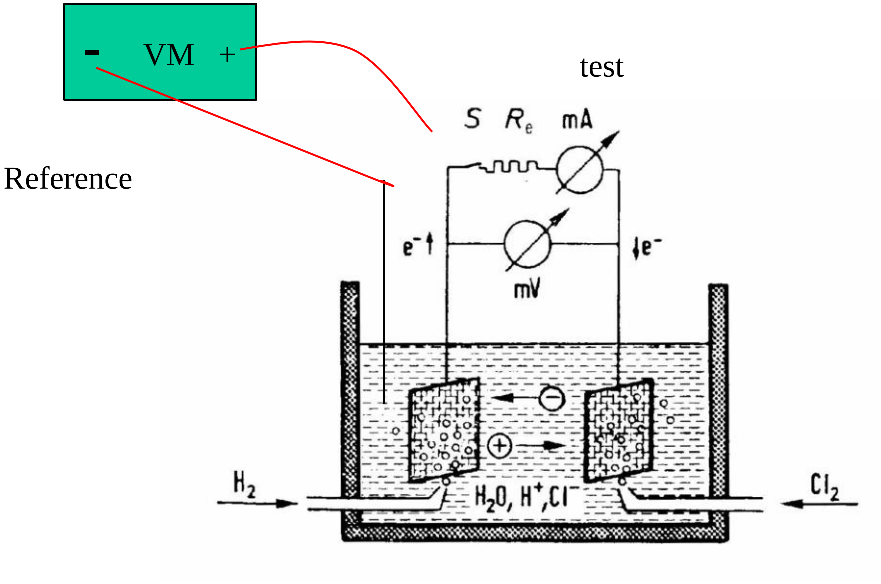
Chapter 3

Electrode Potentials
and
Double – Layer Structure
at Phase Boundaries

Electrical Potential

A. What is the potential?

B. Why is the potential important?
  1. Equilibrium potential (OCV) describes the cell
  2. Potential difference is the driving force for:
    a) Motions of ions (ion conduction)
    b) Transfer of electrons between electrode and solution
  3. So you know how to set up a reference electrode to study the cell



- VM + = voltmeter

Voltmeter should have internal resistance of voltage measuring circuit, R measure > 10^6 Ohm and prefer 10^9 to 10^{11} Ohm.

Chapter 3: Electrode Potentials

Interconversion of electrical and chemical energies occurs in an electrochemical

- An electrolytic cell converts electrical to chemical energy by changing low to high energy chemicals.
- A galvanic cell converts high energy chemicals to low energy chemicals and electrical energy.

The chemical processes occur on 2 separated electrodes in half-reactions at different potentials. The cell reaction and voltage are the differences in the half cell reactions and potentials.

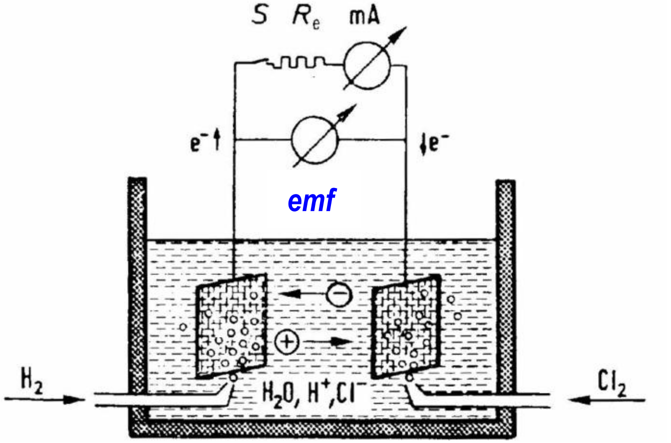
ELECTROLYTIC CELL

For example, recall from chapter 1, the cell with hydrochloric acid (HCl in water) and with H_2 at one Pt electrode and Cl_2 at another Pt electrode.

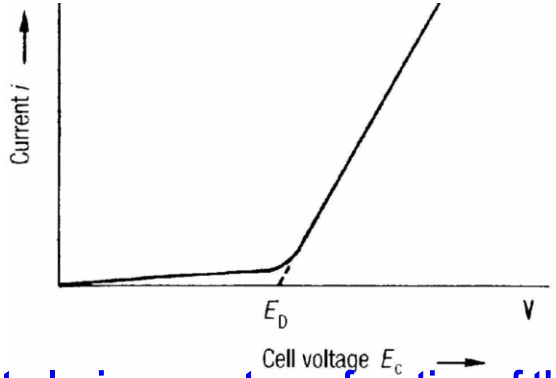
For an electrolytic cell, Cl^- is electrochemical ly formed into Cl_2 at one electrode (called the anode) and H^+ into H_2 at the other (called the cathode) by applying an ***emf*** (also called voltage) E_D across the electrodes,.

$$\begin{array}{lcll} 2\,Cl^- & \rightarrow & Cl_2 + 2\,e^- & Ea \\ 2\,H_3O^+ + 2\,e^- & \rightarrow & H_2 + 2\,H_2O & \underline{Ec} \\ \hline 2\,HCl & \rightarrow & H_2 + Cl_2 & V \end{array}$$

- Cell Voltage = *E*c = V = *E*anode – *E*cathode
- Electromotive Force, ***emf***, is $E_0 = \lim_{t \to 0} V$
- Decomposition Voltage $E_D \approx E_0$



Electrochemical cell with 2 Pt electrodes in hydrochloric acid interconverted to H_2 and Cl_2 .



Electrolysis current as a function of the cell Voltage E_C.. E_D is the decomposition voltage

Galvanic cell, the chlorine (Cl_2) hydrogen (H_2) fuel cell

The chlorine fuel cell reactions (eqns. 1.7)

Half reaction 1 $$Cl_2 + 2e^- \rightarrow 2Cl^-(aq.)$$

Half reaction 2 $$H_2 + 2H_2O \rightarrow 2H_3O^+(aq.) + 2e^-$$

Total cell reaction $$Cl_2 + H_2 \rightarrow 2H_3O^+(aq.) + 2Cl^-(aq.$$

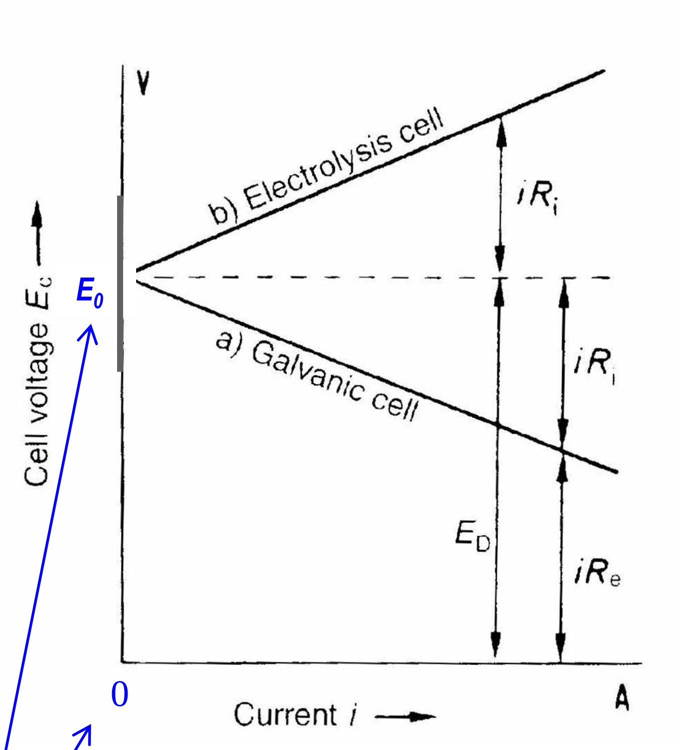
Eqns. 1.7

are a special case of the general scheme equations 3.1:

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

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 :



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

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.

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

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

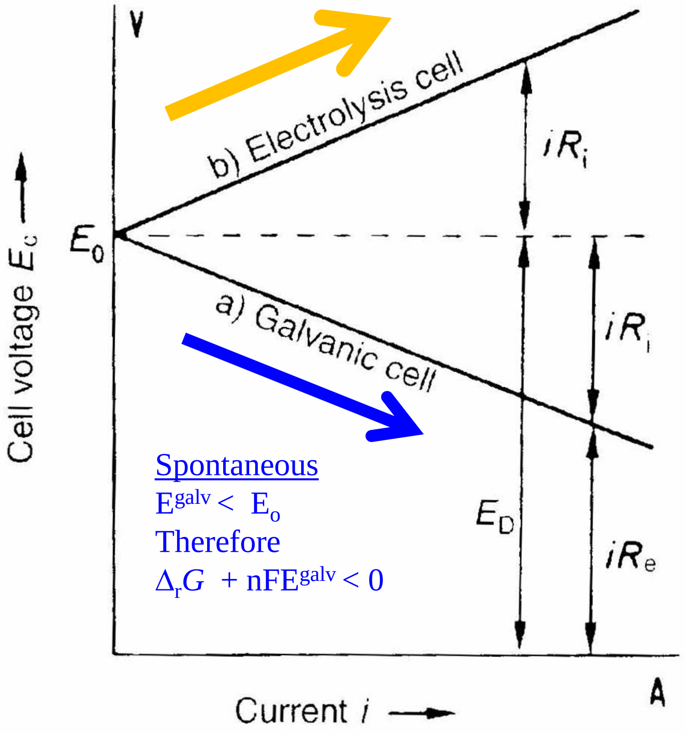
and $$\Delta_r G + nFE_c^{galv} < 0$$

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

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

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

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.

State Functions

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

$$\Delta_r G = -nFE_0$$

Any arbitrary state

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 :

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

Standard state

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

We defined the chemical potential for the i^{th} 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

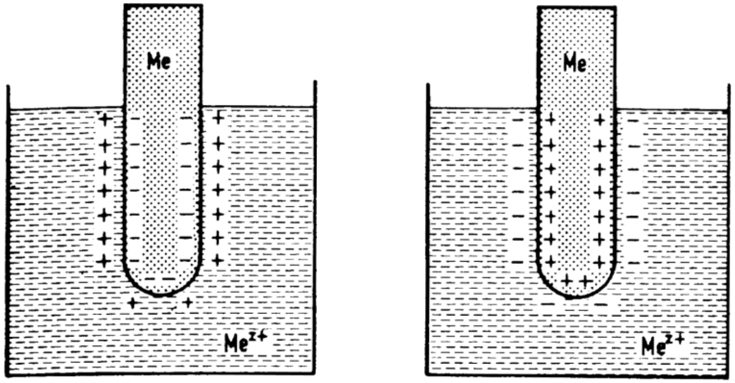
$$\mu_i(\mathrm{I}) = \mu_i(\mathrm{II})$$

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

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

a) If the chemical potential of copper in metal exceeds copper ions in solution and electrons in the metal, then metal dissolution takes place,
the solution next to the metal becomes positively charged compared to the metal.

b) If chemical potential of Cu^{2+} ions in solution and electrons in the metal exceeds copper metal, then metal ions deposit on the copper,
the solution next to the metal becomes negatively charged compared to the metal.



a) **b)**

Origin of the potential difference between electrode and electrolyte.

Adding the potential difference to chemical potential gives at equilibrium eqn. 3.13:

$$\mu_i(\mathrm{I}) + z_i F \varphi_i(\mathrm{I}) = \mu_i(\mathrm{II}) + z_i F \varphi_i(\mathrm{II})$$

Eqn. 3.13

The chemical potential plus the energy of the charge due to the potential difference is the **electrochemical potential** , $\tilde{\mu}_i$, **given in equation 3.14**

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

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 between the 2 potentials inside2 phases is $\Delta\varphi$, the “inner” or “Galvani” potential difference. φ_s is the Galvani potential of the solution and φ_m the Galvani potential of the metal, then for reaction 3.12, $Cu^0 \leftrightarrow Cu^{2+}$ (aq.) + 2 e^- (M) and eqn. 3.15 $\Sigma_i \nu_i \tilde{u}_i = 0$, the equilibrium condition is given by eqn. 3.16 :

$$\tilde{\mu}_{Cu}(M) = \tilde{\mu}_{Cu^{2+}}(aq.) + 2\tilde{\mu}_{e^-}(M)$$ Eqn 3.16

The copper atoms in the metal are neutral, so $\tilde{\mu} = \mu$ and from def of Echem pot., eqn3.14, we have eqn 3.17:

$$\mu^0_{Cu}(M) + RT \ln \cancel{a_{Cu}}(M) = \mu^0_{Cu^{2+}}(aq.) + RT \ln a_{Cu^{2+}} + 2F\varphi_S + \mu^0_{e^-}(M) + \cancel{2RT} \ln a_{e^-} - 2F\varphi_M$$ Eqn 3.17

N.B. activities of copper atoms and electrons in metal are constant

The activity of copper atoms and electrons in copper metal are effectively constant; this gives eqn. 3.18:

$$\Delta\varphi \equiv \varphi_M - \varphi_S = \frac{\mu^0_{Cu^{2+}}(aq.) + \mu^0_{e^-}(M) - \mu^0_{Cu}(M)}{2F} + \frac{RT}{2F} \ln a_{Cu^{2+}}(aq.)$$ Eqn 3.18

$$\Delta\varphi = \Delta\varphi^0 + (RT/2F) \ln a_{Cu^{2+}}$$ Eqn 3.18

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

φ and $\Delta\varphi^0$ above can NOT be measured. But if another electrode with constant $\Delta\varphi'$ is in the solution, then the potential E is the difference of $\Delta\varphi$ and $\Delta\varphi'$ ($E = \Delta\varphi - \Delta\varphi'$) and $E^0 = \Delta\varphi^0 - \Delta\varphi'$, so **$E - E^0 = \Delta\varphi - \Delta\varphi^0$** therefore *although* the Galvani potential of the solution is itself experimentally inaccessible, we can re-write eqn. 3.18 in terms of the electrode potential, E, as eqn. 3.19, which is the Nernst Equation.

$$E = E^0 + \left(\frac{RT}{zF}\right) \ln a_{M^{z+}}$$ **Nernst Equation 3.19**

The Nernst Equation is the equilibrium potential as a function of the concentration of ions (M^{2+}) in solution.

The Nernst Equation for Redox Electrodes

As for metal and metal ions in solution, the electrode potential, *E*, can be found from the Galvani potential difference between two phases, Sox and S red, by inserting an inert electrode, like Pt, in solution to act as a carrier of a electrons in a redox reaction, as written below:

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

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

The equilibrium properties of the redox reaction are 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:

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

Rearranging for the potential difference $\Delta\varphi$, we can write:

$$\Delta\varphi = \varphi_M - \varphi_S = \frac{\mu^{0\dagger}_{ox} + n\mu^{0}_{e^-} - \mu^{0\dagger}_{red}}{nF} + \frac{RT}{nF}\ln\frac{a_{ox}}{a_{red}}$$

$$= \Delta\varphi_0 + \left(\frac{RT}{nF}\right)\ln\left(\frac{a_{ox}}{a_{red}}\right)$$

if there is another electrode with constant $\Delta\varphi'$ is in the solution then the potential *E* is:

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

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 be :

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

Take a breath

Measurement of Electrode Potentials and Cell Voltages p.84-88

- A direct measurement of the Galvani potential difference (voltage) between electrode and electrolyte is not possible since any device to measure such a voltage would have to be simultaneously in contact with both phases.
- At zero current, the actual *emf* measured for a galvanic cell will be the difference between the two Galvani voltages $\Delta\varphi(\mathrm{I})$ and $\Delta\varphi(\mathrm{II})$ for the two interfaces.

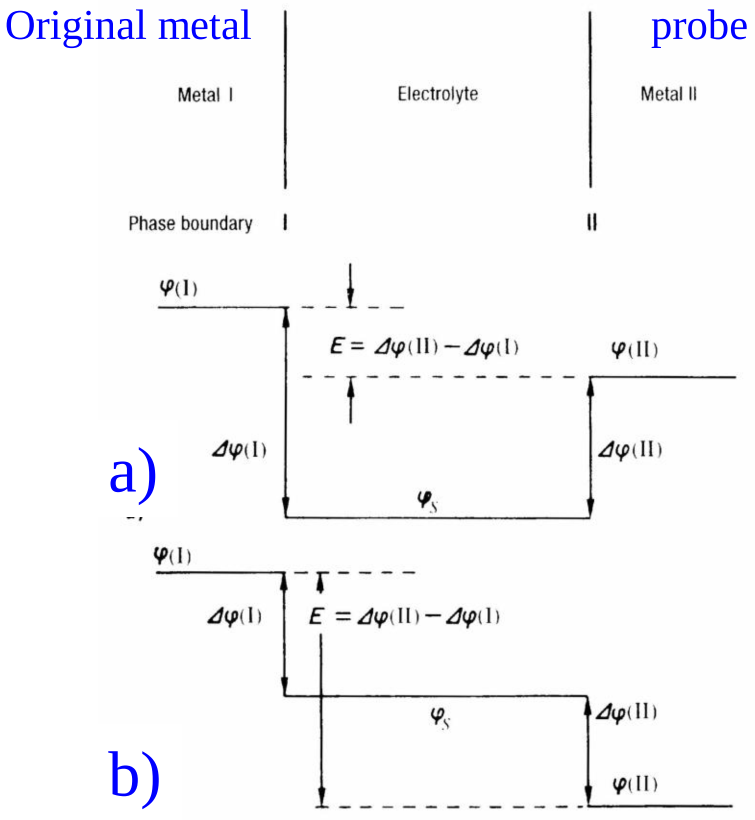
The figure demonstrates two specific cases:

a) the solution Galvani potential φ_s lies below the metal φ_m Galvani potentials

b) the solution Galvani potential φ_s lies between the metal φ_m Galvani potentials (a)

Since φ_s is considered constant, from the figure it is clear that the *emf* or potential difference, E, between the two metals is given by:

$$E = \Delta\varphi(\mathrm{II}) - \Delta\varphi(\mathrm{I}) = \varphi(\mathrm{II}) - \varphi(\mathrm{I})$$

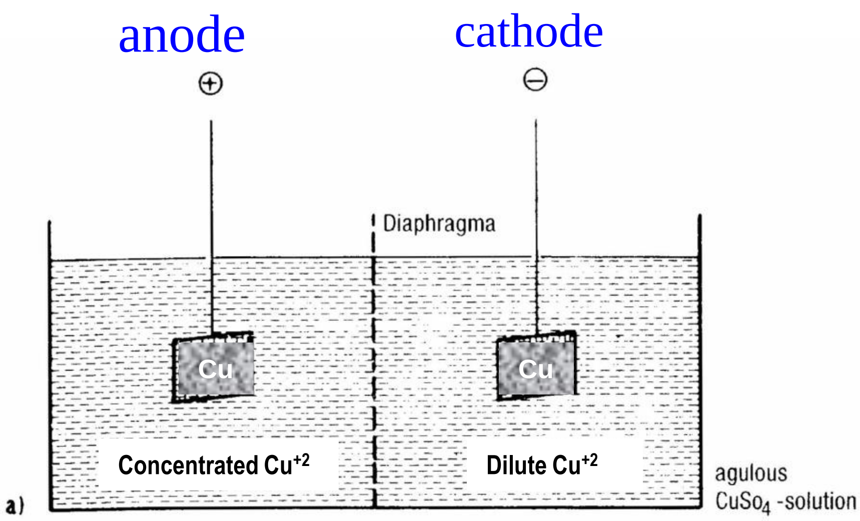


The *EMF* of a galvanic cell as the difference of the equilibrium Galvani potentials at the two electrodes

The Nernst Equation and the Electrolyte Concentration

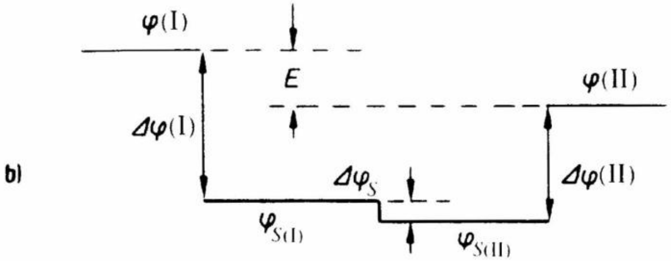
If the two electrodes in a cell are made from the same metal, but these are now in contact with two solutions of different ionic activities (separated from each other by a glass frit that permits contact but impedes diffusion), then the *emf* , *E,* of such a cell, which is termed a *concentration cell,* is given :

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



a) Schematic of the concentration cell

The above Equation shows that the *emf* increases by 0.059V per decade change in the activity ratio in the two solutions.



b) Magnitude of Galvani potentials from anode to cathode

An example for a galvanic cell description

anode $M \mid M^{z+}(I) \,\vdots\, M^{z+}(II) \mid M$ cathode

| is solid-liquid phase boundary

¦ is liquid-liquid phase boundary maintained by a frit or diaphram

Why is it that in cell a) the cell voltage, *E* ≠ 0 ?
Because φ's shift to φ (I) and φ (II)

- **as 2 electrodes of the same metal (Cu)**
- **come to 2 different electrochemical equilibriums with solutions of 2 different Cu^{+2} ion concentrations**

Temperature dependence of Cell Voltage

Relationship between cell *emf*, E_{cell}, and Thermodynamics, ΔG p.88

$E_c^o = -\Delta_r G^o / nF$ Eqn. 3.5

E_c^o *is the emf* of the cell at standard state

$$E_c = -\Delta_r G / nF$$

Eqn. 3.46

E_c *is the emf* of the cell at any arbitrary state

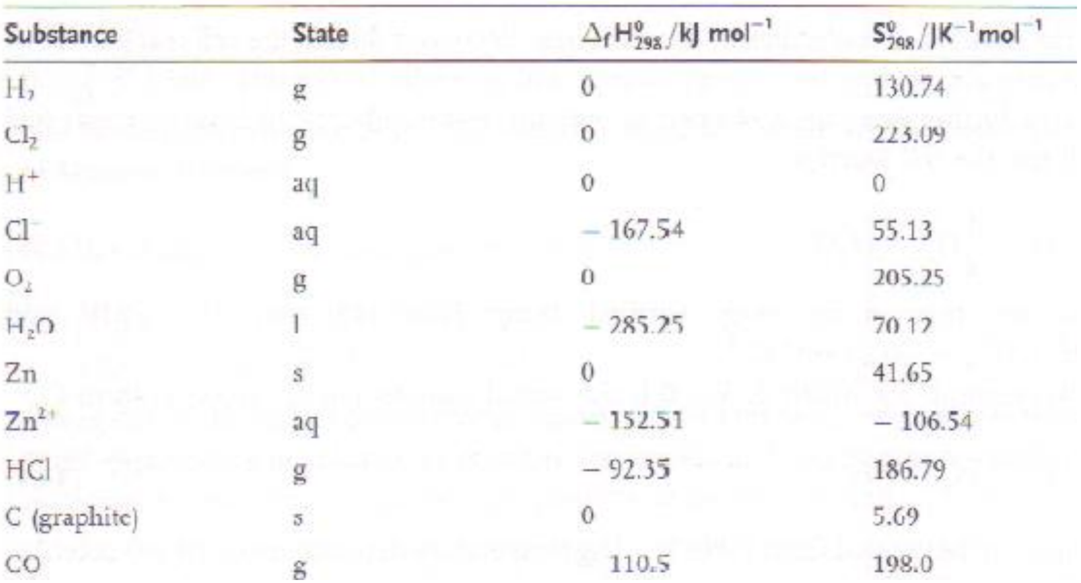
$$\Delta_r G = \sum_i v_i \mu_i = \sum_i v_i \mu_i^{0\dagger} + \sum_i v_i RT \ln a_i = \Delta_r G^0 + \sum_i RT \ln a_i$$

Eqn. 3.47

$$\Delta_r G^0 = \Delta_r H^0 - T\Delta_r S^0$$

Eqn. 3.51

Table 3.1 Enthalpies and entropies of formation for selected elements and compounds at 298 K. Abbreviations: g – gas phase; l – liquid phase; s – solid phase; aq – in aqueous solution with unit activity.



Substance	State	$\Delta_f H^0_{298}$/kJ mol^{-1}	S^0_{298}/JK^{-1}mol^{-1}
H_2	g	0	130.74
Cl_2	g	0	223.09
H^+	aq	0	0
Cl^-	aq	− 167.54	55.13
O_2	g	0	205.25
H_2O	l	− 285.25	70.12
Zn	s	0	41.65
Zn^{2+}	aq	− 152.51	− 106.54
HCl	g	− 92.35	186.79
C (graphite)	s	0	5.69
CO	g	110.5	198.0

The electrochemical cell potential, *E*, is a state function which can be calculated from Thermodynamic data, like ΔS and ΔH, found in Table 3.1 and elsewhere.

Note well

- The enthalpy, $\boldsymbol{\Delta H}$, and entropy, $\boldsymbol{\Delta S}$, of the solvated proton, H^+ aq., is defined as 0.
- All other ions are referenced to this standard.

The change in *E* with *T*, *P* etc. can be found as any thermodynamic quantity.

The Temperature Dependence of the Cell Voltage

From the expression ***E* = Δ**** $E = \Delta_r G/nF$ which relates the cell voltage to the free energy of the reaction, we can calculate the temperature dependence of the *EMF* by direct differentiation:

$$\left(\frac{\partial E}{\partial T}\right)_p = -\frac{1}{nF}\cdot\left(\frac{\partial \Delta_r G}{\partial T}\right)_p = +\frac{\Delta_r S}{nF}$$

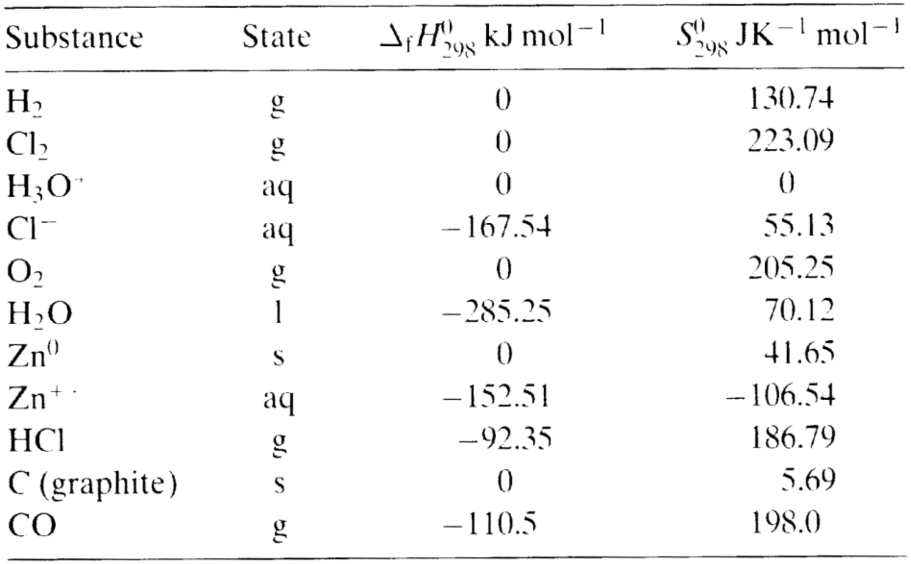
If the number of molecules in the gas phase decreases as in the case of the cell reaction $H_2 + Cl_2 \rightarrow 2\,H^+_{aq..} + 2\,Cl^-_{aq.}$, then the system becomes more ordered and the entropy change ($\Delta_r S$) and cell potential, *E*, decrease as shown below.

$$\left(\frac{\partial E^0}{\partial T}\right)_p = \frac{2S^0_{H^+} + 2S^0_{Cl^-} - S^0_{H_2} - S^0_{Cl_2})}{2 \times 96485}$$

$$= -1.2\,\mathrm{mV\,K^{-1}}$$

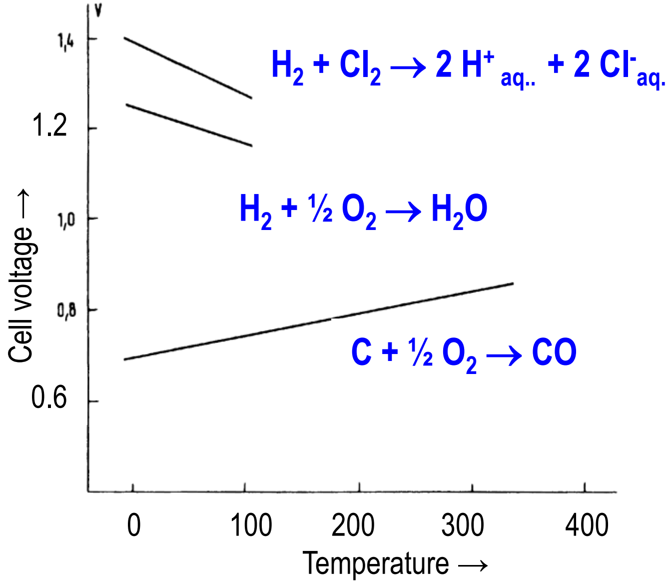
An example for which the entropy change increases ($\Delta_r S > 0$) and cell potential, *E*, increases is the partial combustion of carbon to form CO and could be derived from Table 3.1:

$$C + \tfrac{1}{2}O_2 \rightarrow CO$$



Substance	State	$\Delta_f H^0_{298}$ kJ mol^{-1}	S^0_{298} JK^{-1} mol^{-1}
H_2	g	0	130.74
Cl_2	g	0	223.09
H_3O^+	aq	0	0
Cl^-	aq	−167.54	55.13
O_2	g	0	205.25
H_2O	l	−285.25	70.12
Zn^0	s	0	41.65
Zn^{2+}	aq	−152.51	−106.54
HCl	g	−92.35	186.79
C (graphite)	s	0	5.69
CO	g	−110.5	198.0

Enthalpies and entropies of formation for selected elements and compounds at 298 K



Temperature dependence of the cell voltages

The Pressure Dependence of the Cell Voltage

For the change of *emf* with pressure we have:

$$\left(\frac{\partial E}{\partial p}\right)_T = -\frac{1}{nF}\cdot\left(\frac{\partial \Delta_r G}{\partial p}\right)_T = -\frac{\Delta_r \overline{V}}{nF}$$

The dependence of volume on pressure for liquids and solids is very small, so it is usually only necessary to gases. Considering the ideal gas law, we have for the gaseous components of the cell reaction:

$$\Delta_r \overline{V} = \sum_j \nu_j \frac{RT}{p_j}$$

Eqn. 3.61

Combining the first two equations we get:

$$\left(\frac{\partial E}{\partial p}\right)_T = -\sum \nu_j \frac{RT}{nFp_j} \equiv \sum_j \left(\frac{\partial E}{\partial p_j}\right)_T$$

Eqn. 3.62

After an integration, the result is Eqn. 3.63

$$E = E^0 - \sum_j \nu_j \left(\frac{RT}{nF}\right) \ln \frac{p_j}{p^0}$$

Eqn. 3.63

for which E^o is the *emf* at standard state including for partial pressures of all gases being 1 atmosphere

Applying that to the specific example of the chlorine/hydrogen cell:

$$E = E^0 + \tfrac{1}{2}\cdot 0.059 \log_{10}(p_{H_2}/p^0)\cdot(p_{Cl_2}/p^0)$$

E^o = 1.36 V (at 1 atm)

A simultaneous increase of the pressure of both working gases. Cl_2 and H_2, from 1 to 10 bar leads, from the above equations, to E^0 = 1 .43 V, whereas a simultaneous decrease from 1 bar to 1 mbar in the gas pressures at both electrodes leads to a reduction of the cell potential difference to 1.19 V

Reference Electrodes and the Electrochemical Series

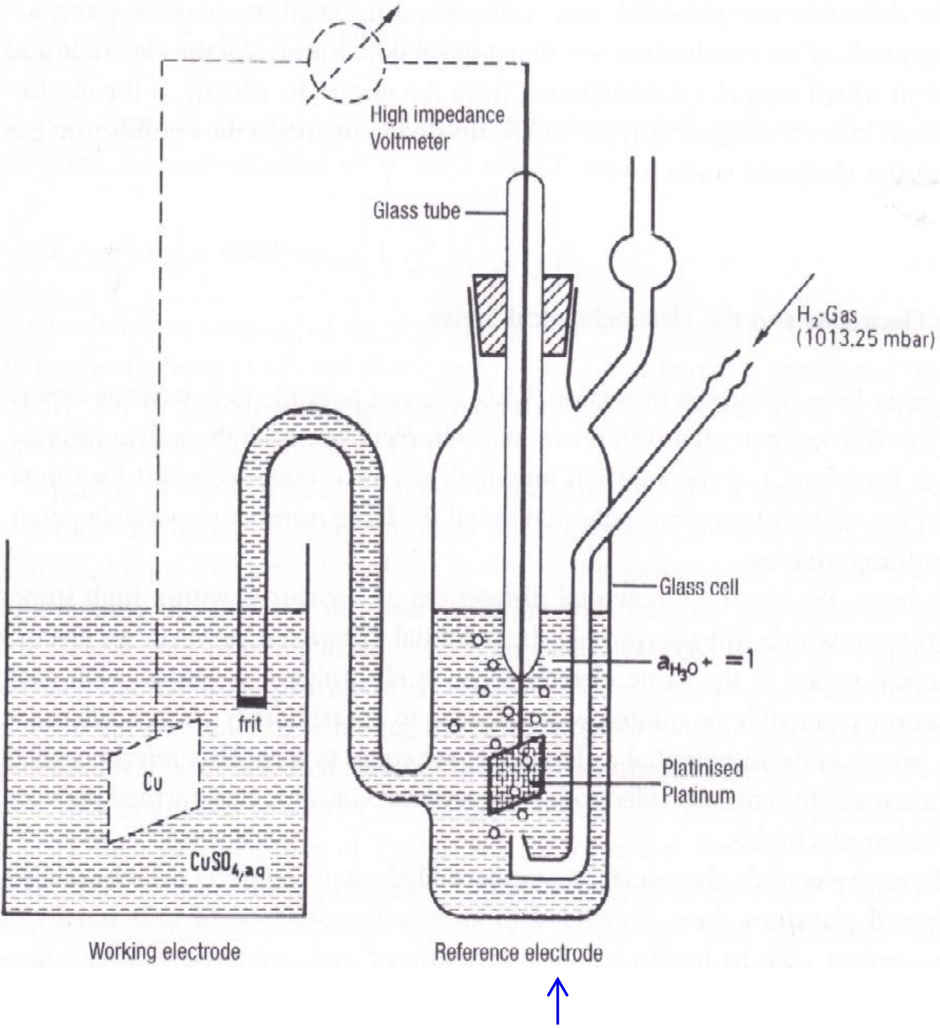
As has already been discussed it is not possible to determine experimentally the Galvani potential difference between electrode and electrolyte interiors. That is why one arbitrarily chooses a reference electrode, whose Galvani potential is set equal to zero.

The most accepted reference is, $E^{0,\,\mathrm{SHE}}$, is assigned 0 volts for the standard hydrogen electrode (SHE), which is a high surface area platinum electrode in contact with aqueous proton, H^+, solution whose activity is 1 and saturated with H_2 gas at activity of 1 atmosphere for the reaction, below.

$$2H^+(aq.) + 2e^- \rightleftharpoons H_2$$

At any other proton activity or hydrogen gas pressure, the reference potential of the resulting hydrogen electrode is E^{HE}, which is given versus SHE by the Nernst Equation, as follows:

$$E^{\mathrm{HE}} = E^{0,\mathrm{SHE}} + \frac{RT}{F}\ln\left\{a_{\mathrm{H}^+}/\sqrt{p_{\mathrm{H}_2}}\right\}$$

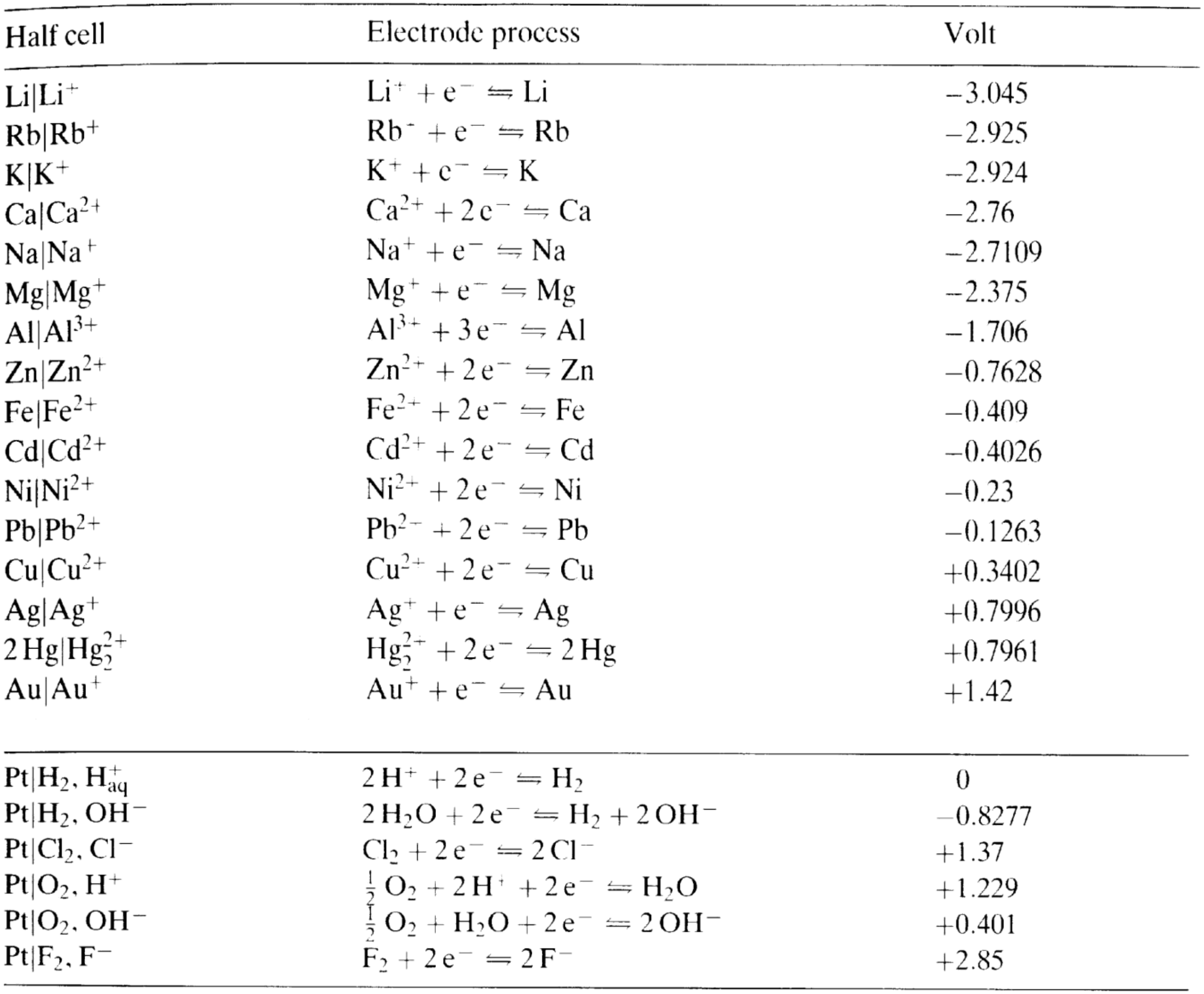


Construction of a Standard Hydrogen Electrode (SHE)

All other electrode potential are tabulated against SHE, and the potential values obtained are termed ***standard electrode potentials***.

Standard Electrode Potentials

for different metal-ion, gas or redox electrodes versus SHE at 25^0C



Half cell	Electrode process	Volt
$Li\|Li^+$	$Li^+ + e^- \rightleftharpoons Li$	−3.045
$Rb\|Rb^+$	$Rb^+ + e^- \rightleftharpoons Rb$	−2.925
$K\|K^+$	$K^+ + e^- \rightleftharpoons K$	−2.924
$Ca\|Ca^{2+}$	$Ca^{2+} + 2e^- \rightleftharpoons Ca$	−2.76
$Na\|Na^+$	$Na^+ + e^- \rightleftharpoons Na$	−2.7109
$Mg\|Mg^+$	$Mg^+ + e^- \rightleftharpoons Mg$	−2.375
$Al\|Al^{3+}$	$Al^{3+} + 3e^- \rightleftharpoons Al$	−1.706
$Zn\|Zn^{2+}$	$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0.7628
$Fe\|Fe^{2+}$	$Fe^{2+} + 2e^- \rightleftharpoons Fe$	−0.409
$Cd\|Cd^{2+}$	$Cd^{2+} + 2e^- \rightleftharpoons Cd$	−0.4026
$Ni\|Ni^{2+}$	$Ni^{2+} + 2e^- \rightleftharpoons Ni$	−0.23
$Pb\|Pb^{2+}$	$Pb^{2+} + 2e^- \rightleftharpoons Pb$	−0.1263
$Cu\|Cu^{2+}$	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.3402
$Ag\|Ag^+$	$Ag^+ + e^- \rightleftharpoons Ag$	+0.7996
$2Hg\|Hg_2^{2+}$	$Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg$	+0.7961
$Au\|Au^+$	$Au^+ + e^- \rightleftharpoons Au$	+1.42
$Pt\|H_2, H^+_{aq}$	$2H^+ + 2e^- \rightleftharpoons H_2$	0
$Pt\|H_2, OH^-$	$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	−0.8277
$Pt\|Cl_2, Cl^-$	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.37
$Pt\|O_2, H^+$	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$	+1.229
$Pt\|O_2, OH^-$	$\frac{1}{2}O_2 + H_2O + 2e^- \rightleftharpoons 2OH^-$	+0.401
$Pt\|F_2, F^-$	$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.85

Pseudo - reference electrodes or electrodes from the first kind

Metals (usually noble metals) with a relatively stable electrode potential could be used as *pseudo-reference electrodes:* **Example:**

$$\mathrm{Pt} \mid \mathrm{H_2} \mid \mathrm{H_3O^+ . SO_4^{2-}} \mid \mathrm{Cu^{2+} . SO_4^{2-}} \mid \mathrm{Cu}$$

For this cell the reactions are:

$$\mathrm{H_2} + 2\,\mathrm{H_2O} \longrightarrow 2\,\mathrm{H_3O^+} + 2\,\mathrm{e^-}; \quad \textit{anode}$$

$$\mathrm{Cu^{2+}} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Cu}; \quad \textit{cathode}$$

and the *emf* is given by

$$E^0 = E^{0,\mathrm{copper}} - E^{0,\mathrm{SHE}} \equiv E^{0,\mathrm{copper}}$$

If we know $E^{0,SHE} = 0$, then $E^0 = E^{0\ Cu} = 0.342$

and the Cu^{2+}/Cu electrode could be used as a *pseudo-reference electrode*

The cupric sulfate / copper reference electrode is popular in the corrosion community but it is usually not a good idea to use a reference electrode of the first kind unless you *really* need to and really know what you are doing.

Reference Electrodes of the Second Kind

Disadvantages of the normal hydrogen electrode:

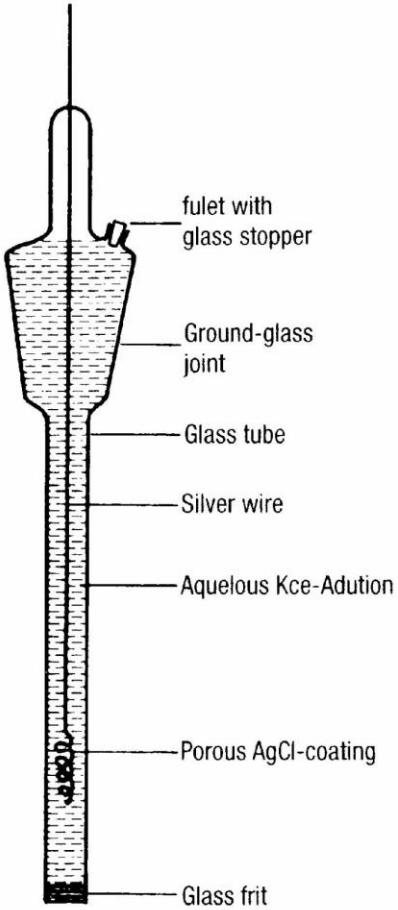
- the electrolyte must be prepared with an accurately known H_30^+ activity
- the hydrogen gas used must be purified
- the platinum electrode employed must be frequently re-platinised
- impurities could poison it.

A good alternative:

The most important types of secondary reference electrode are metal-ion electrodes where the activity of the potential-determining metal $\boldsymbol{a_M^{z+}}$ in the solution phase is itself controlled by ensuring that the solution is in contact with a second solid phase composed of a sparingly soluble salt of the M^{z+}

An example of a RE of 2nd kind:

The well-known silver-silver chloride reference electrode where the activity of silver is controlled by the interaction between the sparingly soluble AgCl and the solution containing Cl^- ions



Construction of a silver-silver chloride electrode.

If we take the silver ion as an example. then for the silver electrode we have:

$$E^{\mathrm{Ag}^+|\mathrm{Ag}} = E^{0,\mathrm{Ag}^+|\mathrm{Ag}} + \frac{RT}{F}\ln a_{\mathrm{Ag}^+}$$

Now, if the sparingly soluble salt AgCl is present then we must have the equilibrium:

$$\mathrm{AgCl} \leftrightharpoons \mathrm{Ag}^+ + \mathrm{Cl}^- \qquad \text{and} \qquad a_{\mathrm{Ag}^+}\cdot a_{\mathrm{Cl}^-} = K_s^{\mathrm{AgCl}}$$

Replacing in the Nernst Equation:

$$E^{\mathrm{Cl}^-|\mathrm{AgCl}|\mathrm{Ag}} = E^{0,\mathrm{Ag}^+|\mathrm{Ag}} + \frac{RT}{F}\ln K_s^{\mathrm{AgCl}} - \frac{RT}{F}\ln a_{\mathrm{Cl}^-}$$

Combining the constants in a standard potential of the Ag/AgCl electrode:

$$E^{\mathrm{Cl}^-|\mathrm{AgCl}|\mathrm{Ag}} = E^{0,\mathrm{Cl}^-|\mathrm{AgCl}|\mathrm{Ag}} - (RT/F)\ln a_{\mathrm{Cl}^-}$$

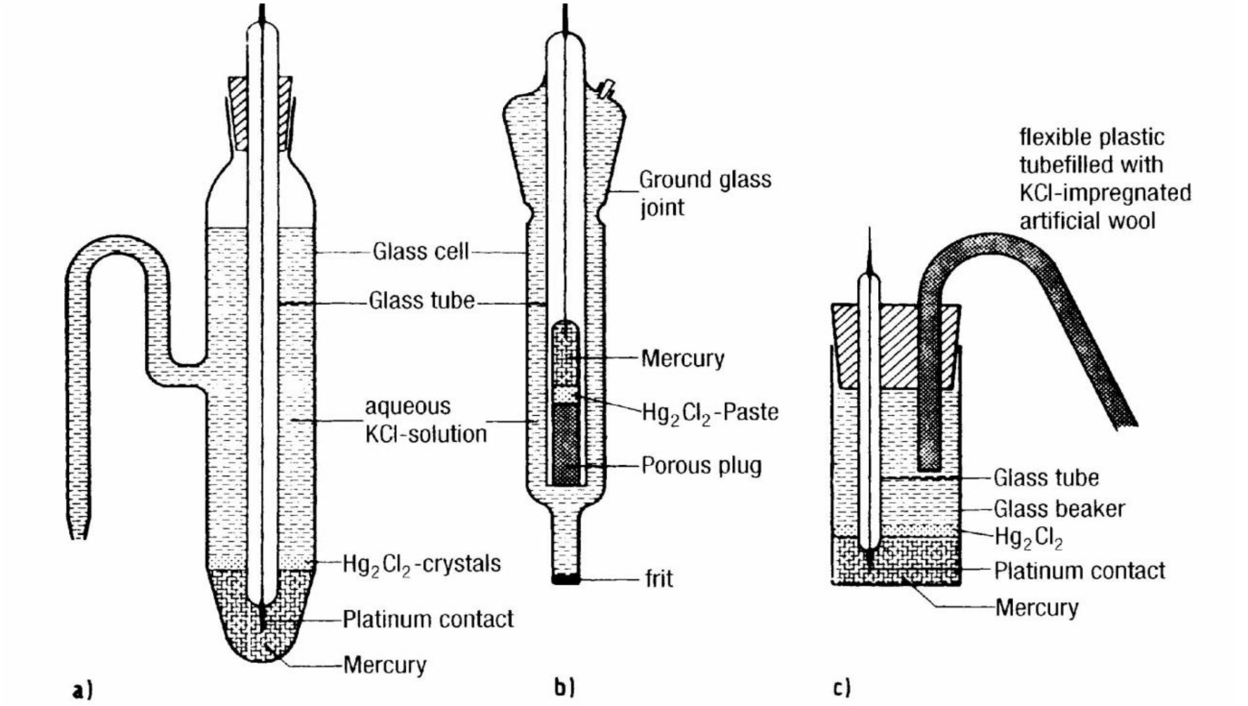
Where: $E^{0,\,\mathrm{Ag/AgCl}} = 0.2224$ *V (SHE) for* $a_{Cl^-} = 1$ (see table below for $E^{\mathrm{Ag/AgCl}}$ at other Cl^- concentrations)

Half Cell	Conditions	Electrode Process	a^{Cl^-}	Potential/V
$\mathrm{Ag}\vert\mathrm{AgCl}\vert\mathrm{Cl}^-$ (silver-silver chloride electrode)	$a_{\mathrm{Cl}^-} = 1$	$\mathrm{AgCl} + e^- \rightarrow \mathrm{Ag} + \mathrm{Cl}^-$	1	0.2224
	saturated KCl		>1	0.1976
	KCl ($c = 1$M)**($\gamma^{\mathrm{Cl}^-} < 1$)**		<1	0.2368
	KCl ($c = 0.1$M)		<<1	0.2894

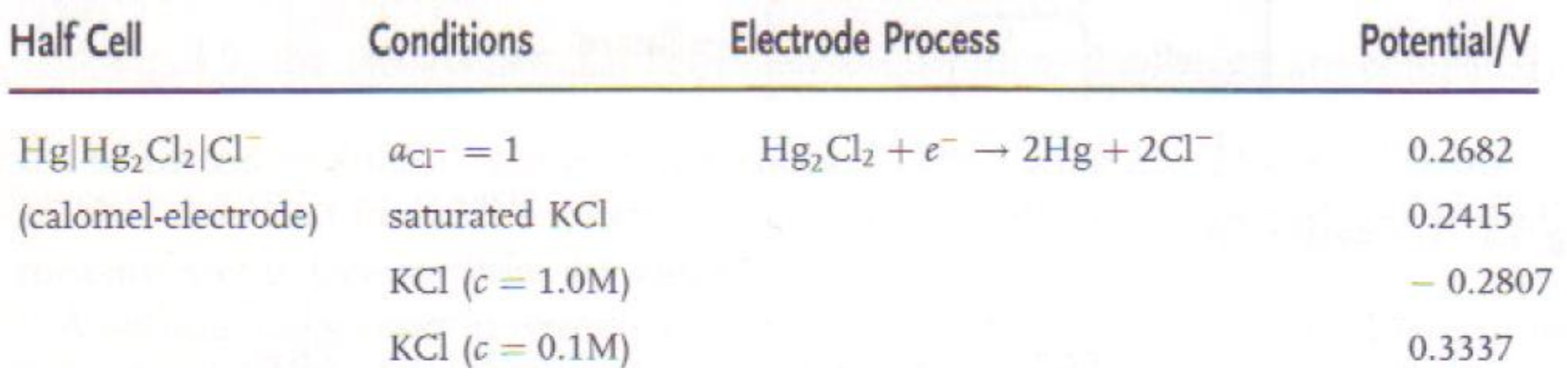
Calomel Electrode p100

$$E^{Cl^-|Hg_2Cl_2|Hg} = E^{0,Cl^-|Hg_2Cl_2|Hg} - (RT/F)\ln a_{Cl^-}$$

Where: $E^{0,\,Cl^-/HgCl/Hg} = 0.2682\ V\ (nhe)$



Technical forms of the calomel electrode (s) standard form (b) form manufactured as a miniature: (c) form suitable for technical measurements



Half Cell	Conditions	Electrode Process	Potential/V
$Hg\|Hg_2Cl_2\|Cl^-$	$a_{Cl^-} = 1$	$Hg_2Cl_2 + e^- \rightarrow 2Hg + 2Cl^-$	0.2682
(calomel-electrode)	saturated KCl		0.2415
	KCl ($c = 1.0$M)		− 0.2807
	KCl ($c = 0.1$M)		0.3337

Skip pp. 103 -144
Non-aqueous solvents and diffusion, liquid junction potential

Next: Electrical Double-layer *p 115*