Chem!stry

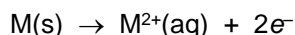### Electrode Potentials – Macroconcept: Systems

Essential Understanding: Oxidation is the loss of electrons. Reduction is the gain of electrons (OIL RIG).

Metals:

If a metal strip is placed in a solution of its ions, atoms of the metal may oxidise and dissolve as positive ions, leaving a build-up of electrons on the metal:

$$M(s) \rightarrow M^{2+}(aq) + 2e^-$$

Consequently, the metal will become negatively charged. Alternatively, metal ions in solution may be reduced as they remove electrons from the strip of metal and discharge as metal atoms:

$$M^{2+}(aq) + 2e^- \rightarrow M(s)$$
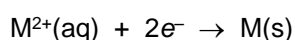
In this case, the metal strip will become positively charged. The potential difference between the strip of metal and the solution of metal ions depends upon the nature of the metal and on the concentration of the metal ions. Zinc acquires a more *negative* potential than copper, since zinc atoms are more readily oxidised (compared to the tendency for zinc ions to be reduced). In order to compare electrode potentials for different metals, *standard electrode potentials* are quoted at 25 °C with an ionic concentration of 1.0 mol dm^{-3}. The zero on the standard electrode potential scale is the potential of a strip of platinum metal in contact with hydrogen gas at 1 atm pressure and hydrogen ions at a concentration of 1.0 mol dm^{-3}. **Figure 1** shows the experimental set-up to measure the standard electrode potential of a zinc half-cell. In this set-up, a zinc half-cell (shown on the right-hand-side) is connected to a hydrogen half-cell (shown on the left-hand-side). In this particular system, the zinc metal is oxidised to form zinc ions:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$
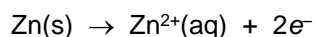
While the hydrogen ions are reduced to form hydrogen gas:

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$
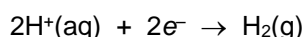
Figure 1: Experimental set-up to measure the standard electrode potential of a zinc half-cell.

The flow of electrons through the external circuit is from the zinc half-cell towards the hydrogen half-cell. **Note**: the anode is defined as *the electrode at which oxidation takes place*. In this particular system, the zinc electrode is therefore designated as the anode, even though it is also the *negative electrode*!
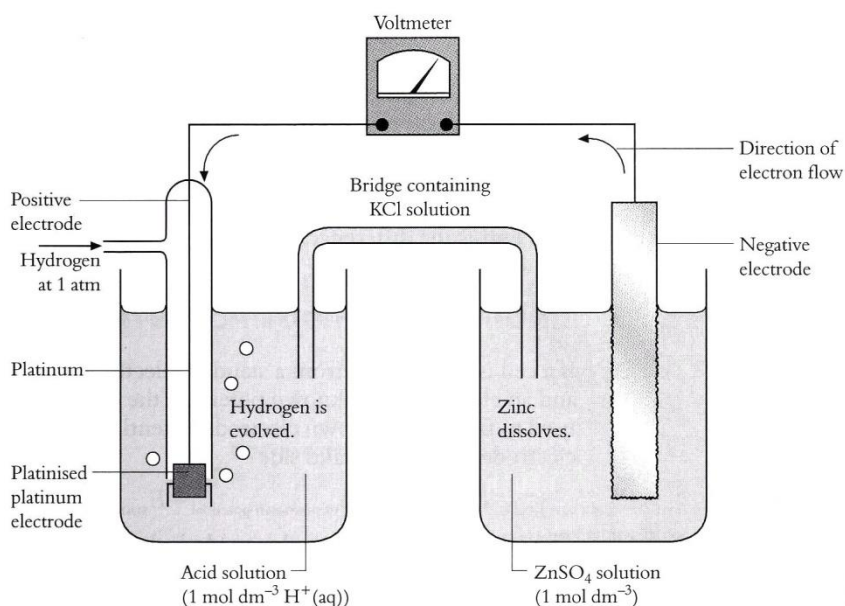
Redox Systems:

Metals are generally good reducing agents, *i.e.* they readily donate electrons to other chemicals. Other oxidation-reduction systems also have electrode potentials. The standard electrode potential of a redox system is the potential acquired by a piece of platinum immersed in a solution of the redox system in which the concentration of each dissolved component is 1.0 mol dm^{-3}. A powerful oxidising agent removes electrons and gives the platinum a high positive potential. Conversely, a powerful reducing agent donates electrons and gives the platinum a high negative potential. When all of the redox systems are arranged in order of their standard electrode potentials, the *electrochemical series* is obtained. **Table 1** shows some of the redox systems in the series:

Reaction	E / V
$K^+(aq) + e^- \rightleftharpoons K(s)$	−2.92
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	−2.87
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.36
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	−1.66
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.44
$Cr^{3+}(aq) + e^- \rightleftharpoons Cr^{2+}(aq)$	−0.41
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	−0.25
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	−0.14
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	−0.13
$2H_3O^+(aq) + 2e^- \rightleftharpoons H_2(g) + H_2O(l)$	0.00
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	+0.15
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.09
$MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$	+1.23
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$PbO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2H_2O(l)$	+1.46
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.78
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.85

Table 1: The electrochemical series.

Electrochemical Cells:

Figure 2 shows two different metals inserted into solutions of their ions. The two solutions are joined by a salt bridge, and the two metal electrodes are connected by an external circuit. The cell has an electromotive force (e.m.f.) or voltage, which is equal to the difference between the standard electrode potentials of the two metals, and this electromotive force makes a current flow through the external circuit.
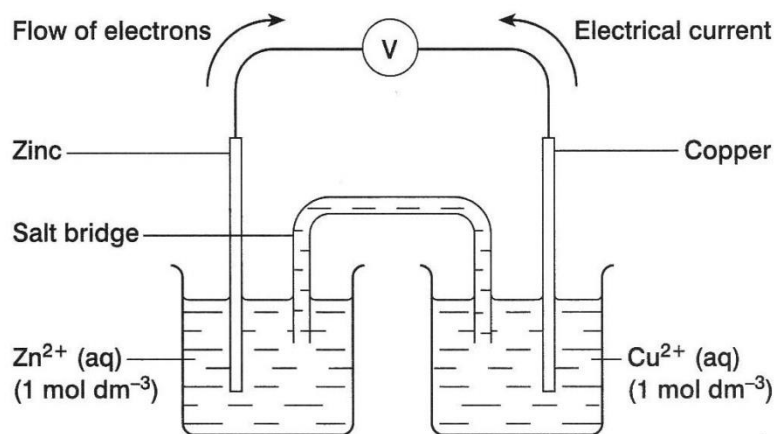
Figure 2: An electrochemical cell.

The cell in **Figure 2** can be represented by:

$$Zn(s) \mid Zn^{2+}(aq) \; \vdots \; Cu^{2+}(aq) \mid Cu(s)$$
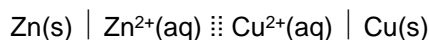
By convention, the e.m.f. of the cell is taken as:

$$E_{cell} = E \text{ (right-hand-side electrode)} - E \text{ (left-hand-side electrode)}$$

$$E_{cell} = E \text{ (Cu)} - E \text{ (Zn)}$$

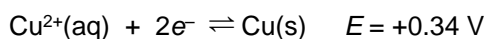$$E_{cell} = +0.34 - (-0.76)$$

$$E_{cell} = +1.10 \text{ V}$$

The flow of electrons is clockwise through the external circuit (from zinc to copper). Conventional electricity flows anticlockwise through the external circuit (from copper to zinc).

Note: A redox reaction will go almost to completion if the two redox systems differ by 0.3 V or more in their electrode potentials.

> ● Will a cell reaction happen? **Yes, if *E* for the cell is positive.**
> ● Will the cell reaction go to completion? **Yes, if *E* for the cell is > 0.3 V.**
> ● How fast will the reaction be? **This is difficult to predict and depends upon kinetic factors.**

Which Electrode is Which?

When two electrodes are combined, a cell reaction will take place if the e.m.f. for the cell is *positive*. The values of *E* for the two electrodes will tell you which will be the positive electrode and which the negative. For example:

$$Cu^{2+}(aq) \; + \; 2e^- \rightleftharpoons Cu(s) \quad E = +0.34 \text{ V}$$

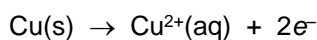$$Ag^+(aq) \; + \; e^- \rightleftharpoons Ag(s) \quad E = +0.80 \text{ V}$$

At one electrode, reduction will occur, and the half-cell reaction will take place from left-to-right as written. At the other electrode, oxidation will take place and the half-cell reaction will take place from right-to-left. Which is which? For the overall *E* of the cell to be positive, the half-reaction at the silver electrode must go from left-to-right as a reduction, with $E = +0.80$ V, *i.e.* with the silver electrode being positive. Then the half-reaction at the copper electrode must go from right-to-left as an oxidation with $E = -0.34$ V, *i.e.* with the copper electrode being negative. For the cell, $E_{cell} = (+0.80) + (-0.34) = +0.46$ V. What would happen if the two reactions took place in opposite directions? Then $E_{cell} = (-0.80) + (+0.34) = -0.46$ V. With a negative value for *E*, this reaction does not take place.
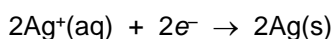
The Anti-clockwise Rule:

An alternative way to work out which reaction will happen is to use the *anti-clockwise rule*. Write the two systems with the less positive or more negative value of E at the top. Next, draw a circle *anti-clockwise* around the system:
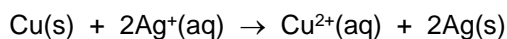

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \quad E = +0.34 \text{ V}$$

$$Ag^+(aq) + e^- \rightleftharpoons Ag(s) \quad E = +0.80 \text{ V}$$
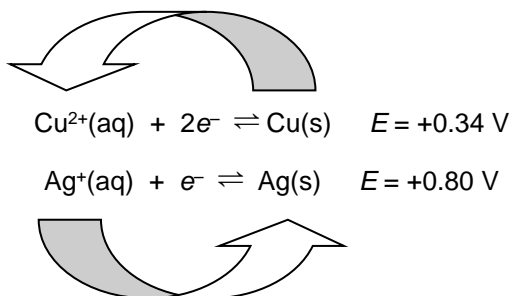
The circle tells you that the reaction that takes place is:

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

and:

$$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$$

gives:

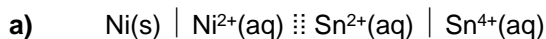$$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

Oxidation takes place at the copper electrode, electrons are released, and the electrode is therefore negative. Reduction takes place at the silver electrode, electrons are supplied to discharge the silver ions and the electrode is therefore positive.
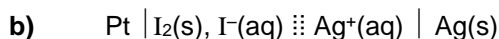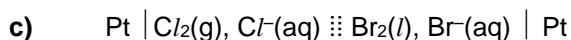
Questions:

Question 1:
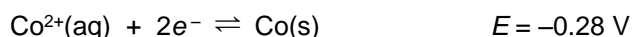
Calculate the e.m.f.s of the following cells at 298 K:

a) $Ni(s) \mid Ni^{2+}(aq) \vdots\vdots Sn^{2+}(aq) \mid Sn^{4+}(aq)$

....

b) $Pt \mid I_2(s), I^-(aq) \vdots\vdots Ag^+(aq) \mid Ag(s)$

....

c) $Pt \mid Cl_2(g), Cl^-(aq) \vdots\vdots Br_2(l), Br^-(aq) \mid Pt$

....

Question 2:

Two standard electrode potentials are given below:

$$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq) \qquad E = +1.07 \text{ V}$$

$$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s) \qquad E = -0.28 \text{ V}$$
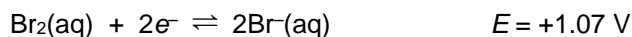
a)   Calculate the e.m.f. generated by this cell.

....

b)   Write the ionic equation for the overall cell reaction.

....

c)   Identify the electrode at which reduction occurs.

....

Question 3:

The standard electrode potentials for two systems are:

$$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq) \qquad E = +0.54 \text{ V}$$

$$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq) \qquad E = +1.70 \text{ V}$$
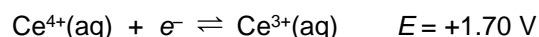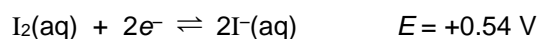
a) Calculate the standard cell potential that is generated when these two half-cells are connected together:

....

b) Write the ionic equation for the chemical reaction that takes place:

....

c) Identify the positive electrode, the negative electrode, the anode and the cathode in this system:

Positive electrode: ………………………… Negative electrode: …………………………

Anode: ……………………… Cathode: …………………………

Answers:

Question 1:

a) $E_{cell} = (+0.15) - (-0.25) = \underline{+0.40 \text{ V}}$

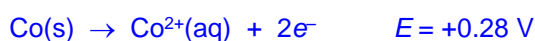**b)** $E_{cell} = (+0.80) - (+0.54) = \underline{+0.26 \text{ V}}$

c) $E_{cell} = (+1.09) - (+1.36) = \underline{-0.27 \text{ V}}$

Question 2:

a) E for the cell must be positive, therefore the two reactions that take place must be:

$$Br_2(aq) + 2e^- \rightarrow 2Br^-(aq) \qquad E = +1.07 \text{ V}$$
$$\text{and}$$
$$Co(s) \rightarrow Co^{2+}(aq) + 2e^- \qquad E = +0.28 \text{ V}$$
$$E_{cell} = (+1.07) + (+0.28)$$
$$E_{cell} = \underline{1.35 \text{ V}}$$

b) $Br_2(aq) + Co(s) \rightarrow 2Br^-(aq) + Co^{2+}(aq)$

c) Reduction takes place in the bromine half-cell as reduction is the gain of electrons.

Question 3:

a) E for the cell must be positive, therefore the two reactions that take place must be:
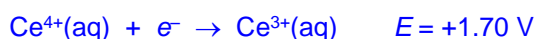
$$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq) \qquad E = +1.70 \text{ V}$$
$$\text{and}$$
$$2I^-(aq) \rightarrow I_2(aq) + 2e^- \qquad E = -0.54 \text{ V}$$
$$E_{cell} = (+1.70) + (-0.54)$$
$$E_{cell} = \underline{1.16 \text{ V}}$$

b) $2Ce^{4+}(aq) + 2I^-(aq) \rightarrow 2Ce^{3+}(aq) + I_2(aq)$

c) Positive electrode = cerium   Negative electrode = iodine

Anode = iodine   Cathode = cerium

Ramsden, E. N. (2001). Calculations for A-level chemistry (4th Edition). Nelson Thornes. ISBN: 978 0 7487 5839 5.