

Topic 12 – Redox Equilibria

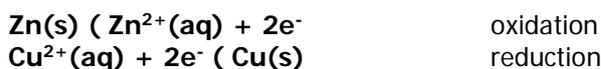
Revision Notes

1) Redox Reactions

- Redox reactions involve the transfer of electrons e.g. in the reaction between zinc metal and copper (II) sulphate, electrons are transferred from zinc atoms to copper (II) ions

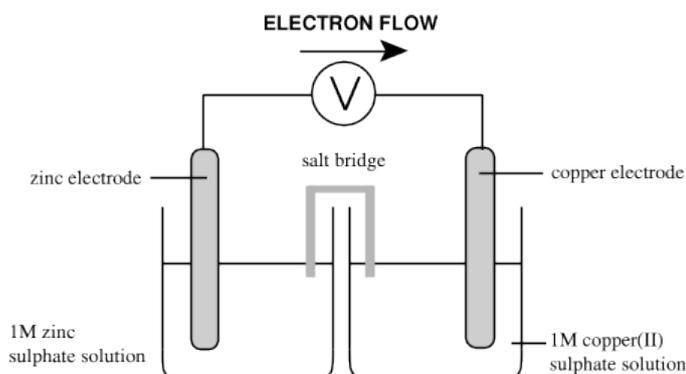


- The overall equation can be split into half-equations



2) Electrodes and cells

- The two half-reactions for zinc and copper can be carried out in separate beakers
- In this case the beakers would typically contain a piece of copper dipping into copper sulphate solution and a piece of zinc dipping into zinc sulphate solution
- The combination of a metal dipping a solution containing its ions is called an electrode
- Electrons can transfer from the zinc electrode to the copper electrode through a wire and a voltmeter.
- The circuit is completed by connecting the two electrodes with a salt bridge which is usually a piece of filter paper soaked in saturated potassium nitrate solution
- Ions can move through the salt bridge (to complete the circuit) but KNO_3 is unreactive (so won't react with the electrodes)

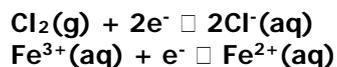


- Two electrodes joined in this way make up an electrochemical cell
- The zinc/copper cell can be represented as follows. This is called the standard cell notation

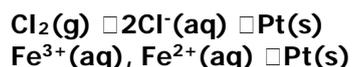


- The vertical line represents a boundary between different phases (states)
- Two vertical lines denotes the salt bridge

- Electrodes can also consist of non-metals and their ions or transition metals in two different oxidation states e.g.

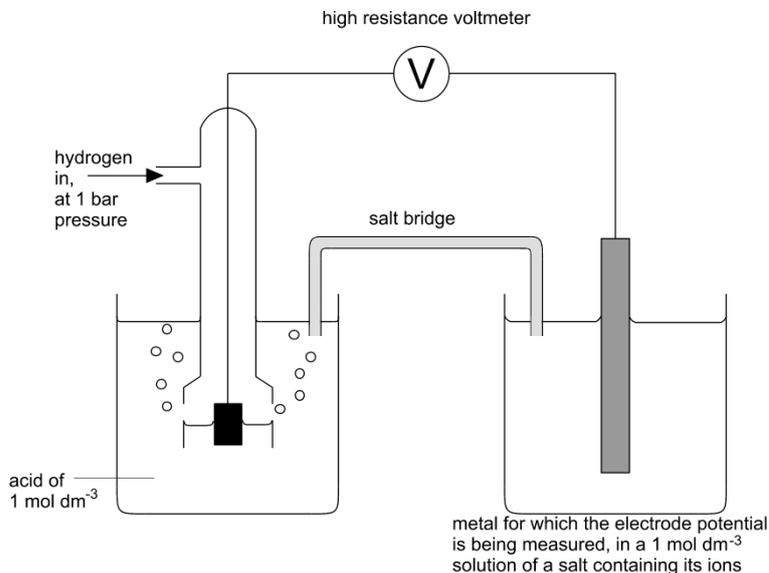
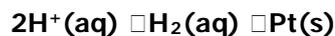
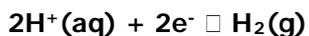


- With both of these electrodes a piece of platinum is needed to transfer electrons into or out of the solution (platinum is inert and a good conductor). The notation for these electrodes, as reductions, is as follows



3) Electrode potentials

- The voltage, or potential, measured on the voltmeter will be different for different pairs of electrodes
- The voltages produced by different electrodes can be measured by pairing up each electrode with a standard electrode
- The electrode used for comparison is called the standard hydrogen electrode (SHE), which is deemed to have a potential of 0.00 V (zero volts) – see diagram below. The acid must be identified e.g. 1 mol dm⁻³ HCl
- The half equation and conventional notation for the SHE are:



Source of these two diagrams: <http://www.btinternet.com/~chemistry.diagrams/>

- To measure standard electrode potentials the following conditions are needed: temperature of 298K, pressure of 100 kPa and solutions of concentration 1 mol dm⁻³
- The hydrogen electrode is normally drawn on the left in diagrams showing how standard electrode potentials are measured
- Electrode potentials are always quoted as reductions (gain of electrons)

a) Secondary standards

- The SHE is tricky to set up, cumbersome and hazardous. In practice, simpler secondary standards are used. Two secondary standards are the silver/silver chloride electrode and the calomel electrode (which uses Hg and Hg₂Cl₂)

4) Calculating cell voltage

- Electrode potentials can be used to calculate the voltage produced when electrodes are paired up
- The convention is to put the more positive electrode on the right and the less positive electrode on the left
- The electrode with the more positive potential is the positive electrode
- Electrons will then flow from left to right through the external circuit (wire and voltmeter)
- The cell voltage, E_{cell} , is calculated from

$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}}$$

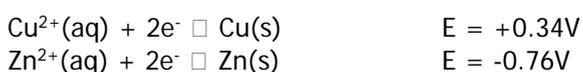
In the copper and zinc example

$$\begin{aligned} E_{\text{R}} &= +0.34\text{V} \\ E_{\text{L}} &= -0.76\text{V} \\ E_{\text{cell}} &= 0.34 - (-0.76) \\ &= 1.10\text{V} \end{aligned}$$

5) Predicting reaction feasibility

- The electrode potential is a measure the willingness of a substance to be reduced
- The more positive the potential, the more willing the substance to be reduced
- Electrode potentials can be used to predict which substance will be oxidised and which substance will be reduced when half equations are paired up in a beaker
- The half-reaction with the more positive potential will stay as a reduction
- The half-reaction with the less positive potential will flip round and go as an oxidation

Example – copper and zinc



Cu^{2+}/Cu potential is more positive so this stays as a reduction
 Zn^{2+}/Zn flips round to become an oxidation i.e. $\text{Zn}(\text{s}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-}$

- The overall equation for the feasible reaction can then be written adding the half equations together and cancelling electrons
- As with any redox reaction, one or both of the half equations may have to be multiplied to make the number of electrons equal

Overall equation



Cancelling electrons gives



The reaction is not feasible in the other direction i.e. $\text{Cu(s)} + \text{Zn}^{2+}(\text{aq}) \rightleftharpoons$ no reaction

6) Electrochemical series

- A list of reduction half-equations in ascending or descending order of electrode potential is known as the electrochemical series
- Remember that the electrode potential measures willingness to be reduced which is also strength as an oxidising agent
- The strongest oxidising agent is on the LHS of the half-equation with the most positive potential
- The strongest reducing agent is on the RHS of the half-equation with the least positive potential
- Any substance on the LHS of a half-equation will oxidise the substance on the RHS of a half-equation with a less positive potential
- Any substance on the RHS of a half-equation will reduce the substance on the LHS of a half-equation with a more positive potential

7) Effect of concentration

- The effect of changing concentration can be illustrated using the Cu^{2+}/Cu electrode as an example



- If the concentration of $\text{Cu}^{2+}(\text{aq})$ is reduced, the equilibrium will shift to the left (by Le Chatelier's principle)
- This means that reduction (the forward reaction) is less likely, so the electrode potential will be reduced from its standard value

8) Uses of electrochemical cells

Electrochemical cells can be used as a commercial source of electrical energy

a) **Non-rechargeable cells**

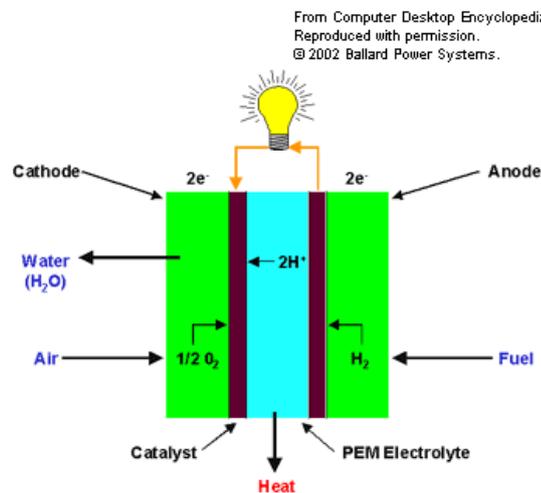
- Most AA and AAA batteries used in electrical items are non-rechargeable because the reactions involved are not reversible
- When the reactants are used up the voltage will drop and the cell will be sent for land-fill

b) Rechargeable cells

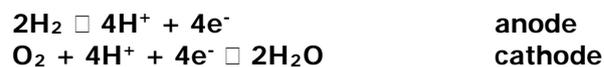
- Car batteries and the batteries used in mobile phones and mp3 players are re-chargeable because the reactions involved are reversible
- When cells are recharged, the reactions that take place are the reverse of those occurring in normal use
- Use of rechargeable cells means the metals involved are re-used so there is less mining, less waste and less energy needed for metal extraction compared with non-rechargeable cells

c) Fuel cells

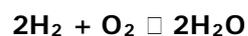
- Fuel cells (as used in experimental cars) do not need to be recharged but do require a supply of fuel such as hydrogen
- Refuelling is a quick process, similar to visiting a petrol station.
- A fuel cell converts the energy from the reaction of a fuel with oxygen into electrical energy
- The fuel is oxidised at the positive electrode (anode)
- Electrons travel through an external circuit doing work
- Oxygen is reduced at the negative electrode (cathode)
- In the example below, the fuel is hydrogen which reacts with oxygen to form water. PEM stands for proton exchange membrane as H^+ needs to move from anode to cathode to react with O_2



- The two half reactions for acidic conditions are:



- The overall equation is:



- The reactions take place over precious metal catalysts, usually platinum or an alloy of platinum, palladium, or ruthenium

Answering Exam Questions

Example (1)

Use the standard electrode potentials below to explain why Au^+ ions are **not** normally found in aqueous solution. Write an equation to show how Au^+ ions would react with water.



First mark: $1.68 > 1.23$ (or $E(\text{Au}^+) > E(\text{O}_2)$ i.e. species on LHS)

Second mark: Au^+ will oxidise H_2O or H_2O will reduce Au^+ (say what reaction will occur)

Third mark: Overall equation from flipping $\text{O}_2/\text{H}_2\text{O}$ half-equation and doubling Au^+/Au to equalise electrons: $2\text{Au}^+ + \text{H}_2\text{O} \rightleftharpoons 2\text{Au} + \frac{1}{2}\text{O}_2 + 2\text{H}^+$

Example (2)

Use the standard electrode potentials below to predict and explain the reactions that occur when iron powder is added to an excess of $\text{AgNO}_3(\text{aq})$



Note plural reactions in the question

$0.80 > -0.44$, Ag^+ will oxidise Fe to Fe^{2+}

$0.80 > 0.77$, Ag^+ will then oxidise Fe^{2+} to Fe^{3+}