G$ and $\Delta H$ for the cell reaction can be evaluated.

We can also use measurements of equilibrium cell potentials to determine the concentration of a redox active substance present at the electrode/solution interface. This is the basis for potentiometric chemical sensing.
Standard Electrode Potentials

Standard reduction potential ($E^0$) is the voltage associated with a reduction reaction at an electrode when all solutes are 1 M and all gases are at 1 atm.

Reduction Reaction

\[ 2e^- + 2H^+ (1 \text{ M}) \rightarrow 2H_2 (1 \text{ atm}) \]

\[ E^0 = 0 \text{ V} \]

Standard hydrogen electrode (SHE)

Measurement of standard redox potential $E^0$ for the redox couple $A(aq)/B(aq)$.

$E^0$ provides a quantitative measure for the thermodynamic tendency of a redox couple to undergo reduction or oxidation.
We should recall from our CH1101 electrochemistry lectures that any combination of two redox couples may be used to fabricate a galvanic cell. This facility can then be used to obtain useful thermodynamic information about a cell reaction which would be otherwise difficult to obtain. Herein lies the usefulness of electrochemical thermodynamics.

Given any two redox couples A/B and P/Q we can readily use tables of standard reduction potentials to determine which of the two couples is preferentially reduced. Once this is known the galvanic cell can be constructed, the net cell potential can be evaluated, and knowing this useful thermodynamic information can be obtained for the cell reaction.

The procedure is simple to apply. One determines the couple with the most positive standard reduction potential (or the most positive equilibrium potential $E_E$ determined via the Nernst equation if the concentrations of the reactants differ from 1 mol dm$^{-3}$). This couple will undergo reduction at the cathode. The other redox couple will consequently undergo oxidation at the anode. This information can also be used to determine the direction of electron flow, for upon placing a load on the cell electrons will flow out of the anode because of the occurrence of a spontaneous de-electronation (otherwise known as oxidation or electron loss) reaction, through the external circuit and into the cathode causing a spontaneous electronation (aka reduction or electron gain) reaction to occur. Hence in a driven cell the anode will be the negative pole of the cell and the cathode the positive pole. Now according to the IUPAC convention if the cell reaction is spontaneous the resultant cell potential will be positive. We ensure that such is the case by writing the cathode reaction on the rhs, and the anode reaction on the lhs of the cell diagram. Then since $E_E$ is more positive that $E_{cell}$ a positive cell potential $V_e$ will be guaranteed.

### Table 19.1 Standard Reduction Potentials at 25°C

<table>
<thead>
<tr>
<th>Half-Reaction</th>
<th>$E^\circ$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$</td>
<td>-0.77</td>
</tr>
<tr>
<td>$\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}$</td>
<td>-2.87</td>
</tr>
<tr>
<td>$\text{Cu}^{2+} + e^- \rightarrow \text{Cu}$</td>
<td>1.35</td>
</tr>
<tr>
<td>$\text{Ag}^+ + e^- \rightarrow \text{Ag}$</td>
<td>0.80</td>
</tr>
<tr>
<td>$\text{H}^+ + e^- \rightarrow \text{H}_2$</td>
<td>-0.00</td>
</tr>
<tr>
<td>$\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$</td>
<td>-1.23</td>
</tr>
</tbody>
</table>

### Standard electrode potential

- $E^\circ$ is for the reaction as written
- The more positive $E^\circ$ the greater the tendency for the substance to be reduced
- The half-cell reactions are reversible
- The sign of $E^\circ$ changes when the reaction is reversed
- Changing the stoichiometric coefficients of a half-cell reaction does not change the value of $E^\circ$
When a spontaneous reaction takes place in a galvanic cell, electrons are deposited in one electrode (the site of oxidation or anode) and collected from another (the site of reduction or cathode), and so there is a net flow of current which can be used to do electrical work $W_e$.

- From thermodynamics we note that maximum electrical work done at constant temperature and pressure $W_e$ is equal to the change in Gibbs free energy $\Delta G$ for the net cell reaction.
- We use basic physics to evaluate the electrical work $W_e$ done in moving $n$ mole electrons through a potential difference of $E_{\text{cell}}$.

\[
W_e = q E_{\text{cell}} = -n e E_{\text{cell}} 
\]

Relation between thermodynamics of cell reaction and observed cell potential

\[
\Delta G = W_e = -n e N_A E_{\text{cell}} = -n F E_{\text{cell}}
\]

$E_{\text{cell}} = E_{\text{HIS}}^0 - E_{\text{LHS}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0$
We subtract the two reactions to obtain the following result.

\[ mA - nP \rightarrow mB - nQ \]
\[ mA + nQ \rightarrow mB + nP \]

To proceed we subtract the corresponding thermodynamic state functions.

In this case \( \Delta G^0 \):

\[
\Delta G_{\text{cell}}^0 = m \Delta G_{A,B}^0 - n \Delta G_{P,Q}^0 = m \left( -nF E_A^0 \right) - \left( -mF E_P^0 \right) = -nmF \left( E_A^0 - E_P^0 \right) = -nmF E_{\text{cell}}^0
\]

Note that \( nm \) denotes the number of electrons transferred per mole of reaction as written.

Net Cell Reaction:

\[
\begin{align*}
A + ne^- & \rightarrow B & \text{ Cathode} \\
P & \rightarrow Q + me^- & \text{ Anode}
\end{align*}
\]

\[ mA + nP \rightarrow mB + nQ \]

The establishment of equilibrium does not imply the cessation of redox activity at the interface. The condition of equilibrium implies an equality in the electrochemical potentials of the transferring species in the two phases and in the establishment of a compensating two way flow of charge across the interface resulting in a definite equilibrium potential difference \( \Delta \phi_e \) or \( E_e \). A single equilibrium potential difference may not be measured. Instead a potential is measured between two electrodes (a test or indicator electrode and a reference electrode). This is a potentiometric measurement.

The potential of the indicator electrode is related to the activities of one or more of the components of the test solution and it therefore determines the overall equilibrium cell potential \( E_e \). Under ideal circumstances, the response of the indicator electrode to changes in analyte species activity at the indicator electrode/solution interface should be rapid, reversible and governed by the Nernst equation. The ET reaction involving the analyte species should be kinetically facile and the ratio of the analyte/product concentration should depend on the interfacial potential difference via the Nernst equation.
In a potentiometric measurement two electrodes are used. These consist of the indicator or sensing electrode, and a reference electrode. Electroanalytical measurements relating potential to analyte concentration rely on the response of one electrode only (the indicator electrode). The other electrode, the reference electrode is independent of the solution composition and provides a stable constant potential. The open circuit cell potential is measured using a potential measuring device such as a potentiometer, a high impedance voltmeter or an electrometer.

**Equilibrium condition between phases: chemical potential.**

It is well known from basic chemical thermodynamics that if two phases \( \alpha \) and \( \beta \) with a common uncharged species \( j \), are brought together, then the tendency of species \( j \) to pass from phase \( \alpha \) to phase \( \beta \) will be determined by the difference \( \Delta \mu \) in the chemical potential between the two phases. The condition for equilibrium is

\[
\Delta \mu_j = \mu_j(\alpha) - \mu_j(\beta) = 0
\]

The standard thermodynamic definition of the chemical potential is:

\[
\mu_j(\alpha) = \frac{\partial G}{\partial n_j} \Bigg|_{n_{j,\alpha}, T}
\]

Alternatively we can view the chemical potential of a species \( j \) in a phase \( \alpha \) as a measure of the work that must be done for the reversible transfer of one mole of uncharged species \( j \) from the gaseous state of unit fugacity (the reference state) into the bulk of phase \( \alpha \).

In electrochemistry we deal with charged species and charged phases.
Electrochemical Activity

We consider the work done \( W \), in transferring a species \( i \) from the interior of a standard phase to the interior of the phase of interest. We also assume that the species \( i \) has a charge \( q_i = z_i e \).

The electrochemical activity can be defined in the following manner.

\[
\pi_i = a_i \exp \left( \frac{q_i \phi - \phi_0}{k_B T} \right) = a_i \exp \left( \frac{z_i F \phi - \phi_0}{k_B T} \right) = \exp \left( \frac{W_i}{k_B T} \right)
\]

In the latter expression \( a_i \) represents the activity of species \( i \).

If two phases \( \alpha \) and \( \beta \) contain a species \( i \) with different electrochemical activities such that the electrochemical activity of species \( i \) in phase \( \beta \) is greater than that of phase \( \alpha \) then there is a tendency for species \( i \) to leave phase \( \beta \) and enter phase \( \alpha \).

The driving force for the transport of species \( i \) is the difference in electrochemical activity between the two phases.

Now from the definition of electrochemical activity

\[
\pi_i(\beta) = a_i(\beta) \exp \left( \frac{z_i F \phi - \phi_0}{k_B T} \right)
\]

\[
\pi_i(\alpha) = a_i(\alpha) \exp \left( \frac{z_i F \phi - \phi_0}{k_B T} \right)
\]

Hence

\[
\frac{\pi_i(\beta)}{\pi_i(\alpha)} = \frac{a_i(\beta)}{a_i(\alpha)} \exp \left( \frac{z_i F \phi}{k_B T} \right)
\]

We can follow the lead of Lewis and introduce the difference in electrochemical potential as follows.

\[
\Delta \pi_i = \Delta \pi_i(\beta) - \Delta \pi_i(\alpha)
\]

Hence the difference in electrochemical potential is split up into two distinct components: first, the difference in chemical potential \( \Delta \mu \), and second the difference in electrical potential \( \Delta \phi \).

Hence we note that the electrochemical potential is defined as the work required to transfer 1 mole of charged species from infinity in vacuum into a material phase. This work consists of three separate terms. The first constitutes a chemical term which includes all short range interactions between species (such as an ion) and its environment (ion/dipole interaction, ion/induced dipole interactions, dispersion forces etc.). This constitutes the chemical potential term \( \mu_i \).

The second constitutes an electrostatic term linked to the crossing of the layer of oriented interfacial dipoles (\( z_i F \phi_\alpha \)).

The third constitutes an electrostatic term linked to the charge of the phase (\( z_i F \phi_\beta \)).

The outer potential \( \gamma \) is the work done in bringing a test charge from infinity up to a point outside a phase where the influence of short range image forces can be neglected.

The surface potential \( \kappa \) defines the work done to bring a test charge across the surface layer of oriented dipoles at the interface.

Hence the inner Galvani potential \( \phi \) is then defined as the work done to bring the test charge from infinity to the inside of the phase in question and so we define:

\[
\phi = \gamma + \kappa
\]
In electrochemistry we deal with charged species and charged phases, and one introduces the idea of the electrochemical potential which is defined as the work expended in transferring one mole of charged species \( j \) from a given reference state at infinity into the bulk of an electrically charged phase.

\[
\bar{\mu}_j = \mu_j + z_j F \phi = \mu_j + z_j F (\chi + \psi)
\]

\[
= \mu_j^0 + RT \ln a_j + z_j F \phi
\]

It is sometimes useful to separate the electrochemical potential into chemical and electrical components as follows.

\[
\bar{\mu}_j = \mu_j + z_j F \phi = \mu_j + q \phi
\]

Equilibrium involving charged species transfer between two adjacent phases is attained when no difference exists between the electrochemical potentials of that species in the two phases.
Rigorous Analysis of Electrochemical Equilibrium

When two phases come into contact the electrochemical potentials of the species in each phase equate. For equilibrium at metal/solution interface the electrochemical potential of the electron in both phases equate.

Before Contact
\[ \mu^0_e(\alpha) = \mu^0_e(\beta) \]

After Contact
\[ \mu^0_e(\alpha) = \mu^0_e(\beta) \]

Via process of Charge transfer
\[ \mu^0_e(\alpha) = \mu^0_e(\beta) \]

The Nernst Equation

We consider the following ET reaction.
\[ \text{Ox}^{z_{\text{Ox}}} + ne^- \rightarrow \text{Red}^{z_{\text{Red}}} \]

At equilibrium
\[ \mu_e(\beta) = \mu_e(\alpha) = \mu_e^0(\beta) + RT \ln \frac{a_e(\beta)}{a_e(\alpha)} = \mu_e^0(\beta) + RT \ln \frac{a_e(\beta)}{a_e(\alpha)} \]

Simplifying we get
\[ n \mu_e(\beta) = \mu_e^0(\beta) - \mu_e^0(\beta) + RT \ln \frac{a_e(\beta)}{a_e(\alpha)} = nF \phi \]

Hence
\[ \mu_e(\beta) = \mu_e^0(\beta) + RT \ln \frac{a_e(\beta)}{a_e(\alpha)} = \mu_e(\alpha) = \mu_e^0(\beta) + RT \ln \frac{a_e(\beta)}{a_e(\alpha)} \]

Simplifying we get
\[ \mu_e^0(\beta) - \mu_e^0(\beta) + RT \ln \frac{a_e(\beta)}{a_e(\alpha)} = \mu_e(\beta) - \mu_e(\alpha) = F(\phi - \phi_e) \]

This is the Nernst Equation.
We recall that the Gibbs energy $G$ is used to determine whether a chemical reaction proceeds spontaneously or not. We consider the gas phase reaction $A(g) \rightarrow B(g)$. We let $\xi$ denote the extent of reaction. Clearly $0 < \xi < 1$. When $\xi = 0$ we have pure $A$ and when $\xi = 1$ we have 1 mol $A$ destroyed and 1 mol $B$ formed. Also $dn_A = -d\xi$ and $dn_B = +d\xi$ where $n$ denotes the quantity (mol) of material used up or formed. By definition the change in Gibbs energy $dG$ at constant $T$ and $P$ is related to the chemical potential $\mu$ as follows:

$$dG = \mu_A dn_A + \mu_B dn_B$$
$$= -\mu_A d\xi + \mu_B d\xi = (\mu_B - \mu_A) d\xi$$

Furthermore

$$dG = \left( \frac{\partial G}{\partial \xi} \right)_{P,T} d\xi$$

Hence we get from eqn. 1 and 2

$$\left( \frac{\partial G}{\partial \xi} \right)_{P,T} = \Delta_r G = \mu_B - \mu_A$$

In the latter the symbol $\Delta = \left( \frac{\partial G}{\partial \xi} \right)_{P,T}$

$\Delta_r G =$ reaction Gibbs free energy

Since $\mu_j$ varies with composition, then so also does $\Delta_r G$.

### Review of Thermodynamics

We recall that the Gibbs energy $G$ is used to determine whether a chemical reaction proceeds spontaneously or not. We consider the gas phase reaction $A(g) \rightarrow B(g)$. We let $\xi$ denote the extent of reaction. Clearly $0 < \xi < 1$. When $\xi = 0$ we have pure $A$ and when $\xi = 1$ we have 1 mol $A$ destroyed and 1 mol $B$ formed. Also $dn_A = -d\xi$ and $dn_B = +d\xi$ where $n$ denotes the quantity (mol) of material used up or formed. By definition the change in Gibbs energy $dG$ at constant $T$ and $P$ is related to the chemical potential $\mu$ as follows:

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### Reaction Gibbs energy

$\Delta_r G = \left( \frac{\partial G}{\partial \xi} \right)_{P,T}$

extent of reaction $= \xi$

$\Delta_r G$ is the slope of the $G$ versus $\xi$ graph at any degree of advancement $\xi$ of the chemical reaction.
If $\mu_A > \mu_B$ then $A \rightarrow B$ is spontaneous and $\Delta_rG$ is negative.
If $\mu_A > \mu_B$ then $B \rightarrow A$ is spontaneous and $\Delta_rG$ is positive.
If $\mu_A = \mu_B$ then $\Delta_rG = 0$ and chemical equilibrium has been achieved.

Since $A$ and $B$ are ideal gases then we write

$$
\mu_A = \mu_A^0 + RT \ln \frac{P_A}{P_A^0}
$$

$$
\mu_B = \mu_B^0 + RT \ln \frac{P_B}{P_B^0}
$$

$$
\mu_A - \mu_B = \mu_B^0 - \mu_A^0 + RT \ln \left( \frac{P_A}{P_A^0} \right) - RT \ln \left( \frac{P_B}{P_B^0} \right)
$$

$$
= \mu_B^0 - \mu_A^0 + RT \ln \left( \frac{P_A}{P_B} \right)
$$

$$
= \Delta_rG + RT \ln Q_R
$$

$$
\Delta_rG = \Delta_rG^0 + RT \ln Q_R
$$

At equilibrium $Q_R = K$ and $\Delta_rG = 0$

$$
\Delta_rG = -RT \ln K
$$

Gibbs energy and chemical equilibrium.

Reaction not spontaneous
In forward direction

$P \rightarrow R$

$\Delta G < 0$

Equilibrium $Q = K$

Q large, $Q > K$
$[P] >> [R]$
$\Delta G$ positive

Q small, $Q < K$
$[P] << [R]$
$\Delta G$ negative

Standard state
$Q = 1$
$\ln Q = 0$

$R \rightarrow P$

Reaction spontaneous
In forward direction

$\Delta G^0 + RT \ln Q$

$\Delta G = \Delta G^0 + RT \ln Q_R$
The expression just derived for the special case $A \to B$
can also be derived more generally. If we set $n_j$ as the
stoichiometric coefficient of species $j$ (negative for reactants and positive for
products, we can derive the following.

$$dG = \sum_j v_j \mu_j d\xi = \left(\frac{\partial G}{\partial \xi}\right)_{\xi, T} d\xi$$

$$\Delta_G = \left(\frac{\partial G}{\partial \xi}\right)_{\xi, T} = \sum_j v_j \mu_j$$

We can relate chemical potential $\mu_j$ to activity $a_j$ as follows.

$$\mu_j = \mu_j^0 + RT \ln a_j$$

In the latter we have introduced the following definitions.

$$Q_s = \prod_j a_j^{v_j}$$

$$\sum_j \ln a_j^{v_j} = \ln \left\{ \prod_j a_j^{v_j} \right\}$$

Again at equilibrium

$$\Delta_G = 0$$

$$Q_s = K$$

$$\Delta_G^0 = -RT \ln K$$

$$K = \prod_j a_j^{v_j}$$

$$\Delta_G^0 = \sum_j v_j \Delta_j G^0$$

Standard free energy

$\text{of formation of species } j.$

Potentiometric Measurements

We now mention the practicalities of conducting a potentiometric
measurement. A two electrode electrochemical cell is used. This
consists of a reference electrode and an indicator electrode. The object of
the exercise is to make a measurement of the equilibrium cell potential
without drawing any significant current since we note that the
equilibrium cell potential is defined as $E = \Delta \phi_{i \to 0}$ where $\Delta \phi$ denotes the
Galvani potential difference measured between the cell terminals. This
objective is achieved either using a null detecting potentiometer or a high
impedance voltmeter.
The second measurement protocol involves use of an electrometer. The latter is based on a voltage follower circuit. A voltage follower employs an operational amplifier. The amplifier has two input terminals called the summing point S (or inverting input) and the follower input F (or non-inverting input). Note that the positive or negative signs at the input terminals do not reflect the input voltage polarity but rather the non-inverting and inverting nature respective of the inputs. Now the fundamental property of the operational amplifier is that the output voltage \( V_o \) is the inverted, amplified voltage difference \( V_i \) where \( V_i = V_o - V \), denotes the voltage of the inverting input with respect to the non inverting input. Hence we can write that

\[
V_o = -AV_i + AV_+ = -AV_i
\]

In the latter \( A \) denotes the open loop gain of the amplifier. Although ideally \( A \) should be infinite it will typically be \( 10^5 \).

\[
V_o = -AV_i = -A(V_o - V_i)
\]

\[
V_o = \frac{V_i}{1 + \frac{1}{A}} \approx V_i
\]

Also ideally the amplifier should exhibit an infinite input impedance so that they can accept input voltages without drawing any current from the voltage source. This is why we can measure a voltage without any perturbation. In practice the input impedance will be large but finite (typically \( 10^5 \Omega \)). An ideal amplifier should also be able to supply any desired current to a load. The output impedance should be zero. In practice amplifiers can supply currents in the mA range although higher current output can also be achieved.

Keeping these comments in mind we can now discuss the operation of the voltage follower circuit presented. In this configuration the entire output voltage is returned to the inverting input. If \( V_i \) represents the input voltage then we see from the analysis outlined across that the circuit is called a voltage follower because the output voltage is the same as the input voltage. The circuit offers a very high input impedance and a very low output impedance and can therefore be used to measure a voltage without perturbing the voltage significantly.

The Nernst equation.

The potential developed by a Galvanic cell depends on the composition of the cell.

From thermodynamics the Gibbs energy change for a chemical reaction \( \Delta G \) varies with composition of the reaction mixture in a well defined manner. We use the relationship between \( \Delta G \) and \( E \) to obtain the Nernst equation.

\[
\Delta_G = -nFE \ \ \ \ \ \Delta_G^0 = -nFE^0
\]

\[
-nFE = -nFE^0 + RT \ln Q_R
\]

\[
E = E^0 - \frac{RT}{nF} \ln Q_R
\]

\[
E = E^0 - \frac{0.0592}{n} \log Q_R
\]

RT/F = 25.7 mV
At T = 298 K

\[
Q_R \approx \frac{[\text{products}]}{[\text{reactants}]}
\]

Nernst eqn. holds for single redox couples and net cell reactions.

Walther Hermann Nernst

The Nernst equation.
Determination of thermodynamic parameters from $E_{\text{cell}}$ vs temperature data.

Measurement of the zero current cell potential $E$ as a function of temperature $T$ enables thermodynamic quantities such as the reaction enthalpy $\Delta H$ and reaction entropy $\Delta S$ to be evaluated for a cell reaction.

Gibbs-Helmholtz eqn.

\[
\Delta H = \Delta G - T \left( \frac{\partial \Delta G}{\partial T} \right)_p
\]

\[
\Delta G = -nFE
\]

\[
\Delta H = -nFE - T \left( \frac{\partial (-nFE)}{\partial T} \right)_p
= -nFE + nFT \left( \frac{\partial E}{\partial T} \right)_p
\]

\[
\Delta H = -nF \left( E - T \frac{\partial E}{\partial T} \right)_p
\]

Temperature coefficient of zero current cell potential obtained from experimental $E$ vs $T$ data. Typical values lie in range $10^{-4} - 10^{-5}$ VK$^{-1}$.
• Once $\Delta H$ and $\Delta G$ are known then $\Delta S$ may be evaluated.

\[
\Delta_r G = \Delta_r H - T \Delta_r S \\
\Delta_r S = \frac{\Delta_r H - \Delta_r G}{T} \\
\frac{\Delta_r S}{T} = \frac{1}{T} \left\{ -n F E + n F T \left( \frac{\partial E}{\partial T} \right)_P + n F E \right\} \\
\Delta_r S = n F \left( \frac{\partial E}{\partial T} \right)_P
\]

• Electrochemical measurements of cell potential conducted under conditions of zero current flow as a function of temperature provide a sophisticated method of determining useful thermodynamic quantities.

**Fundamentals of potentiometric measurement: the Nernst Equation.**

The potential of the indicator electrode is related to the activities of one or more of the components of the test solution and it therefore determines the overall equilibrium cell potential $E_e$. Under ideal circumstances, the response of the indicator electrode to changes in analyte species activity at the indicator electrode/solution interface should be rapid, reversible and governed by the Nernst equation. The ET reaction involving the analyte species should be kinetically facile and the ratio of the analyte/product concentration should depend on the interfacial potential difference via the Nernst equation.
Hydrogen/oxygen fuel cell

Anode reaction

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

H$_2$O$_2$ fuel cell

H$^+$ ion Conducting membrane

Cathode reaction

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

Δ$G = -nF\Delta E_{eq,cell}$

$E_{eq,cell} = E_{eq,C} - E_{eq,A}$

Ballard PEM Fuel Cell.
Efficiency of fuel cell (I).

\[ \Delta G = -nFE_{\text{eq,cell}} \]
\[ E_{\text{eq,cell}} = E_{\text{eq,C}} - E_{\text{eq,A}} \]

Efficiency \( \varepsilon = \frac{\text{work output}}{\text{heat input}} \)

For electrochemical or 'cold' combustion:
Heat input \( \rightarrow \) enthalpy change \( \Delta H \) for cell reaction
Work output \( \rightarrow \) Gibbs energy change \( \Delta G \) for cell reaction

\[ \varepsilon_{\text{max}} = \frac{\Delta G}{\Delta H} = \frac{\Delta H - T\Delta S}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H} \]

\[ \varepsilon_{\text{max}} = -\frac{nFE_{\text{eq,cell}}}{\Delta H} \]

Usually
\[ \Delta_r G \approx \Delta_r H \]
\[ \varepsilon \approx 1 \]

\[ \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O} (l) \]
\[ \Delta G^0 = -56.69 \text{ kcal mol}^{-1}; \]
\[ \Delta H^0 = -68.32 \text{ kcal mol}^{-1} \]

\[ n = 2, E_{\text{eq}} = 1.229 \text{ V, } \varepsilon = 0.830. \]

Efficiency of fuel cell (II).

• For all real fuel cell systems terminal cell potential \( E \) does not equal the equilibrium value \( E_{\text{eq}} \), but will be less than it.

• Furthermore \( E \) will decrease in value with increasing current drawn from the fuel cell.

\[ \varepsilon_{\text{real}} = -\frac{nFE_{\text{cell}}}{\Delta H} = -\frac{nF(E_{\text{eq}} - \sum |\eta|)}{\Delta H} \]

• This occurs because of:
  - Slowness of one or more intermediate steps of reactions occurring at one or both electrodes.
  - Slowness of mass transport processes either reactants to, or products from, the electrodes.
  - Ohmic losses through the electrolyte.

\[ \text{Sum of all overpotential Losses.} \]
Nernst Equation involving both an electron and proton transfer.

We consider the following reaction which involves both the transfer of m protons and n electrons. This is a situation often found in biochemical and organic reactions.

\[ A + mH^+ + ne^- \rightarrow B \]

The Nernst equation for this type of proton/electron transfer equilibrium is given by the following expression.

\[ E = E^0 - \frac{RT}{nF} \ln \left( \frac{a_y}{a_y^0} \right) \]

This expression can be readily simplified to the following form

\[ E = E^0 - \frac{2.303RT}{nF} \ln \left( \frac{a_y}{a_y^0} \right) - 2.303 \frac{mRT}{F} \frac{pH}{n} \]

Hence we predict that a Nernst plot of open circuit or equilibrium Potential versus solution pH should be linear with a Nernst slope \( S_n \) whose value is directly related to the redox stoichiometry of the redox reaction through the \( \frac{m}{n} \) ratio.

When \( m = n \) then we predict that \( S_n = -\frac{2.303RT}{F} \left( \frac{m}{n} \right) \) Which is close to 60 mV per unit change in pH at 298 K.

Membrane Potential

Since we are considering charged species we define equilibrium in terms of equality of electrochemical potentials:

\[ \Pi(a) = \Pi(b) \]
\[ \mu_i(a) + z_iF\phi = \mu_i(b) + z_iF\phi_i \]
\[ \Delta \mu_{\text{geo}} = \phi_i - \phi > 0 \]
\[ a_i(a) > a_i(b) \]
\[ \phi_i < \phi \]

Now
\[ \mu_i(a) = \mu_i^0(a) + RT \ln a_i(a) \]
\[ \mu_i(b) = \mu_i^0(b) + RT \ln a_i(b) \]

Hence
\[ z_iF(\phi_i - \phi) = z_iF(\phi_i - \phi) = \mu_i(a) - \mu_i(b) \]
\[ \phi_i = \phi + \frac{RT}{z_iF} \ln \left( \frac{a_i(a)}{a_i(b)} \right) \]

\( \Delta \phi \) is the electric potential necessary to prevent equalization of ionic activities by diffusion across the membrane.

Now if we assume that \( \mu_i^0(a) = \mu_i^0(b) \)

We get the final expression for the membrane potential

\[ \Delta \phi_m = \frac{RT}{z_iF} \ln \left( \frac{a_i(a)}{a_i(b)} \right) \]

Of course a similar result for the membrane potential can be obtained by equalizing the ratio of electrochemical activities and noting that the following pertains.