$$ {}^{\alpha}\Delta^{\beta}\mu = \mu_j(\alpha) - \mu_j(\beta) = 0 $$
$$ \mu_j(\alpha) = \mu_j(\beta) $$

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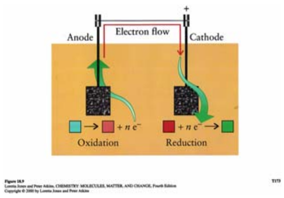
Physical and Interfacial Electrochemistry 2013

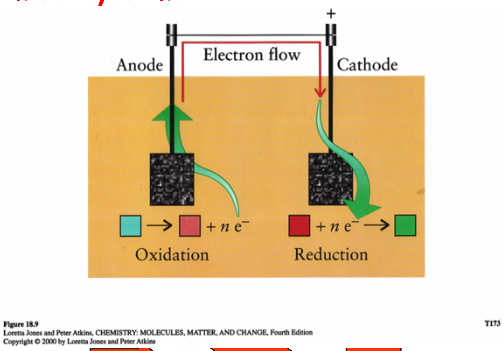


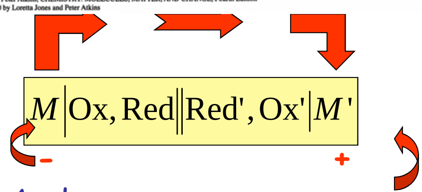
Lecture 4.
Electrochemical Thermodynamics

Module JS CH3304 MolecularThermodynamics and Kinetics

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 ΔG, ΔH and ΔS for a chemical reaction by determining how the open circuit cell potential E_{cell} varies with solution temperature. We can compute the thermodynamic efficiency of a fuel cell provided that ΔG and ΔH 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.



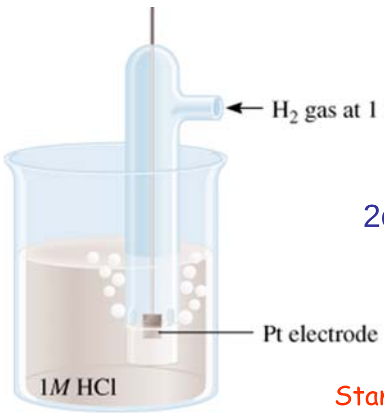


Anode
Oxidation
e^- loss
LHS

Cathode
Reduction
e^- gain
RHS

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.



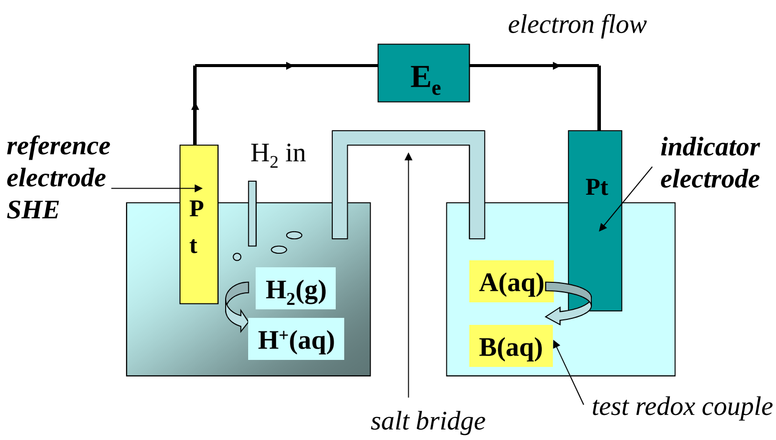
Reduction Reaction

$$2e^- + 2H^+ (1\ M) \longrightarrow 2H_2\ (1\ atm)$$

$$E^0 = 0\ V$$

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.

Table 19.1 Standard Reduction Potentials at 25°C*

Half-Reaction	$E°$(V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O$	+2.07
$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$	+1.70
$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.50
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O$	+1.23
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$	+0.96
$2Hg^{2+}(aq) + 2e^- \longrightarrow Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow SO_2(g) + 2H_2O$	+0.20
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	−0.28
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.76
$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \longrightarrow Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.66
$Be^{2+}(aq) + 2e^- \longrightarrow Be(s)$	−1.85
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \longrightarrow Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	−2.90
$K^+(aq) + e^- \longrightarrow K(s)$	−2.93
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.05

Increasing strength as oxidizing agent (↑)

Increasing strength as reducing agent (↓)

* For all half-reactions the concentration is 1 M for dissolved species and the pressure is 1 atm for gases. These are the standard-state values.

Standard electrode potential

- *E^0* is for the reaction as written
- The more positive *E^0* the greater the tendency for the substance to be reduced
- The half-cell reactions are reversible
- The sign of *E^0* changes when the reaction is reversed
- Changing the stoichiometric coefficients of a half-cell reaction ***does not*** change the value of *E^0*

19.3

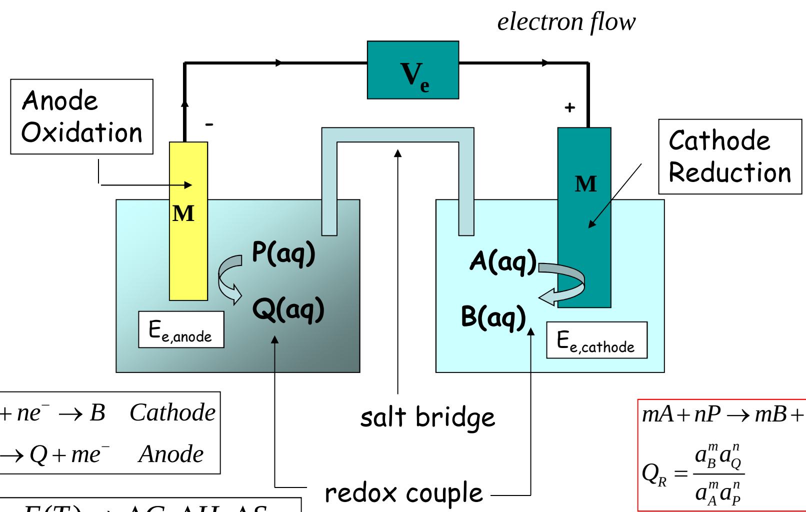
We should recall from our CH1101 electrochemistry lectures that any combination of two redox couples may be used to fabricate a galvanic cell . This facility can then be used to obtain useful thermodynamic information about a cell reaction which would be otherwise difficult to obtain. Herein lies the 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 $E_{e,rhs}$ is more positive than $E_{e,lhs}$ a positive cell potential V_e will be guaranteed

$$A + P \rightarrow B + Q$$

$$E^0_{cell} = E^0_{RHS} - E^0_{LHS} = E^0_{cathode} - E^0_{anode}$$



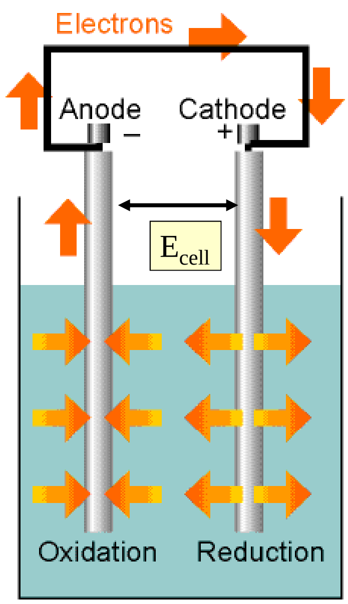
$A + ne^- \rightarrow B$ *Cathode*

$P \rightarrow Q + me^-$ *Anode*

$$E = E(T) \Rightarrow \Delta G, \Delta H, \Delta S, \varepsilon$$

$$mA + nP \rightarrow mB + nQ$$

$$Q_R = \frac{a_B^m a_Q^n}{a_A^m a_P^n}$$



- 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 ΔG 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_{cell}.

1 electron : $W_e = q\,E_{cell} = -e\,E_{cell}$

1 mole electrons : $W_e = -N_A e\,E_{cell}$

n mole electrons : $W_e = -n\,N_A\,e\,E_{cell}$

$\Delta G = W_e$

Relation between thermodynamics of cell reaction and observed cell potential

$$\Delta G = W_e = -n\,e\,N_A\,E_{cell} = -n\,F\,E_{cell}$$

$$A + ne^- \rightarrow B \quad E^0(A,B)$$

$$P + me^- \rightarrow Q \quad E^0(P,Q)$$

$$mA + mne^- \rightarrow mB$$

$$nP + nme^- \rightarrow nQ$$

We assume that $E^0_{A,B}$ is more positive than $E^0_{P,Q}$ and so is assigned as the cathode reaction.

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 ΔG^0

$$\Delta G_{cell}^{\ 0} = m\Delta G^0_{A,B} - n\Delta G^0_{P,Q} = m\left(-nFE^0_{A,B}\right) - \left(-mFE^0_{P,Q}\right) = -nmF\left\{E^0_{A,B} - E^0_{P,Q}\right\} = -nmFE^0_{cell}$$

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

Net Cell Reaction

$$A + ne^- \rightarrow B \quad Cathode$$
$$P \rightarrow Q + me^- \quad Anode$$

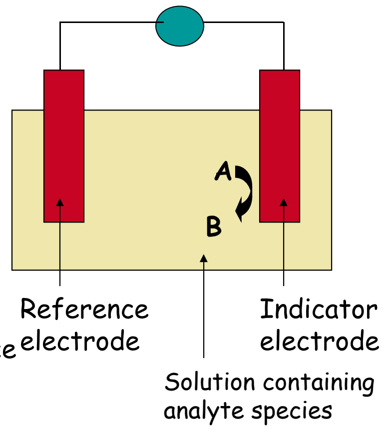
$$mA + nP \rightarrow mB + nQ$$
$$Q_R = \frac{a_B^m a_Q^n}{a_A^m a_P^n}$$

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.

The potentiometric measurement.

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 voltameter or an electrometer.



Equilibrium condition between phases: chemical potential.

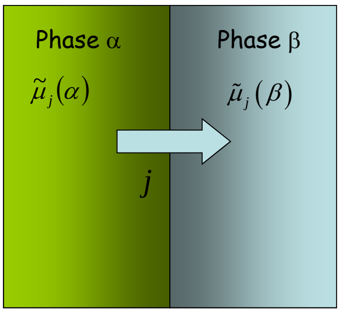
It is well known from basic chemical thermodynamics that if two phases α and β with a common *unchanged* species j, are brought together, then the tendency of species j to pass from phase α to phase β will be determined by the difference ${}^{\alpha}\Delta^{\beta}\mu$ in the chemical Potential between the two phases. The condition for equilibrium is

$$^{\alpha}\Delta^{\beta}\mu = \mu_j(\alpha) - \mu_j(\beta) = 0$$
$$\mu_j(\alpha) = \mu_j(\beta)$$

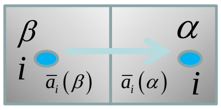
The standard thermodynamic definition of the chemical potential is:

$$\mu_j(\alpha) = \left(\frac{\partial G}{\partial n_j}\right)_{n_k, P, T}$$

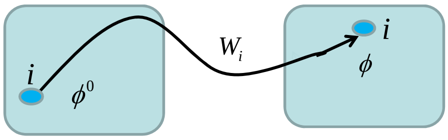
Alternatively we can view the chemical potential of a species j in a phase α as a measure of the work that must be done for the reversible transfer of one mole of uncharged species j from the gaseous state of unit fugacity (the reference state) into the bulk of phase α . In electrochemistry we deal with *charged* species and charged phases .



Electrochemical Activity



We consider the work done W_i 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 $q_i = z_i e$.



Standard Phase

Destination Phase

The electrochemical activity can be defined in the following manner.

$$\bar{a}_i = a_i \exp\left[\frac{q_i}{k_B T}\left(\phi - \phi^0\right)\right] = a_i \exp\left[\frac{z_i F}{RT}\left(\phi - \phi^0\right)\right] = \exp\left[\frac{W_i}{k_B T}\right]$$

In the latter expression a_i represents the activity of species i.

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

$$\bar{a}_i(\beta) = a_i(\beta)\exp\left[\frac{z_i F}{RT}\left[\phi_\beta - \phi^0\right]\right]$$

$$\bar{a}_i(\alpha) = a_i(\alpha)\exp\left[\frac{z_i F}{RT}\left[\phi_\alpha - \phi^0\right]\right]$$

Hence

$$\frac{\bar{a}_i(\beta)}{\bar{a}_i(\alpha)} = \frac{a_i(\beta)}{a_i(\alpha)}\exp\left[\frac{z_i F}{RT}\left(\phi_\beta - \phi_\alpha\right)\right] = \frac{a_i(\beta)}{a_i(\alpha)}\exp\left[\frac{z_i F}{RT}\Delta_{\alpha\beta}\phi\right]$$

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

$$\Delta\bar{\mu}_i = \bar{\mu}_i(\beta) - \bar{\mu}_i(\alpha)$$

We can immediately deduce a relationship between the electrochemical potential difference and the ratio of electrochemical activities between two phases α and β via the following relationships.

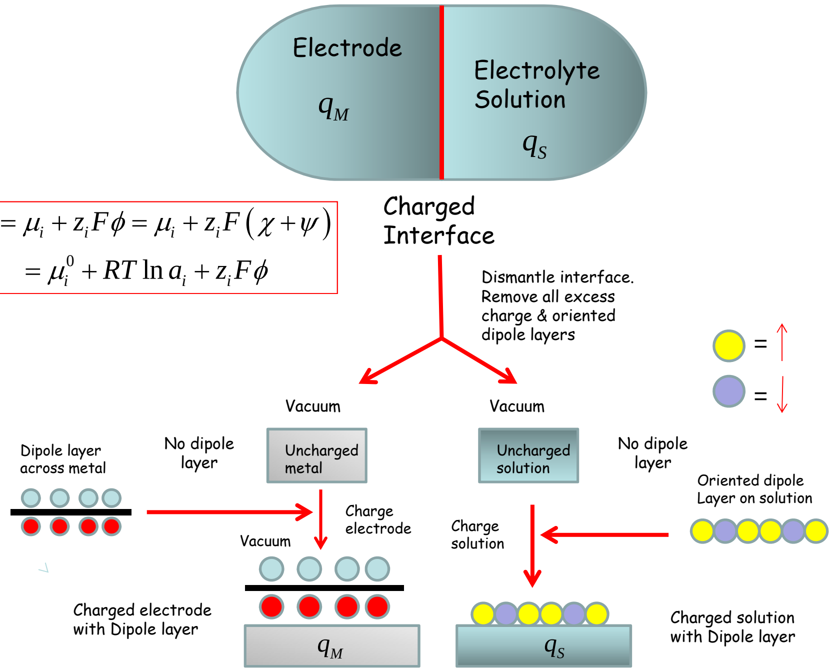
$$\Delta\bar{\mu}_i = RT\ln\left\{\frac{\bar{a}_i(\beta)}{\bar{a}_i(\alpha)}\right\} = RT\ln\left\{\frac{a_i(\beta)}{a_i(\alpha)}\right\} + z_i F\Delta_{\alpha\beta}\phi = \Delta\mu_i + z_i F\Delta_{\alpha\beta}\phi$$

Hence the difference in electrochemical potential is split up into two distinct components. First, the difference in chemical potential $\Delta\mu_i$ and second the difference in electrical potential $\Delta_{\alpha\beta}\phi$.

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 μ_j.
The second constitutes an electrostatic term linked to the crossing of the layer of oriented interfacial dipoles ($z_i F\chi$).
The third constitutes an electrostatic term linked to the charge of the phase ($z_i F\psi$).
The outer potential y 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 c defines the work done to bring a test charge across the surface layer of oriented dipoles at the interface.
Hence the inner Galvani potential f 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:

$$\phi = \chi + \psi$$

$$\bar{\mu}_i = \mu_i + z_i F\phi = \mu_i + z_i F(\chi + \psi)$$
$$= \mu_i^0 + RT\ln a_i + z_i F\phi$$



Electrochemical Potential

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 .

$$\bar{\mu}_j(\alpha) = \left(\frac{\partial G}{\partial n_j}\right)_{n_k,P,T}$$

$\bar{\mu}_j =$ Electrochemical potential

$\tilde{G} =$ Electrochemical Gibbs energy

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

$$\bar{\mu}_j = \mu_j + z_j F\phi = \mu_j + q_j\phi$$

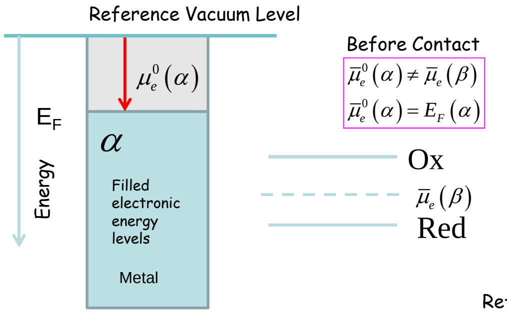
Chemical potential (μ_j); Species valence (z_j); Species charge (q_j); Galvani electrical potential (ϕ)

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 .

$$^{\alpha}\Delta^{\beta}\bar{\mu} = \bar{\mu}_j(\alpha) - \bar{\mu}_j(\beta) = 0$$
$$\bar{\mu}_j(\alpha) = \bar{\mu}_j(\beta)$$

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.



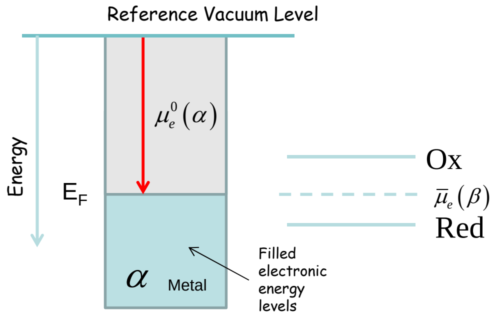
Before Contact

$$\bar{\mu}_e^0(\alpha) \neq \bar{\mu}_e(\beta)$$
$$\bar{\mu}_e^0(\alpha) = E_F(\alpha)$$

After Contact

$$\bar{\mu}_e^0(\alpha) = \bar{\mu}_e(\beta)$$

Via process of Charge transfer



The Nernst Equation

We consider the following ET reaction.

$$Ox^{z_{ox}} + ne^- \rightarrow Red^{z_{red}}$$

$$n = z_{ox} - z_{red} = z_O - z_R$$

At equilibrium

$$\bar{\mu}_O(\beta) + n\bar{\mu}_e(\beta) = \bar{\mu}_R(\beta)$$

We note the following

$$\bar{\mu}_e(\beta) = \mu_e^0 - F\phi_\beta$$
$$\bar{\mu}_O(\beta) = \mu_O(\beta) + z_O F\phi_\beta$$
$$\bar{\mu}_R(\beta) = \mu_R(\beta) + z_R F\phi_\beta$$

Also

$$\mu_O(\beta) = \mu_O^0(\beta) + RT\ln a_O(\beta)$$
$$\mu_R(\beta) = \mu_R^0(\beta) + RT\ln a_R(\beta)$$

Hence

$$\mu_O^0(\beta) + RT\ln a_O(\beta) + n\bar{\mu}_e(\beta) + z_O F\phi_\beta = \mu_R^0(\beta) + RT\ln a_R(\beta) + z_R F\phi_\beta$$

Simplifying we get

$$n\bar{\mu}_e(\beta) = \mu_R^0(\beta) - \mu_O^0(\beta) + RT\ln\left\{\frac{a_R(\beta)}{a_O(\beta)}\right\} + (z_R - z_O)F\phi_\beta$$

$$n\bar{\mu}_e(\beta) = \mu_R^0(\beta) - \mu_O^0(\beta) + RT\ln\left\{\frac{a_R(\beta)}{a_O(\beta)}\right\} - nF\phi_\beta$$

Hence

$$\bar{\mu}_e(\beta) = \frac{\mu_R^0(\beta) - \mu_O^0(\beta)}{n} + \frac{RT}{n}\ln\left\{\frac{a_R(\beta)}{a_O(\beta)}\right\} - F\phi_\beta$$

Also

$$\bar{\mu}_e(\alpha) = \mu_e^0(\alpha) - F\phi_\alpha$$

At equilibrium

$$\bar{\mu}_e(\beta) = \bar{\mu}_e(\alpha)$$

$$\frac{\mu_R^0(\beta) - \mu_O^0(\beta)}{n} + \frac{RT}{n}\ln\left\{\frac{a_R(\beta)}{a_O(\beta)}\right\} - \mu_e^0(\alpha) = F(\phi_\beta - \phi_\beta)$$

Simplifying we get

$$\phi_\alpha - \phi_\beta = \frac{\mu_O^0(\beta) - \mu_R^0(\beta) + n\mu_e^0(\alpha)}{nF} + \frac{RT}{nF}\ln\left\{\frac{a_O(\beta)}{a_R(\beta)}\right\}$$

$$\Delta_{\alpha\beta}\phi = \Delta_{\alpha\beta}\phi^0 + \frac{RT}{nF}\ln\left\{\frac{a_O(\beta)}{a_R(\beta)}\right\}$$

$$\Delta_{\alpha\beta}\phi^0 = \frac{\mu_O^0(\beta) - \mu_R^0(\beta) + n\mu_e^0(\alpha)}{nF}$$

This is the Nernst Equation.

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) → B (g).
We let ξ 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
μ as follows:

$$
\begin{aligned}
dG &= \mu_A dn_A + \mu_B dn_B \\
&= -\mu_A d\xi + \mu_B d\xi = (\mu_B - \mu_A) d\xi
\end{aligned} \qquad (1)
$$

Furthermore

$$dG = \left(\frac{\partial G}{\partial \xi}\right)_{P,T} d\xi \qquad (2)$$

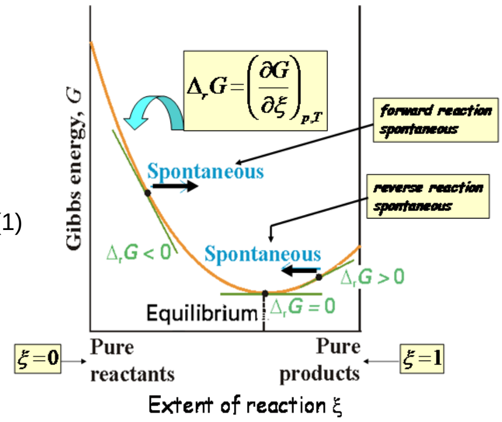
Hence we get from eqn. 1 and 2

$$\left(\frac{\partial G}{\partial \xi}\right)_{P,T} = \Delta_r G = \mu_B - \mu_A \qquad (3)$$

In the latter the symbol $\Delta = \frac{\partial}{\partial \xi}$

$\Delta_r G$ = reaction Gibbs free energy

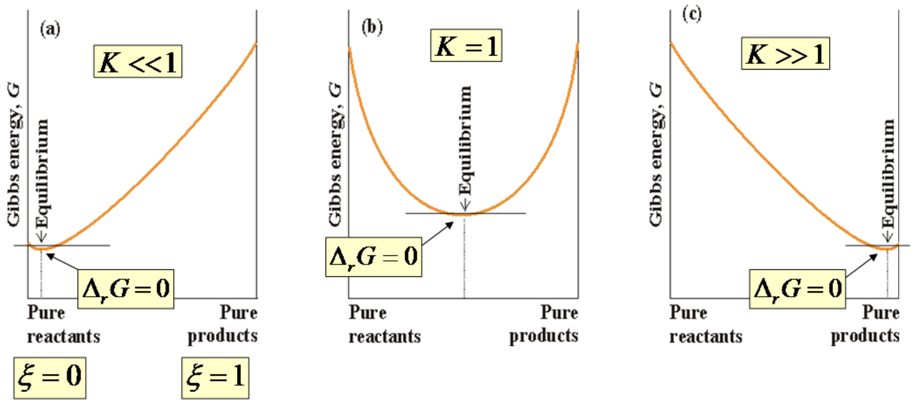
Since μ_j varies with composition
Then so also does $\Delta_r G$.



Reaction Gibbs energy

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

extent of reaction = ξ



$\Delta_r G$ is the slope of the G versus ξ graph at any degree of advancement ξ of the chemical reaction.

If $\mu_A > \mu_B$ then A → B is spontaneous and $\Delta_r G$ is negative.
If $\mu_A > \mu_B$ then B → A is spontaneous and $\Delta_r G$ is positive.
If $\mu_A = m_B$ then $\Delta_r G = 0$ and chemical equilibrium has been achieved.

Since A and B are ideal gases then we write

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

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

$$\mu_B - \mu_A = \mu_B^0 - \mu_A^0 + RT\ln\left(\frac{p_B}{p^0}\right) - RT\ln\left(\frac{p_A}{p^0}\right)$$

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

$$= \Delta_r G^0 + RT\ln Q_R$$

Q_R = reaction quotient
K = Equilibrium constant

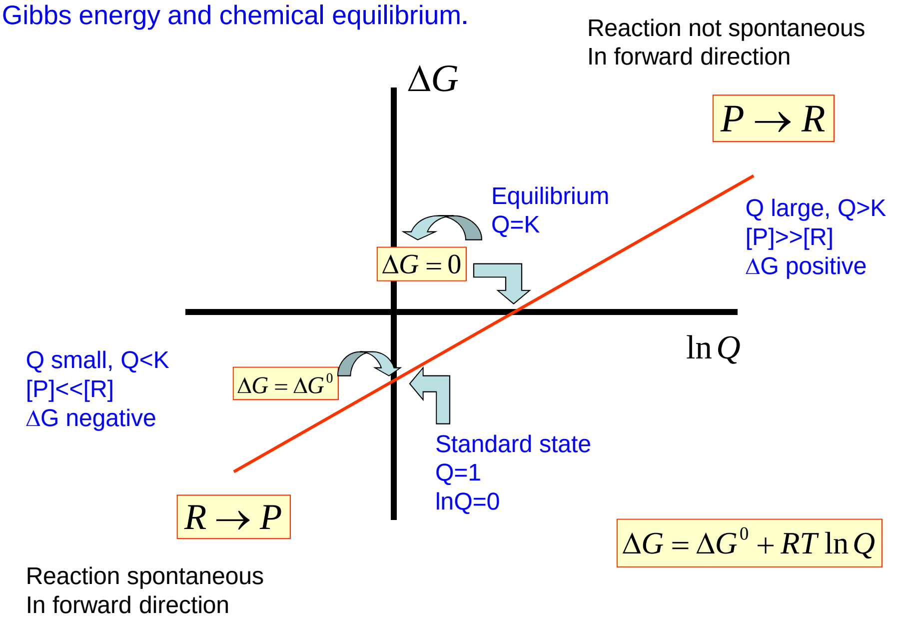
$$\Delta_r G = -RT\ln K + RT\ln Q_R = RT\ln\left(\frac{Q_R}{K}\right)$$

$$\Delta_r G = \Delta_r G^0 + RT\ln Q_R$$

At equilibrium Q_R = K and $\Delta_r G = 0$

$$\Delta_r G = -RT\ln K$$

Gibbs energy and chemical equilibrium.



The expression just derived for the special case A → 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.

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

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

We can relate chemical potential μ_j to activity a_j as follows.

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

$$\Delta_r G = \sum_j \upsilon_j \mu_j^0 + RT \sum_j \upsilon_j \ln a_j$$
$$= \Delta_r G^0 + RT \sum_j \ln a_j^{\upsilon_j}$$
$$= \Delta_r G + RT \ln \left\{ \prod_j a_j^{\upsilon_j} \right\}$$
$$\Delta_r G = \Delta_r G^0 + RT \ln Q_R$$

In the latter we have introduced the following definitions.

$$Q_R = \prod_j a_j^{\upsilon_j}$$

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

Again at equilibrium

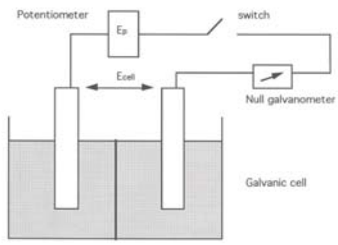
$$\Delta_r G = 0 \quad Q_R = K$$
$$\Delta_r G^0 = -RT \ln K$$
$$K = \prod_j a_j^{\upsilon_j}$$
$$\Delta_r G^0 = \sum_j \upsilon_j \Delta_f G^0$$

$\Delta_f G^0 =$

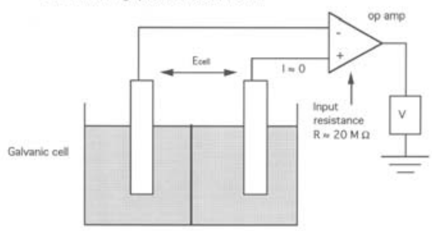
Standard free energy oOf formation of species j.

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 Df 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 .



Classical method : The voltage E p is manually adjusted until it equals E cell and the galvanometer reads zero deflection. This method is based on the principle of voltage compensation and is still used for high precision measurements.



Modern method uses an electronic voltage follower based on operational amplifier circuits (digital voltmeter DVM). The voltge follower reproduces the cell voltage E cell and does not draw any significant current from the cell since its input impedance is very large.

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 respectively 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_Δ where $V_\Delta = V_- - V_+$ denotes the voltage of the inverting input with respect to the non inverting input. Hence we can write that

$$V_o = -AV_- + AV_+ = -AV_\Delta$$

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

$$V_o = -AV_\Delta = -A(V_o - V_i)$$

$$V_o = \frac{V_i}{1+\frac{1}{A}} \approx V_i$$

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 $10^6\ \Omega$). 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.

Walther Hermann Nernst

The potential developed by a Galvanic cell depends on
the composition of the cell.
From thermodynamics the Gibbs energy change for a chemical reaction ΔG varies with composition of the reaction mixture in a well defined manner. We use the relationship between ΔG and E to obtain the Nernst equation.

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

$$\Delta_r G = \Delta_r G^0 + RT \ln Q_R$$

Reaction quotient

$$\Delta_r G = -nFE \quad \Delta_r G^0 = -nFE^0$$

$$-nFE = -nFE^0 + RT \ln Q_R$$

RT/F = 25.7 mV
At T = 298 K

$$Q_R \cong \frac{[\text{products}]}{[\text{reactants}]}$$

T = 298K

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

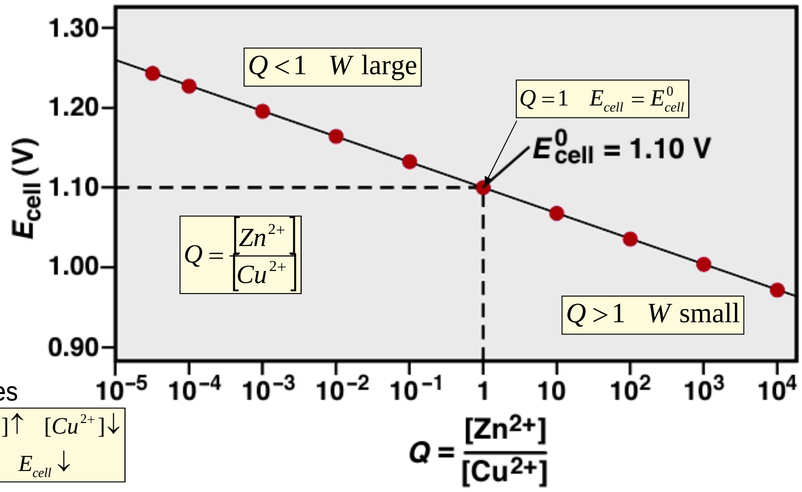
$$E = E^0 - \frac{0.0592}{n} \log Q_R$$

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

$$E_{cell} = E^0_{cell} - \frac{0.059}{2}\log\left\{\frac{[Zn^{2+}]}{[Cu^{2+}]}\right\}$$

Equilibrium $\Delta G = 0$
$E_{cell} = 0 \quad Q_R = K$
$W = 0$

Dead cell



As cell operates

$[Zn^{2+}]\uparrow \quad [Cu^{2+}]\downarrow$
$Q_R\uparrow \quad E_{cell}\downarrow$

Determination of thermodynamic parameters from E_{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 ΔH and reaction entropy ΔS to be evaluated for a cell reaction.

$$E = a + b(T - T_0) + c(T - T_0)^2 + \cdots$$

a, b and c etc are constants, which can be positive or negative.
T_0 is a reference temperature (298K)

$$\left(\frac{\partial E}{\partial T}\right)_P$$

← Temperature coefficient of zero current cell potential obtained from experimental E=E(T) data. Typical values lie in range 10^{-4} – 10^{-5} VK^{-1}

Gibbs-Helmholtz eqn.

$$\Delta_r H = \Delta_r G - T\left(\frac{\partial \Delta_r G}{\partial T}\right)_P$$

↓

$$\Delta_r G = -nFE$$

→

$$\Delta_r H = -nFE - T\left\{\frac{\partial}{\partial T}(-nFE)\right\}$$

$$= -nFE + nFT\left(\frac{\partial E}{\partial T}\right)_P$$

$$\Delta_r H = -nF\left\{E - T\left(\frac{\partial E}{\partial T}\right)_P\right\}$$

- Once ΔH and ΔG are known then ΔS may be evaluated.

$$\Delta_r G = \Delta_r H - T\Delta_r S$$

$$\Delta_r S = \frac{\Delta_r H - \Delta_r G}{T}$$

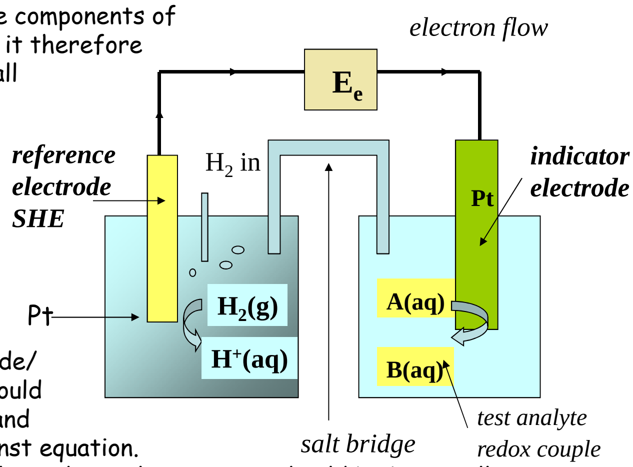
$$\Delta_r S = \frac{1}{T}\left\{-nFE + nFT\left(\frac{\partial E}{\partial T}\right)_P + nFE\right\}$$

$$\Delta_r S = nF\left(\frac{\partial E}{\partial T}\right)_P$$

- 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.

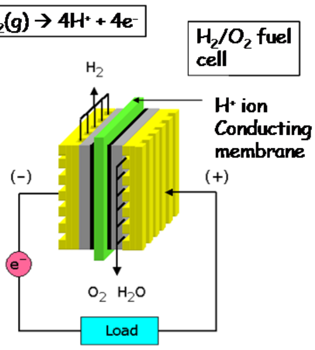


The ET reaction involving the analyte species should be kinetically facile and the ratio of the analyte/product concentration should depend on the interfacial potential difference via the Nernst equation.

Hydrogen/oxygen fuel cell

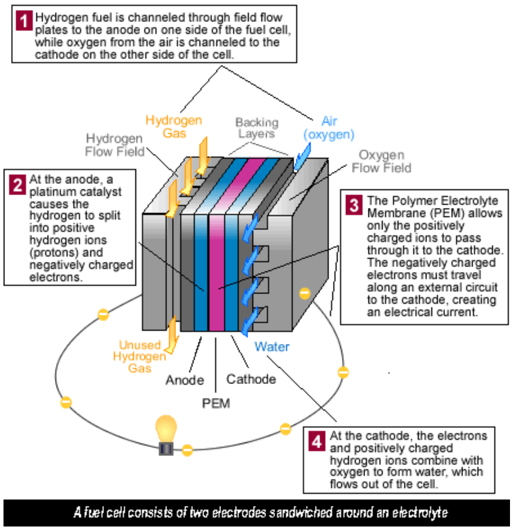
Anode reaction

$2H_2(g) \rightarrow 4H^+ + 4e^-$



Cathode reaction

$O_2(g) + 4e^- + 4H^+ \rightarrow 2H_2O$



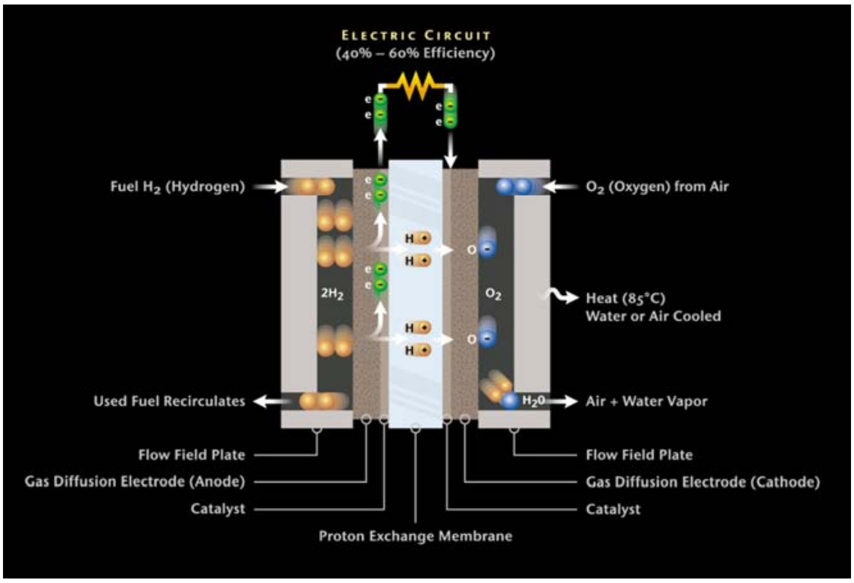
A fuel cell consists of two electrodes sandwiched around an electrolyte

Remember CH1101 Electrochemistry:

$$\Delta G = -nFE_{eq,cell}$$

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

Ballard PEM Fuel Cell.



Efficiency of fuel cell(I) .

Efficiency ε =work output/heat input

$\Delta G = -nFE_{eq,cell}$

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

For electrochemical or 'cold' combustion:
Heat input → enthalpy change ΔH for cell reaction
Work output → Gibbs energy change ΔG for cell reaction

$$\varepsilon_{max} = \frac{\Delta_r G}{\Delta_r H} = \frac{\Delta_r H - T\Delta_r S}{\Delta_r H} = 1 - \frac{T\Delta_r S}{\Delta_r H}$$

$$\varepsilon_{max} = -\frac{nFE_{eq,cell}}{\Delta_r H}$$

Usually

$\Delta_r G \cong \Delta_r H$

$\varepsilon \cong 1$

$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O$ (l) ΔG^0 = -56.69 kcal mol^{-1}; ΔH^0 = - 68.32 kcal mol^{-1}
n = 2, E^0_{eq} = 1.229 V , ε = 0.830.

Efficiency of fuel cell (II).

- For all real fuel cell systems terminal cell potential E does not equal the equilibrium value E_{eq}, but will be less than it.
- Furthermore E will *decrease* in value with increasing current drawn from the fuel cell.

- 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.

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

← 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.

$$A + mH^+ + ne^- \rightarrow B$$

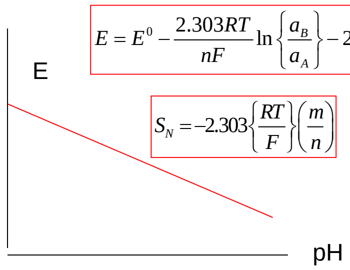
The Nernst equation for this type of proton/electron transfer equilibrium is given by the following expression.

$$E = E^0 - \frac{RT}{nF}\ln\left\{\frac{a_B}{a_A a_{H^+}^m}\right\}$$

Idea:
Potentiometric measurements can give rise to accurate pH measurements (especially metal oxide electrodes Lyons TEECE Group Research 2012/2013).

This expression can be readily simplified to the following form

$$E = E^0 - \frac{2.303RT}{nF}\ln\left\{\frac{a_B}{a_A}\right\} - 2.303\left(\frac{m}{n}\right)\frac{RT}{F}pH$$



$$S_N = -2.303\left\{\frac{RT}{F}\right\}\left(\frac{m}{n}\right)$$

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 m/n ratio.
When m = n then we predict that S_N = - 2/303RT/F
Which is close to 60 mV per unit change in pH at 298 K.

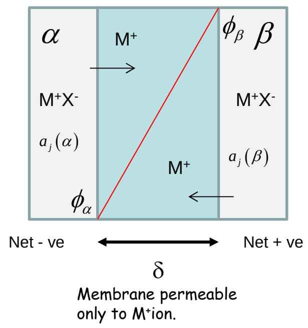
Membrane Potential

Since we are considering charged species we define equilibrium
In terms of equality of elctrochemical potentials.

$$\bar{\mu}_j(\alpha) = \bar{\mu}_j(\beta)$$
$$\mu_j(\alpha) + z_jF\phi_\alpha = \mu_j(\beta) + z_jF\phi_\beta$$

$$\Delta_{\beta\alpha}\phi = \phi_\beta - \phi_\alpha > 0$$

$$a_j(\alpha) > a_j(\beta) \qquad \phi_\alpha < \phi_\beta$$



$$z_jF\phi_\beta - z_jF\phi_\alpha = z_jF(\phi_\beta - \phi_\alpha) = \mu_j(\alpha) - \mu_j(\beta)$$

Now

$$\mu_j(\alpha) = \mu_j^0(\alpha) + RT\ln a_j(\alpha)$$
$$\mu_j(\beta) = \mu_j^0(\beta) + RT\ln a_j(\beta)$$

Hence

$$z_jF(\phi_\beta - \phi_\alpha) = \left(\mu_j^0(\alpha) - \mu_j^0(\beta)\right) + RT\ln a_j(\alpha) - RT\ln a_j(\beta)$$
$$= \left(\mu_j^0(\alpha) - \mu_j^0(\beta)\right) + RT\ln\left\{\frac{a_j(\alpha)}{a_j(\beta)}\right\}$$
$$\Delta_{\beta\alpha}\phi = \frac{\left(\mu_j^0(\alpha) - \mu_j^0(\beta)\right)}{z_jF} + \frac{RT}{z_jF}\ln\left\{\frac{a_j(\alpha)}{a_j(\beta)}\right\}$$

Now if we assume that $\mu_j^0(\alpha) = \mu_j^0(\beta)$

We get the final expression for the membrane potential

$$\Delta\phi_M = \frac{RT}{z_jF}\ln\left\{\frac{a_j(\alpha)}{a_j(\beta)}\right\}$$

Δϕ is the electric potential necessary
To prevent equalization of ionic activities
by Difusion across the membrane.

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.

$$\bar{a}_j(\beta)/a_j(\alpha) = \frac{a_j(\beta)}{a_j(\alpha)}\exp\left[\frac{z_jF}{RT}(\phi_\beta - \phi_\alpha)\right] = 1$$
$$\Delta\phi_M = \frac{RT}{z_jF}\ln\left\{\frac{a_j(\alpha)}{a_j(\beta)}\right\}$$