

## **Chapter 4:**

# **Thermodynamics of Electrochemical Systems**

1. Gibbs free energy defining the spontaneous direction of chemical reactions
2. Chemical potential, the Gibbs equation and equilibria
3. Activity of ions
4. Electrode standard potentials
5. The Nernst equation
6. Pourbaix diagrams, region of aqueous electrochemistry and corrosion
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## Chapter 4: Thermodynamics of Electrochemical Systems

Thermodynamics is the study of equilibria states. Thus, it provides us information on systems which do not carry current. Thermo applies also to pseudo-steady states, i.e., systems whose response time is faster (shorter) than the imposed change (perturbation), and therefore if the reaction is fast, thermo will still apply. However, electrochemical systems are often characterized by sluggish electrode kinetics and slow diffusion, hence; one should apply thermodynamic analysis with care to such systems, since it can be misleading. Accordingly, thermo indicates that we cannot plate zinc out of acidic solutions, the lead acid battery cannot exist, and that we cannot plate InSb, GaAs and other compounds from aqueous solutions – all of which are wrong.

Nonetheless, thermo provides the ‘base line’ – i.e., the ideal or the basis from which we start to analyze our system. This relates primarily to the standard potential, direction of spontaneous reactions, energy content in chemicals, etc.

We focus our discussion on electrochemical systems, i.e., systems involving ionic species in contact with electrodes.

### Energy Expressions used in thermo:

- $G$  = Gibbs Free energy
- $A$  = Helmholtz free energy

We can determine the change in Gibbs Free energy of a system undergoing a reaction readily from thermodynamic measurable and tabulated values:

$$\Delta G = \Delta H - T\Delta S \quad [4-1]$$

Where  $\Delta H$  is the change in the enthalpy ( $\sim$  heat content) of the system, and  $\Delta S$ , the change in its entropy. The latter term is typically quite small at ambient temperatures.

We shall also see that  $\Delta G$  is directly linked to the standard potential of the electrode reaction,  $E$ :

$$\Delta G = -nFE \quad [4-2]$$

Where  $n$  is the number of electrons transferred in the electrode reaction, and  $F$  is Faraday’s constant.

The Gibbs free energy can be viewed (imprecisely) as the chemical energy stored in a system. Hence a change in the Gibbs free energy will tell us if the system will react spontaneously (negative  $\Delta G$  for the reaction).

### Criterion for Spontaneity:

$\Delta G$  provides a criterion for determining the spontaneous direction a chemical reaction will take.

The change in free energy for any process is either negative or remains constant, at constant temperature and pressure, for any closed system. The change in  $\Delta G$  provides the clue whether a reaction will spontaneously proceed in a particular direction. This is why  $G$  is also called the thermodynamic or chemical potential. It is analogous as far as equilibrium and changes are concerned to potential energy in mechanical systems.

Note:

1.  $\Delta G$  determines the possibility and direction of change in a chemical system - not its rate.
2. Never try to propose a process in which  $\Delta G$  increases.
3.  $\Delta G$  and direction of the chemical reaction can change with the temperature. (Why do we often heat systems where  $\Delta G$  is already negative?)
4. Will reaction "1" proceed more readily than reaction "2" if  $\Delta G_1 < \Delta G_2$  both being negative.  
[define "readily" faster (no) or to a further extent (yes)].
5. In electrochemical systems  $\Delta G = -nFE$ , hence we can drive any reaction to any extent by externally applying the appropriate voltage.

### Gibbs Equation and the Chemical Potential

Gibbs free energy is a function of the temperature, pressure and chemical composition of the system:

$$G = G(T, P, n_i) \quad [4-3]$$

A complete differential becomes,

$$dG = \left( \frac{\partial G}{\partial T} \right)_{P, n_i} dT + \left( \frac{\partial G}{\partial P} \right)_{T, n_i} dP + \sum \left( \frac{\partial G}{\partial n_i} \right)_{T, P, n_j} dn_i \quad [4-4]$$

Gibbs defined the chemical potential of species  $i$ ,  $\mu_i$ ,

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T, P, n_j} = \left( \frac{\partial A}{\partial n_i} \right)_{T, V, n_j} \quad [4-5]$$

We can now re-write the Gibbs equation 4-4,

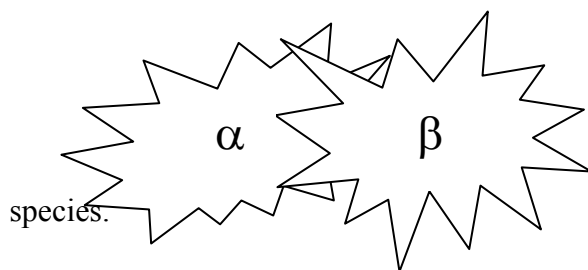
$$dG = -SdT + VdP + \sum \mu_i dn_i \quad [4-6]$$

## Reversible Work

$dW=dG$       const.  $T,P$     at equilibrium, no work  $\rightarrow dG=0$

The chemical potential provides the criterion for phase equilibrium:

For two phases  $\alpha$  and  $\beta$ , in contact, in which species can transfer from one to the other,



at equilibrium:

$$\mu_i^\alpha = \mu_i^\beta$$

For all species, including charged

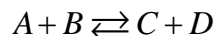
$$\text{Also: } T^\alpha = T^\beta$$

$$p^\alpha = p^\beta$$

## Activity

We cannot measure directly the chemical potential and also its mathematical behavior is inconvenient (goes to negative infinity when a species is absent), hence we want to account for it in terms of another parameter, the activity.

Availability of a species in solution for a chemical reaction is equal to its concentration only in the absence of any intermolecular forces. In any non-ideal solution such forces will exist between the -solvent and the solute molecules. In the case of ionic solutions, in particular those of strong electrolytes, strong long range coulombic forces also exist between the ions. Therefore, in all these practical solutions we must replace the concentration with an "effective concentration" which we will designate as the activity,  $a$ . Hence for the reaction



$$K = \frac{a_C \cdot a_D}{a_A \cdot a_B} \neq \frac{C_C \cdot C_D}{C_A \cdot C_B}$$

Also, when the ionic solution is extremely dilute the activity approach the concentration:

$$a_i \sim C_i \quad \text{as } C \rightarrow 0$$

We would like to speak about the absolute activity of a species  $i$ ,  $a_i$  (dimensionless) irrespective of the concentration units used. We will say that the absolute activity is equal to the concentration times an activity coefficient.

$$a_i = f_i C_i$$

Since we have two major concentration systems:

*m* - molality [gr moles solute/1000 gr solvent]

or

*c* - molarity [gr moles solute/liter solution]

We must define two systems of activity coefficients:

$$a_i = \gamma_i m_i \quad \text{or} \quad a_i = f_i C_i$$

We relate the activity to the chemical potential:

$$\mu_i = RT \ln a_i \quad (\text{absolute activity according to Gugenheim})$$

$$\mu_i = \mu_i^0 + RT \ln a_i \quad (\text{activity defined by Lewis and Randall})$$

### Mean Properties

While conceptually we may discuss the activity of an ionic species, in reality, we are always faced with a solution containing multiple species (as required by electroneutrality). Since the activity of an ion is strongly affected by its neighboring ions, we must therefore discuss (and measure) the activity of an ion in combination with the other constituents of the solution. We do this by defining the mean properties of the neutral combination:

$$a_{+/-} = \gamma_{+/-} m_{+/-}$$

### Calculating the activity

Consider the salt:  $\text{BaCl}_2 \rightarrow \text{Ba}^{++} + 2\text{Cl}^-$

Or in a general form:  $\text{A}_{v^+}\text{B}_{v^-} \rightarrow v^+ \text{A} + v^- \text{B}$

Define:  $v = v^+ + v^-$

Mean molality  $m_{+/-} = m \left( v_+^{v^+} \cdot v_-^{v^-} \right)^{1/v}$

Mean activity  $a_{+/-} = \gamma_{+/-} m_{+/-}$

Activity:  $a = \left( a_{+/-} \right)^v$

### Determining the activity coefficients:

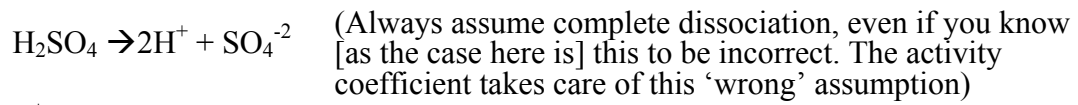
a. Use tabulated values (hard to find, but available)

b. Use the Debye-Huckel limiting law:  $\log \gamma_{+/-} = -0.51 |z_+ \cdot z_-| \sqrt{I}$

Where *I* is the ionic strength of the solution, given by:  $I = \frac{1}{2} \sum_i z_i^2 C_i$

**Example:**

Determine the activity of 0.1 m H<sub>2</sub>SO<sub>4</sub> given that  $\gamma_{+/-} = 0.265$



$$v^+ = 2; \quad v^- = 1$$

$$v = v^+ + v^- = 2 + 1 = 3$$

$$m_{+/-} = m \left( v_+^{v^+} \cdot v_-^{v^-} \right)^{1/v} = 0.1(2^2 * 1^1)^{1/3} = 0.1587$$

$$a_{+/-} = \gamma_{+/-} m_{+/-} = 0.265 * 0.1587$$

$$a = (a_{+/-})^v = (0.1587 * 0.265)^3 = 7.4 * 10^{-5}$$

# Standard Electrode Potentials

Measured vs. Normal Hydrogen Electrode.

In Practice, we use secondary 'reference electrodes'

Expresses the relative tendency of an electrode to give up or accept electrons and change its oxidation state.

Conventionally written as reduction potentials for the half-cell reaction:



or:



$E^0$  = 'Standard' Electrode potentials; refers to potential of electrode in contact with unit activity solution ( $a_{M^{n+}} = 1$ )

Related definitions for: Equilibrium potentials, Galvani potentials, Open circuit potential (OCP), EMF:

Because of the need for a charge balance we must have an accompanying oxidation reaction which provides the electrons. E.g.:



## Standard electrode potentials:

### *Active (anodic)*

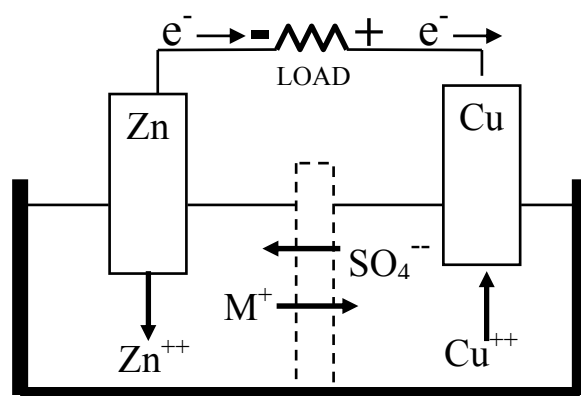
$\text{Li}^+ + \text{e} \rightarrow \text{Li}^0$	-3.045 V	$\text{H}^+ + \text{e} \rightarrow 1/2\text{H}_2$	0 V
$\text{K}^+ + \text{e} \rightarrow \text{K}^0$	-2.935	$\text{HgO} + \text{H}_2\text{O} + 2\text{e} \rightarrow \text{Hg} + 2\text{OH}^-$	0.098
$\text{Ca}^{2+} + 2\text{e} \rightarrow \text{Ca}^0$	-2.866	$\text{Cu}^{++} + \text{e} \rightarrow \text{Cu}^+$	0.153
$\text{Na}^+ + \text{e} \rightarrow \text{Na}^0$	-2.714	$\text{AgCl} + \text{e} \rightarrow \text{Ag} + \text{Cl}^-$	0.2224
$\text{Mg}^{++} + 2\text{e} \rightarrow \text{Mg}^0$	-2.363	$\text{HgCl}_2 + 2\text{e} \rightarrow 2\text{Hg} + 2\text{Cl}^-$	0.2676
$\text{Al}^{+3} + 3\text{e} \rightarrow \text{Al}^0$	-1.662	$\text{Cu}^{++} + 2\text{e} \rightarrow \text{Cu}^0$	0.337
$\text{Ti}^{++} + 2\text{e} \rightarrow \text{Ti}^0$	-1.628	$\text{Fe}(\text{CN})_6^{-3} + \text{e} \rightarrow \text{Fe}(\text{CN})_6^{-4}$	0.36
$\text{Zn}(\text{OH})_2 + 2\text{e} \rightarrow \text{Zn}^0 + 2\text{OH}^-$	-1.245	$\text{I}_2 + 2\text{e} \rightarrow 2\text{I}^-$	0.536
$\text{Mn}^{++} + 2\text{e} \rightarrow \text{Mn}^0$	-1.180	$\text{O}_2 + 2\text{H}^+ + 2\text{e} \rightarrow \text{H}_2\text{O}_2$	0.682
$2\text{H}_2\text{O} + 2\text{e} \rightarrow \text{H}_2 + 2\text{OH}^-$	-0.822	$\text{Fe}^{+3} + \text{e} \rightarrow \text{Fe}^{+2}$	0.771
$\text{Zn}^{++} + 2\text{e} \rightarrow \text{Zn}^0$	-0.764	$\text{Ag}^+ + \text{e} \rightarrow \text{Cu}^0$	0.9
$\text{Cr}^{3+} + 3\text{e} \rightarrow \text{Cr}$	-0.744	$\text{Br}_2 + 2\text{e} \rightarrow 2\text{Br}^-$	1.065
$\text{Fe}^{++} + 2\text{e} \rightarrow \text{Fe}^0$	-0.441	$\text{O}_2 + 4\text{H}^+ + 4\text{e} \rightarrow 2\text{H}_2\text{O}$	1.229
$\text{Cd}^{++} + 2\text{e} \rightarrow \text{Cd}^0$	-0.403	$\text{Cl}_2 + 2\text{e} \rightarrow 2\text{Cl}^-$	1.358
$\text{Ni}^{++} + 2\text{e} \rightarrow \text{Ni}^0$	-0.250	$\text{PbO}_2 + 4\text{H}^+ + \text{e} \rightarrow \text{Pb}^{+2} + 2\text{H}_2\text{O}$	1.455
$\text{Sn}^{++} + 2\text{e} \rightarrow \text{Sn}^0$	-0.136	$\text{Ce}^{+4} + \text{e} \rightarrow \text{Ce}^{+3}$	1.61
$\text{Pb}^{++} + 2\text{e} \rightarrow \text{Pb}^0$	-0.126	$\text{Au}^+ + \text{e} \rightarrow \text{Au}^0$	1.692
$\text{H}^+ + \text{e} \rightarrow 1/2\text{H}_2$	0	$\text{F}_2 + 2\text{e} \rightarrow 2\text{F}^-$	1.87

### *Nobel (Cathodic)*



These are half cell potentials. Obviously, for a process we require two half cells: one with anodic reaction, the other with cathodic (why?)

For example consider the Zn/Cu cell



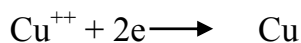
Battery or Fuel-Cell

A spontaneous chemical reaction is used to produce electrical energy

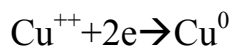
**Anodic Oxidation:**



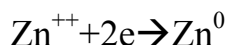
**Cathodic Reduction:**



Assume:



$$E^0 = 0.34 \text{ V}$$

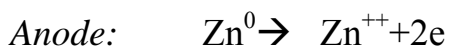


$$E^0 = -0.76 \text{ V}$$

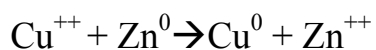
We must reverse one of the reactions (Why?). Note also, that when we add the standard potentials we get -0.42 and hence  $\Delta G$  will be positive. This indicates impossible reaction. We will pick the half cell reaction with the lower standard potential and reverse it:



$$E^0 = 0.34 \text{ V}$$



$$- E^0 = +0.76 \text{ V}$$



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$$V = +1.1 \text{ V} \rightarrow \Delta G = -nFE^0 < 0$$

Now we can sum up the reactions and the standard potentials:

We note that the cell voltage is:  $V_{\text{Cell}} = E^0_{\text{Anode}} - E^0_{\text{Cathode}}$

Materials that are active (very negative) tend to get easily oxidized. This will reverse the cathodic reaction and yield a positive  $E^0$  corresponding to negative (spontaneous)  $\Delta G$ . They are suitable to be anodes in batteries.

The other electrode reaction in the battery during discharge will be cathodic reduction. However, here we have a problem, since we do not want the proton to be reduced to hydrogen gas, which will tend to explode the battery.

Possible materials are those that inhibit hydrogen evolution kinetically – Zinc, and lead, or mercury, or Cd. Alternatively, if we want to e.g., use Li, we must use non-aqueous (a-protic) solvents.

Note: Battery applications - Cathodes  $\text{Li} = -3 \text{ V}$

$\text{Zn} = -0.176$

$\text{Pb} = -0.126$

The highest voltage: Li-F Battery:  $1.87 \text{ V} - (-3.045 \text{ V}) = 4.91 \text{ V}$

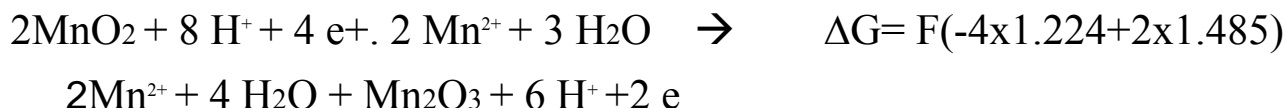
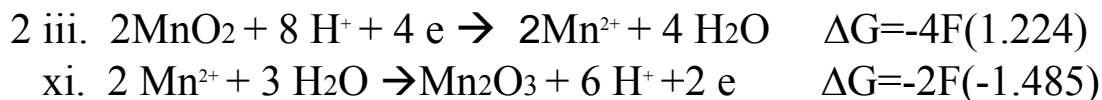
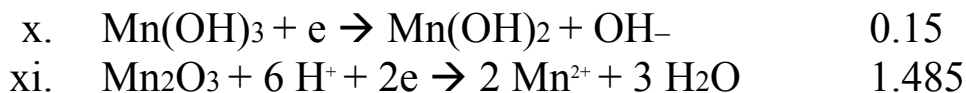
## Leclanche Cell (Zn-Carbon)

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

Cathode:  $2\text{MnO}_2(s) + 2 \text{H}^+(aq) + 2 e^- \rightarrow \text{Mn}_2\text{O}_3(s) + \text{H}_2\text{O}(l)$   
 $[\text{Mn}^{+4} \rightarrow \text{Mn}^{+3} + e^-]$

We find for Mn:

i.	$\text{Mn}^{++} + 2 e^- \rightarrow \text{Mn}$	-1.185
ii.	$\text{Mn}^{3+} + 3e^- \rightarrow \text{Mn}^{2+}$	1.5415
iii.	$\text{MnO}_2 + 4 \text{H}^+ + 2 e^- \rightarrow \text{Mn}^{2+} + 2 \text{H}_2\text{O}$	1.224
iv.	$\text{MnO}_4^- + e^- \rightarrow \text{MnO}_4^{2-}$	0.558
v.	$\text{MnO}_4^- + 4 \text{H}^+ + 3 e^- \rightarrow \text{MnO}_2 + 2 \text{H}_2\text{O}$	1.679
vi.	$\text{MnO}_4^- + 8 \text{H}^+ + 5 e^- \rightarrow \text{Mn}^{2+} + 4 \text{H}_2\text{O}$	1.507
vii.	$\text{MnO}_4^- + 2 \text{H}_2\text{O} + 3 e^- \rightarrow \text{MnO}_2 + 4 \text{OH}^-$	0.595
viii.	$\text{MnO}_4^{2-} + 2 \text{H}_2\text{O} + 2 e^- \rightarrow \text{MnO}_2 + 4 \text{OH}^-$	0.60
ix.	$\text{Mn}(\text{OH})_2 + 2 e^- \rightarrow \text{Mn} + 2 \text{OH}^-$	-1.56



When considering energetics we never add voltages. We add and subtract energies or  $\Delta G$ . When  $n$  is identical in the two reactions, we may add and subtract voltages, since  $\Delta G = -nFE$ . However when adding half cell reactions with different  $n$  we must add or subtract  $\Delta G$ .

Combining identical terms:



$$\Delta G = F(-4 \times 1.224 + 2 \times 1.485) = F(-1.926)$$

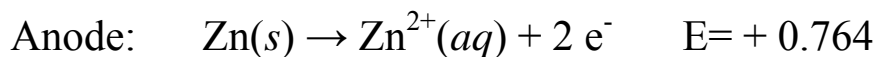
Switching back to voltage:

$$E = -\Delta G/nF = 1.926/2 = 0.963 \text{ V}$$

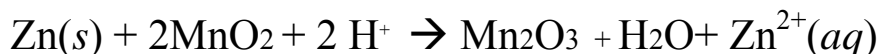
Combining with the Zinc reaction:



Reversing the zinc reaction:

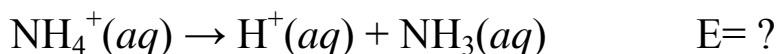


Summing the anode and cathode reactions we get:



$$E = 0.963 + 0.764 = 1.727 \text{ V (in reality we have } V \sim 1.5 \text{ V)}$$

This difference is mainly due to the fact that the proton comes from ammonia:

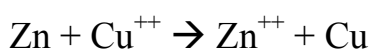


## Corrosion implications:

All very negative material 'love' to give electrons (are readily oxidized). All very positive materials tend to be reduced (accept electrons). This is why we find in nature the alkali metals only as cations, and all 'active' metals are found as oxides. On the other hand, noble metals such as gold or platinum might be found in nature in the reduced form, as e.g., gold metallic nuggets (if we are lucky to find them). We will never find active metal as a reduced (non oxidized) species.

By the same token, we never want to have an active element in its reduced form (e.g., Li, zinc, or even iron) in contact with a 'noble' species in its oxidized form. The active metal will readily give its electrons to the noble material.

This is why we never want to store  $\text{CuSO}_4$  solution in zinc or iron container. We will have the reaction:



which will have a Positive E (or negative  $\Delta G$ ), indicating a spontaneous reaction.

### Dissimilar metal corrosion

## The Cementation reaction

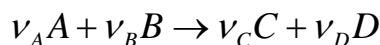


Copper (in the form of carbonates, sulfates, etc.) is dug from the ground and leached with sulfuric acid, producing impure copper sulfate. Iron scrap is then thrown into the bath, causing the reaction above. The copper 'mud' precipitates, with codeposits of iron. Gold. Silver..

The copper 'mud' is then used as anode in a copper refining cell.

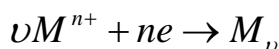
## Nernst equation:

Correcting for activities different from unity:



$$E = E^0 - \frac{RT}{nF} \ln \frac{a_C^{\nu_C} \cdot a_D^{\nu_D}}{a_A^{\nu_A} \cdot a_B^{\nu_B}} \sim E^0 - \frac{RT}{nF} \ln \frac{C_C^{\nu_C} \cdot C_D^{\nu_D}}{C_A^{\nu_A} \cdot C_B^{\nu_B}} \quad (\text{assuming } \gamma_i=1)$$

For the half cell reaction:



$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{M_\nu}}{a_{M^{n+}}^\nu} = E^0 - \frac{RT}{nF} \ln \frac{a_{\text{reduced}}}{a_{\text{oxidized}}^\nu} = E^0 - \frac{RT}{nF} \ln \frac{a_{\text{right}}}{a_{\text{left}}^\nu}$$

At 25 C = 298 K:

$$\frac{RT}{F} = 0.02565 \text{ V}$$

$$\frac{RT}{F} \ln X = 0.02565 \ln X = 2.3 \cdot 0.02565 \log X = 0.059 \log X$$

$$E = E^0 - \frac{0.02565}{n} \ln \frac{a_{M_\nu}}{a_{M^{n+}}^\nu} = E^0 - \frac{0.059}{n} \log \frac{a_{M_\nu}}{a_{M^{n+}}^\nu}$$

Also,

$$a_{\text{element}} = 1$$

$$\ln a^\nu = \nu \ln a$$

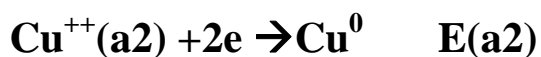
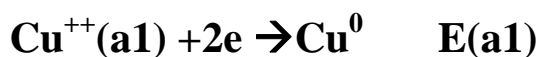
$$\ln \frac{1}{X} = -\ln X$$

$$\ln a - \ln b = \ln \frac{a}{b}$$

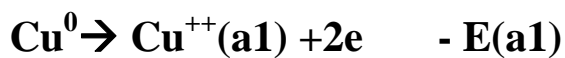
$$E = E^0 - \frac{RT}{n} \ln \frac{a_{M_\nu}}{a_{M^{n+}}^\nu} = E^0 - \frac{RT}{n} \ln \frac{1}{a_{M^{n+}}^\nu} = E^0 + \frac{RT}{n} \ln a_{M^{n+}}^\nu = E^0 + \frac{RT}{\nu n} \ln a_{M^{n+}}$$

## Cells with Varying Concentrations

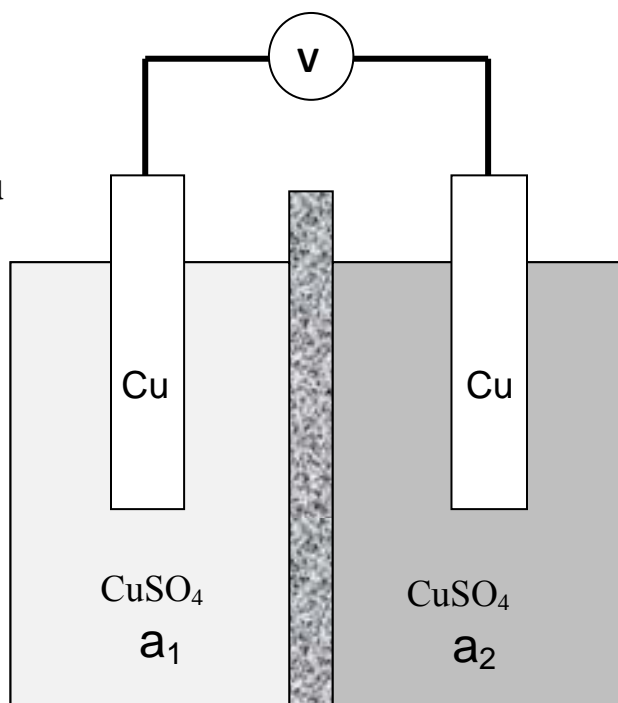
### A. Identical Species



Reverse the more negative:



Add up:



$$a_1 < a_2$$

$$E(a_1) = E^0 - (RT/nF)\ln(1/a_1)$$

$$E(a_2) = E^0 - (RT/nF)\ln(1/a_2)$$

$$-E(a_1) = -E^0 + (RT/nF)\ln(1/a_1)$$

Add up potentials ( $\Delta G$ ):

$$E = -E(a_1) + E(a_2) = -E^0 + (RT/nF)\ln(1/a_1) + E^0 - (RT/nF)\ln(1/a_2)$$

$$E = (RT/nF)\ln(a_2/a_1) > 0 \quad [\text{Spontaneous}]$$

$a_1$  = anode (dissolves)

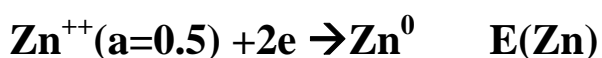
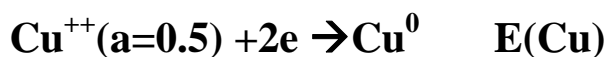
$a_2$  = cathode (plates)

## Cells with Varying Concentrations

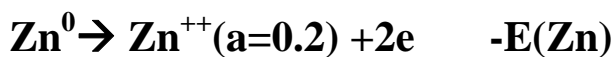
### B. Non- Identical Species



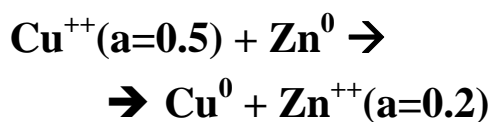
**E<sub>cell</sub>=?**



**Reverse the more negative:**



**Add up:**



$$E_{Cu} = E_{Cu}^0 - \frac{RT}{2F} \ln \frac{a_{Cu^0}}{a_{Cu^{++}}}$$

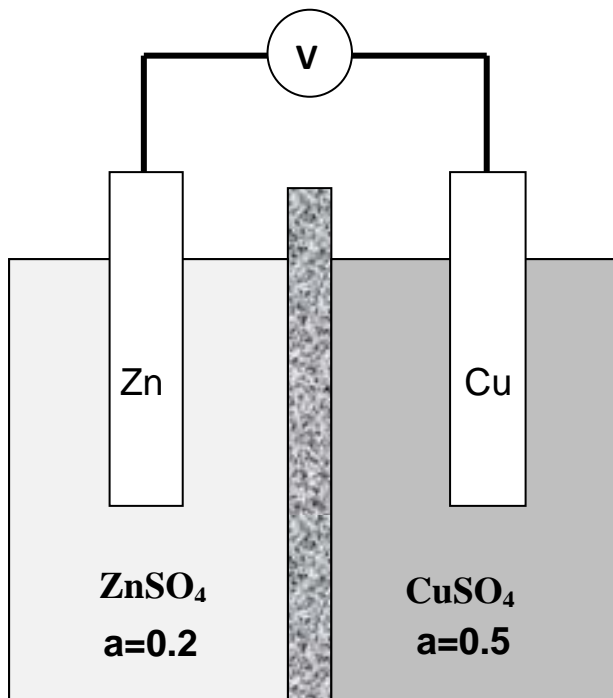
$$E_{Zn} = E_{Zn}^0 - \frac{RT}{2F} \ln \frac{a_{Zn^0}}{a_{Zn^{++}}}$$

$$-E_{Zn} = -E_{Zn}^0 + \frac{RT}{2F} \ln \frac{a_{Zn^0}}{a_{Zn^{++}}}$$

$$E_{Cell} = E_{Cu} + (-E_{Zn}) = E_{Cu}^0 - E_{Zn}^0 - \frac{RT}{2F} \ln \frac{a_{Cu^0}}{a_{Cu^{++}}} + \frac{RT}{2F} \ln \frac{a_{Zn^0}}{a_{Zn^{++}}}$$

$$E_{Cell} = (E_{Cu}^0 - E_{Zn}^0) + \frac{RT}{2F} \ln \frac{a_{Zn^0} a_{Cu^{++}}}{a_{Zn^{++}} a_{Cu^0}} = (E_{Cu}^0 - E_{Zn}^0) + \frac{RT}{2F} \ln \frac{a_{Cu^{++}}}{a_{Zn^{++}}}$$

$$E_{Cell} = (0.34 - [-0.784]) + \frac{0.059}{2} \log \frac{0.5}{0.2} = 1.115 + 0.03 * 0.398 = 1.127V$$



**Determine now the concentrations upon short circuit:**

$$E_{\text{cell}} = 0 \text{ V}$$

$$\begin{aligned} E_{\text{cell}} = 0 &= \left( E_{\text{Cu}}^0 - E_{\text{Zn}}^0 \right) + \frac{RT}{2F} \ln \frac{a_{\text{Cu}^{++}}}{a_{\text{Zn}^{++}}} = \\ &= (0.34 - [-0.784]) + \frac{0.059}{2} \log \frac{a_{\text{Cu}^{++}}}{a_{\text{Zn}^{++}}} = 1.115 + 0.03 * \log \frac{a_{\text{Cu}^{++}}}{a_{\text{Zn}^{++}}} \end{aligned}$$

$$\frac{a_{\text{Cu}^{++}}}{a_{\text{Zn}^{++}}} = 10^{-37}$$

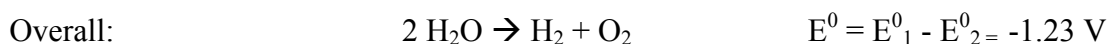
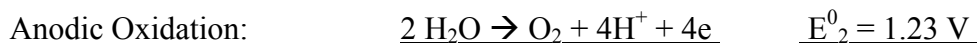
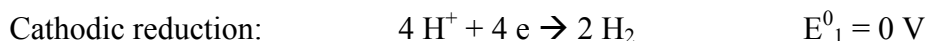
Since  $a_{\text{Zn}}$  cannot be significantly larger than 1, very few atoms of cupric ions remain in solution

Industrial application: Copper displacement by iron scrap.



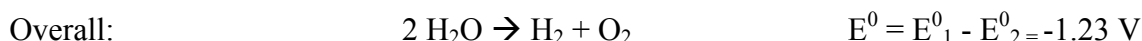
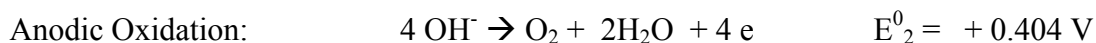
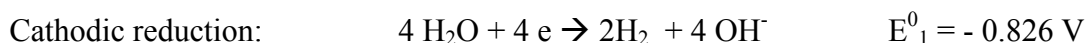
## E-pH diagrams (Pourbaix diagrams)

Water may be electrolytically decomposed (= ‘electrolyzed’) according to:



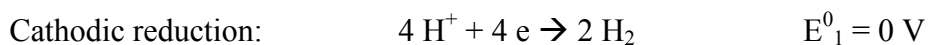
The negative standard potential tells us that the reaction is not spontaneous (positive  $\Delta G$ ). Acidic medium has been assumed at pH=0, however a similar reaction can be written for neutral or basic environment, remembering that under neutral conditions we have both  $\text{H}^+$  and  $\text{OH}^-$  species, and in base environment we only have  $\text{OH}^-$  and water.

In base environment (pH= 14) we have:



Obviously, both reactions exhibit the same overall standard potential (- 1.23 V), and it should be so, because the overall reaction is the same, and does not involve the pH.

It is instructive to write the potential for each of the electrode reactions separately. We will assume, here, arbitrarily for this illustration) that we are in acidic environment (pH=0).



$$E = E^0 - \frac{RT}{nF} \log \frac{\Pi a^v_{\text{products}}}{\Pi a^v_{\text{reactants}}}$$

$$E_{\text{H}_2} = 0 - \frac{0.059}{4} \log \frac{p_{\text{H}_2}}{a_{\text{H}^+}^4} = -\frac{0.059}{4} \log a_{\text{H}^+}^{-4} \cdot p_{\text{H}_2} = +0.059 \log a_{\text{H}^+} \cdot p_{\text{H}_2}$$

Since:

$$\text{pH} \equiv -\log a_{\text{H}^+}$$

$$E_{\text{H}_2} = -0.059 \cdot \text{pH} \cdot \log p_{\text{H}_2}$$

Assuming that the partial pressure of hydrogen is 1 ( $p_{\text{H}_2}=1$ ),

$$E_{\text{H}_2} = -0.059 \cdot \text{pH}$$

We can show, similarly, for the oxygen:

$$E_{O_2} = 1.23 - 0.059 \cdot pH$$

The overall reaction,  $E_{H_2} - E_{O_2}$

$$E_{H_2} - E_{O_2} = -1.23$$

The same as before. Clearly, from Nernst Eq., only reactions that exhibit explicitly either  $H^+$  or  $OH^-$  will show a dependence of  $E$  on the  $pH$ .

We now will plot a diagram of the dependence of each of the electrode reactions on the  $pH$ :

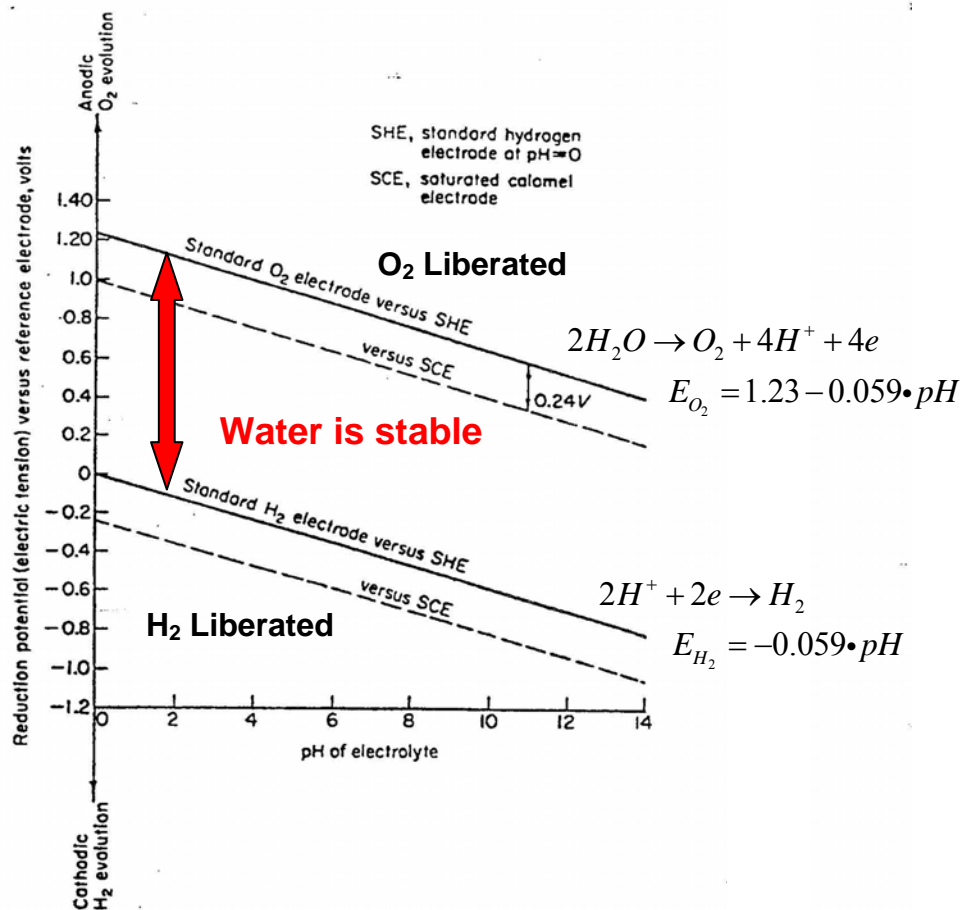
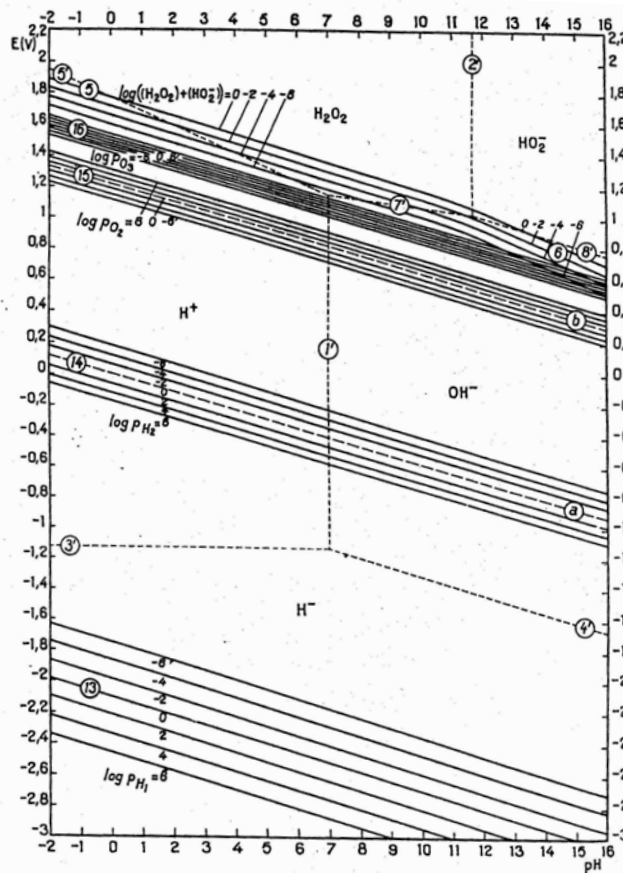


Fig. 4 Potentials of standard-state hydrogen and oxygen electrodes versus  $pH$  of electrolyte, using the reduction potential sign convention.



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#### CHAPTER IV. SECTIONS 3.1-3.5

##### 3.2. STABILITY AND FORMATION OF THE ALKALI METALS

The alkali metals, as well as the alkaline earth metals, exert extremely low solution potential.

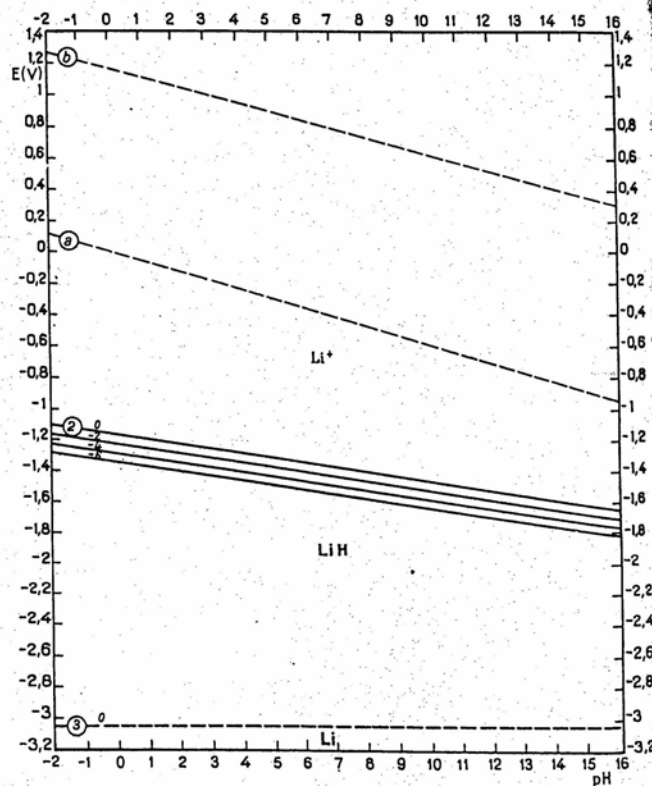


FIG. 1. Potential-pH equilibrium diagram for the system lithium-water, at 25°C.

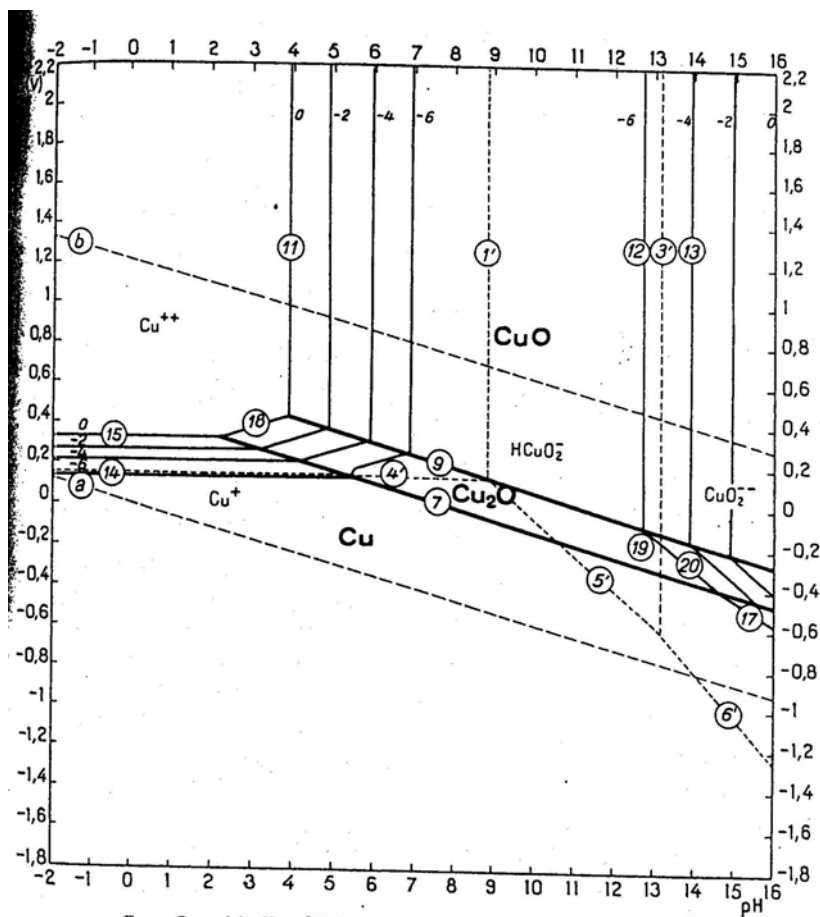
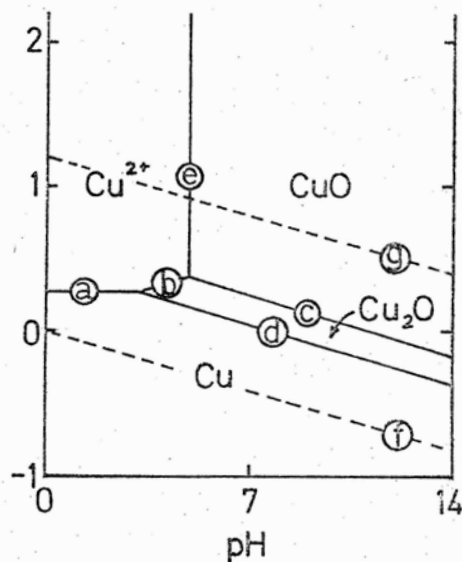


FIG. 1. Potential-pH equilibrium diagram for the system copper-water, at 25°C.  
[Considering the solid substances Cu, Cu<sub>2</sub>O and CuO. Cu(OH)<sub>2</sub> is not considered.]



Pourbaix Diagram for the System Cu-Cu<sup>2+</sup>-Cu<sub>2</sub>O-CuO-H<sub>2</sub>O. Activity of Cupric Ion is assumed to be 0.01.

Line	Reaction
a	$\text{Cu} = \text{Cu}^{2+} + 2\text{e}^-$
b	$\text{Cu}_2\text{O} + 2\text{H}^+ = 2\text{Cu}^{2+} + \text{H}_2\text{O} + 2\text{e}^-$
c	$\text{Cu}_2\text{O} + \text{H}_2\text{O} = 2\text{CuO} + 2\text{H}^+ + 2\text{e}^-$
d	$2\text{Cu} + \text{H}_2\text{O} = \text{Cu}_2\text{O} + 2\text{H}^+ + 2\text{e}^-$
e	$\text{Cu}^{2+} + \text{H}_2\text{O} = \text{CuO} + 2\text{H}^+$
f	$\text{H}_2 = 2\text{H}^+ + 2\text{e}^-$
g	$\text{H}_2\text{O} = 1/2 \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$

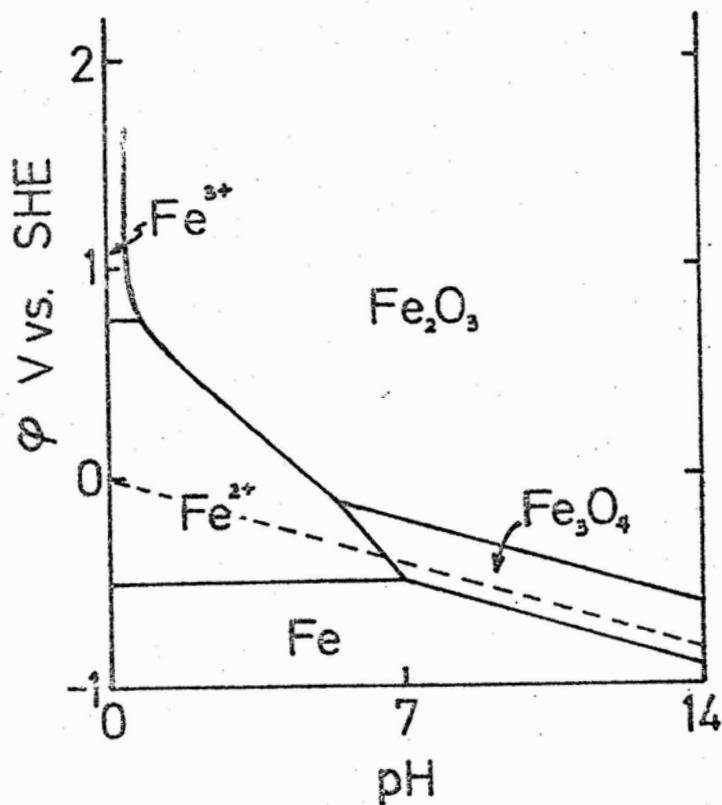
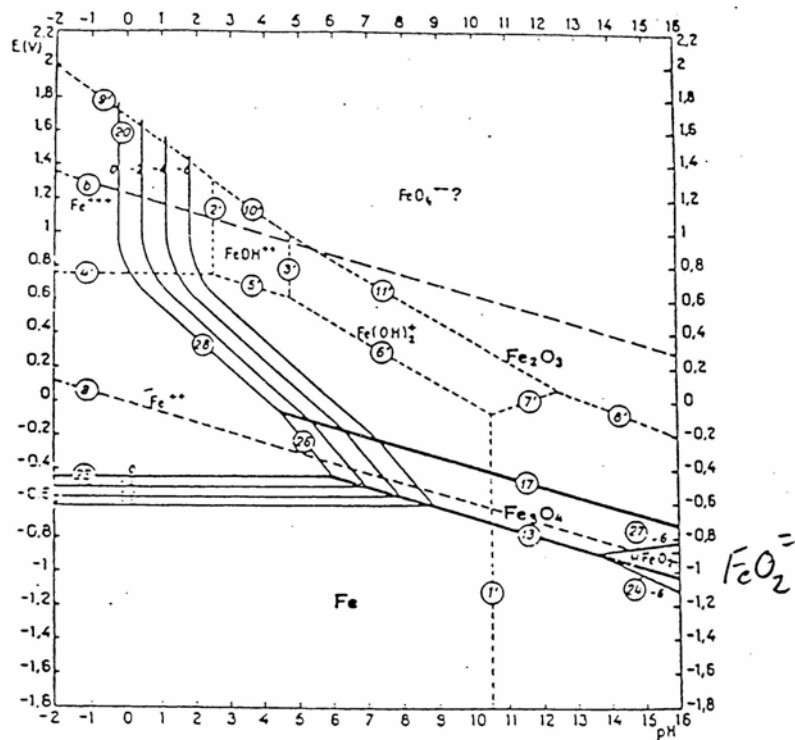


FIGURE III-10. Pourbaix Diagram for Iron.

Effect of complexing agents on codeposition of alloys.

The normal deposition potentials for copper and zinc are far apart. Nevertheless, it is possible to plate brass (a Cu-Zn alloy) directly by electrolysis. Suggest how simultaneous deposition of these two metals is possible:



$$\Delta E = 1.102 \text{ V}$$

↑ This is clearly too much of a difference

$$(107) \quad E_1 = E_1^\circ + \frac{RT}{2F} \ln \text{Zn}^{++}$$

$$(108) \quad E_2 = E_2^\circ + \frac{RT}{2F} \ln \text{Cu}^{++}$$

$$(109) \quad E_1 = E_2: \text{ for codeposition}$$

$$(110) \quad -0.758 + \frac{0.059}{2} \lg \text{Zn}^{++} = +0.344 + \frac{0.059}{2} \lg \text{Cu}^{++}$$

$$(111) \quad \lg \frac{[\text{Zn}^{++}]}{[\text{Cu}^{++}]} = \frac{2.204}{0.059}; \quad \frac{[\text{Zn}^{++}]}{[\text{Cu}^{++}]} = 1.7 \times 10^{37}$$

Clearly, not many copper ions are allowed to be in the solution. A "permissible" concentrations ratio can be obtained by the addition of a complexing agent such as cyanide. The cuprocyanide anion dissociates into cuprous and cyanide ions according to:



And for the zinc:



Assume 0.05 M copper cyanide solution and 0.025 M  $\text{Zn}(\text{CN})_4^{2-}$

$$(112) \quad \frac{[\text{Cu}^+][\text{CN}^-]^3}{[\text{Cu}(\text{CN})_3^{2-}]} = \frac{[x][3x]^3}{[0.05-x]} = 5.6 \times 10^{-28} \quad \begin{array}{l} [\text{Cu}^+] = 3.19 \times 10^{-8} \\ [\text{CN}^-] = 9.57 \times 10^{-8} \end{array}$$

for the Zn:

$$[\text{Zn}^{++}] = 6.62 \times 10^{-5}; \quad [\text{CN}] = 2.65 \times 10^{-4}$$

When the two solutions are mixed the cyanide concentration will be mostly due to the  $\text{An}$  complex dissociation. Calculate again the cuprous ion conc.:

$$(113) \quad \frac{[\text{Cu}^+]}{0.05} [2.65 \times 10^{-4}]^3 = 5.6 \times 10^{-28} \quad [\text{Cu}^+] = 1.50 \times 10^{-18}$$

The new deposition potentials are:

$$\text{For Zn:} \quad E_1 = -0.758 + \frac{0.059}{2} \lg 6.62 \times 10^{-5} \approx -0.90\text{V}$$

$$\text{For Cu:} \quad E_1 = +0.52 + \frac{0.059}{1} \lg 1.5 \times 10^{-18} \approx -0.54\text{V}$$

$$E^\circ \text{ Cu}^+/\text{Cu} \quad \Delta V \approx 0.36\text{V}$$

This  $\Delta V$  is considerably closer than 1.1 V, and can be "bridged over" by surface overpotential terms.

#### Temperature Effects on the EMF

$$(114) \quad \Delta G = \Delta H - T\Delta S = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_p; \quad \Delta G = -nFe$$

$$(115) \quad -nFE = \Delta H - nFT\left(\frac{\partial E}{\partial T}\right)_p$$

$$(116) \quad \Delta H = -nF \left[ E - T\left(\frac{\partial E}{\partial T}\right)_p \right]$$

Note that:

$$(117) \quad \Delta S = nF \left(\frac{\partial E}{\partial T}\right)_p \quad \begin{array}{l} \text{slope of } E \text{ vs. } T \text{ gives entropy change on the} \\ \text{order of } 0.5\text{mV}/^\circ\text{C} \end{array}$$

Also:

$$(118) \quad \Delta C_p = nFT\left(\frac{\partial^2 E}{\partial T^2}\right)_p \quad \leftarrow \text{Difficult to determine accurately}$$

$$\left(\frac{\partial E}{\partial T}\right)_p = \frac{\Delta S}{nF}$$

$\Delta S$  can be either negative or positive, but it is a small number under ambient temperatures

#### Effects of Pressure on EMF

$$(119) \quad \left(\frac{\partial E}{\partial p}\right)_T = -\frac{\Delta V}{nF} \quad \begin{array}{l} \text{For solids and liquids pressure dependence} \\ \text{of volume is normally negligible} \end{array}$$

Considering only the volume change of a gas:

$$(120) \quad E_p = E_1 - \frac{1}{nF} \int_1^p \Delta V dp \quad \text{dependence of } V \text{ on } P \text{ must be specified}$$

Assuming ideal gas behavior  $PV = NRT$

$$E_p = E_1 - \frac{NRT}{nF} \int_1^P d \ln P = E_1 - \frac{NRT}{nF} \ln P$$

Values of  $N$  and  $n$  have to be established with care.

Example: Decomposition potential of water at 25°C and 100 At.



$$E_{100} = -1.23 - \frac{3 \times 0.059}{4} \lg_{10} 100 = -1.23 - 0.09 = -1.32 \text{ V}$$

The negative sign is indicative that this reaction (decomposition of water) is not spontaneous,  $\Delta E$  is positive.

### Current Flow and Heat Effects

The potential of a cell under equilibrium is called the "EMF". Equilibrium implies that there is no current flow. When current flows the cell deviates from equilibrium and for a case of a galvanic cell the terminal voltage  $E_T$  will be lower than the EMF because of ohmic dissipation on the internal cell resistance.

The current flowing through the cell:

$$i = \frac{EMF}{R_e + R_i}$$

where  $R_e$  - external resistance

$R_i$  - internal resistance

The component  $i R_e = E_T$  = Terminal voltage.

The relationship between EMF and  $E_T$ :

$$\frac{E_T}{EMF} = \frac{R_e}{R_e + R_i}$$

for  $n$  cells in series  $i = \frac{nEMF}{R_e + nR_i}$

(same as for single  
if  $R_i \gg R_e$ ;  $i = \frac{EMF}{R_i}$   
if  $R_i \ll R_e$ ;  $i = n \cdot \frac{EMF}{R_e}$



if  $n$  cells //:

5)

$$i = \frac{\text{EMF}}{R_e + \frac{R_i}{n}}$$

(for batteries  $R_i = 0.05 - 0.5 \Omega$ )

$$\text{if } R_i \gg R_e, i = n \frac{\text{EMF}}{R_1}$$

current prop. to number of cells

$$\text{if } R_i \ll R_e, i = \frac{\text{EMF}}{R_e}$$

current same as for single cell

## Heat Effects in Cells

Heat effects are measured either in terms of either:

$Q$  [cal/mole] - heat of reaction

or

$q$  [cal/sec] - rate of heat flow

The two are related through:

$$q = Q \dot{m} \left[ = \frac{\text{cal}}{\text{mole}} \frac{\text{mole}}{\text{sec}} = \frac{\text{cal}}{\text{sec}} \right]$$

Where  $\dot{m}$ , the rate of material reacted is related to the current through Faraday's law:

$$\dot{m} = \frac{w}{Mt} = \frac{I}{Fz} \left[ \frac{\text{mole}}{\text{sec}} \right]$$

In order to analyze the heat effects we must first assign a sign convention. Accordingly, heat evolved (giving rise to cell temperature) will be considered with a negative sign. Conversely, heat absorbed (causing cell cooling) will be positive.

Heat effects (cooling or heating) of electrochemical cells are due to two classes of phenomena:

- Reversible ("thermodynamic") heat effects
- Heat due to irreversible (dissipative processes).

The heat associated with the thermodynamic (reversible) process is *associated with electrical work*

$$Q_{\text{rev}} = T \Delta S$$

or

I

$$q_{\text{rev}} = \dot{m} T \Delta S$$

$$\Delta S < 0 \rightarrow \text{heat is evolved}$$

$\Delta S$  can either be positive or negative hence the cell may heat or cool down due to reaction.  $\Delta S$ , however, is typically a small quantity and unless the temperature is very high the reversible heat effect is rather small.

- The heat associated with the irreversible processes is always negative (heat evolved). It is given by the various dissipative processes in the cell, including diffusion, kinetics and ohmic migration. Typically the later, given by  $I\eta_a$  or  $I^2R$ , is dominant. Hence,

$$q_{\text{irr}} = -0.24 |I\eta_a| = -0.24 I^2 R = -0.24 \frac{\eta_a^2}{R} \quad \left[ \frac{\text{cal}}{\text{sec}} \right]$$

The factor of 0.24 is due to the conversion from joules to calories:

$$1 \text{ joule} = 0.24 \text{ cal.}$$

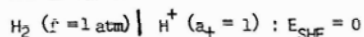
Lastly,

$$q_{\text{total}} = q_{\text{rev}} + q_{\text{irr}} = \dot{m} T \Delta S - 0.24 |I\eta_a| \quad [\text{cal/sec}]$$

# I. THERMODYNAMIC POTENTIALS AND REFERENCE ELECTRODES

## A. REFERENCE ELECTRODES FOR AQUEOUS SOLUTIONS

### 1. PRIMARY REFERENCE: THE STANDARD HYDROGEN ELECTRODE (SHE)



AT ALL TEMPERATURES BY DEFINITION.

### 2. SECONDARY REFERENCES: FOR USE WITHOUT LIQUID JUNCTIONS

#### A) TABLE I: TYPICAL REFERENCE ELECTRODES

$[E_{\text{red}}^{\circ} \text{ AT } 25^{\circ}\text{C}]^{\text{A}}$

Hg / $\text{Hg}_2\text{Cl}_2$ / HCl (stable)	+ 0.26823 V	(calomel)
Hg / $\text{Hg}_2\text{SO}_4$ / $\text{H}_2\text{SO}_4$	+ 0.6151	
Hg / HgO / KOH	+ 0.098	
Ag / AgCl / HCl	+ 0.2224	
Cd / $\text{Cd}(\text{OH})_2$ / KOH	- 0.809	
$\text{H}_2$ / $\text{H}^+$	0	
$\text{H}_2$ / $\text{OH}^-$	- 0.828	
$\alpha$ H-Pd / $\text{H}^+$	+ 0.050	
DYNAMIC (Pt) $\text{H}_2 \uparrow$ / $\text{H}^+$	PROVISIONAL <sup>B</sup>	

<sup>A</sup> STANDARD REDUCTION POTENTIALS IN AQUEOUS SYSTEMS. NOTE THAT THE REDUCTION POTENTIALS AND ELECTRODE POTENTIALS HAVE THE SAME SIGNS. ALL POTENTIALS VS. SHE.

<sup>B</sup>  $\text{H}_2$  GENERATED BY SMALL CATHODIC POLARIZING CURRENT ON HIGH AREA Pt CATHODE. POTENTIAL SHOULD BE CHECKED AGAINST A KNOWN REFERENCE. POTENTIAL USUALLY CLOSE TO REVERSIBLE  $\text{H}_2$  /  $\text{H}^+$  ELECTRODE.

### 3. SECONDARY REFERENCES: FOR USE WITH SALT BRIDGES TO MINIMIZE LIQUID JUNCTION POTENTIALS

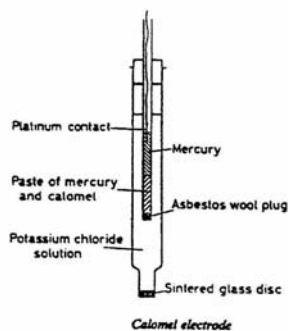
#### A) REQUIREMENTS OF SALT BRIDGE TO MINIMIZE LIQUID JUNCTION POTENTIALS

- 1) HIGH CONCENTRATION
- 2) TRANSFERENCE NO.  $t_+ \approx t_-$

#### B) TYPICAL ELECTROLYTES: KCl, $\text{NH}_4\text{NO}_3$

TABLE II: CALOMEL REFERENCES WITH SALT BRIDGES

	$E_{25^{\circ}\text{C}}$
Hg / $\text{Hg}_2\text{Cl}_2$ / KCl (sat'd) / salt bridge	+ 0.2445V
Hg / $\text{Hg}_2\text{Cl}_2$ / KCl (1M) / salt bridge	+ 0.2830
Hg / $\text{Hg}_2\text{Cl}_2$ / KCl (0.1M) / salt bridge	+ 0.3356



#### 4. REFERENCE ELECTRODES FOR NON AQUEOUS SYSTEMS

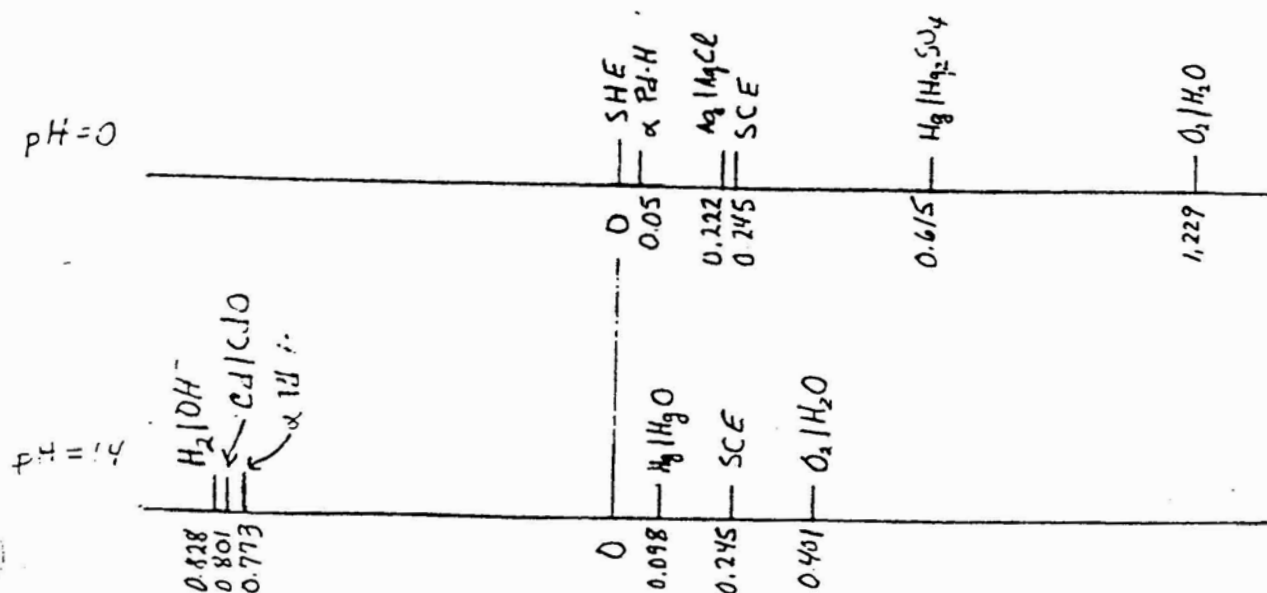
TABLE III: APPLICATIONS OF REFERENCE ELECTRODES

Electrode	Suitability				Special applications
	Aqueous solutions	Organic solvents	Fused salts	Biological systems	
standard hydrogen	****	**	*	*	Electrode standardization
silver-silver halide	****	***	***	***	Secondary reference standard; thermodynamic studies
calomel	****	**	*	*	Thermodynamic studies
glass	****	**	*	***	pH measurement; potentiometric titration
quinhydrone	****	*	*	**	Potentiometric studies
metal-metal oxide and sulfide	***	*	***	**	Alkaline systems; high-temperature studies
metal-metal halide	**	**	***	**	Thermodynamics of molten inorganic halides
metal-metal sulfate	***	**	**	**	Thermodynamic studies
membrane	***	**	*	**	Membrane performance studies; colloidal solutions
halogen	*	*	**	*	Molten inorganic halides
oxygen	**	*	*	**	Oxygen tension measurement
thiol	*	*	*	**	Biological oxidation-reduction experiments

Key: \*\*\*\* generally applicable  
 \*\*\* applicable to selected systems  
 \*\* occasionally suitable  
 \* insufficiently explored and/or inapplicable

G. Janz and F. Kelly in Encyclopedia of Electrochemistry, C. Hampel, ed., Reinhold, NYC, 1964, p. 1015.

#### 5. COMPARISON OF REFERENCE ELECTRODE POTENTIALS



## Liquid Junction Potential (LJP)

- A small (few mV) potential that typically exists over regions of electrolyte with varying concentrations.
- The origin of liquid Junction potential is in diffusion and electrostatics, and it is present in cells without current passage (equilibrium), hence it lies in the border region between thermo and transport.
- The liquid junction potential is a function of the electrolyte type and the structure of the region of varying concentrations; hence it is typically a constant value for a given system.
- The determination of the LJP is complicated since it requires detailed knowledge of the concentration profile in the junction region
- LJP is always present when using reference electrodes, since those involve a concentration gradient across a salt bridge.
- LJP is of little importance to engineers. Areas where it is important are:
  - The determination of accurate absolute equilibrium potentials
  - Biological systems (e.g., cell membranes) that are characterized by a small potential.

Consider a two compartment cell, separated by a diaphragm.

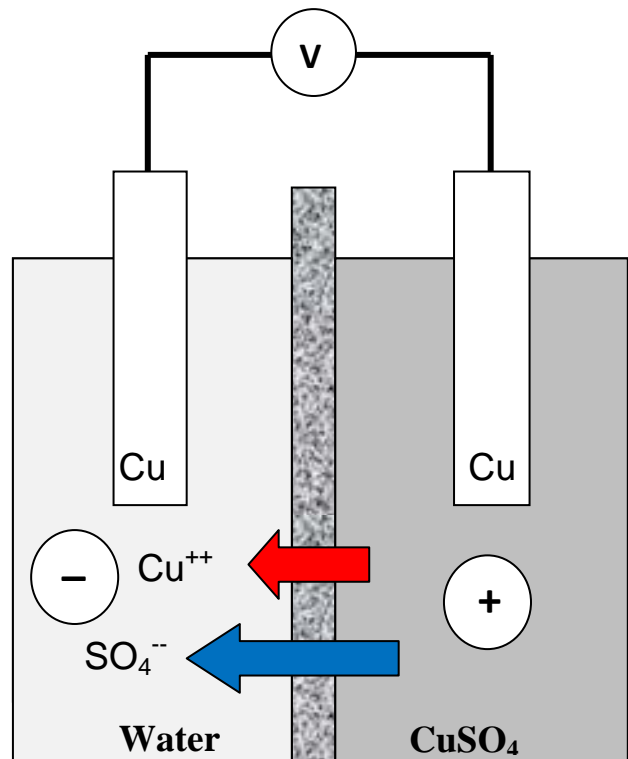
One compartment contains copper sulfate; the other water.

Clearly, Cupric and sulfate ions will diffuse From the right compartment to the left one.

However their properties are different:

**Cu:**  $\lambda_{\text{Cu}} = 54$      $D \sim 5 \cdot 10^{-6}$

**SO<sub>4</sub>:**  $\lambda_{\text{SO}_4} = 80$      $D \sim 7.4 \cdot 10^{-6}$



As a consequence of the different diffusivity, the Sulfate ion will diffuse faster than the cupric ion. Since the sulfate is negatively charged, the left compartment 4-66 will build-up a negative charge, the right one will become positive.

The different charge gives rise to a potential. The potential will now slow down the fast moving sulfate ion and will enhance (electrostatically) the transport of the slow moving copper. This potential difference which causes both ions to continue diffusing at the same speed is the LJP.

The preferred salt in salt bridges for reference electrodes is KCl. The reason being is that

$$\lambda_K \sim \lambda_{Cl}$$

Hence both ions diffuse at about the same rate, minimizing the LJP.