Module 2, Lecture 8
Electron Transfer Reactions
Part 2

Learning Objectives:

- Understand the relationship between $E^o_{reaction}$ and ΔG^o and K
- Use the Nernst Equation to calculate $E_{reaction}$ and E under non-standard conditions
- Appreciate how oxidant strength can depend on pH
- The definition of biological standard state $E^{o'}$
- Appreciate how concentrations can be determined electrochemically
- Understand the concept of a concentration cell
- Understand the concepts of concentration gradients and how they lead to membrane potentials, which in turn can be used to do work.

Textbook: Chapter 20

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Predicting spontaneous redox reactions

Earlier we found that reaction spontaneity was determined by considering the value of $\Delta_r G^o$, and since V is a unit of energy:

(V = J C^{-1} – energy per unit charge)

$$\Delta_r G^o = -nFE^o_{reaction}$$

*where n is the number of electrons transferred in the reaction and **F** is the **Faraday Constant** (96 485 C mol^{-1})*

Also, we have seen that we can relate $\Delta_r G^o$ to K so: (remember $\Delta_r G^o = -RT\ln K$)

$$E^o_{reaction} = \frac{RT}{nF} \ln K$$

(see worked example 20.10 in textbook)

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Non-standard conditions

Everything we have so far considered has been at standard conditions: 1 mol L^{-1} concentrations and 1 bar (approx 1 atmosphere) pressure. But most redox reactions (and probably all biological redox reactions) do not occur under these conditions.

We have seen that $\Delta_r G$, the Gibbs Energy under non-standard conditions, could be calculated from:

$$\Delta_r G = \Delta_r G^o + RT\ln Q \qquad \text{where } Q = \frac{[\text{products}]}{[\text{reactants}]}$$

A similar equation can be used for calculating E
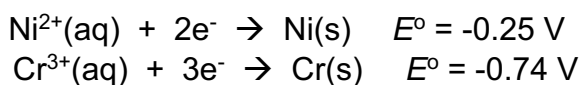
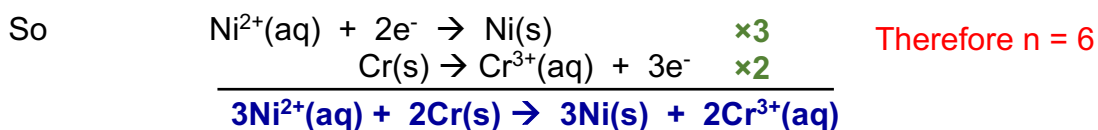🚩 **Careful** Sign difference! $$E = E^o - \frac{RT}{nF} \ln Q$$ **The Nernst Equation**

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Example

Consider the redox reaction between the following redox couples:

$$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s) \qquad E^o = -0.25 \text{ V}$$
$$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s) \qquad E^o = -0.74 \text{ V}$$

Calculate the potential difference, $E_{reaction}$, when: $[Ni^{2+}] = 1.0 \times 10^{-4}$ mol L^{-1} and $[Cr^{3+}] = 2.0 \times 10^{-3}$ mol L^{-1}

The standard reduction potentials tell us that Ni^{2+} should be the oxidant in the spontaneous reaction.

So $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ **×3**   Therefore n = 6
                     $Cr(s) \rightarrow Cr^{3+}(aq) + 3e^-$ **×2**

$3Ni^{2+}(aq) + 2Cr(s) \rightarrow 3Ni(s) + 2Cr^{3+}(aq)$

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3Ni²⁺(aq) + 2Cr(s) → 3Ni(s) + 2Cr³⁺(aq)

$E^o_{reaction}$ = E^o(Ni²⁺/Ni) - E^o(Cr³⁺/Cr)
= (-0.25 V) – (-0.74 V)
= 0.49 V

$E_{reaction} = E^o_{reaction} - \dfrac{RT}{nF} \ln Q$ = $E^o_{reaction} - \dfrac{RT}{6F} \ln \dfrac{[Cr^{3+}]^2}{[Ni^{2+}]^3}$

= $0.49\text{ V} - \dfrac{8.314 \times 298}{6 \times 96\ 485} \ln \dfrac{(2.0 \times 10^{-3})^2}{(1.0 \times 10^{-4})^3}$

= 0.42 V

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3Ni²⁺(aq) + 2Cr(s) → 3Ni(s) + 2Cr³⁺(aq)

$E^o_{reaction}$ = E^o(Ni²⁺/Ni) - E^o(Cr³⁺/Cr)
= (-0.25 V) – (-0.74 V)
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$E_{reaction} = E^o_{reaction} - \dfrac{RT}{nF} \ln Q$ = $E^o_{reaction} - \dfrac{RT}{6F} \ln \dfrac{[Cr^{3+}]^2}{[Ni^{2+}]^3}$

Extra for experts practice
• Calculate K from $E^o_{reaction}$
• Why can you not use $E_{reaction}$ to calculate K?

= $0.49\text{ V} - \dfrac{8.314 \times 298}{6 \times 96\ 485} \ln \dfrac{(2.0 \times 10^{-3})^2}{(1.0 \times 10^{-4})^3}$

= 0.42 V

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Balancing redox equations

So far reduction potentials have only contained simple ions.
Reducation potentials involving more complex ions often depend on pH
To explain this we have to learn how to balance half equations:

For example, balancing the reduction of MnO_4^- (aq) to Mn^{2+} (aq)

$$MnO_4^-(aq) \quad \rightarrow \quad Mn^{2+}(aq)$$

We start by balancing for atoms. There is one Mn on each side already, so OK.

There are 4 oxygens on the left and none on the right.

We balance these by adding **H_2O** to the right, in this case 4 of them.

$$MnO_4^-(aq) \quad \rightarrow \quad Mn^{2+}(aq) \; + \; 4H_2O(l)$$

Balancing redox equations

Now we balance the hydrogens from the water by adding H^+ to the left (note that for redox equations we use H^+ rather than H_3O^+)

$$MnO_4^-(aq) \; + \; 8H^+ \quad \rightarrow \quad Mn^{2+}(aq) \; + \; 4H_2O(l)$$

Now that the half equation is balanced for atoms we balance for charges.

$$MnO_4^-(aq) \; + \; 8H^+ \quad \rightarrow \quad Mn^{2+}(aq) \; + \; 4H_2O(l)$$

Total charge = -1 + (8 × +1)   Total charge = +2 + (4 × 0)
               = +7   = +2

$$MnO_4^-(aq) \; + \; 8H^+(aq) + 5e^- \quad \rightarrow \quad Mn^{2+}(aq) \; + \; 4H_2O(l)$$

Total Charge = -1 + (8 × +1) + (5 x -1)   Total charge = +2 + (4 × 0)
               = +2   = +2

Summary: Balancing redox equations

1. Balance for non oxygen and hydrogens first

$$MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$$

2. Balance oxygens by adding water

$$MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

3. Balance hydrogens by adding H^+ ions

$$MnO_4^-(aq) + 8H^+ \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

4. Balance charges by adding electrons

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

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An example of a pH dependent reaction

Under standard conditions, the standard reduction potential for acidic permanganate, $E^o(MnO_4^-, H^+/ Mn^{2+}) = 1.51$ V

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

Q) What is the reduction potential if $[MnO_4^-] = [Mn^{2+}] = 1.0$ mol L^{-1} but pH = 4.0?

Write out the Nernst Eq.:

$$E(MnO_4^-,H^+/Mn^{2+}) = E^o(MnO_4^-,H^+/Mn^{2+}) - \frac{RT}{5F} \ln\left(\frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}\right)$$

$$= 1.51 \text{ V} - \frac{8.314 \times 298}{5 \times 96\,485} \ln \frac{1}{(1.0 \times 10^{-4})^8}$$

$$= 1.13 \text{ V}$$

i.e. the oxidising strength of the MnO_4^- ion is **pH dependent** (at pH 7 E = 0.85 V)

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Biological standard state, $E^{o\prime}$

All species at 1 mol L^{-1} concentrations **EXCEPT H$^+$, which has a concentration of 1×10^{-7} mol L^{-1} (pH = 7)** – a realistic biological value.

Consider the reduction of $O_2(g)$ to water (at standard pressure and 298 K):

$$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E^o = 1.23 \text{ V}$$

At pH = 7: $E_{reaction} = E^o_{reaction} - \dfrac{RT}{nF} \ln Q = 1.23 \text{ V} - \dfrac{RT}{4F} \ln \dfrac{1}{[H^+]^4}$

$$= 1.23 \text{ V} - \dfrac{RT}{4F} \ln \dfrac{1}{(1 \times 10^{-7})^4}$$

$$= 0.82 \text{ V}$$

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Finding unknown concentrations

Galvanic cells can be used to find concentrations of unknown solutions.

e.g. A galvanic cell made from a silver half cell under standard conditions combined with a copper half cell made with unknown $[Cu^{2+}]$.

Cu(s)   0.62 V   Ag(s) E_{cell} = 0.62 V

Cu^{2+}(aq)
??? mol L^{-1}

Ag$^+$(aq)
1.00 mol L^{-1}
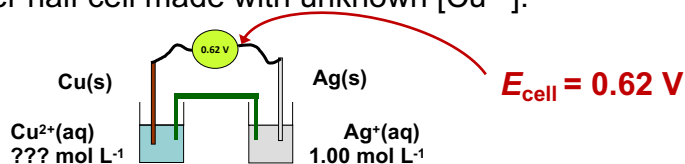
The **SIGN** of the E_{cell} tells us reduction is occuring at the RHS so the spontaneous reaction can be written;

$$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

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Finding unknown concentrations

Cu(s) + 2Ag$^+$(aq) → Cu^{2+}(aq) + 2Ag(s)

The Nernst equation for this reaction will be:

$$E_{cell} = E^o{}_{cell} - \frac{RT}{nF} \ln Q \qquad = E^o{}_{cell} - \frac{RT}{2F} \ln \frac{[Cu^{2+}]}{[Ag^+]^2}$$

From standard reduction potentials

$$E^o{}_{cell} = E^o(Ag^+/Ag) - E^o(Cu^{2+}/Cu)$$
$$= 0.80\ V - 0.34\ V$$
$$= 0.46\ V$$

Since R, T and F are all known and [Ag$^+$] = 1.0 mol L^{-1} it is possible to calculate [Cu^{2+}]!

$$(3.87 \times 10^{-6}\ mol\ L^{-1})$$

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Ion selective electrodes

The same method can be used to measure concentrations VERY accurately in **ion selective electrodes** that can measure the concentration of specific ions in aqueous solutions.

A **pH meter** is an ion selective electrode – one that is able to measure [H$^+$] – as low as [H$^+$] = 1 x 10^{-14} mol L^{-1}

The difference in [H$^+$] from inside the electrode to that outside produces a potential across the glass membrane proportional [H$^+$] in the sample solution. See Sample exercise 20.13, page 982, for an explanation of how this works

Ag/AgCl electrodes

H$^+$ (aq, buffer)
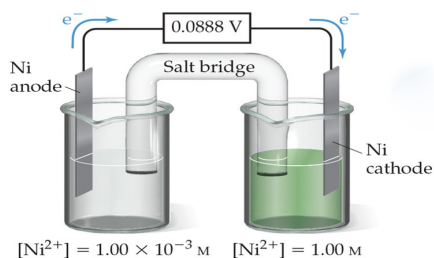
porous plug

glass membrane

Solution
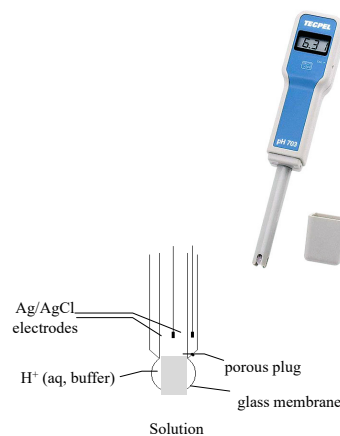
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Concentration cells

What happens if both sides of the cell contain the same ions but at different concentrations? Will we see a flow of electrons?
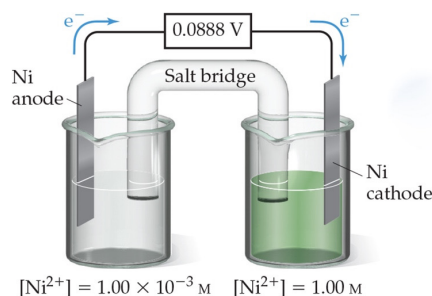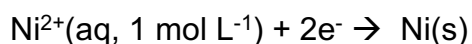

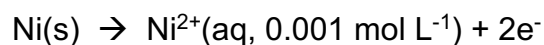We still see a reading on the potentiometer so electrons must flow through the circuit….

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The **SIGN** tell us **reduction** is at RHS:

$$Ni^{2+}(aq, 1 \text{ mol L}^{-1}) + 2e^- \rightarrow Ni(s)$$

And **oxidation** at LHS:

$$Ni(s) \rightarrow Ni^{2+}(aq, 0.001 \text{ mol L}^{-1}) + 2e^-$$

Spontaneous reaction is: **Ni^{2+}(aq, 1 mol L^{-1}) → Ni^{2+}(aq, 0.001 mol L^{-1})**

$$E_{cell} = E^o{}_{cell} - \frac{RT}{nF} \ln \frac{[Ni^{2+}{}_{0.001 \text{ mol/L}}]}{[Ni^{2+}{}_{1 \text{ mol/L}}]}$$

$$= 0 - \frac{8.314 \times 298}{2 \times 96\,485} \ln \frac{1.00 \times 10^{-3}}{1.00}$$

🚩 **Check:** E$_{cell}$ must be positive for spontaneous reaction.

$$= +0.0888 \text{ V}$$

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Membrane potentials – biological conc. cells

The idea of concentration cells is very important in many biological systems, where a membrane separates two solutions of different concentrations of an ion.

The membrane is able to let the ions through but in a controlled way, such that the **concentration gradient** is maintained.

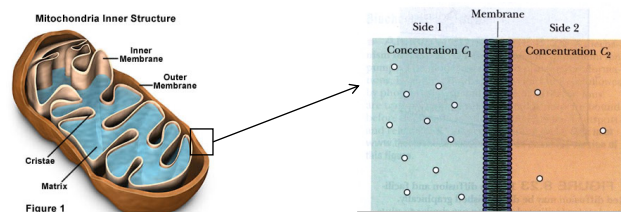The potential difference resulting from the concentration gradient can be utilised to **do work**.
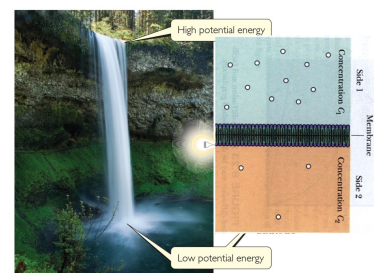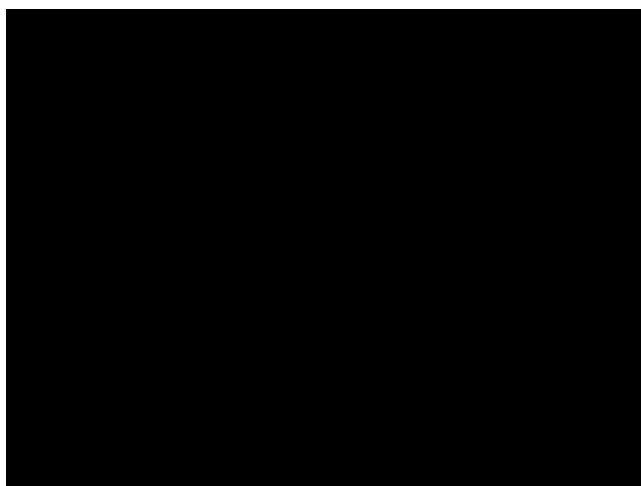

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ATP synthesis

In the mitochondria, an H^+ ion concentration gradient of about 0.5 pH units* is maintained across the membrane.

The energy released as the H^+ ions cross the membrane is harnessed by an enzyme called ATP synthase to make ATP from ADP and P.

*[H^+] on the 'outside' is about 5 times larger than that on the 'inside'

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✳ **Homework** ✳

Chemistry – the central science 15th Ed

Brown *et al.*

Problems 20.30 20.31 20.32 and 20.33

Answers on Blackboard

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