CHEM465/865, 2006-3, Lecture 8, 22nd Sep., 2006

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

$$E = E^0 - \frac{RT}{|\nu_e| F} \ln Q \qquad \text{with} \qquad Q = \frac{[C]^{|\nu_C|}\,[D]^{|\nu_D|}}{[A]^{|\nu_A|}\,[C]^{|\nu_B|}}$$

has two parts:

- Standard EMF E^0 (tabulated values)

  standard conditions:
  - 25℃
  - gases: 1 bar, solutions: 1M, unit activities

- composition-dependent part, deviations from standard conditions (involving T-variation)!

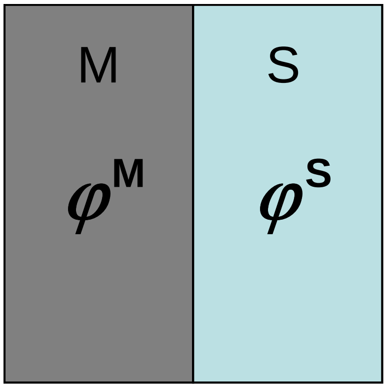
Known standard potentials and composition of system → in principle EMFs of all systems can be determined!

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: $E_{\mathrm{el}} = \varphi^{\mathrm{M}} - \varphi^{\mathrm{S}}$ **(cathodic)**

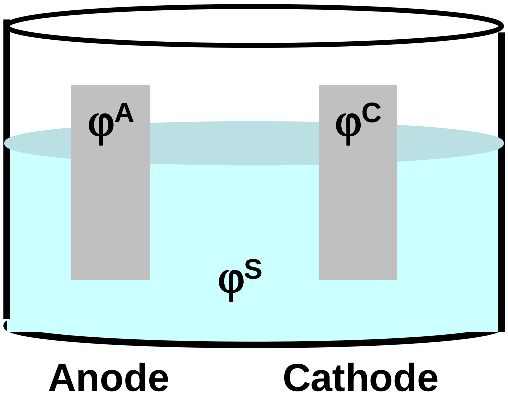


Remember: E_{el} **proportional to the amount of work required to move a test charge across the metal|solution interface**

Measurement: two electrodes needed

Electrochemical Cell

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



Electrical work performed by system in bringing electron from anode to cathode.

Can be calculated for known E_{el} **at the two distinct M|S interfaces**

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

Measurable! What do we need?

- **metal connection between electrodes**
- **voltmeter with high electronic resistance (“close to” electrochemical equilibrium).**

Classification of electrodes

Based on nature of species involved in electrochemical equilibria: electrode material, components of electrolyte, other substances (gases, liquids, solids)

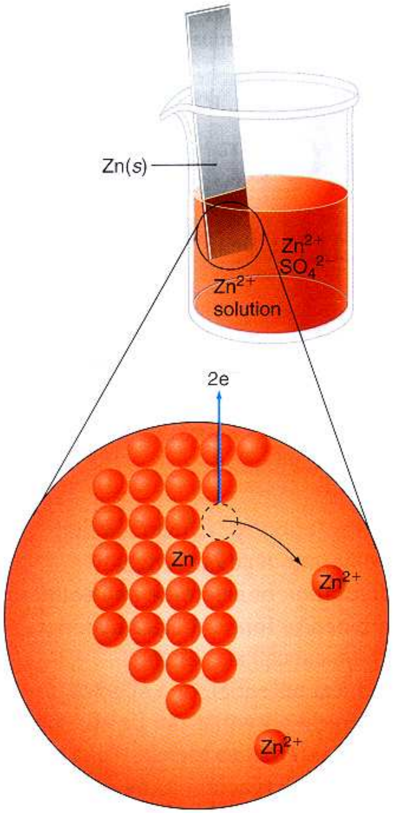
Conventionally, four types of electrodes distinguished:

1) Electrodes of the first type

- **Metal electrode in contact with solution of its ions:** $M^{z+} + ze^- \rightarrow M$ **(ion transfer)**

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

e.g. $Zn^{2+}|Zn$ or $Au|[Au(CN)_2]^-$



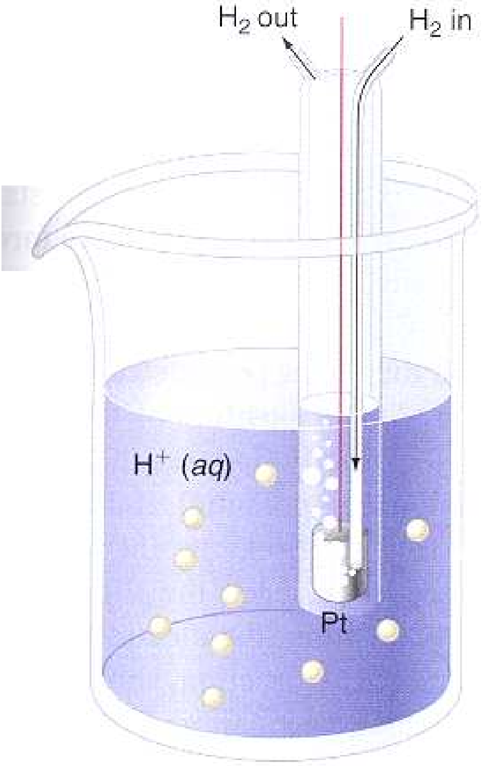
- **Nonmetal in contact with its ions on the surface of an inert metal electrode, e.g. the HYDROGEN ELECTRODE: $H^+|H_2(g)|Pt$**

  $$E_{el} = E^0 - \frac{RT}{F}\ln\left(\frac{p_{H_2}^{1/2}}{a_{H^+}}\right)$$ **(here: cathodic)**

  or $Pt,Cl_2|Cl^-$ (these are gaseous electrodes)

  e^- transfer between neutral species and its ion

Hydrogen electrode



2) Metal electrodes in contact with solution containing anions that form a poorly soluble salt with the metal ions, e.g. the

CALOMEL ELECTRODE: $Hg|Hg_2Cl_2|Cl^-$

$$E = E^0 - \frac{RT}{F}\ln\left(a_{Cl^-}\right)$$

Salt: almost entirely in solid form (~ unit activity). Electrode potential: function anion activity only. Low solubility of the salt: electrodes are very stable – good reference electrodes.

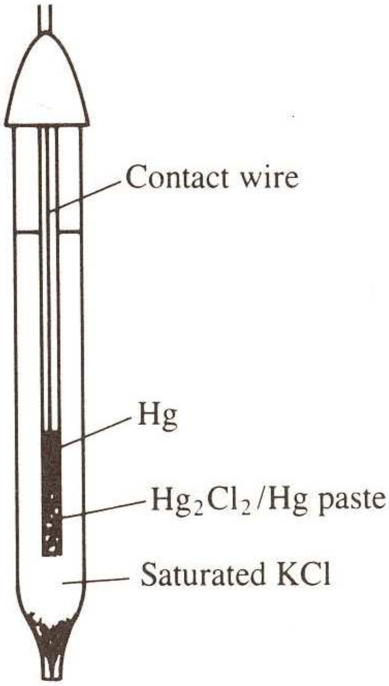


Fig. 2.3. The saturated calomel electrode.

Another example: $Ag|AgCl|Cl^-$

3) Redox or inert electrodes: simultaneous equilibria with respect to anions and cations, no surface reaction occurring
4) Other, e.g. pH sensitive glass electrode.

Most important reference electrode:

standard hydrogen electrode (SHE)

Potential fixed (at all T) at $E^0_{\mathrm{SHE}} = 0$.

Tabulated standard electrode potentials:

- EMF of an electrochemical cell
- standard hydrogen electrode on the left (ANODE)
- considered electrode on the right (CATHODE)
- all components of the system are at unit activity
- very reproducible scale

Another important reference electrode:

standard calomel electrode (SCE), $Hg|Hg_2Cl_2|Cl^-$

Recommended literature (electrochemical equilibria, electrode potentials, EMF, measurements of potentials):

- Encyclopedia of Electrochemistry, Edited by A.J. Bard and M. Stratmann, vol. 1, ch. 1, Weinheim, Wiley-VCH, 2002-...

From R.A. Silbey and R.J. Alberty, Physical Chemistry, Wiley, NY, 2001.

Table 7.2 Standard Electrode Potentials at 25 °C[a,e]

Electrode	$E°/\mathrm{V}$	*Electrode Reaction*
$\mathrm{F^- \mid F_2(g) \mid Pt}$	2.87	$\frac{1}{2}\mathrm{F_2(g)} + \mathrm{e^-} = \mathrm{F^-}$
$\mathrm{Au^{3+} \mid Au}$	1.50	$\frac{1}{3}\mathrm{Au^{3+}} + \mathrm{e^-} = \frac{1}{3}\mathrm{Au}$
$\mathrm{Pb^{2+} \mid PbO_2 \mid Pb}$	1.455	$\frac{1}{2}\mathrm{PbO_2} + 2\mathrm{H^+} + \mathrm{e^-} = \frac{1}{2}\mathrm{Pb^{2+}} + \mathrm{H_2O}$
$\mathrm{Cl^- \mid Cl_2(g) \mid Pt}$	1.3604	$\frac{1}{2}\mathrm{Cl_2(g)} + \mathrm{e^-} = \mathrm{Cl^-}$
$\mathrm{H^+ \mid O_2(g) \mid Pt}$	1.2288	$\mathrm{H^+} + \frac{1}{4}\mathrm{O_2(g)} + \mathrm{e^-} = \frac{1}{2}\mathrm{H_2O}$
$\mathrm{Ag^+ \mid Ag}$	0.7992	$\mathrm{Ag^+} + \mathrm{e^-} = \mathrm{Ag}$
$\mathrm{Fe^{3+}, Fe^{2+} \mid Pt}$	0.771	$\mathrm{Fe^{3+}} + \mathrm{e^-} = \mathrm{Fe^{2+}}$
$\mathrm{I^- \mid I_2(s) \mid Pt}$	0.5355	$\frac{1}{2}\mathrm{I_2} + \mathrm{e^-} = \mathrm{I^-}$
$\mathrm{Cu^+ \mid Cu}$	0.521	$\mathrm{Cu^+} + \mathrm{e^-} = \mathrm{Cu}$
$\mathrm{OH^- \mid O_2(g) \mid Pt}$[b]	0.4009	$\frac{1}{4}\mathrm{O_2(g)} + \frac{1}{2}\mathrm{H_2O} + \mathrm{e^-} = \mathrm{OH^-}$
$\mathrm{Cu^{2+} \mid Cu}$	0.3394	$\frac{1}{2}\mathrm{Cu^{2+}} + \mathrm{e^-} = \frac{1}{2}\mathrm{Cu}$
$\mathrm{Cl^- \mid Hg_2Cl_2(s) \mid Hg}$[c]	0.268	$\frac{1}{2}\mathrm{Hg_2Cl_2} + \mathrm{e^-} = \mathrm{Hg} + \mathrm{Cl^-}$
$\mathrm{Cl^- \mid AgCl(s) \mid Ag}$	0.2224	$\mathrm{AgCl} + \mathrm{e^-} = \mathrm{Ag} + \mathrm{Cl^-}$
$\mathrm{Cu^{2+}, Cu^+ \mid Pt}$[d]	0.153	$\mathrm{Cu^{2+}} + \mathrm{e^-} = \mathrm{Cu^+}$
$\mathrm{Br^- \mid AgBr(s) \mid Ag}$	0.0732	$\mathrm{AgBr} + \mathrm{e^-} = \mathrm{Ag} + \mathrm{Br^-}$
$\mathrm{H^+ \mid H_2(g) \mid Pt}$	0.0000	$\mathrm{H^+} + \mathrm{e^-} = \frac{1}{2}\mathrm{H_2(g)}$
$\mathrm{D^+ \mid D_2(g) \mid Pt}$	−0.0034	$\mathrm{D^+} + \mathrm{e^-} = \frac{1}{2}\mathrm{D_2(g)}$
$\mathrm{Pb^{2+} \mid Pb}$	−0.126	$\frac{1}{2}\mathrm{Pb^{2+}} + \mathrm{e^-} = \frac{1}{2}\mathrm{Pb}$
$\mathrm{Sn^{2+} \mid Sn}$	−0.140	$\frac{1}{2}\mathrm{Sn^{2+}} + \mathrm{e^-} = \frac{1}{2}\mathrm{Sn}$
$\mathrm{Ni^{2+} \mid Ni}$	−0.250	$\frac{1}{2}\mathrm{Ni^{2+}} + \mathrm{e^-} = \frac{1}{2}\mathrm{Ni}$
$\mathrm{Cd^{2+} \mid Cd}$	−0.4022	$\frac{1}{2}\mathrm{Cd^{2+}} + \mathrm{e^-} = \frac{1}{2}\mathrm{Cd}$
$\mathrm{Fe^{2+} \mid Fe}$	−0.440	$\frac{1}{2}\mathrm{Fe^{2+}} + \mathrm{e^-} = \frac{1}{2}\mathrm{Fe}$
$\mathrm{Zn^{2+} \mid Zn}$	−0.763	$\frac{1}{2}\mathrm{Zn^{2+}} + \mathrm{e^-} = \frac{1}{2}\mathrm{Zn}$
$\mathrm{OH^- \mid H_2(g) \mid Pt}$	−0.8279	$\mathrm{H_2O} + \mathrm{e^-} = \frac{1}{2}\mathrm{H_2(g)} + \mathrm{OH^-}$
$\mathrm{Mg^{2+} \mid Mg}$	−2.37	$\frac{1}{2}\mathrm{Mg^{2+}} + \mathrm{e^-} = \frac{1}{2}\mathrm{Mg}$
$\mathrm{Na^+ \mid Na}$	−2.714	$\mathrm{Na^+} + \mathrm{e^-} = \mathrm{Na}$
$\mathrm{Li^+ \mid Li}$	−3.045	$\mathrm{Li^+} + \mathrm{e^-} = \mathrm{Li}$

[a] All ions are at unit activity (on the molal scale) in water, and all gases are at 1 bar.

[b] See problem 7.59.

[c] The electrode potential of the normal calomel electrode is 0.2802 V and that of the calomel electrode containing saturated KCl is 0.2415 V.

[d] The order of writing the ions in the electrolyte solution is immaterial.

[e] Many more standard electrode potentials at 298.15 K are given in S. G. Bratsch, *J. Phys. Chem. Ref. Data* **18:**1 (1989).

From: Encyclopedia of Electrochemistry, Edited by A.J. Bard and M. Stratmann, vol. 1, ch. 1, Weinheim, Wiley-VCH, 2002-...

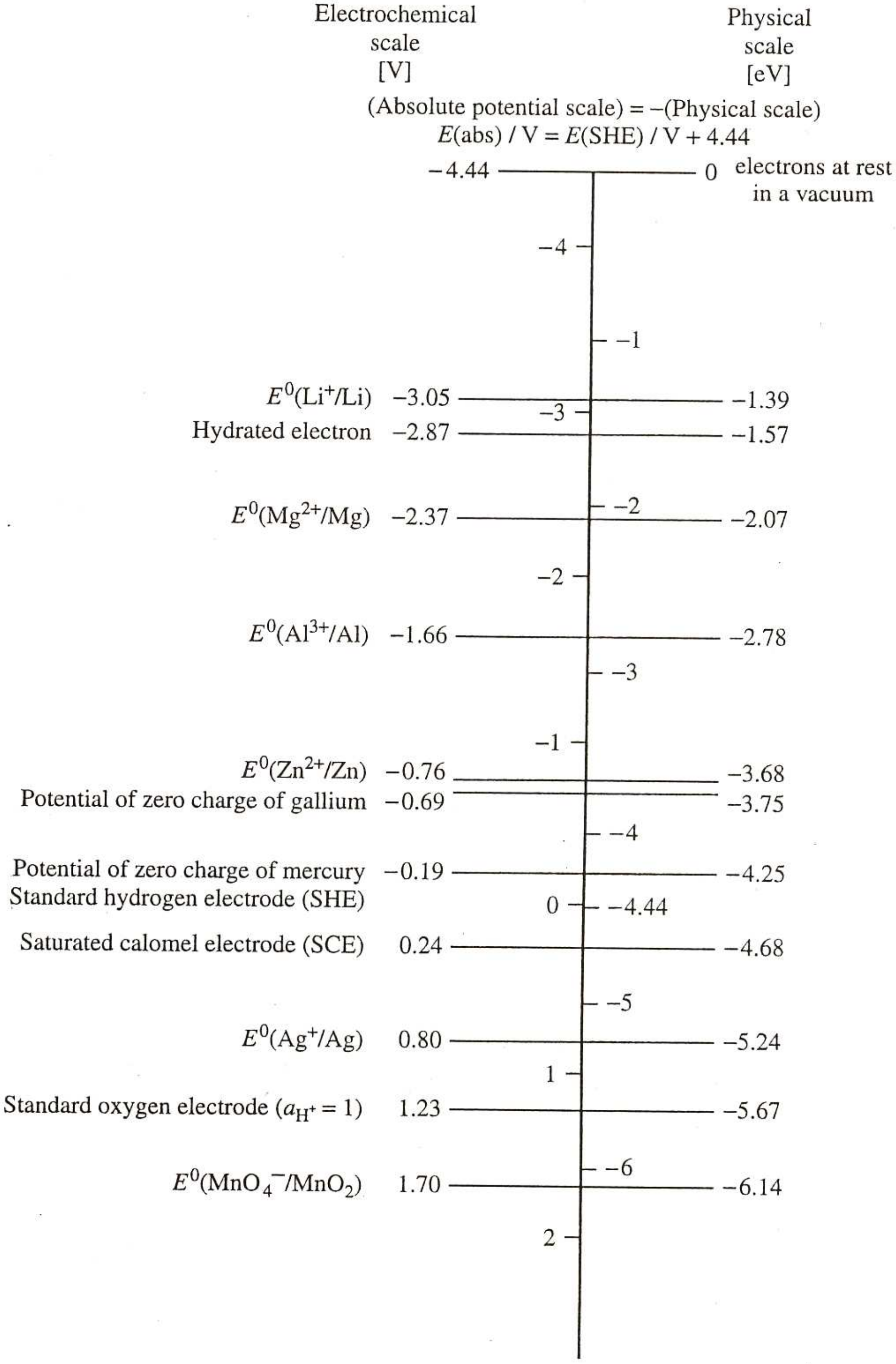


Fig. 4 Comparison of SHE and "absolute" scales, as reported in Ref. [9].

The Electrical Double layer

This part is about charged solid surfaces in liquids:

- **the most important liquid is water**
- **high dielectric constant – good solvent for ions**
- **most surfaces in water are charged**

Here: consider case, when external electric potential between the considered metal|electrolyte interface and a counterelectrode is applied
(see previous topic: electrochemical cell and EMF).

- **Excess charges on metal surface →**
  internal electric field at metal|electrolyte interface
- **Electric field attracts counterions, i.e. ions of opposite charge**
- **Surface charge and counterions form the so-called “electric double layer” (EDL)**

We will see some characteristic experimental data for the capacitance at the interface. Employing some ideas about the distributions of ions in solution will help to rationalize these data and understand in more detail the nature of the interfacial region.

Whenever two dissimilar phases are in direct contact with each other, forces become active:

- **Short-range forces (chemical forces, dispersion forces)**
- **Long-range forces (coulombic interactions)**

They following phenomena can be observed:

- **Orientation of solvent molecules**
- **Accumulation of ionic species**
- **Specific adsorption of ionic/non-ionic species**

Experimental techniques in surface electrochemistry:

- **Traditional: cyclic voltammetry, impedance spectroscopy, electrocapillary measurements – no spatial resolution of structures and processes, indirect information**
- **Modern techniques: spectroscopy (IR reflection, X-ray diffraction and absorption, second harmonic generation) and microscopy (e.g. scanning tunneling microscopy) – study processes with molecular/atomistic resolution**

In any electrochemical experiment, one applies a potential to the electrode and measures the charge flowing to the electrode surface. This charge generates an electric field of 10^7-10^8 V/m that drives ions and dipolar molecules. We want to understand in more detail the effects of this electric field.

We start first with the purely electrostatic effects (due to coulomb potential). Later on, we will consider specific adsorption and then charge transfer processes.

For the studies of the pure electrostatic effects (i.e. no specific adsorption, no charge transfer for the time being), we need suitable model systems. These are called...