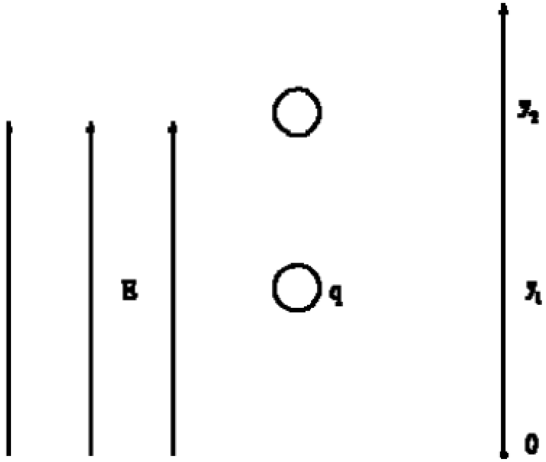
Review of Electrostatics

Review of Electric Force, F, Field,E, Potential, V, and Energy, PE

The magnitude of the force, F, between the charges is Coulomb's Law

$F = k Q_1 Q_2 / r^2$ (units Newtons) Coulomb's constant $k = 9.0 \times 10^9$ N m^2/C^2

If there are more than two charges present, then the force on any one charge must be found by adding vectorially the forces found by Coulomb's law between each pair of charges



The electric field $\vec{E}$ associated with this charge distribution is defined through the relation

$$\vec{F} = q\,\vec{E}$$

The units of $\vec{E}$ are thus seen to be N/C. The vector nature of the electric force and field makes problems involving more than a few point charges prohibitively difficult. In many instances it is possible to attack a problem using a scalar quantity called the **electric potential**. To introduce it, suppose we have a region of space where the electric field is constant.

Motion of a point charge, *q*, in a constant electric field, E

We now place a charge *q* at y_1 which moves, by the electric force, to the point y_2 . The work done by the electric force is given by

$W = Fd = qE(y_2 - y_1)$.

We can write this relation in terms of a change in an **electric potential energy** *PE*

1) $W = \Delta PE = -(PE_2 - PE_1)$

and also introduce the electric **potential difference** ΔV as

2) $\Delta PE = q\Delta V = q(V_2 - V_1)$

and from the above 3 equations we find

3) $E = -\Delta V/\Delta y = -V_2 - V_1/y_2 - y_1$

4) $F = qE$

1) the units of electric potential energy *PE* are the same as those of work, which are Joules (J.).
2) The units of potential difference ΔV are J/C, which is given the special name **Volt** (V).
3) The units of electric field, *E*, which we found to be N/C, can also be expressed as V/m.
4) The units of electric force, *F*, are N.

Expressions giving the electric potential energy *PE* and potential *V* at any point involve an *arbitrary* constant *C* :

$PE = -qEy + C \Rightarrow -\Delta PE = qE(y_2 - y_1)$

$= -Ey + C \Rightarrow -\Delta V = E(y_2 - y_1)$

The presence of the constant *C* stems from the fact that it is only *differences* in potential energy or potential which enter into the definitions for *W* and *PE*; this is exactly analogous to the situation for gravitational potential energy, where one is free to choose the zero point at will.

Chapter 3

Electrode Potentials
&
Double – Layer Structure at Phase Boundaries

Electrode Potentials and their Dependence on Concentration, Gas-Pressure and Temperature

The discharge of a galvanic cell always corresponds to a chemical process that can be divided into two spatially separated electrochemical half-reactions. The chlorine fuel cell reactions (eqns. 1.7)

Half reaction 1	$Cl_2 + 2\,e^- \rightarrow 2\,Cl^-(aq.)$
Half reaction 2	$H_2 + 2\,H_2O \rightarrow 2\,H_3O^+(aq.) + 2\,e^-$
Total cell reaction	$Cl_2 + H_2 \rightarrow 2\,H_3O^+(aq.) + 2\,Cl^-(aq.)$

Eqns. 1.7

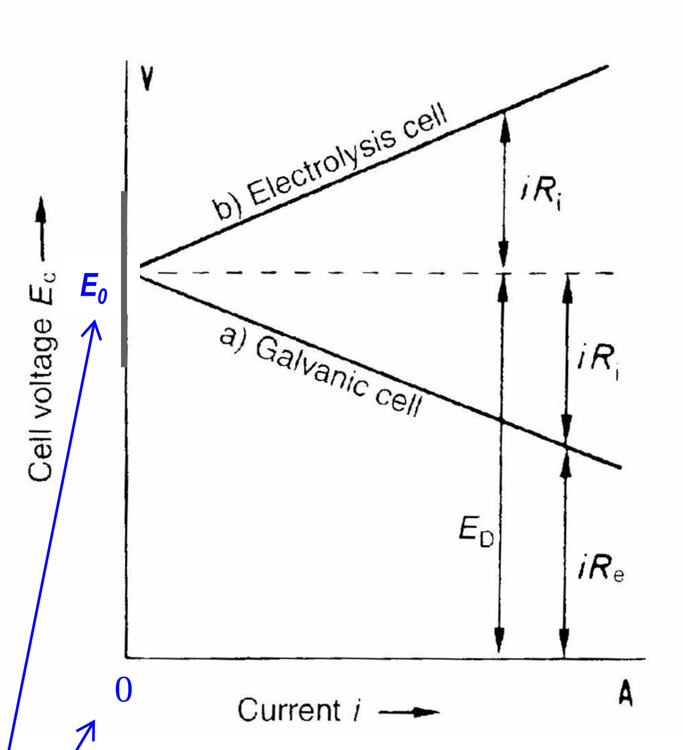
are a special case of the general scheme equations 3.1:

$$\begin{array}{ll} \nu_1 S_1 + \ldots + \nu_i S_i + ne^- & \rightleftharpoons \nu_j S_j + \ldots + \nu_k S_k \\ \nu_l S_l + \ldots + \nu_m S_m & \rightleftharpoons \nu_n S_n + \ldots + \nu_p S_p + ne^- \\ \hline \nu_1 S_1 + \ldots + \nu_m S_m & \rightleftharpoons \nu_j S_j + \ldots + \nu_p S_p \end{array}$$

Eqns 3.1

In order for the overall reaction to be stoichiometrically balanced, the number of electrons , *n*, exchanged in each half reaction must be equal, which dictates the values of the stoichiometric factors, v_i :

The maximum electrical work obtainable is given by the change in the Gibbs function for the cell reaction, $\Delta_r G$, which equals nFE_0 in which E_0 is the open cell voltage ($E_{c,0} = E_0$ =OCV =OCP) also called zero-current voltage, as shown in the figure to the right.



Schematic variation of cell voltage ***Ec*** against load current ***i*** for
(a) a galvanic cell:
(b) an electrolvsis cell.

Cell voltage, E_o , is the clearest experimental indicator of the energy of reactions in a cell

Spontaneous (Galvanic) and Driven (Electrolytic) Cells

For the transformation of one mole of reactants, the molar free energy of the reaction and is designated as $\Delta_r G$

$$\Delta_r G = -nFE_0$$

If the current flows as a result of a spontaneous chemical process this is called a galvanic cell and

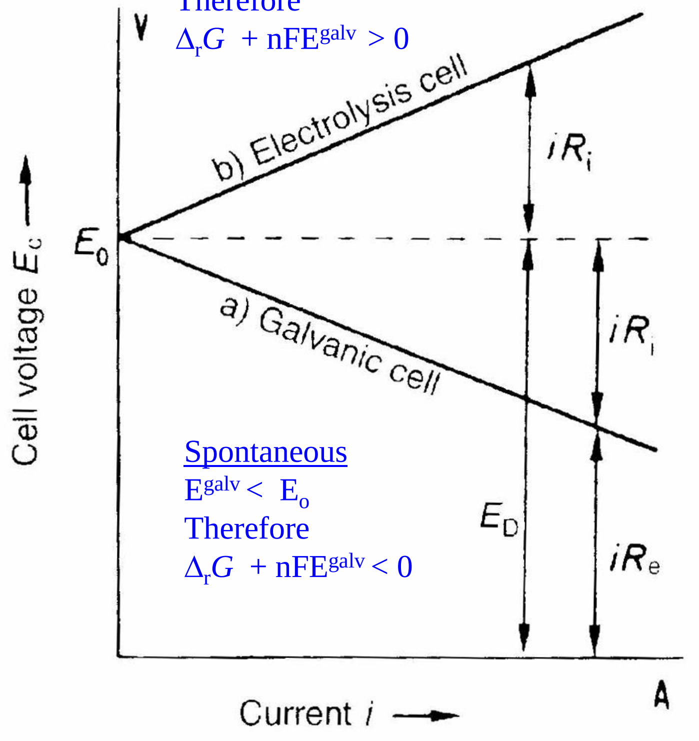
$$E_c^{\text{galv}} < E^0$$

and $$\Delta_r G + nFE_c^{\text{galv}} < 0$$

If an electrical current drives the cell, this is called an electrolysis cell

$$E_c^{\text{elec}} > E^0$$

and $$\Delta_r G + nFE_c^{\text{elec}} > 0$$



Non- Spontaneous
$E^{galv} > E_o$
Therefore
$\Delta_r G + nFE^{galv} > 0$

Spontaneous
$E^{galv} < E_o$
Therefore
$\Delta_r G + nFE^{galv} < 0$

Schematic variation of cell voltage ***Ec*** against load current ***i*** for (a) a galvanic cell: b) an electrolvsis cell.

In general, for the transformation of one mole of reactants, the molar free energy of the reaction is designated as $\Delta_r G$ and the relationship between free energy and potential is

$$\Delta_r G = -nFE_0$$

If the reactants and products of the cell reaction are in their standard states at the temperature of transformation, then $\Delta_r G$ is replaced by the standard free energy, $\Delta_r G^o$ and the potential, E_0 becomes the standard potential, E^0 and the the relationship between free energy and potential of thesystem is described by :

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

The Origin of Electrode Potentials, Galvani Potential Differences and the Electrochemical Potential pp. 78-90

We defined the chemical potential for the ith component of a mixture through the equation:

$$\mu_i = \mu_i^{0\dagger} + RT \ln a_i$$

a_i is activity of i
$\mu^{\dagger}_i$ is the chemical potential of i at unit activity
† indicate i is not a pure substance

The chemical potential, μ_i, can be regarded as
the change in free energy of one mole reactant or product,

$$\mu_i = \left(\frac{\partial G}{\partial n}\right)_{n_j \neq n_i, p, T}$$

The total free energy is:

$$G = \sum_i n_i \mu_i$$

In a large excess reactants and products, as the reaction proceeds,
the free energy change, $\Delta_r G$, for reaction 3.1 (given on slide 1) is:

$$\Delta_r G = \sum_i \nu_i \mu_i$$

At equilibrium $\Delta_r G = 0$ and so

$$\sum_i \nu_i \mu_i = 0$$

If two mixtures or solutions are in contact with each other such that chemical equilibrium is established between the phases, then for each component i present in the two phases (I and II) we have

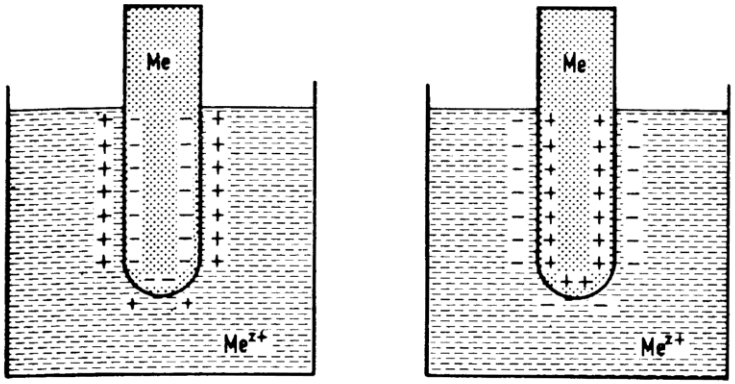
$$\mu_i(\mathrm{I}) = \mu_i(\mathrm{II})$$

If a metal, such as copper, is placed in contact with a solution containing the ions of that metal,

$$\mathrm{Cu}^0 \rightleftharpoons \mathrm{Cu}^{2+}(\mathrm{aq.}) + 2\,e^-_m$$

a) If the *chemical potential of the copper in the metal* exceeds that of the *copper ions in solution and electrons in the metal*, then metal *dissolution* will take place, and the *solution next to the metal will become positively charged* with respect to the metal itself.

b) If the *chemical potential of Cu*$^{2+}$ *ions in solution and electrons in the metal* exceeds that of *copper metal* itself, then *deposition* of ions takes place. When metal ions *deposit* on the copper, the *solution next to the metal will become negatively charged* with respect to the metal itself.



a) **b)**

Origin of the potential difference between electrode and electrolyte.

Incorporating the effects of the potential difference into our thermodynamic equations we get:

$$\mu_i(\mathrm{I}) + z_i F \varphi_i(\mathrm{I}) = \mu_i(\mathrm{II}) + z_i F \varphi_i(\mathrm{II})$$ **Eqn. 3.13**

This way we can introduce the **electrochemical potential** , $\tilde{\mu}_i$.

$$\tilde{\mu}_i = \mu_i + z_i F \varphi_i = \mu_i^{0\dagger} + RT \ln a_i + z_i F \varphi_i$$ **Eqn. 3.14**

Upon electrochemical equilibrium we would expect: $$\sum_i \nu_i \tilde{\mu}_i = 0$$ **Eqn. 3.15**

The Nernst Equation

The difference in inner potentials between 2 phases is the Galvani potential difference, $\Delta\varphi$ (slide 9).

If we represent by φ_s the Galvani potential of the solution and by φ_m the Galvani potential of the metal, then for $Cu^o \leftrightarrow Cu^{2+}$ (aq.) + 2 e^- (M) and eqn. 3.15, the equilibrium condition can be written as:

$$\tilde{\mu}_{Cu}(M) = \tilde{\mu}_{Cu^{2+}}(aq.) + 2\tilde{\mu}_{e^-}(M)$$

Eqn 3.16

Assuming the copper atoms in the metal to be neutral, so that, $\tilde{\mu} = \mu$ and using eqn. 3.14, we have:

Eqn 3.17

$$\mu^0_{Cu}(M) + \cancel{RT \ln a_{Cu}(M)} = \mu^0_{Cu^{2+}}(aq.) + RT \ln a_{Cu^{2+}} + 2F\varphi_S + \mu^0_{e^-}(M) + \cancel{2RT \ln a_{e^-}} - 2F\varphi_M$$

Activities of copper atoms and electrons in metal are constant

The concentration of both copper atoms and electrons in copper metal are effectively constant; this gives:

$$\Delta\varphi \equiv \varphi_M - \varphi_S = \frac{\mu^0_{Cu^{2+}}(aq.) + \mu^0_{e^-}(M) - \mu^0_{Cu}(M)}{2F} + \frac{RT}{2F}\ln a_{Cu^{2+}}(aq.)$$

Eqn 3.18

$$= \Delta\varphi_0 + \left(\frac{RT}{2F}\right)\ln a_{Cu^{2+}}$$

$\Delta\varphi^o$ = standard Galvani potential difference between Cu^0 and Cu^{2+} + 2 e^- for when Cu^{2+} in solution is at unit activity

We replace $\Delta\varphi$ by the electrode potential E, as the Galvani potential of the solution is itself experimentally inaccessible, yielding the Nernst Equation:

$$E = E^0 + \left(\frac{RT}{zF}\right)\ln a_{M^{z+}}$$

Nernst Equation 3.19

Which is the dependence of the equilibrium potential on the concentration of ions (M^{2+}) in solution.

The Nernst Equation for Redox Electrodes

The Galvani potential difference between two phases Sox and S red can be found by inserting an inert electrode, like Pt, to act as a carrier of a electrons in redox reaction, as written below:

$$S_{ox} + n\,e^{-} \leftrightharpoons S_{red}$$

e.g., $Fe^{+3} + e^{-} \longrightarrow Fe^{+2}$

The equilibrium properties of the redox reaction can be described by the following equation:

$$\tilde{\mu}_{ox} + n\tilde{\mu}_{e^-}(M) = \tilde{\mu}_{red}$$

If we are to have electroneutrality. The above equation becomes:

$$\mu_{ox}^{0\dagger} + RT\ln a_{ox} + nF\varphi_S + n\mu_{e^-}^{0} - nF\varphi_M = \mu_{red}^{0\dagger} + RT\ln a_{red}$$

This way for the potential difference $\Delta\varphi$ we can write:

$$\begin{aligned}\Delta\varphi = \varphi_M - \varphi_S &= \frac{\mu_{ox}^{0\dagger} + n\mu_{e^-}^{0} - \mu_{red}^{0\dagger}}{nF} + \frac{RT}{nF}\ln\frac{a_{ox}}{a_{red}} \\ &= \Delta\varphi_0 + \left(\frac{RT}{nF}\right)\ln\left(\frac{a_{ox}}{a_{red}}\right)\end{aligned}$$

Accepting the reference electrode convention:

$$E = E^{0} + \left(\frac{RT}{nF}\right)\ln\left(\frac{a_{ox}}{a_{red}}\right)$$

The Nernst Equation for Gas Electrodes

The Nernst equation above for the dependence of the equilibrium potential of redox electrodes on the activity of solution species *is also valid for uncharged species* in the gas phase that take part in electron exchange reactions at the electrode-electrolyte interface. For the Chlorine reduction:

$Cl_2 + 2e \leftrightharpoons 2Cl$ we have: $E = E^0 + \left(\frac{RT}{2F}\right) ln \left(\frac{a_{Cl_2}(aq.)}{a^2_{Cl^-}}\right)$

If the gas-liquid system is in equilibrium: $\mu_{Cl_2}(gas) = \mu_{Cl_2}(aq.)$

Writing the chemical potential equations and transforming we get:

$$a_{Cl_2}(aq.) = \left(\frac{p_{Cl_2}}{p^0}\right) \cdot \exp\left(\frac{\mu^0_{Cl_2}(gas - \mu^0_{Cl_2}(aq.)}{RT}\right)$$

The Nernst Equation will then :

$$E = E^{\dagger 0} + \left(\frac{RT}{2F}\right) \ln \left(\frac{p_{Cl_2}}{p^0 a^2_{Cl^-}}\right)$$

Take a breath