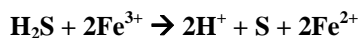


## E23 OXIDATION AND REDUCTION

### Electron Transfer Reactions

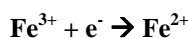
#### Electron Transfer

There are many reactions that involve electron transfers. For example, the reaction between  $\text{Fe}^{3+}$  and  $\text{H}_2\text{S}$  below involves the transfer of electrons from sulfur to iron.



In any such transfer of electrons there is a change in the oxidation number of the species involved. For the example above, iron goes from +III on the left of the equation to +II on the right through a process of gaining electrons; sulfur changes from -II to 0 by a loss of electrons. When the oxidation number of a species becomes more positive in value, then that species is said to have been *oxidised*. If the oxidation state becomes less positive then the species is said to have been *reduced*. Thus, in our example, iron has been reduced and sulfur has been oxidised.

The overall reaction above is termed an oxidation/reduction (or *redox*) reaction and can be broken up into several half-equations that show the two processes of oxidation and reduction in isolation, as shown below. These half-equations are more properly termed *ion/electron half-equations*.



In a redox reaction, the species that causes oxidation of another species is called the *oxidant* and is itself reduced in the process.

On the other hand, the species that causes reduction in another species is called the *reductant*, and undergoes oxidation in the process. In our example, then, iron(III) is the oxidant and hydrogen sulfide is the reductant.

Importantly, for a redox reaction to occur there must exist *both* a simultaneous oxidation and reduction process.

#### Redox Equations

The process for constructing ion/electron half-equations and combining them to give a redox equation is given below.

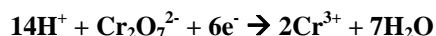
Also, see the worked example at the end of this document.

#### Constructing Half-Equations

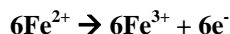
1. Balance the numbers of all the atoms other than O and H.
2. Balance O by adding  $\text{H}_2\text{O}$  to either side.
3. Balance H by adding  $\text{H}^+$  to either side.
4. Balance the charges by adding electrons to either side.
5. **If basic conditions are specified:** eliminate any  $\text{H}^+$  present by adding enough  $\text{OH}^-$  to each side of the reaction equation to turn  $\text{H}^+$  into  $\text{H}_2\text{O}$ .

#### Combining Half-Equations

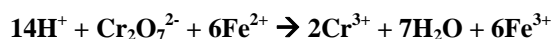
If two half-equations are to be combined, the electrons must be algebraically eliminated by multiplying each half-equation by a whole number. Take the following example:



In order to combine these two half-equations together, first multiply the iron oxidation half-equation by 6, giving



Then, when this is added to the dichromate reduction half-equation, cancel anything that appears on both sides of the equation, including the electrons. Hence, the overall redox reaction is



## Electrochemical Couples

### Homogeneous Couples

The combination of the reactant and product in a single ion/electron half-equation is described as an *electrochemical couple*. If all species are in solution, the couple is described as being homogeneous. An example is a solution containing iron(III) sulfate and iron(II) sulfate, where the couple is represented as  $\text{Fe}^{3+} / \text{Fe}^{2+}$  (in this type of shorthand representation, the oxidised species appears first). In isolation the solution containing the couple is stable, but when it is mixed with a solution containing another couple a redox reaction almost always occurs. One couple moves towards its reduced species, the other towards its oxidised species, until equilibrium is established. Treatment of the above couple with a suitable reductant converts the  $\text{Fe}^{3+}$  of the couple into  $\text{Fe}^{2+}$ , while treatment with a suitable oxidant converts  $\text{Fe}^{2+}$  into  $\text{Fe}^{3+}$ .

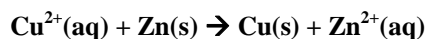
The extent to which these movements occur is determined by two factors:

- The relative reducing/oxidising power of a particular couple
- The relative concentrations of the four solutes.

### Heterogeneous Couples

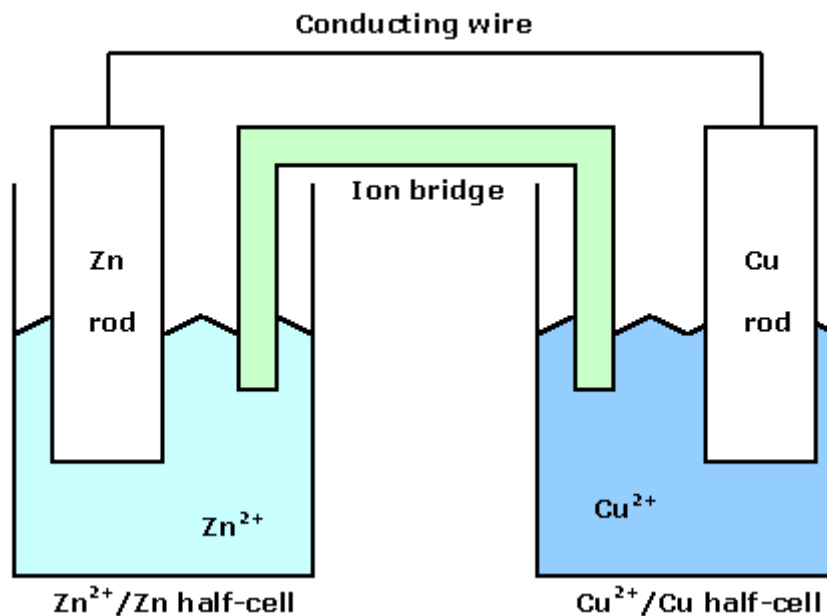
The species that make up a couple need not all be in solution: one member may be a solid, as in  $\text{Cu}^{2+}(\text{aq}) / \text{Cu}(\text{s})$ , or a gas, as in  $\text{H}^+(\text{aq}) / \text{H}_2(\text{g})$ . Any such couple that involves transition between species in different states is called a heterogeneous couple.

For instance, when combined with a  $\text{Cu}^{2+} / \text{Cu}$  couple, a  $\text{Zn}^{2+} / \text{Zn}$  couple undergoes oxidation. The equation for the reaction is



### Electrochemical Cells

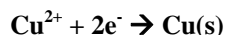
When the  $\text{Cu}^{2+} / \text{Cu}$  couple and  $\text{Zn}^{2+} / \text{Zn}$  couple are combined as shown in the diagram below, electron-transfer will take place through the conducting wire.



This system is called an electrochemical cell. The half-reaction taking place in the  $\text{Zn}^{2+} / \text{Zn}$  half-cell is



and in the  $\text{Cu}^{2+} / \text{Cu}$  half-cell is



Thus the electrons flow through the wire from the Zn rod (or electrode) to the Cu rod. A solution of an electrolyte must always be electrically neutral. Consequently, because positive ions are produced at the surface of the Zn rod and are removed from solution at the surface of the Cu rod, electrical neutrality can only be maintained if ions "flow" between the two half-cells. This flow of ions is provided by the ion bridge, which consists of a solution of electrolyte supported by absorbent paper (or other means). In the cell above, the neutrality is maintained by the movement of positive ions within the ion bridge towards the  $\text{Cu}^{2+} / \text{Cu}$  half-cell and of negative ions towards the  $\text{Zn}^{2+} / \text{Zn}$  half-cell. Note that it is the ions within the bridge that provide the balance and not the transfer of ions from one solution to the other.

In this example, the metal electrode which is one component of each couple provides the link between the half-cell and the conducting wire. In a half-cell lacking a metal electrode, such as in a homogeneous couple, the link is provided by a non-reacting solid conductor such as a graphite or platinum electrode. Moreover, a measure of the potential difference between the half-cells can be determined through the inclusion of a voltmeter in the conducting wire.

See Appendix 1.

### Experimental Notes

In this exercise, some redox reactions and their applications to cells are investigated. The ion/electron half-reactions corresponding to the following couples are to be ranked in the order of their tendency to undergo reduction. That is, in the order of their electrode potentials.



In each experiment only one member of each couple being investigated is present initially. This has two consequences:

- Where reaction occurs, this is shown by the appearance of the second member of the couple and/or by the disappearance of the first.
- When the reaction occurs, the second member of each couple is formed.

## EXAMPLE 1

### Constructing Redox Equations

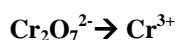
The process for constructing ion/electron half-equations is given below. Please note that unless otherwise stated, always assume acidic or neutral conditions. Only if basic conditions are specified is *Step 5* required.

1. Balance the numbers of all the atoms other than O and H.
2. Balance O by adding H<sub>2</sub>O to either side.
3. Balance H by adding H<sup>+</sup> to either side.
4. Balance the charges by adding electrons to either side.
5. **If** basic conditions are specified: eliminate any H<sup>+</sup> present by adding enough OH<sup>-</sup> to each side of the reaction equation to turn H<sup>+</sup> into H<sub>2</sub>O.

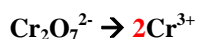
**Example (i)** Construct the ion/electron half-equation for the reduction of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> to Cr<sup>3+</sup> in the presence of H<sup>+</sup>.

1. Balance Cr (ie. elements other than O or H)

The reaction is Cr(VI) to Cr(III)



The Cr atoms are balanced by doubling the Cr<sup>3+</sup>



2. Balance O

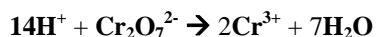
To balance for oxygen, 7 atoms must be added to the right-hand side of the equation. Since an ion/electron half-equation is for the oxidation or reduction of only one species (and hence for a change in oxidation number of only one atom, Cr in this case), the O atoms must have the same oxidation number as those on the left-hand side, namely -II.

It is convenient to insert these as H<sub>2</sub>O molecules.



3. Balance H

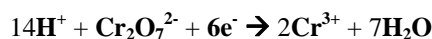
To balance for hydrogen, 14 atoms must be added to the left-hand side. As with oxygen, the H atoms added must have the same oxidation number as those on the right-hand side, namely +I. It is convenient to insert them as H<sup>+</sup>.



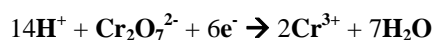
4. Balance the charge

There is a total of 12 positive charges on the left side of the equation and 6 positive charges on the right. In order to balance charges, we add electrons (which have a charge of -1). Thus, if we add 6 electrons to the left side, the charges become balanced (both +6).

*Note, the purpose of balancing charges is **not** to make both sides of the equation zero!*



Note that acidic conditions were specified, so the balanced half-equation for the reduction of Cr(VI) to Cr(III) is



**Example (ii)** Construct the ion/electron half-equation for the oxidation of Ag to Ag<sub>2</sub>S through reaction with HS<sup>-</sup> in the presence of OH<sup>-</sup>.

1. Balance Ag and S (ie. elements other than O or H)

The reaction is Ag(0) to Ag(I). Sulfur remains at -II.



The Ag atoms are balanced by doubling the Ag



The S atoms are already balanced.

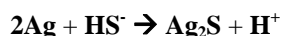
2. Balance O

There is no oxygen present in this example to balance.



3. Balance H

To balance for hydrogen, add sufficient  $\text{H}^+$ . In our example, this requires the addition of one  $\text{H}^+$  to the right-side of the equation.



4. Balance the charge

There is a total of 1 negative charge on the left side of the equation and 1 positive charge on the right. In order to balance charges, we need to add 2 electrons to the right side.



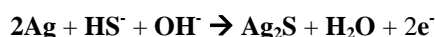
Note that basic conditions were specified, so we need to complete Step 5 as well so as to remove any acid present.

5. Basic conditions

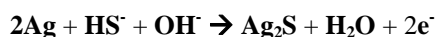
There is 1  $\text{H}^+$  present in our current equation. To eliminate this we need to add sufficient  $\text{OH}^-$  to both sides of the equation so that the  $\text{H}^+$  will be neutralised.



This can be simplified to:



If water molecules had existed on the left-side of the equation, we could further simplify by cancelling out water molecules. The final balanced reaction is thus:



### Alternative Method

Note that there is an alternative method for handling basic conditions that is given in some textbooks. This involves a different set of steps as outlined below:

1. Balance the numbers of all the atoms other than O and H.
2. Balance O by adding  $\text{H}_2\text{O}$  to either side.
3. Balance H by adding  $\text{H}_2\text{O}$  to the side deficient in H and an equal amount of  $\text{OH}^-$  to the other side.
4. Balance the charges by adding electrons to either side.

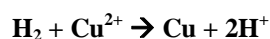
However, it is suggested that you use the steps given at the top of the page as these are simpler and easier to remember as they do not involve a change in procedure between acidic and basic conditions.

## APPENDIX 1 - HALF-CELL POTENTIALS

If a cell is constructed from two half-cells, and a voltmeter included in the conducting wire, then the observed potential difference is a measure of the *difference in reducing power* of the two couples. In this way, the reducing power of a particular couple can be specified as the potential of its half-cell relative to another half-cell. This can only ever be a relative measure as it is not possible to measure the potential of a half-cell in isolation.

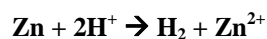
By choosing a particular half-cell (couple) as a reference standard, the reducing power of any other half-cell can be specified as a particular potential. For this purpose the reference standard chosen is the *standard hydrogen half-cell*. This consists of the couple  $\text{H}^+(\text{aq})/\text{H}_2(\text{g})$  (with platinised platinum as the solid conductor), the pressure of  $\text{H}_2(\text{g})$  being 101 kPa exactly, and the concentration of  $\text{H}^+(\text{aq})$  being 1 M exactly. The potential of this half-cell is then defined as zero at all temperatures. If any other half-cell is connected to this reference half-cell, the observed potential difference between them is then a measure of the electrode potential,  $E$ , of the half-cell under test. If the components of this half-cell also have concentrations of 1 M exactly for a solute and pressure equal to 101 kPa exactly for a gas, then the potential difference is defined as the **standard electrode-potential**,  $E^\circ$ . This is also sometimes called the reduction potential.

The potential difference of the cell composed of the  $\text{Pt}/\text{H}^+/\text{H}_2$  and  $\text{Cu}^{2+}/\text{Cu}$  couples (all components in their standard states) is 0.34 volt and the copper half-cell is positive with respect to the hydrogen half-cell. Hence the value of  $E^\circ$  for the  $\text{Cu}^{2+}/\text{Cu}$  couple is +0.34 volt. The reaction that occurs is



It is seen that the  $\text{Cu}^{2+}/\text{Cu}$  couple undergoes reduction while the  $\text{Pt}/\text{H}^+/\text{H}_2$  couple undergoes oxidation.

The potential difference of the cell composed of the  $\text{Pt}/\text{H}^+/\text{H}_2$  and  $\text{Zn}^{2+}/\text{Zn}$  couples (all components in their standard states) is 0.76 volt and the zinc half-cell is negative with respect to the hydrogen half-cell. Hence the value of  $E^\circ$  for the  $\text{Zn}^{2+}/\text{Zn}$  couple is -0.76 volt. The reaction that occurs is



It is seen that the  $\text{Zn}^{2+}/\text{Zn}$  couple undergoes oxidation while the  $\text{Pt}/\text{H}^+/\text{H}_2$  couple undergoes reduction.