CHEM465/865, 2006-3, Lecture 7, 20th Sep., 2006

Electrochemical Equilibrium – Electromotive Force

Relation between chemical and electric driving forces

Electrochemical system at constant T and p: consider $\tilde{G}$

Consider electrochemical reaction (involving transfer of e^-):

(1) $$|\nu_A|A + |\nu_B|B + |\nu_e|e_R^- \rightarrow |\nu_C|C + |\nu_D|D + |\nu_e|e_L^-$$

reactants **products**

Note:

- **Stoichiometric coefficients** (ν_i) of reactants (A, B) have negative sign, those of products (C,D) are positive
- **Electrons** are written explicitly in this equation since they will appear in the condition of electrochemical equilibrium!

Objective: use thermodynamic arguments to derive electrical potential (the so-called **electromotive force**, **EMF**) of a cell and relate this EMF to the composition of electrochemical cells

$$\text{Thermodynamics} \xrightarrow{\text{Composition}} \text{Electrical potential, EMF}$$

Reaction (1) advances by small amount dξ from left to right

⇒ amount of A changes by $\mathrm{d}N_\mathrm{A} = \nu_\mathrm{A}\mathrm{d}\xi < 0$

amount of B changes by $\mathrm{d}N_\mathrm{B} = \nu_\mathrm{B}\mathrm{d}\xi < 0$

amount of C changes by $\mathrm{d}N_\mathrm{C} = \nu_\mathrm{C}\mathrm{d}\xi > 0$

amount of D changes by $\mathrm{d}N_\mathrm{D} = \nu_\mathrm{D}\mathrm{d}\xi > 0$

Example:

$$2Al_2O_3(s) + 3Si(s) + 12e_R^- \rightarrow 3SiO_2(s) + 4Al(s) + 12e_L^-$$

$$\nu_\mathrm{A} = -2, \quad \nu_\mathrm{B} = -3, \quad \nu_\mathrm{C} = 3, \quad \nu_\mathrm{D} = 4$$

Change in electrochemical Gibbs free energy:

$\mathrm{d}\tilde{G} = \sum_{i,\alpha} \tilde{\mu}_i^\alpha \mathrm{d}N_i^\alpha$ (distinguish species and phases)

$= \sum_i \nu_i \tilde{\mu}_i \mathrm{d}\xi$ (i: all species and all phases)

and, thus,

$$\Delta_r\tilde{G} = \left(\frac{\partial \tilde{G}}{\partial \xi}\right)_{T,p} = \sum_i \nu_i \tilde{\mu}_i$$

(general relation, involves all species, all phases)

Condition of electrochemical equilibrium: $\Delta_r\tilde{G} = 0$

System is not in chemical equilibrium!

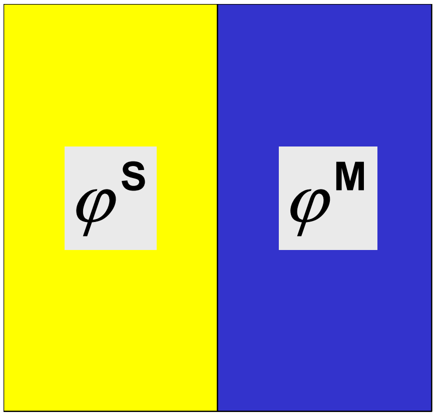
$\Delta_r G < 0$ (spontaneous reaction)

→ this is the chemical driving force of the reaction

Let's consider some examples first:

1. Metal|solution interface, solution contains ions of the metal

Ion-transfer: $M^{z+} + ze^- \rightleftharpoons M$ (cathodic reaction, reduction)



Write equilibrium condition: $\tilde{\mu}_M^M - z\tilde{\mu}_e^M - \tilde{\mu}_{M^{z+}}^S = 0$

where

$$\tilde{\mu}_{M^{z+}}^S = \mu_{M^{z+}}^{0,S} + RT\ln\left(a_{M^{z+}}\right) + zF\varphi^S$$

$$\tilde{\mu}_e^M = \mu_e^{0,M} - F\varphi^M$$

$\tilde{\mu}_M^M = \mu_M^{0,M}$ (standard value, unit activity)

Here, $\mu_i^{\alpha,0}$ is the standard chemical potential of species *i* in phase α, referring to standard conditions.

Conventions:

- activities of solvated species: $a^0 = 1$
- partial pressures of gaseous components: $p^0 = 1$ bar
- concentrations of dilute solutions: $c^0 = 1$ mol/l
- metals, solids, liquids: for practical purposes always at standard conditions!

Insert all the relations into condition of electrochemical equilibrium and solve for $\Delta_{\mathrm{S}}^{\mathrm{M}}\varphi$. Result is an expression for the electrode potential *E* or EMF of the M^{z+}|M redox couple:

$$E = \Delta_{\mathrm{S}}^{\mathrm{M}}\varphi = \varphi^{\mathrm{M}} - \varphi^{\mathrm{S}} = \frac{\mu_{\mathrm{M}^{z+}}^{0,\mathrm{S}} + \mathrm{z}\mu_{\mathrm{e}}^{0,\mathrm{M}} - \mu_{\mathrm{M}}^{0,\mathrm{M}}}{\mathrm{z}F} + \frac{RT}{\mathrm{z}F}\ln\left(a_{\mathrm{M}^{z+}}\right)$$

and, thus,

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

***E* depends on activities of potential determining ions.**

E^0 is the standard EMF: $$E^{0} = \frac{\mu_{\mathrm{M}^{z+}}^{0,\mathrm{S}} + \mathrm{z}\mu_{\mathrm{e}}^{0,\mathrm{M}} - \mu_{\mathrm{M}}^{0,\mathrm{M}}}{\mathrm{z}F}$$

2. Non-metal in contact with its ions on surface of an inert, conducting substance, e.g. $H_2|H^+$ on Pt

H_2 (g) $\rightleftharpoons$ 2 H^+ + 2 e^- (anodic reaction, oxidation)

$$\Delta_r\tilde{G} = 0 \Rightarrow$$

$$2\mu_{\mathrm{H^+}}^{0,\mathrm{S}} + 2RT\ln\left(a_{\mathrm{H^+}}\right) + 2F\varphi^{\mathrm{S}} + 2\mu_{\mathrm{e}}^{0,\mathrm{Pt}} - 2F\varphi^{\mathrm{Pt}} - \mu_{\mathrm{H_2}}^{0,\mathrm{g}} - RT\ln\left(p_{\mathrm{H_2}}\right) = 0$$

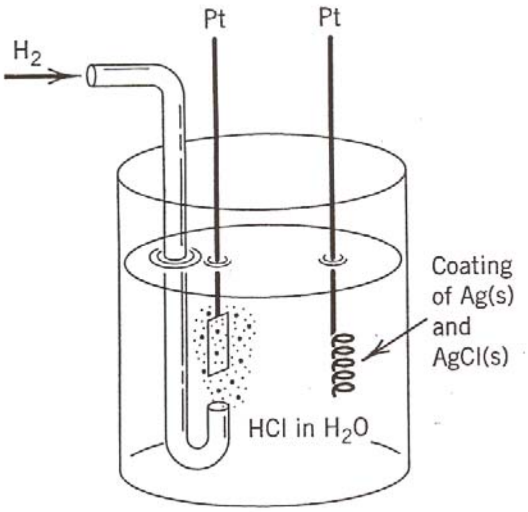
chemical potential of hydrogen gas: $\mu_{\mathrm{H_2}}^{\mathrm{g}} = \mu_{\mathrm{H_2}}^{0,\mathrm{g}} + RT\ln\left(p_{H_2}\right)$

Electrode potential:

$$E = \Delta_{\mathrm{Pt}}^{\mathrm{S}}\varphi = \varphi^{\mathrm{S}} - \varphi^{\mathrm{Pt}} = \frac{\mu_{\mathrm{H_2}}^{0,\mathrm{g}} - 2\mu_{\mathrm{H^+}}^{0,\mathrm{S}} - 2\mu_{\mathrm{e}}^{0,\mathrm{Pt}}}{\mathrm{z}F} + \frac{RT}{F}\ln\left(\frac{p_{\mathrm{H_2}}^{1/2}}{a_{\mathrm{H^+}}}\right)$$

$$\boxed{E = E^0 + \frac{RT}{F}\ln\left(\frac{p_{\mathrm{H_2}}^{1/2}}{a_{\mathrm{H^+}}}\right)}$$

3. Consider the following galvanic cell:



$Pt_L|H_2(g)|HCl(m)|AgCl(s)|Ag(s)|Pt_R$

(m: molality of the electrolyte solution)

Left electrode: ANODE, oxidation

$H_2\,(g) \rightleftharpoons 2\,H^+ + 2\,e^-$ (at Pt_L)

Right electrode: CATHODE, reduction

$2\,AgCl(s) + 2e^-$ (at Pt_R) $\rightleftharpoons 2\,Ag(s) + 2\,Cl^-$

overall:

$H_2\,(g) + 2\,AgCl(s) + 2e^-$ (at Pt_R) $\rightleftharpoons 2\,HCl\,(m) + 2\,Ag(s) + 2\,e^-$ (at Pt_L)

Electrochemical equilibrium (all species, all phases):

$$2\tilde{\mu}^{aq}_{HCl} + 2\tilde{\mu}^{s}_{Ag} + 2\tilde{\mu}^{Pt_L}_{e} - \tilde{\mu}^{g}_{H_2} - 2\tilde{\mu}^{S}_{AgCl} - 2\tilde{\mu}^{Pt_R}_{e} = 0$$

Again: solids, metals, liquids → unit activity

Only electrochemical potentials of electrons in Pt-wires are potential dependent.

Why can $\tilde{\mu}^{aq}_{HCl}$ be considered as one electroneutral species?

Insert expressions for electrochemical potentials:

$$2\mu^{aq}_{HCl} + 2\mu^{s}_{Ag} - \mu^{g}_{H_2} - 2\mu^{S}_{AgCl} + 2\mu^{Pt_L}_{e} - 2\mu^{Pt_R}_{e} - 2F\varphi^{Pt_L} + F\varphi^{Pt_R} = 0$$

$$\Rightarrow \Delta_r G + 2F\left(\varphi^{Pt_R} - \varphi^{Pt_L}\right) = 0$$

$$\Rightarrow E = \varphi^{Pt_R} - \varphi^{Pt_L} = -\frac{\Delta_r G}{2F}, \text{ with } \Delta_r G = \Delta_r G^0 + 2RT\ln\left(\frac{a_{HCl}}{p_{H_2}^{1/2}}\right)$$

Relation between EMF *E* and reaction Gibbs free energy $\Delta_r G$

How is EMF determined by the chemical composition of the system? → leads to Nernst's equation

Again: consider electrochemical cell with overall reaction

$$|\nu_A| A + |\nu_B| B + |\nu_e| e_R^- \rightarrow |\nu_C| C + |\nu_D| D + |\nu_e| e_L^-$$

(could be for instance a Daniell element)

Reaction Gibbs free energy vs. composition of the mixture:

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

The relation between EMF E and $\Delta_r G$ is

$$E = \varphi^R - \varphi^L = -\frac{\Delta_r G}{|\nu_e| F} = -\frac{\Delta_r G^0}{|\nu_e| F} - \frac{RT}{|\nu_e| F} \ln Q$$

or

$$E = E^0 - \frac{RT}{|\nu_e| F} \ln Q$$

This is Nernst equation!

Here, Q is the so-called reaction quotient:

$$Q = \frac{[C]^{|\nu_C|} [D]^{|\nu_D|}}{[A]^{|\nu_A|} [C]^{|\nu_B|}}$$

Note: instead of concentrations, there could be activities or partial pressures in the reaction quotient as well – depends on type of species.

The Nernst equation is just another way to formulate the condition of electrochemical equilibrium.

Now: what would be the equivalent expression to Nernst-equation for chemical equlibrium???

Connection between two electrodes through external metal wire: system will go to chemical equilibrium (by electrons flowing spontaneously from anode to cathode).

Discharged battery: chemical equilibrium

Fuel cell: cannot reach chemical equilibrium due to continuous supply of reactants (open system)

Electrode configurations and reference electrodes

Nernst equation: in principle possible to calculate and measure EMFs for half reactions and electrochemical cells (examples in problem sets)

In general, the EMF

$$E = E^0 - \frac{RT}{|\nu_e| F} \ln Q$$

has to parts:

- **Standard EMF E^0**

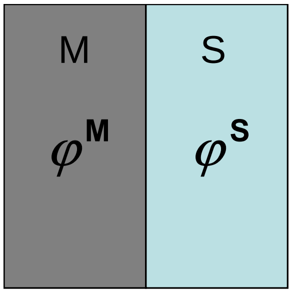
  standard conditions are:
  - **25°C**
  - **partial pressures of gaseous species: 1 bar**
  - **1M solutions**
  - **unit activities of ions**
- **composition-dependent part due to deviations from standard conditions (involving temperature variation)!**

If standard potentials and composition of the system are known, then in principle EMFs of all systems could be determined!

However: there is no absolute scale, only differences in electrode potentials can be determined. Is that bad?

Electrode potential of single electrode configuration:

Metal|solution interface

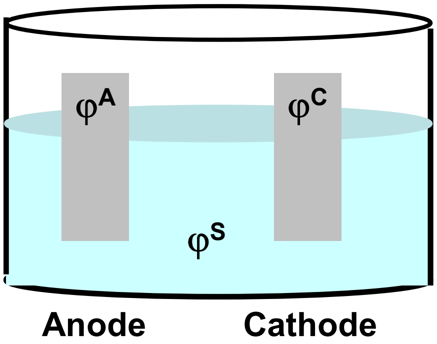


Electrode potential: $\boxed{E_{el} = \varphi^{M} - \varphi^{S} \text{ (cathodic)}}$

Remember: this is proportional to the amount of work required to move a test charge across the metal|solution interface

Measurement: at least two electrodes are required

Electrochemical Cell



EMF: $E_{cell} = \varphi^{C} - \varphi^{A}$

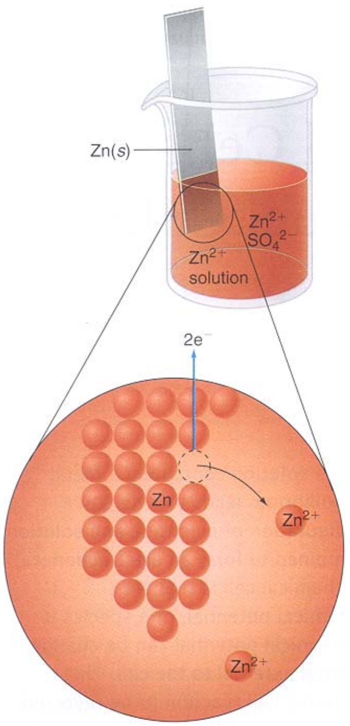
Electrical work that the system can perform in bringing single electron from anode to cathode.

This value can be calculated if the electrode potentials are known at the two distinct M|S interfaces

$$E_{cell} = E_{el}^{C} - E_{el}^{A}$$

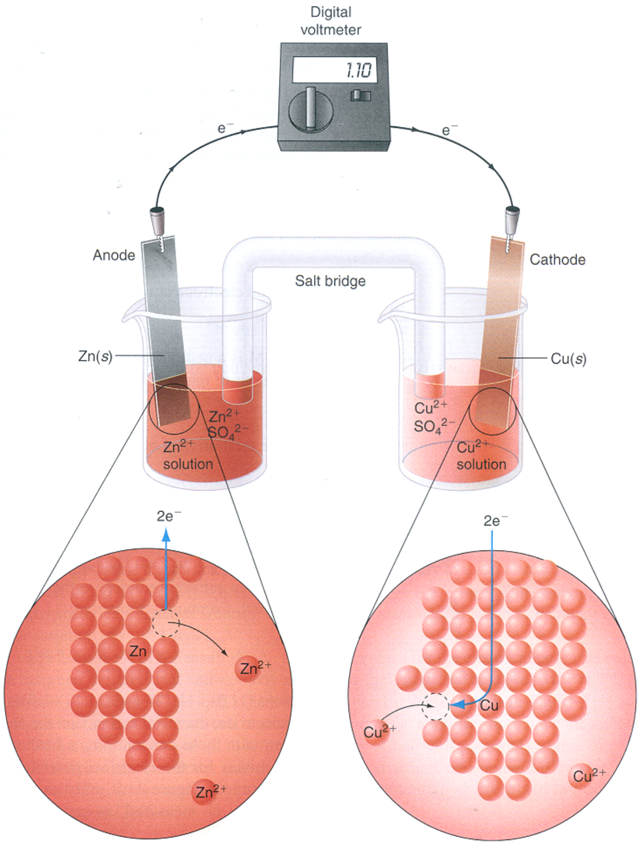
This is measurable (metal connection between electrodes, voltmeter with high electronic resistance, that allows only a very small current to flow - measurement performed practically under conditions of electrochemical equilibrium.

Zinc electrode immersed in water



Small amount of Zn^{2+} ions go into solution, leaving negative charge on electrode.
Potential difference: $\varphi^{M} - \varphi^{S} \sim -1V$

Schematic diagram of Daniell cell



Zn^{2+}|Zn and Cu^{2+}|Cu halfcells are connected through salt bridge (internal circuit).
Voltmeter in external circuit.