

*Centre of Excellence*

Training course

**abc-ELECTROCHEMISTRY**

**Part IV**

**4. Electrodes**

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## 4. Electrodes

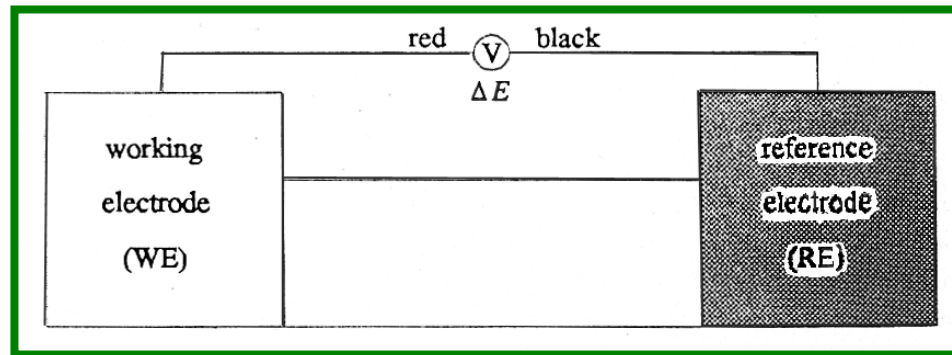
Often electrochemical studies are interested in **one of the electrodes of the cell** only. The second electrode is present to complete the cell.

Electrode of interest is named **working electrode** or the **indicator electrode**; the second electrode is known as **reference electrode** or **auxiliary electrode (counter electrode)**.

In practice the potential of the **working electrode (WE)** is measured with respect to the **reference electrode (RE)**.

Many electrochemical cells employ three electrodes (working, reference and counter electrodes).

### 4.1 Electrode potentials

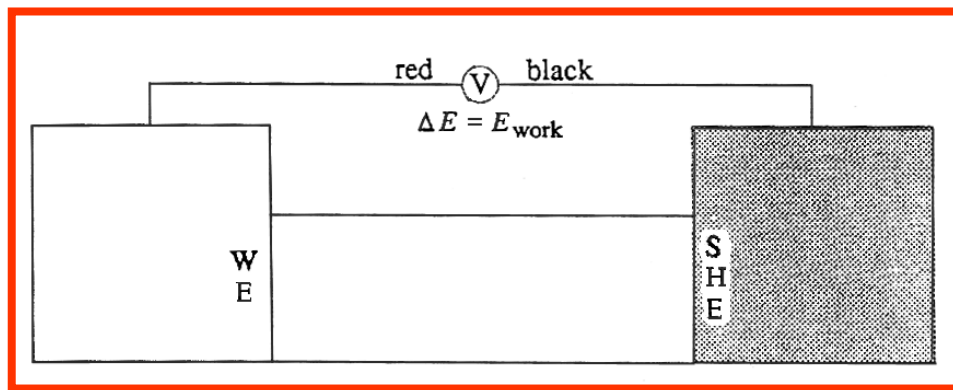
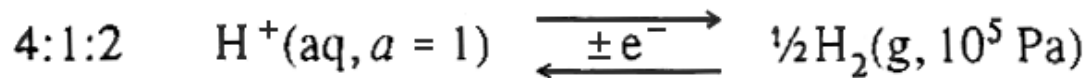


The potential difference developed by the cell  $\Delta E$  may be thought of as the **difference** between the potential of the **working electrode**  $E_{\text{work}}$  and the **reference electrode**  $E_{\text{ref}}$

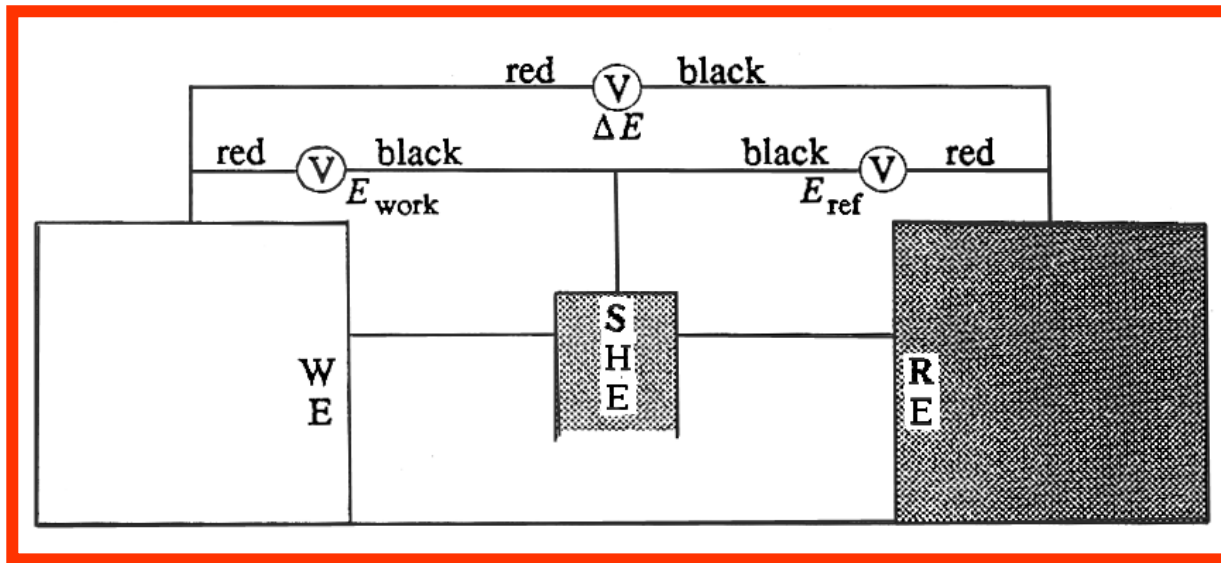
$$4:1:1 \quad \Delta E = E_{\text{work}} - E_{\text{ref}}$$

In fact there is **no straight forward way** to measure a **single electrode potential**. Nevertheless the **concept of electrode potential** is such a useful one that electrochemists have invented away to get around the fact that single electrode potential can not be measured. What is done is to **select one electrode as a standard** and **define its potential as a zero**.

The **universally accepted standard** is the **standard hydrogen electrode (SHE)**, at which the electrode process is:



Because this electrode **is defined to have zero potential**, the voltmeter in the diagram is set to measure the electrode potential  $E_{\text{work}}$  of the working electrode. **In reality** the voltmeter **measures a cell voltage**, but by convention **we all agree to speak** of this potential difference as the **potential of the WE**.



In effect, we **split the measured voltage  $\Delta E$**  across the cell into the **difference  $E_{\text{work}}$**  and  **$E_{\text{ref}}$**  (as in equation 4:1:1), by **imagining an extra electrode - a standard hydrogen electrode** - to be dipped in the solution as shown above.

We don't actually need to use a SHE: provided that we know  $E_{\text{ref}}$  and measure  $\Delta E$  we can always calculate  $E_{\text{work}}$  as  $\Delta E + E_{\text{ref}}$

## 4.2 Reference electrode

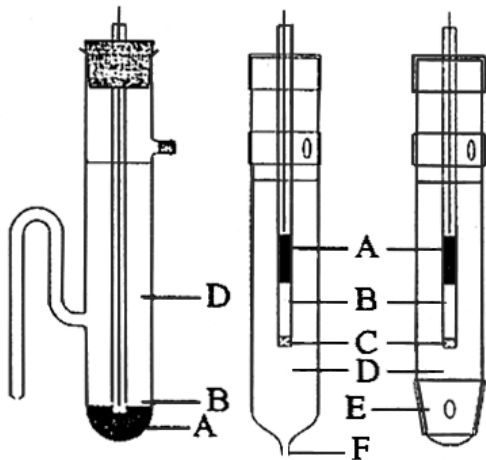
**Ideal reference electrode** - maintains a constant potential  $E_{\text{ref}}$  independent if it operates as cathode or as an anode, irrespective of the current that passes through it.

To come close to this requirements among other things it must be:

- **continuous supply of all species** involved in the reference electrode reaction
- **activities** of all these species are **constant**
- **electrode process** must be **without polarization**.
- electrode must be robust and unaffected by processes (such as evaporation) that occur when use is intermittent.

The above criteria are best met by the **saturated calomel electrode (SCE)** which is therefore the most popular **reference electrode** for use in **aqueous solutions**.

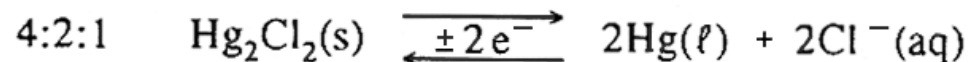
### Versions of SCE:



- A = mercury
- B = mercury-calomel paste
- C = asbestos or glass wool plug
- D = potassium chloride solution
- E = sleeve junction
- F = ceramic, quartz or asbestos fiber junction

**SCE** consists of a pool of **Hg** in contact with a paste of mercurous chloride ( $\text{Hg}_2\text{Cl}_2$  - **virtually insoluble salt** also known as **calomel**) - which in turn contacts a **solution of KCl**, which is maintained saturated by presence of **solid KCl**.

The electrode reaction



involves only **species at unit activity** ( $\text{Hg}_2\text{Cl}_2$  and  $\text{Hg}$ ) and  $\text{Cl}^-$  ion whose **activity is constant** because the **KCl solution is saturated**.

The potential of the electrode has been accurately measured (against the SHE standard) as

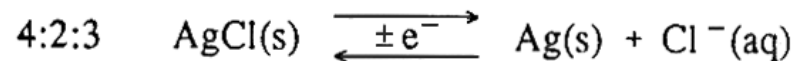
$$4:2:2 \quad E_{\text{ref}} = 0.244 \text{ V at } 298.15 \text{ K}$$

The **advantage** of the use of **saturated KCl** as the solution in the **SCE** is that the **junction potential difference** created when it is dipped into most other **aqueous solution is negligible** in all but the most precise studies.

The potential of SCE has a **large temperature coefficient** ( $dE_{\text{ref}}/dT = 0.67 \text{ mV K}^{-1}$ ), but **unsaturated calomel electrodes** (e.g. with **0.10 M KCl**  $E_{\text{ref}} = 0.336 \text{ V}$ ) can be substituted to **alleviate this drawback**.

Sometimes it is **inconvenient to use a liquid metal** in a reference electrode and therefore an **alternative reference electrode** - the **silver/silver chloride** electrode - is often employed instead of SCE.

The process



occurs and **generates a potential (0.199 V at 298.15 K with saturated KCl)** that is **almost as stable as that of SCE**.

From a **theoretical viewpoint** the **best reference electrode** would be SHE because the **cell voltage would than measure  $E_{\text{work}}$  directly**.

Unfortunately the SHE is **temperamental and difficult to use**: it is **employed only in calibration studies**.

### 4.3 Standard electrode potentials

In the equation

$$4:1:1 \quad \Delta E = E_{\text{work}} - E_{\text{ref}}$$

the cell voltage is divided up into **working component**  $E_{\text{work}}$  and **reference component**  $E_{\text{ref}}$ .

Similarly we could partition equation

3:2:25

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

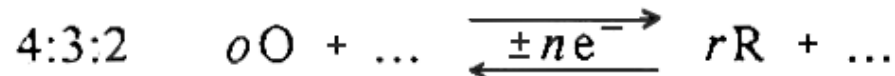
into

4:3:1

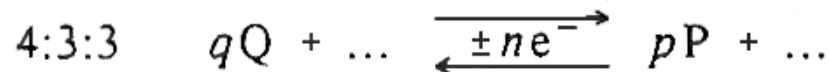
$$\Delta E_n = E_{\text{work}} - E_{\text{ref}}$$

$$= \left[ E_{\text{work}}^\circ - \frac{RT}{nF} \ln \frac{a_R^r \dots}{a_O^o \dots} \right] - \left[ E_{\text{ref}}^\circ - \frac{RT}{nF} \ln \frac{a_P^p \dots}{a_Q^q \dots} \right]$$

where the electrode **reaction at the working electrode** is



and the electrode **reaction at the reference electrode** is



Because the **reference electrode is always selected** to have **constant activities** there is **no need to split  $E_{\text{ref}}$**  into a **standard potential term** and **activity term**.

Instead it can be written

$$4:3:4 \quad \Delta E_n = E_{\text{work}}^{\circ} - \frac{RT}{nF} \ln \frac{a_{\text{R} \dots}^r}{a_{\text{O} \dots}^o} - E_{\text{ref}}$$

Which differs from

$$3:2:25 \quad \Delta E_n = \Delta E^{\circ} - \frac{RT}{nF} \ln \left\{ \frac{a_{\text{Q}}^q a_{\text{R} \dots}^r}{a_{\text{O}}^o a_{\text{P}}^p \dots} \right\}$$

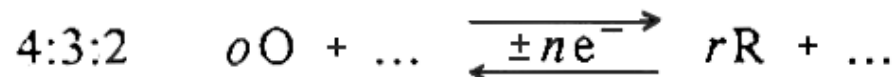
in including the **activities of only those species that are involved in the reaction at the working electrode**. Alternatively, since

$$\Delta E_n = E_{\text{work}} - E_{\text{ref}}$$

We can write

$$4.3.5 \quad E_{\text{work}} = E_{\text{work}}^{\circ} - \frac{RT}{nF} \ln \frac{a_{\text{R} \dots}^r}{a_{\text{O} \dots}^o}$$

This is the **Nernst equation** for the **working electrode** at which occurs **reaction**



When **Nernst equation** is written with **negative sign** the **product of reaction appear in a numerator** of the log term and the **oxidized reactant in the denominator**

The term  $E_{\text{work}}^{\circ}$  is the **standard electrode potential** of the **working electrode**.

It is the value that the **potential of the WE** would adopt if **all the species R, O,...** were in **unit activity**.

Extensive **tables of standard electrode potentials exist** and representative selection is given on the next slide table.

It is more **economical** of space to **tabulate  $G^{\circ}$**  values and to **calculate standard potential** from the **standard Gibbs energies** of the species involved, via the relationship

$$4:3:6 \quad E^{\circ} = -\frac{\Delta G^{\circ}}{nF} = -\frac{rG_{\text{R}}^{\circ} + \dots - oG_{\text{O}}^{\circ} - \dots}{nF}$$

For calculating the **strandard electrode potentials** it is **useful to remember** the value of the conversion factor

$$4:3:7 \quad \frac{1}{F} = 10.3643\text{mV (kJ mol}^{-1}\text{)}^{-1}$$

Standard electrode potentials (at 25.00°C)

#	Electrode reaction	$E^\circ/V$
1	$\text{MnO}_4^- (\text{aq}) + 8\text{H}^+ (\text{aq}) \xrightleftharpoons{\pm 5e^-} \text{Mn}^{2+} (\text{aq}) + 4\text{H}_2\text{O} (\ell)$	+1.512
2	$\text{Cl}_2 (\text{g}) \xrightleftharpoons{\pm 2e^-} 2\text{Cl}^- (\text{aq})$	+1.3578
3	$\text{Cr}_2\text{O}_7^{2-} (\text{aq}) + 14\text{H}^+ (\text{aq}) \xrightleftharpoons{\pm 6e^-} 2\text{Cr}^{3+} (\text{aq}) + 7\text{H}_2\text{O} (\ell)$	+1.33
4	$\text{O}_2 (\text{g}) + 4\text{H}^+ (\text{aq}) \xrightleftharpoons{\pm 4e^-} 2\text{H}_2\text{O} (\ell)$	+1.2288
5	$\text{Ag}^+ (\text{aq}) \xrightleftharpoons{\pm e^-} \text{Ag} (\text{s})$	+0.7989
6	$\text{Hg}_2^{2+} (\text{aq}) \xrightleftharpoons{\pm 2e^-} 2\text{Hg} (\ell)$	+0.7958
7	$\text{Fe}^{3+} (\text{aq}) \xrightleftharpoons{\pm e^-} \text{Fe}^{2+} (\text{aq})$	+0.771
8	$\text{O}_2 (\text{g}) + 2\text{H}^+ (\text{aq}) \xrightleftharpoons{\pm 2e^-} \text{H}_2\text{O}_2 (\text{aq})$	+0.6946
9	$\text{I}_3^- (\text{aq}) \xrightleftharpoons{\pm 2e^-} 3\text{I}^- (\text{aq})$	+0.5362
10	$\text{O}_2 (\text{g}) + 2\text{H}_2\text{O} (\ell) \xrightleftharpoons{\pm 4e^-} 4\text{OH}^- (\text{aq})$	+0.4008
11	$\text{Fe}(\text{CN})_6^{3-} (\text{aq}) \xrightleftharpoons{\pm e^-} \text{Fe}(\text{CN})_6^{4-} (\text{aq})$	+0.355
12	$\text{Ag}_2\text{O} (\text{s}) + \text{H}_2\text{O} (\ell) \xrightleftharpoons{\pm 2e^-} 2\text{Ag} (\text{s}) + 2\text{OH}^- (\text{aq})$	+0.3428
13	$\text{Cu}^{2+} (\text{aq}) \xrightleftharpoons{\pm 2e^-} \text{Cu} (\text{s})$	+0.340
14	$\text{Hg}_2\text{Cl}_2 (\text{s}) \xrightleftharpoons{\pm 2e^-} 2\text{Hg} (\ell) + 2\text{Cl}^- (\text{aq})$	+0.2680
15	$\text{AgCl} (\text{s}) \xrightleftharpoons{\pm e^-} \text{Ag} (\text{s}) + \text{Cl}^- (\text{aq})$	+0.22216
16	$2\text{H}^+ (\text{aq}) \xrightleftharpoons{\pm 2e^-} \text{H}_2 (\text{g})$	0
17	$\text{Pb}^{2+} (\text{aq}) \xrightleftharpoons{\pm 2e^-} \text{Pb} (\text{Hg})$	-0.1207
18	$\text{V}^{3+} (\text{aq}) \xrightleftharpoons{\pm e^-} \text{V}^{2+} (\text{aq})$	-0.255
19	$\text{Zn}^{2+} (\text{aq}) \xrightleftharpoons{\pm 2e^-} \text{Zn} (\text{s})$	-0.7628
20	$2\text{H}_2\text{O} (\ell) \xrightleftharpoons{\pm 2e^-} \text{H}_2 (\text{g}) + 2\text{OH}^- (\text{aq})$	-0.8280

In the table **left-to-right process**, correspond to a reduction.

For this reason these potentials are sometimes called **standard reduction potentials**. The name **redox potential** is also used.

In the table **oxidized species are on the left**, **reduction species are on the right**, with the **strongest oxidizers on the top** and **strongest reducers at the bottom**.

**Redox couple** - two species that are interconvertable by an electronic change

Example:  $\text{Cu}^{2+} (\text{aq})$  and  $\text{Cu} (\text{s})$  or  $\text{Cl}_2 (\text{g})$  and  $\text{Cl}^- (\text{aq})$ . (No 13 and No 2)

This term may be extended to such pairs as  $\text{Cr}_2\text{O}_7^{2-} (\text{aq})$  and  $\text{Cr}^{3+} (\text{aq})$  even though their interconversion involves chemical species as well as electrons. (No 3)

The table includes examples of similar electrode reactions in acidic and in basic solutions (e.g. No. 4 and No. 10). Because the reduction of oxygen (in neutral solutions) may be regarded as proceeding by either of these routes, there must be a **relationship between the two E° values**. In fact, we may derive one standard electrode potential from the other by making use of the ionic product relationship for water

$$4:3:8 \quad a_{\text{H}^+(\text{aq})} a_{\text{OH}^-(\text{aq})} = (1.008 \times 10^{-14}) a_{\text{H}_2\text{O}(\ell)}$$

The **Nernst equation** adopted to entry No 4

$$4:3:9 \quad E_n = 1.2288 \text{ V} - \frac{RT}{4F} \ln \frac{a_{\text{H}_2\text{O}(\ell)}^2}{a_{\text{O}_2(\text{g})} a_{\text{H}^+(\text{aq})}^4}$$

may be combined with the equation 4:3:8 into

$$\begin{aligned} 4:3:10 \quad E_n &= 1.2288 \text{ V} - \frac{RT}{4F} \ln \frac{a_{\text{OH}^-(\text{aq})}^4}{a_{\text{O}_2(\text{g})} (1.008 \times 10^{-14})^4 a_{\text{H}_2\text{O}(\ell)}^2} \\ &= 0.4008 \text{ V} - \frac{RT}{4F} \ln \frac{a_{\text{OH}^-(\text{aq})}^4}{a_{\text{O}_2(\text{g})} a_{\text{H}_2\text{O}(\ell)}^2} \end{aligned}$$

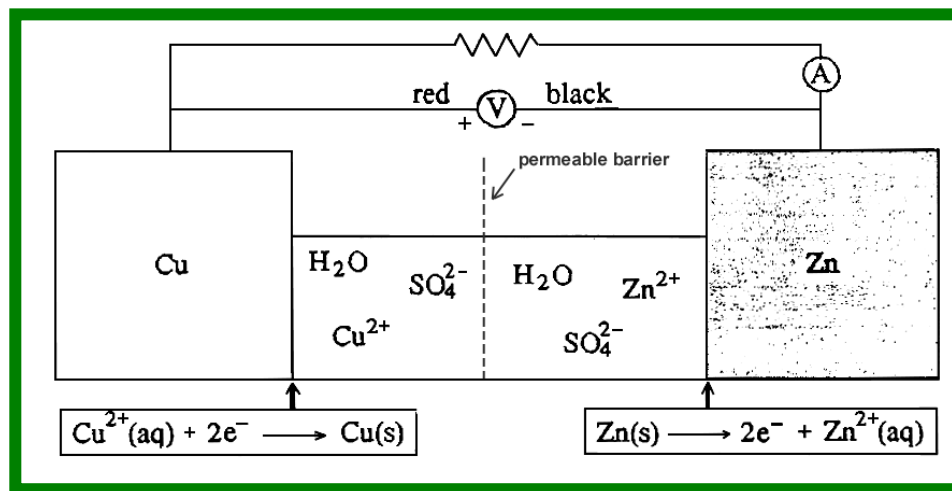
In concurrence with entry No. 10

The **signs** and **magnitudes** of standard electrode potentials are **both important**.

**Example:** for the redox couple:  $\text{Cu}^{2+}(\text{aq})/\text{Cu}(\text{s})$   $E^\circ = +0.340 \text{ V}$

for the redox couple:  $\text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s})$   $E^\circ = -0.763 \text{ V}$

It could be expected that the **zinc electrode** in the Daniel cell would be **negative terminal** (with greater “electron pressure” ) than the **positive copper terminal**. This is indeed the case.



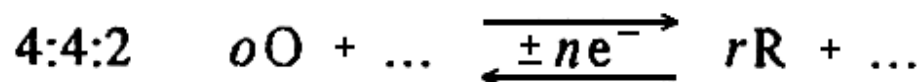
The voltage of the Daniel cell is close to  $0.340 \text{ V} - (-0.763 \text{ V}) = 1.103 \text{ V}$  as expected.

## 4.4 Versions of the Nernst equation

The equation for the **rest potential**  $E_n$

$$4:4:1 \quad E_n = E^\circ - \frac{RT}{nF} \ln \frac{a_R^r \dots}{a_O^o \dots}$$

is the **Nernst relationship** applied to a **working electrode** at which occur the **general reaction**



The **properties of logarithms** permit an **interchange of numbers** between the  $RT/nF$  multiplier in 4:4:1 and the **stoichiometric coefficients** that appear as **powers of the activities**. Thus the **Nernst equation** obtains **alternative form**

$$4:4:3 \quad E_n = E^\circ - \frac{RT}{F} \ln \frac{a_R^{r/n} \dots}{a_O^{o/n} \dots} = E^\circ - \frac{rRT}{nF} \ln \frac{a_R \dots}{a_O^{o/r} \dots}$$

or several other forms

In terms of **logarithms** to the base **10** the **Nernst equation** 4:4:2 becomes

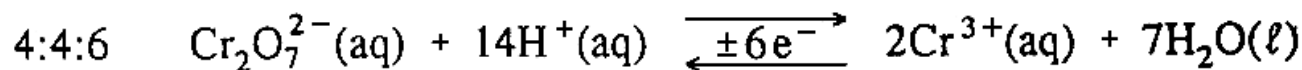
$$4:4:4 \quad E_n = E^\circ - \frac{2.303 RT}{nF} \log_{10} \frac{a_R^r \dots}{a_O^o \dots}$$

Or at temperature **25.0° C**

$$4:4:5 \quad E_n = E^\circ - \frac{59.16 \text{ mV}}{n} \log_{10} \frac{a_R^r \dots}{a_O^o \dots}$$

Sometimes is convenient (e.g. in constructing the **potential - pH diagrams**) to **split off**, from the **Nernst law** activity quotient  $a_R^r \dots / a_O^o \dots$ , the activity of **H<sup>+</sup>(aq)** or **OH<sup>-</sup>(aq)** ions that are **involved in the electrode reaction**, **replacing** their activities  $a_{\text{H}^+(\text{aq})}$  or  $a_{\text{OH}^-(\text{aq})}$  by an **equivalent term involving pH**.

**Example:** For the complicated reaction:

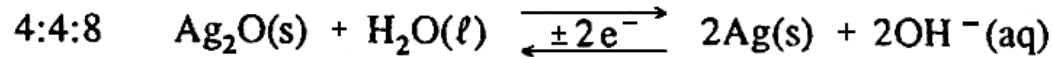


The **Nernst equation** can be **simplified** as follows:

$$\begin{aligned} 4:4:7 \quad E_n &= E^\circ - \frac{RT}{6F} \ln \frac{a_{\text{Cr}^{3+}(\text{aq})}^2 a_{\text{H}_2\text{O}(\ell)}^7}{a_{\text{Cr}_2\text{O}_7^{2-}(\text{aq})} a_{\text{H}^+(\text{aq})}^{14}} \\ &= E^\circ - \frac{RT}{6F} \ln \frac{a_{\text{Cr}^{3+}(\text{aq})}^2 a_{\text{H}_2\text{O}(\ell)}^7}{a_{\text{Cr}_2\text{O}_7^{2-}(\text{aq})}} + \frac{7RT}{3F} \ln a_{\text{H}^+(\text{aq})} \\ &\approx E^\circ - (4.28 \text{ mV}) \ln \frac{a_{\text{Cr}^{3+}(\text{aq})}^2}{a_{\text{Cr}_2\text{O}_7^{2-}(\text{aq})}} - (138.04 \text{ mV}) \text{ pH} \end{aligned}$$

In the final step, an **additional simplification** resulted from taking the **activity of the solvent**  $a_{\text{H}_2\text{O}} = 1$  and the temperature to be **25.0° C**

**Example:** The rest potential of the reaction



can be written as

$$4:4:9 \quad E_n = E^\circ - \frac{RT}{2F} \ln \frac{a_{\text{Ag(s)}}^2 a_{\text{OH}^-(\text{aq})}^2}{a_{\text{Ag}_2\text{O(s)}} a_{\text{H}_2\text{O(l)}} \\ = E^\circ - (12.85 \text{ mV}) \ln \frac{a_{\text{Ag(s)}}^2 a_{\text{H}_2\text{O(l)}}}{a_{\text{Ag}_2\text{O(s)}}} + 828.0 \text{ mV} - (59.16 \text{ mV}) \text{pH}$$

The simplification is obtained by the use of the relation

$$4:3:8 \quad a_{\text{H}^+(\text{aq})} a_{\text{OH}^-(\text{aq})} = (1.008 \times 10^{-14}) a_{\text{H}_2\text{O(l)}}$$

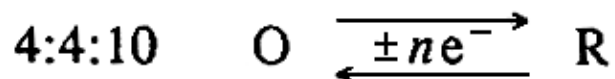
and 
$$-\frac{RT}{F} \ln(1.008 \times 10^{-14}) = 828 \text{ mV}$$

Note that the values of the **remaining activities** of **Ag(s)**; **Ag<sub>2</sub>O**; **H<sub>2</sub>O(e)** are **very close to 1**.

With **E<sup>0</sup> = + 0.3428 V** (# 12 from the table) the potential of the above electrode follows the relation: **E<sub>n</sub> = 1171 mV - (0.59 mV)pH**

In **voltammetry** it is usual to use the equation  $\mathbf{R} \longrightarrow n\mathbf{e}^- + \mathbf{O}$  or  $\mathbf{O} + n\mathbf{e}^- \longrightarrow \mathbf{R}$  when discussing **oxidation** or **reduction** reactions.

In this case, the **general reaction** 4:4:2 is replaced by the **simple redox couple**

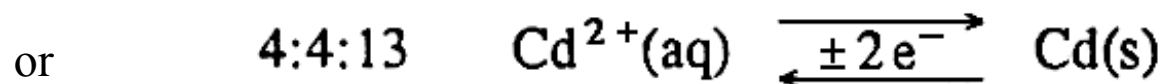
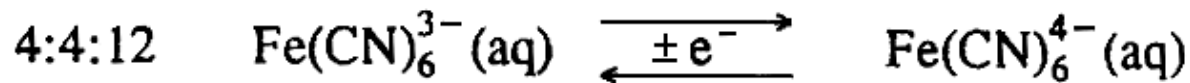


with a **Nernst equation** from which the **stoichiometric coefficients are 1**

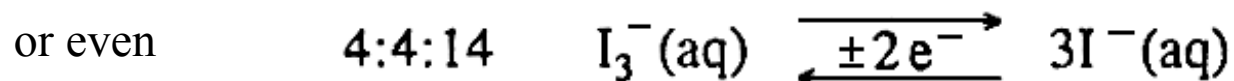
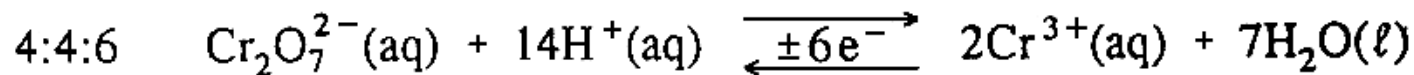
$$4:4:11 \quad E_n = E^\circ - \frac{RT}{nF} \ln \frac{a_{\mathbf{R}}}{a_{\mathbf{O}}}$$

The symbols **O** and **R** are used for the substances **involved** in the **reaction at the working electrode**, as abbreviations for **Oxidized** and **Reduced** species respectively.

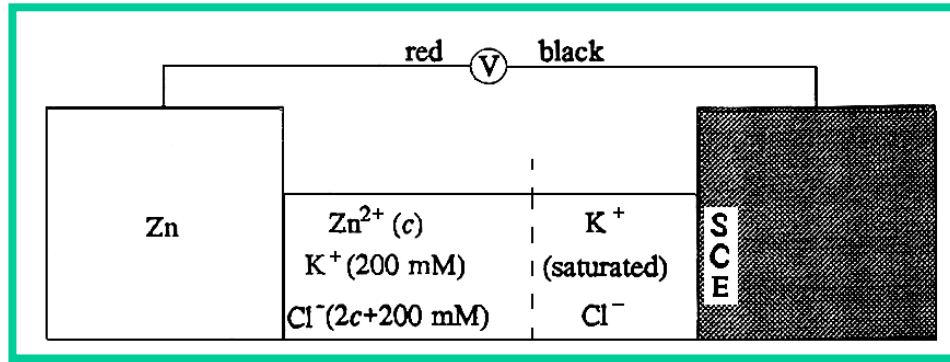
Example: This form of electrode equation is adequate to represent a process such as



but not one with the complexity of the reaction



**Example:**



The **working electrode** consists of **Zn metal** in a **200 mM KCl solution** to which **zinc chloride** has been added to give a small concentration ***c*** of  **$\text{Zn}^{2+}(\text{aq})$**  ions.

The reaction at the working electrode is: 4:4:15  $\text{Zn}^{2+}(\text{aq}) \xrightleftharpoons{\pm 2e^-} \text{Zn}(\text{s})$

The Nernst equation takes the form: 4:4:16 
$$E_n = E^\circ - \frac{RT}{2F} \ln \frac{a_{\text{Zn}(\text{s})}}{a_{\text{Zn}^{2+}(\text{aq})}}$$

The **activity of Zn metal** is **1**. The activity of  **$\text{Zn}^{2+}$**  can be replaced by the **product** of the **concentration ratio**  $c_{\text{Zn}^{2+}(\text{aq})}/c^\circ$  and the **activity coefficient**  $\gamma_{\text{Zn}^{2+}(\text{aq})}$

$$4:4:17 \quad E_n = E^\circ + \frac{RT}{2F} \ln(\gamma_{\text{Zn}^{2+}}) - \frac{RT}{2F} \ln \frac{c^\circ}{c_{\text{Zn}^{2+}(\text{aq})}}$$

In the example, the **concentrations** of  $\text{K}^+$  and  $\text{Cl}^-$  primarily **determine** the **ionic strength**  $\mu$ , as long as we keep the **KCl concentration constant at 200 mM** and  $c_{\text{Zn}^{2+}}$  **much lower** than this, then  $\gamma_{\text{Zn}^{2+}}$  will be **effectively constant**

$$4:4:17 \quad E_n = E^\circ + \frac{RT}{2F} \ln(\gamma_{\text{Zn}^{2+}}) - \frac{RT}{2F} \ln \frac{c^\circ}{c_{\text{Zn}^{2+}(\text{aq})}}$$

Therefore we are able to **combine**  $E^\circ$  and  $(RT/2F) \ln(\gamma_{\text{Zn}^{2+}})$  into a **single constant term**.

Such a constant is known as the **conditional potential**, or **formal potential**, of the working electrode. It is symbolised by  $E^{\circ'}$ .

$$4:4:18 \quad E_n = E^{\circ'} - \frac{RT}{2F} \ln \frac{c^\circ}{c_{\text{Zn}^{2+}(\text{aq})}}$$

The name “**conditional potential**” is used because  $E^{\circ'}$  is **not** an absolute constant: **its value depends** on the conditions in the electrode chamber. If e.g. the **concentration is changed** to 300 mM, or if **KCl is replaced** by HCl,  $E^{\circ'}$  will acquire **somewhat different value**. Usually **conditional potentials** are **measured experimentally**, seldom it is possible to calculate them.

There are two advantages in replacing 4:4:16 by 4:4:18.

$$4:4:16 \quad E_n = E^\circ - \frac{RT}{2F} \ln \frac{a_{\text{Zn(s)}}}{a_{\text{Zn}^{2+}(\text{aq})}}$$

$$4:4:18 \quad E_n = E^{\circ'} - \frac{RT}{2F} \ln \frac{c^\circ}{c_{\text{Zn}^{2+}(\text{aq})}}$$

- **No longer have to worry about activity coefficients** (which are seldom known, when **concentrations are high enough**, so that the Debye-Hueckel theory **becomes invalid**).
- **No longer needed to be concerned about speciation** (the process of **developing new species** through evolution)

In the above example it **was assumed** that **all zinc exists** in a **200 mM KCl as the same ion, Zn<sup>2+</sup> (aq)**, that is present in dilute aqueous solution.

This is certainly **not the case**: some of the zinc will be in the **form of the complex ion ZnCl<sub>4</sub><sup>2-</sup> (aq)**, some as the **ion pair ZnCl<sup>+</sup> (aq)**, and there will be **other species** also.

**Each these species** is present at a **distinct concentration**, has distinct **activity coefficient**, and forms a **redox couple of distinct E<sup>0</sup>** with **Zn(s)**.

As long as discussion is limited to **small zinc concentrations** in **200 mM KCl**, we can utilize the **Nernst equation** in the form

$$4:4:18 \quad E_n = E^{o'} - \frac{RT}{2F} \ln \frac{c^o}{c_{\text{Zn}^{2+}(\text{aq})}}$$

treating  $E^{o'}$  as unknown but **measurable constant**.

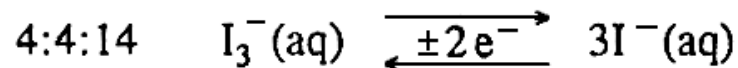
Because of the uncertain speciation, it is sometimes preferable to rewrite this equation in the modified form

$$4:4:19 \quad E_n = E^{o'} - \frac{RT}{2F} \ln \frac{c^o}{c_{\text{Zn}^{II}(\text{aq})}}$$

where  $c_{\text{Zn}^{II}(\text{aq})}$  denotes the **total concentration** of all dissolved Zn species **in oxidation state II**, a quantity that is easily calculable from the **recipe used to prepare the solution**.

The  $c^o$  term in 4:4:19 originated in the **replacement** of  $a_{\text{Zn}^{2+}(\text{aq})}$  by  $\gamma_{\text{Zn}^{2+}(\text{aq})} c_{\text{Zn}^{2+}(\text{aq})} / c^o$

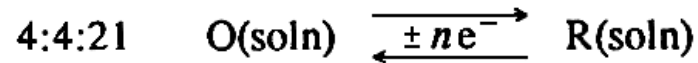
Likewise, for the electrode reaction



$$4:4:20 \quad E_n = E^{o'} - \frac{RT}{3F} \ln \frac{c_{\text{I}^- (\text{aq})}^3}{(c^o)^2 c_{\text{I}_3^- (\text{aq})}}$$

**Nernst equation** again **incorporates** this **standard thermodynamic concentration term**,  $c^o = 1000 \text{ mol m}^{-3}$  (1 M)

When we return to the consideration of the **generic redox couple**



**in which both members** of the couple are **solutes** with **equal stoichiometric coefficients**, then  $c^0$  terms **cancel** and the **Nernst equation** can be cast (involving a **simple concentration ratio**) as

$$4:4:22 \quad E_n = E^{o'} - \frac{RT}{nF} \ln \frac{c_R}{c_O}$$

In tis case the **conditional potential**  $E^{o'}$  equals  $(RT/nF) \ln(\gamma_R/\gamma_O)$

This **various versions** of the Nernst equation all **provide expressions** for the **rest electrode potential**. Each equation can be transformed into an expression for the **open circuit cell potential**  $\Delta E_n$  simply by **subtracting**  $E_{\text{ref}}$  from **each side** of the equation.

$$4:4:23 \quad \Delta E_n = E^{o'} - \frac{RT}{nF} \ln \frac{c_R}{c_O} - E_{\text{ref}}$$

Sometimes is useful to write the Nernst equation

$$4:4:22 \quad E_n = E^{o'} - \frac{RT}{nF} \ln \frac{c_R}{c_O}$$

in exponential form

$$4:4:24 \quad \exp \left\{ \frac{nF}{RT} (E^{o'} - E_n) \right\} = \frac{c_R}{c_O}$$

In all our discussions so far, we have **assumed** that the **concentrations** of **O** and **R** are **uniform** throughout the working electrode compartment.

When concentrations are **nonuniform**, it is the concentrations  $c_O^s$  and  $c_R^s$  of the species **O** and **R** at the electrode surface that determine the cell potential and it is sometimes useful to write the Nernst equation

$$4:4:25 \quad E_n = E^{o'} - \frac{RT}{nF} \ln \frac{c_R^s}{c_O^s}$$

**Thermodynamics implies** that the Nernst equation always holds when no current passes through an electrode.

However, under some conditions (reversible reactions under current) the Nernst law

$$4:4:26 \quad E = E^{o'} - \frac{RT}{nF} \ln \frac{c_R^s}{c_O^s}$$

may hold also and during passage of current

## 4.5 Summary

An electrochemical cell frequently has a working electrode, whose potential  $E$  is of interest, and a reference electrode, designed to have a constant potential.

The measured cell voltage is the difference of the two potentials

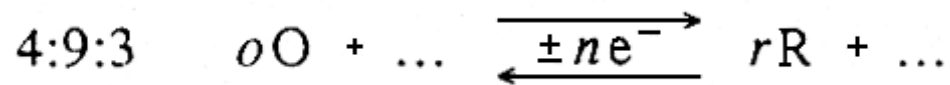
$$4:9:1 \quad \Delta E = E - E_{\text{ref}}$$

and, by defining the SHE to have zero potential, each of these electrode potentials becomes measurable.

One can assign a standard potential to every electrode; it is calculable from the standard Gibbs energies of the products and reactants, e.g.

$$4:9:2 \quad E^\circ = -\frac{\Delta G^\circ}{nF} = -\frac{rG_R^\circ + \dots - oG_O^\circ - \dots}{nF}$$

for the electrode process



The Nernst equation

$$4:9:4 \quad E_n = E^\circ - \frac{RT}{nF} \ln \frac{a_{\text{R}}^r \dots}{a_{\text{O}}^o \dots}$$

expresses the way the electrode's rest potential is affected by the activities at the electrode surface of the species participating in the electrode process

There are many alternative ways of writing the Nernst equation.

For the generic reaction  $\text{O} \xrightleftharpoons{\pm n e^-} \text{R}$  a convenient form is

$$4:9:5 \quad E_n = E^{0'} - \frac{RT}{nF} \ln \frac{c_{\text{R}}}{c_{\text{O}}}$$

where  $E^{0'}$  is a conditional potential, incorporating the activity coefficients.