

Centre of Excellence

Training course

abc-ELECTROCHEMISTRY

Part III

3. Electrochemical cells

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3.3 Cells with junctions

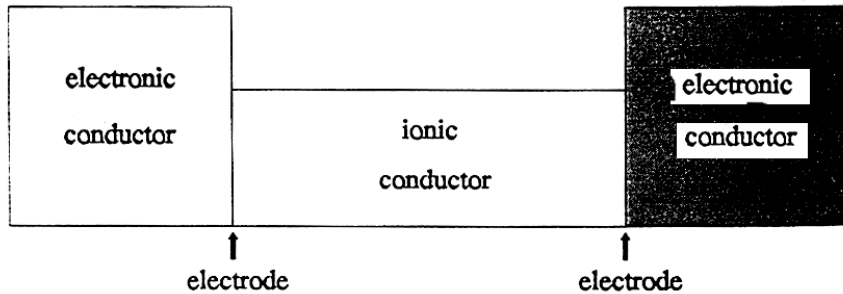
3.4 Utility of equilibrium cells

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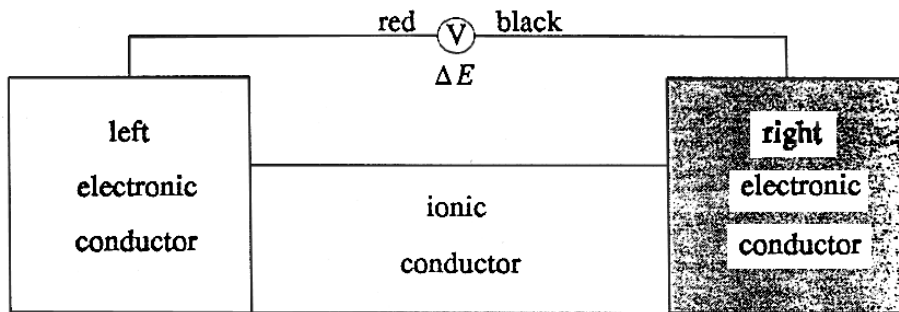
3. Electrochemical cells

Electrode - junction between an electronic conductor and an ionic conductor. At this junction “chemistry” of “electrochemistry “ occur. (“Electrode” is often used to describe the entire electronic conductor or even to one half of a cell)

Electrochemical cell - the simplest electrochemical cell consists of an ionic conductor sandwiched between two electronic conductors. The sandwich is combination of *any* ionic conductor and *any* pair of (similar or dissimilar) electronic conductors.



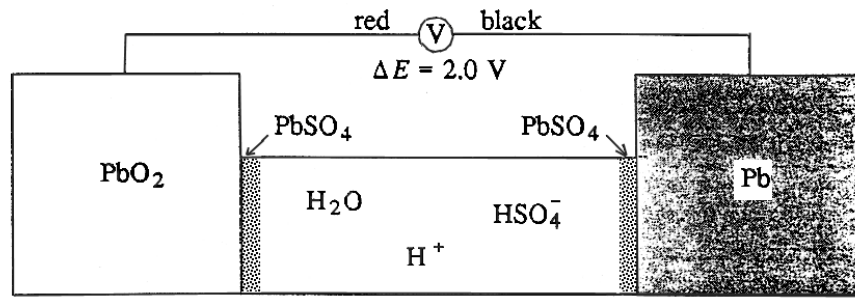
3.1 Cell voltages and currents



The voltmeter attached to the cell measures the **cell voltage** ΔE - the electrical potential difference of the left-hand electronic conductor with respect to the right.

ΔE can be positive, negative or zero. (**EMF, cell potential**)

Example:



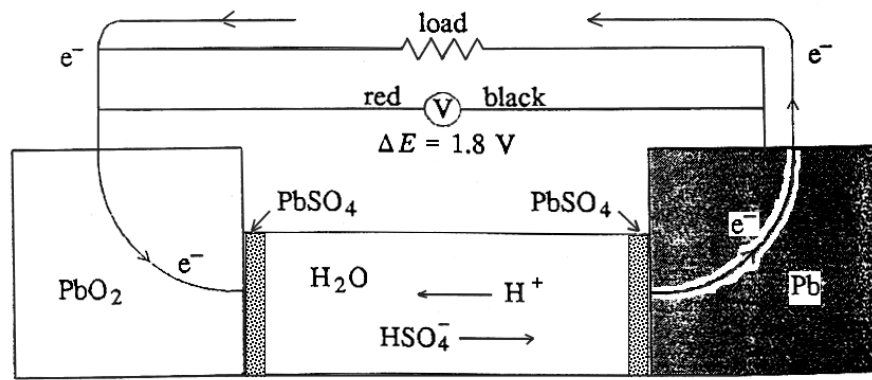
One of the electronic conductors of the **lead/acid cell** is essentially **lead dioxide, PbO_2** ; the other is **lead, Pb** . The ionic conductor is a concentrated aqueous solution of sulfuric acid

(colloquially the phrase “**the electrolyte**” is often used to describe the entire ionic conductor).

At the concentration used in lead/acid battery H_2SO_4 is entirely ionised to H^+ and HSO_4^- ions (some further ionisation to produce SO_4^{2-} occurs but we will ignore it in the moment).

A **porous layer of lead sulfate, PbSO_4** , is found **at the interfaces** between the ionic conductor and each of the electronic conductors.

The voltmeter would read a value **close to 2.0 Volts**, the **PbO_2 being positive** in respect to Pb . The sign of the potential difference can be interpreted that the electrochemical activity of electrons in Pb is greater than that in PbO_2 (or greater “pressure of the electricity” on the PbO_2 than on the Pb).



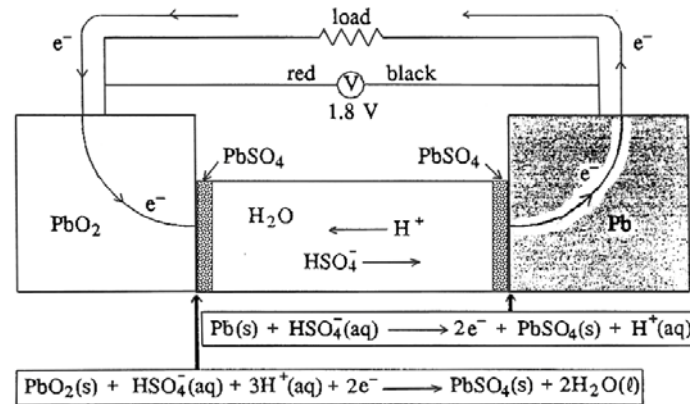
Electricity could pass through each of the electronic conductors by movement of their electrons and through the ionic conductor by motion of H^+ and HSO_4^- ions. A complete circuit can be provided by attaching the so-called “**load**” across the cell (resistor, light bulb, etc.).

Electrons are now able to respond to their greater electrochemical activity in Pb by flowing through the load to the PbO_2 . The electronic conductivity of Pb and PbO_2 allows the passage of electrons through these materials. In the ionic conductor the electricity is carried by the motion of H^+ ions **from right to left** and by the motion of the HSO_4^- ions **from left to right**.

In order to complete the electrical circuit electricity must also be able **to cross the junctions** between the PbO_2 and the H_2SO_4 solution and between the solution and **Pb**.

This is where chemistry enters the picture.

It is possible for electricity **to cross the interface** between an electronic and an ionic conductor only by virtue of an **electrochemical reaction** occurring there. The site of this reaction, the interfacial junction is known as an **electrode**.



The reaction that occurs at the right-hand electrode produces electrons, i.e. it is an **oxidation**; an electrode at which oxidation is occurring is called **anode**.

At the left-hand electrode electrons are consumed, signifying a **reduction**; the name **cathode** is given to such an electrode.

As a result, Pb is converted to lead sulfate at one electrode and the lead oxide - to lead sulfate at the other; the sulfuric acid is destroyed and water is created.

The two electrode reactions complete the circuit and permit electricity to flow **spontaneously** through the load. **Energy is delivered by the cell into the load.**

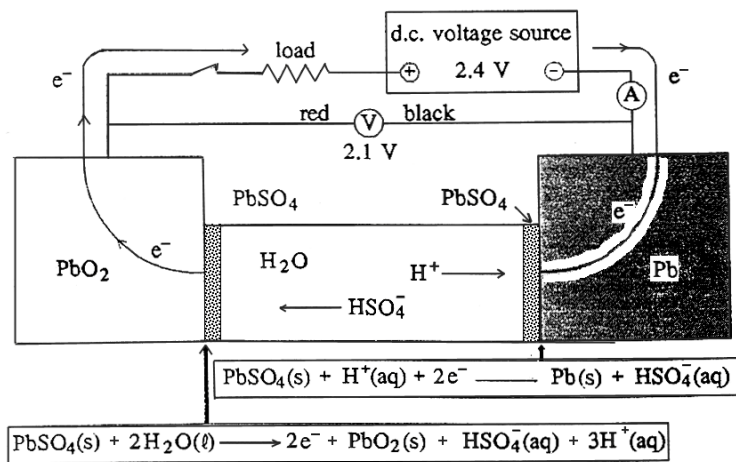
A cell which provides energy in this way is called a **galvanic cell**.

In this **galvanic cell mode** the lead/acid cell is discharged.

Galvanic cells always behave in this way: their voltage decrease in magnitude when energy is taken from them

The phenomenon of deviation of the cell voltage from its equilibrium value is called **polarisation**.

The electric current can be made to flow in the opposite direction through the lead/acid cell (**opposite to the spontaneous direction**) by using an external source to drive electrons from the PbO_2 through the load to the Pb .



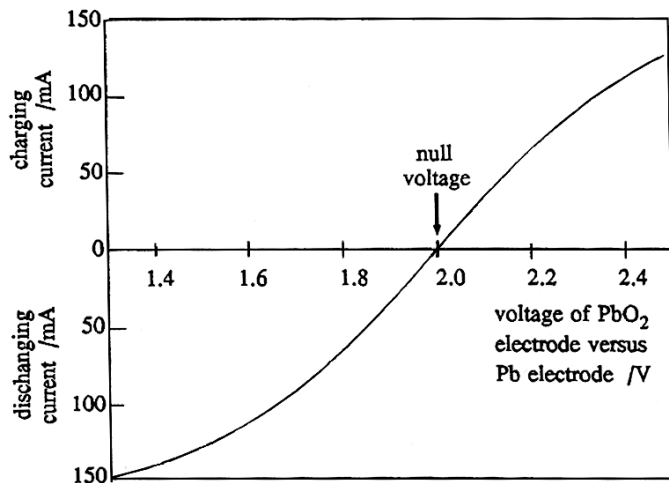
The external source could be another battery, “d.c. voltage source”, etc.

A cell in which the electricity is **driven in the direction counter** to its spontaneous motion is called an **electrolytic cell**.

In this **electrolytic mode** the lead/acid cell is charged. The electrode reactions are now opposite to those on discharge: lead sulfate is converted to lead at one electrode and to lead dioxide at the other; water is destroyed and sulfuric acid created.

In the above case of charging **Pb electrode is a cathode** and **PbO₂ is the anode**. Electric current flows counter clockwise through the circuit and **energy is accumulated in the cell**.

In the case of an **electrolytic cell** the polarisation always leads to a **voltage greater** in magnitude than that in the absence of the current flow.



A plot of cell currents versus the corresponding cell voltage is called a **voltammogram**.

Notice that the voltammogram of the electrochemical cells is not linear even though the conductors of which the cells are composed do obey Ohm's law.

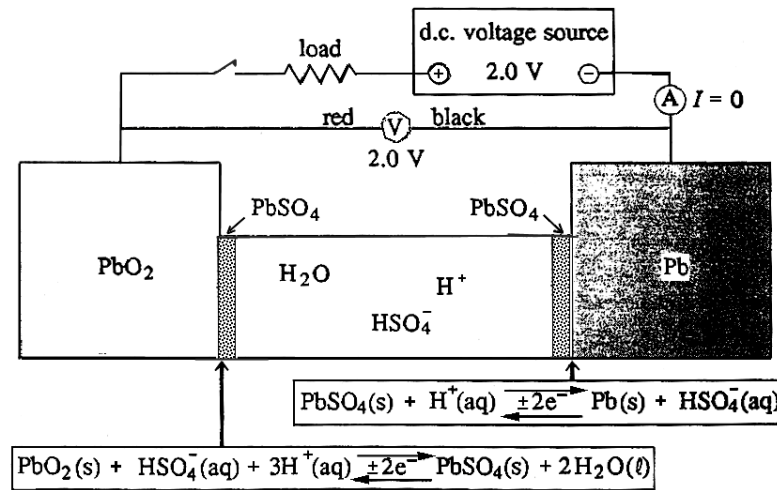
The value of the cell voltage ΔE_n at which **no current flows** is a characteristic voltage known as (five names - not to mention **EMF** or **cell potential**):

equilibrium cell voltage - because the balance exist, or

reversible cell voltage - because a minute change in the applied voltage could cause the current flow to reverse in direction, or

null voltage (rest voltage) - because no current flows, or

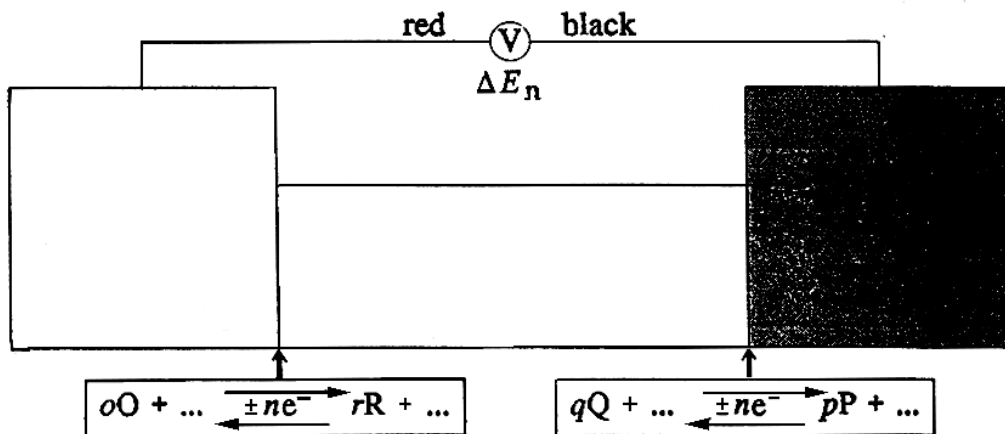
open-circuit voltage -



Electrode reactions are written as equilibria - **oxidised species on the left-hand side**.

When the cell is in its equilibrium state the cell is neither galvanic nor electrolytic - it is an **equilibrium cell**. It is **not appropriate** to apply the names “anode” or “cathode” to either electrode in such a cell.

3.2 Thermodynamics of equilibrium cells



The procedure for predicting the equilibrium voltage ΔE_n of a cell can be generalized as follow:

a. write down the left-hand electrode reaction 3:2:22 $oO + \dots \xrightleftharpoons{\pm ne^-} rR + \dots$

b. write down the right-hand electrode reaction 3:2:23 $qQ + \dots \xrightleftharpoons{\pm ne^-} pP + \dots$

(after first multiplying it, if necessary, to make the number of electrons equal to that in the left-hand electron reaction)

c. subtract the equations to obtain the **cell reaction**



d. The **equilibrium cell voltage** ΔE_n is given by the relationship (known as “Nernst equation”)

$$3:2:25 \quad \Delta E_n = \Delta E^\circ - \frac{RT}{nF} \ln \left\{ \frac{a_Q^q a_R^r \dots}{a_O^o a_P^p \dots} \right\}$$

where ΔE° is the **standard cell voltage**, **n** - number of electrons involved in the cell reaction and the **a** - terms are the activities of the various reactants and products as they exist in the cell.

There are four methods by which the **standard cell voltage** ΔE° may be determined:

i) from the **standard Gibbs energy** change accompanying the cell reaction, by using

$$3:2:27 \quad \Delta E^\circ = - \frac{\Delta G^\circ}{nF} = - \frac{qG_Q^\circ + rG_R^\circ + \dots - oG_O^\circ - pG_P^\circ - \dots}{nF}$$

ii) from the **standard electrode potential** of the left- and the right- hand electrodes by the subtraction

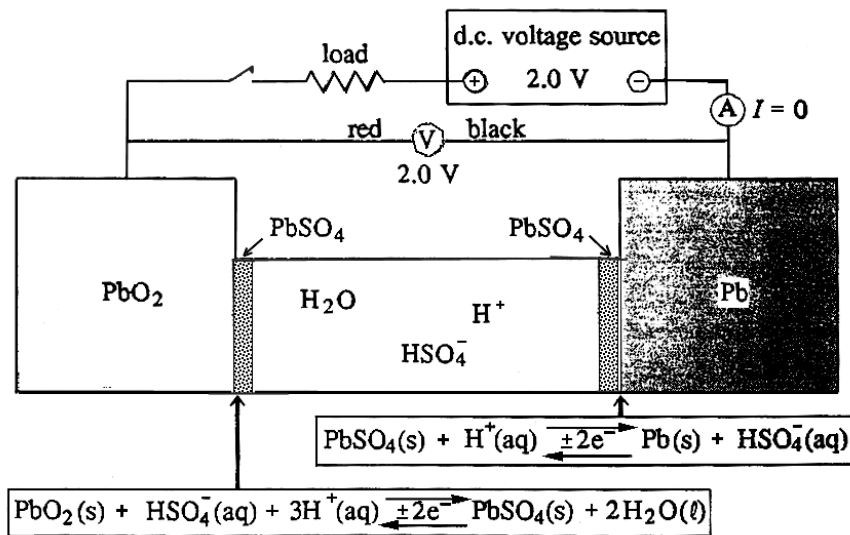
$$3:2:28 \quad \Delta E^\circ = E_l^\circ - E_r^\circ$$

iii) from the **equilibrium constant K** of the cell reaction by using

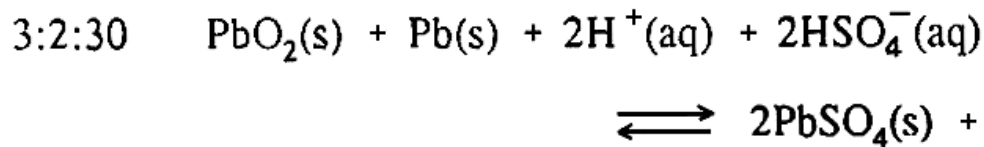
$$3:2:26 \quad \Delta E^\circ = \frac{RT}{nF} \ln \{K\}$$

iv) by extrapolation from experimental measurements

Example:



The electrode reactions in the lead/acid cell above show that the cell reaction (with $n = 2$) is



Using the data to the right, the standard Gibbs energy change for this process is found to be $\Delta G^\circ = -371.0 \text{ kJ mol}^{-1}$ and therefore from equation 3:2:27 one can calculate:

$$\Delta E^\circ = 1923 \text{ mV}$$

Standard Gibbs energies

Species	$G^\circ/\text{kJ mol}^{-1}$
$\text{PbSO}_4(\text{s})$	-813.76
$\text{H}_2\text{O}(\ell)$	-237.13
$\text{PbO}_2(\text{s})$	-218.96
$\text{HSO}_4^-(\text{aq})$	-755.91

The application of **Nernst equation** 3:2:25, with the activity terms for solids replaced by units, leads to

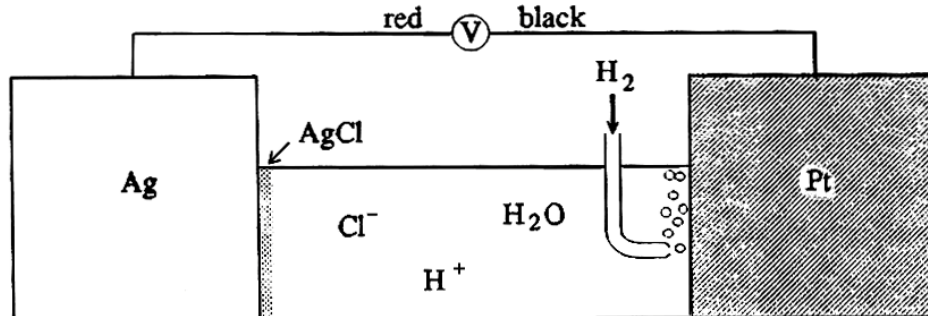
$$3:2:29 \quad \Delta E_n = 1923 \text{ mV} - (12.85 \text{ mV}) \ln \left\{ \frac{a_{\text{H}_2\text{O}(\ell)}^2}{a_{\text{H}^+(\text{aq})}^2 a_{\text{HSO}_4^-(\text{aq})}^2} \right\}$$

In a concentrated sulfuric acid solution used in the batteries it is difficult to estimate the activity coefficients of H_2O , H^+ , HSO_4^- . If we make a crude assumption that they are all unity, than for the battery acid of 5.2 molar concentration, the argument in the logarithm is $1/(5.2)^4$. On this basis one can calculate

$$3:2:31 \quad \Delta E_n = 1923 \text{ mV} + 85 \text{ mV} = 2.008 \text{ V}$$

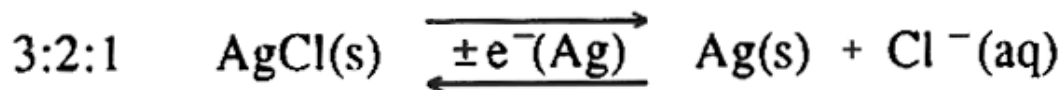
Notice that the activity term is a minor contribution to the cell voltage. This is often the case with electrochemical energy sources and it implies that uncertainties in the values of activity coefficients are seldom of major consequence.

Example:

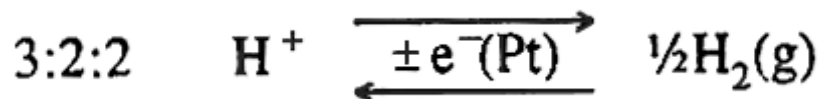


The cell consists of Silver and Platinum electrodes and the ionic conductor is 30.0 millimolar solution of HCl. Hydrogen at 1 bar pressure is bubbled over the Pt-electrode (**standard hydrogen electrode**). The Ag-electrode is covered with porous layer of AgCl. The measured open circuit voltage ΔE_n when the cell is reached equilibrium at 25⁰ C is 410,7 mV, the **Ag being positive**.

The equations

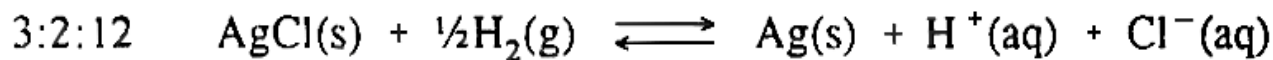


(which has standard electrode potential $E^0 = +0.22216 \text{ V}$) and



(which has standard electrode potential $E^0 = 0 \text{ V}$) describe the equilibria at the left- and the right-hand electrodes respectively. Note that “(Ag)” or “(Pt)” has been added after the electron symbol to recognise that the electrons have different sources.

The overall reaction involves exchange of one electron ($n = 1$) and is:



According to 2:7:11 and 2:7:13

$$K = \exp\left\{-\frac{\Delta G^\circ}{RT}\right\} = \exp\left\{-\frac{\Delta G_{oO+pP \rightarrow qQ+rR}^\circ}{RT}\right\}$$

$$= \exp\left\{-\frac{qG_Q^\circ + rG_R^\circ - oG_O^\circ - pG_P^\circ}{RT}\right\}$$

($RT = 2.4789 \text{ kJmol}^{-1}$)

$$\text{For 3:2:12} \quad \Delta G^\circ = G_{\text{Ag}(s)}^\circ + G_{\text{H}^+(aq)}^\circ + G_{\text{Cl}^-(aq)}^\circ - G_{\text{AgCl}(s)}^\circ - G_{\frac{1}{2}\text{H}_2}^\circ =$$

$$= 0 + 0 + (-131.02 \text{ kJmol}^{-1}) - (-109.59 \text{ kJmol}^{-1}) = -21.43 \text{ kJmol}^{-1}$$

and

$$\mathbf{K = \exp\{-(-21.43)/2.4789\} = \exp\{8.4468\} = 5692}$$

In this way the open circuit potential of the cell is given by

$$3:2:19 \quad \Delta E_n = \frac{RT}{F} \left[\ln \{K\} - \ln \left\{ \frac{a_{\text{Ag(s)}} a_{\text{H}^+(\text{aq})} a_{\text{Cl}^-(\text{aq})}}{a_{\text{AgCl(s)}} a_{\text{H}_2(\text{g})}^{1/2}} \right\} \right]$$

Since the activities of Ag, AgCl and H₂ are all unity

$$3:2:20 \quad \Delta E_n = (25.693 \text{ mV}) \left[\ln \{5692\} - \ln \left\{ \frac{c^2 \gamma_{\pm}^2}{(c^0)^2} \right\} \right]$$

where **c** is the ionic concentration in the HCl (30.0 mM - so that $c^2/(c^0)^2 = 9.00 \times 10^{-4}$) and γ_{\pm} is the mean activity coefficient of H⁺ and Cl⁻.

Hence

$$3:2:21 \quad \Delta E_n = 222.2 \text{ mV} - (25.693 \text{ mV}) \ln \left\{ (9.00 \times 10^{-4}) \gamma_{\pm}^2 \right\}$$

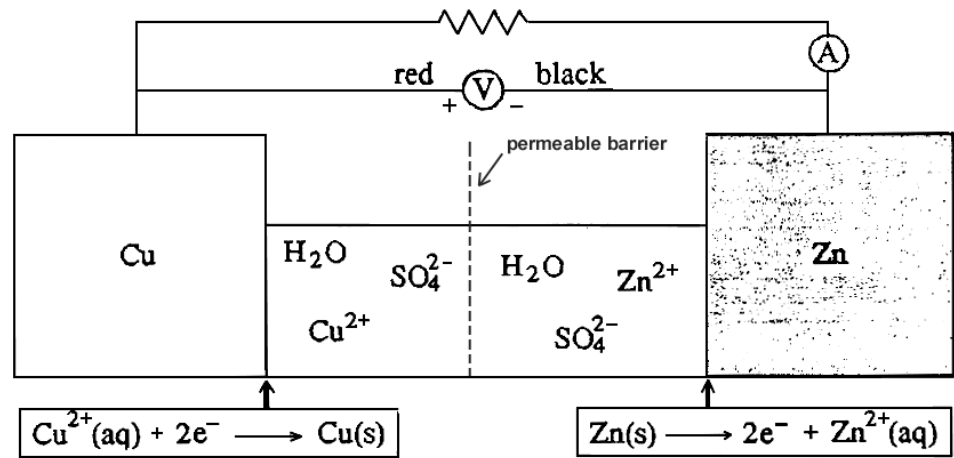
which equals **410.7 mV** if $\gamma_{\pm} = 0.85$

The standard cell voltage according to 3:2:28 is given by $\Delta E^\circ = E_r^\circ - E_c^\circ$ and is equal to **222.2 mV** (the same value as obtained with the use of **K**).

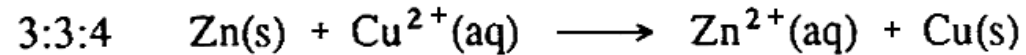
3.3. Cells with junctions

Electrochemical cells are often constructed with one (sometimes two) permeable barrier(s).

Example - Daniel cell



Without the barrier which prevents the mixing of the two solutions, Daniel cell will be completely destroyed by the parasitic reaction



Barriers may consist of finely porous materials (filter paper or fritted glass), gels or membranes of various kinds. Their function is to allow the passage of ions but to inhibit the mixing of the solutions. The presence of **permeable barrier** greatly **increases the resistance** of the ionic conductor.

The magnitude of the **junction potential difference** depends upon the geometry of the pores and on the degree of stirring in the two solutions, but in the simplest circumstances it is given by the **Henderson equation**:

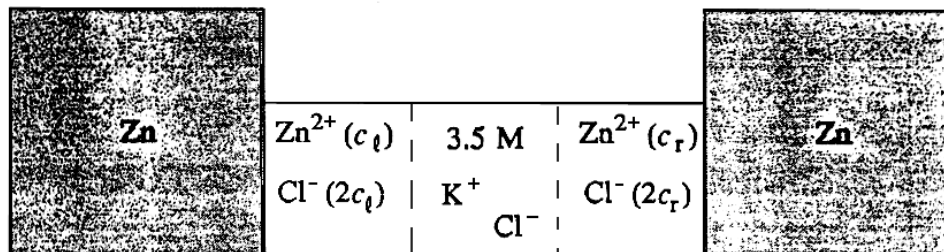
$$3:3:5 \quad \Delta\phi_J = \phi_r - \phi_\ell = -\frac{RT}{F(u_+ + u_-)} \left[\frac{u_+}{z_+} + \frac{u_-}{z_-} \right] \ln \frac{c_r}{c_\ell}$$

For the case of a junction between two different concentrations of a single electrolyte.

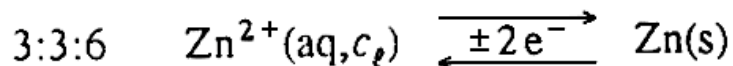
In equation 3:3:5 c_r and c_ℓ refer to the concentration of the cation (or the anion) on the right- and left-hand sides of the barrier. Using tabulated mobilities, a value of **14 mV** may be calculated by the **Henderson equation** for the potential of the junction shown above, but this value is reduced to only **0.8 mV** when **LiBr** is replaced by **KCl**.

The low value of the junction potential for **KCl** arises because the mobilities of the K^+ ($u^0 = 76.2 \times 10^{-9} \text{ m}^2\text{s}^{-1}\text{V}^{-1}$) and Cl^- ($u^0 = 79.1 \times 10^{-9} \text{ m}^2\text{s}^{-1}\text{V}^{-1}$) ions are nearly equal.

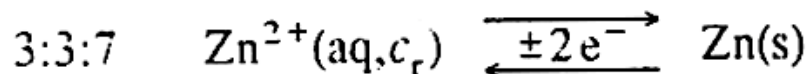
For this reason **KCl** is often used as a **salt bridge**.



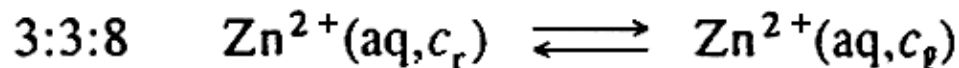
In the above **concentration cell** the **salt bridge** (with high concentration) is used to separate **two zinc chloride** solutions of **low, but different concentrations**. To predict the open circuit voltage we **subtract** the equation (for the equilibrium of the **left-hand** electrode)



from that of the **right-hand** electrode



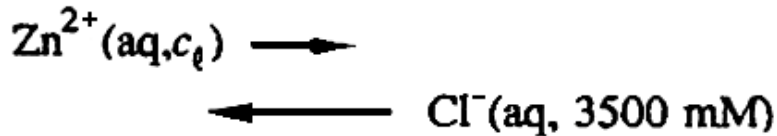
To obtain the overall cell reaction



With $n = 2$ we apply the fundamental (Nernst) equation 3:2:25

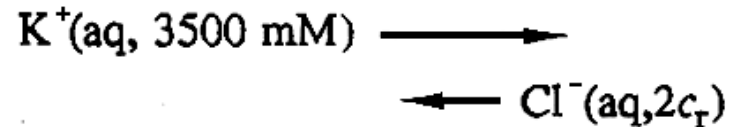
$$3:3:9 \quad \Delta E_n = -\frac{RT}{nF} \ln \left\{ \frac{a_{\text{Zn}^{2+}(\text{aq}, c_\ell)}}{a_{\text{Zn}^{2+}(\text{aq}, c_r)}} \right\} = -\frac{RT}{2F} \ln \left\{ \frac{\gamma_{\pm(\ell)} c_\ell}{\gamma_{\pm(r)} c_r} \right\}$$

There is no standard potential term in 3:3:9 because both electrode reactions involve the same materials.



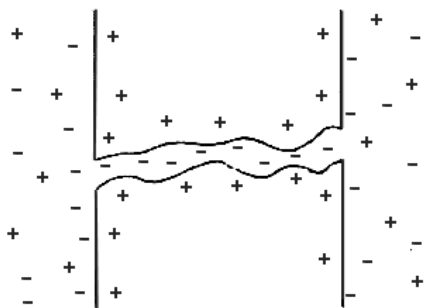
Consider the left-hand barrier and imagine current flowing from left to right through it. The current will be **predominantly carried** across the barrier **by** Cl^- ions because c_ℓ is small compared with **3500 mM** and they are many more Cl^- than Zn^{2+} ions available to carry the current

As shown, a similar situation exist at the second barrier, but in this case the **preponderance of K^+ ions** means that these species **carry most of the current.**



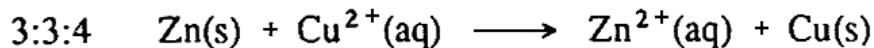
Semipermeable membranes - barriers that allow the passage of some species but not others.

A particular electrochemical value are membranes that allow the passage only of anions or only of cations.



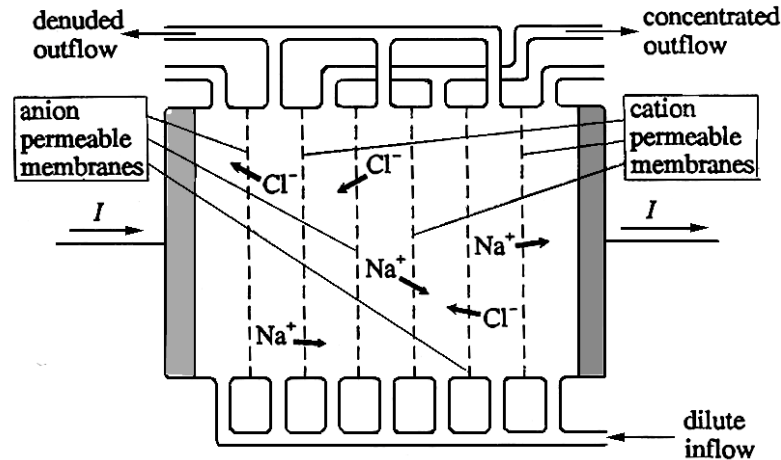
They probably function by having small pores with charge walls that are therefore accessible only to ion of opposite sign. Their use in **concentration cells with transference** has advantages over **less discriminating** barriers.

For example, there would be a clear benefit in employing an **anion selective membranes** as a barrier in Daniell cell: its use would permit the cell to be recharged, which is not possible with a simple porous barrier (because **Cu²⁺** ions would enter the zinc compartment on recharge and undergo reaction



On the other hand, membranes of any kind detrimentally increase the resistance of the cell.

An interesting technological application of **selectively permeable membranes** is in **electrodialysis** - technique for **separating a stream of dilute aqueous electrolyte** into two streams: one of almost **pure water** and one of **concentrated electrolyte**.

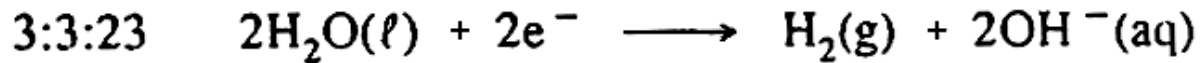
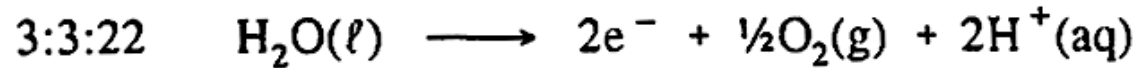


A stack of **alternating anion-permeable and cation-permeable membranes** are arranged as shown above with **electrodes in the end chambers**. Though the diagram shows only three pairs of membranes, industrial installations use hundreds.

The mode of operation is evident from the diagram which uses **NaCl** solution as an example.

Because of the **large number of units** in real installations, much ion transfer occurs with little electrolysis.

Outflows from the end chambers are acidic or basic from the electrode reactions:



and therefore these are not mixed with the other outflows.

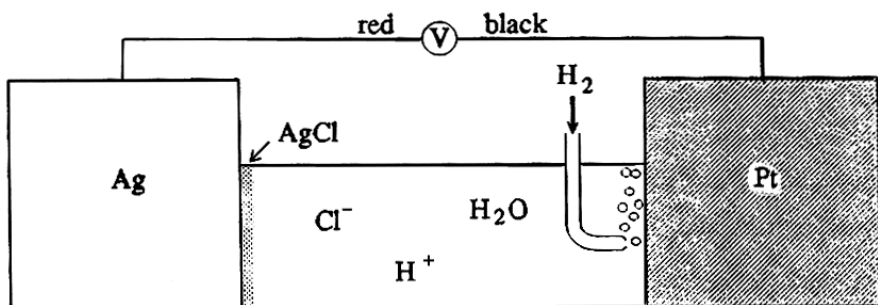
Electrodialysis is used extensively to prepare potable water from brackish water (**desalination**), to extract **NaCl** from **sea water**, to reclaim **toxic ions** from **industrial wastes**, and in processing of foodstuffs.

3.4. Utility of equilibrium cells

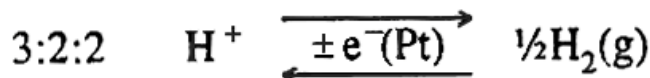
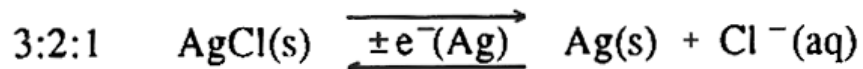
The study of cells in **thermodynamic equilibrium**, and to lesser extend the **concentration cells**, is of great significance because their **open circuit voltages** provide access to **accurate thermodynamic values**.

In fact, in company with **thermochemical** methods and **spectrochemical** techniques, **electrochemical** methods are the source of all **precise thermodynamic data**.

Example:



Electrode reactions:



Very precise measurements have been made of the open circuit voltages of the above cell for variety of concentrations, c , of electrolyte, aqueous hydrochloric acid H^+Cl^- . From the Nernst equation can be obtained that

$$3:4:1 \quad \Delta E_n = -\frac{\Delta G^\circ}{F} - \frac{RT}{F} \ln \left\{ \frac{a_{\text{Ag(s)}} a_{\text{H}^+(\text{aq})} a_{\text{Cl}^-(\text{aq})}}{a_{\text{AgCl(s)}} a_{\text{H}_2(\text{g})}^{1/2}} \right\}$$

It is rather easy to obtain **pure silver** and coat it with **pure AgCl**, and simple to insure that the **hydrogen pressure equals 1 bar** exactly.

Under these conditions the equation for the cell voltage 3:4:1 when the activities are properly replaced simplifies to

$$3:4:2 \quad \Delta E_n = -\frac{\Delta G^\circ}{F} - \frac{2RT}{F} \ln \left\{ \frac{c\gamma_{\pm}}{c^\circ} \right\}$$

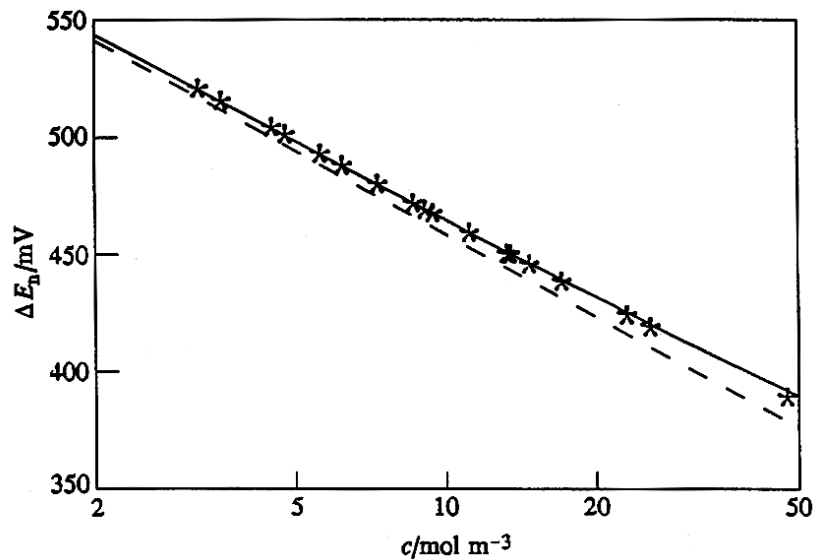
At sufficiently low concentration can be used the Debye- Hueckel low approximation

$$2:5:12 \quad \gamma_{\pm} = \exp \left\{ z_+ z_- \sqrt{\frac{\mu}{727 \text{ mol m}^{-3}}} \right\}$$

To obtain

$$3:4:3 \quad \Delta E_n = -\frac{\Delta G^\circ}{F} - \frac{2RT}{F} \left[\ln \left\{ \frac{c}{c^\circ} \right\} - \sqrt{\frac{c}{727 \text{ mM}}} \right]$$

(because $z^+ = 1$ and $-z^- = 1$ are both unity, the ionic strength of an H^+Cl^- solution equals its concentration c).



The asterisks represent experimental values of the equilibrium cell voltage ΔE_n plotted as a function of H^+Cl^- concentration c (in logarithmic scale).

A careful extrapolation based on 3:4:3 shows that

$$3:4:4 \quad \lim_{c \rightarrow 0} \left[\Delta E_n + (51.396 \text{ mV}) \ln \left\{ \frac{c}{c^0} \right\} \right] = 222.16 \text{ mV}$$

Leading to the conclusion that **222.16 mV** is the value of ΔE^0 .

The full line is very slightly curved down in accordance with 3:4:3 and 3:4:4. The **dashed line** corresponds to prediction **without Debye-Hueckel correction** (it is visible that the correction is valid).

From the ΔE^0 value (**222.16 mV**), is obtained:

$$3:4:5 \quad \Delta G^\circ = -(96485 \text{ C mol}^{-1})(0.22216 \text{ V}) = -21.435 \text{ kJ mol}^{-1}$$

It should be noted that a precision of five significant digits is possible with careful equilibrium voltage measurements.

It should be mentioned that **measurements of equilibrium cell voltages over a range of temperatures** permit **other thermodynamic properties** to be measured.

Thus, analogously the use of $3:4:6 \quad \Delta G^\circ = -nF\Delta E^\circ$

to measure the standard Gibbs energy change, accompanying the cell reaction, there are another two relationships

$$3:4:7 \quad \Delta S^\circ = nF \frac{d\Delta E^\circ}{dT}$$

$$3:4:8 \quad \Delta H^\circ = \Delta G^\circ + T\Delta S^\circ = nFT^2 \frac{d}{dT} \left(\frac{\Delta E^\circ}{T} \right)$$

They are **useful for measuring the changes in entropy and enthalpy** that accompany the cell reaction when all **reactants and products** are in their **standard states**.

It sounds paradoxically **these thermodynamic changes**, which are those accompanying **1 mole of a chemical reaction** can be measured from an **electrochemical cell at equilibrium** in which **no net chemical reaction** occurs at all.

Over the years, using very many pieces of **experimental data**, of which equation 3:4:5 is representative it has been possible to build up a **very large compilation of standard Gibbs energies** for compounds and ions.

The table on the next page is a small form, selected on the basis of utility in electrochemical science. Of course these data can be employed “backwards” to calculate the **standard equilibrium voltages** of a wide variety of cells, as well as such related quantities as **equilibrium constants**.

In using this tabulation it should be remembered that the **Gibbs energies of all elements in their standard states**, as well as that of the **hydrogen ion in its standard state in aqueous solutions** are zero by definition

$$3:4:9 \quad G_{\text{element}}^{\circ} = G_{\text{H}^+(\text{aq})}^{\circ} = 0$$

Standard Gibbs energies $G^\circ/\text{kJ mol}^{-1}$ for selected neutral and ionic species.

AgBr(s)	-95.92	Ag ⁺ (aq)	77.08	Br ⁻ (aq)	-102.76
AgCl(s)	-109.59	Al ³⁺ (aq)	-485	Cl ⁻ (aq)	-131.02
Ag ₂ O(s)	-11.20	Ca ²⁺ (aq)	-553.57	CO ₃ ²⁻ (aq)	-527.82
CaCO ₃ (s)	-1128.79	Cd ²⁺ (aq)	-77.65	Fe(CN) ₆ ³⁻ (aq)	729.4
CO ₂ (g)	-394.38	Cu ⁺ (aq)	50.3	Fe(CN) ₆ ⁴⁻ (aq)	695.08
CO ₂ (aq)	-386.2	Cu ²⁺ (aq)	65.7	HCO ₃ ⁻ (aq)	-586.98
Hg ₂ Cl ₂ (s)	-210.33	Fe ²⁺ (aq)	-78.9	HSO ₄ ⁻ (aq)	-755.91
HgO(s)	-58.54	Fe ³⁺ (aq)	-4.5	HS ⁻ (aq)	12.08
H ₂ O(l)	-237.13	Hg ₂ ²⁺ (aq)	153.57	I ⁻ (aq)	-51.65
H ₂ O ₂ (aq)	-134.03	Hg ²⁺ (aq)	164.67	I ₃ ⁻ (aq)	-51.48
H ₂ S(aq)	-27.84	In ³⁺ (aq)	-97.95	MnO ₄ ⁻ (aq)	-447.1
PbCl ₂ (s)	-313.94	Mn ²⁺ (aq)	-228.1	MnO ₄ ²⁻ (aq)	-500.6
PbO ₂ (s)	-218.96	Ni ²⁺ (aq)	-46.4	OH ⁻ (aq)	-157.24
PbSO ₄ (s)	-813.76	Pb ²⁺ (aq)	-24.18	S ²⁻ (aq)	86.34
ZnO(s)	-318.30	Tl ⁺ (aq)	-32.47	SO ₄ ²⁻ (aq)	-744.53
Zn(OH) ₂ (s)	-555.06	Zn ²⁺ (aq)	-147.19	ZnO ₂ ²⁻ (aq)	-384.4

3.5 Summary

The simplest electrochemical cell consists of an ionic conductor (usually aqueous electrolyte solution), sandwiched between two electronic conductors (usually metals).

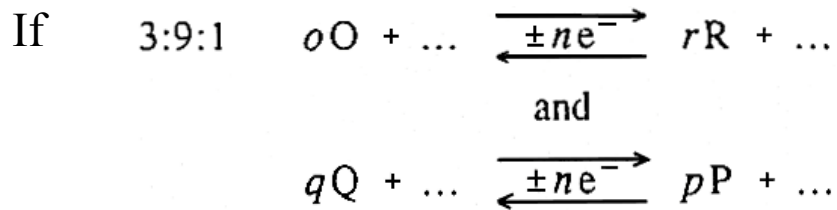
The junctions are electrodes at which electrochemical reaction may occur.

Some external connection from one electronic conductor to the other is needed before an electrode reaction occurs.

When energy is being delivered from the cell into an external load, the cell is functioning galvanically; batteries and fuel cells provide useful examples while corrosion represents an unwonted effect of a galvanic cell.

When energy is being consumed in the cell, it is behaving electrolytically; many chemicals are manufactured in this way.

An open circuit cell develops a voltage that reflex the thermodynamics of the electrode reactions.



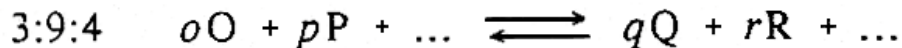
are the electrode processes at the left- and the right-hand electrodes, than the potential of the left-hand electrode with respect to the right is given by

$$3:9:2 \quad \Delta E_n = \Delta E^\circ - \frac{RT}{nF} \ln \left\{ \frac{a_Q^q a_R^r \dots}{a_O^o a_P^p \dots} \right\}$$

The standard cell voltage is related by

$$3:9:3 \quad \Delta E^\circ = \frac{RT}{nF} \ln \{K\} = - \frac{\Delta G^\circ}{nF}$$

To the equilibrium constant \mathbf{K} of the chemical reaction



and to the change to the standard Gibbs energy ΔG^0 that accompanies it.

More complicated cells have two or three ionic conductors separated by one or two barriers.

The use of an efficient salt bridge prevent any significant interaction between two electrode chambers, so that relationships $3:9:2$ and $2:9:3$ still apply.

Without a salt bridge, the open circuit voltage of a two-compartment cell may reflect the transport numbers of the charge-carrying ions and may incorporate a junction potential difference.