

# OXIDATION, REDUCTION AND OXYGEN DEMAND

---

## 1. Introduction

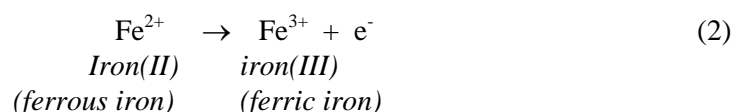
Of all the classes of reaction which take place in the environment one the most important is that which involves reduction and oxidation. Since reduction and oxidation always go hand in hand the reactions are referred to as *redox* reactions.

Their importance lies in the fact that they can influence the movement of materials through the environment and affect the availability of nutrients and pollutants to the biota. For example, certain metals, such as iron and manganese as well as many of the heavy metals, can exist in more than one oxidation, or valency, state. Thus, iron can exist as iron(II), or *ferrous*, iron in which the valency is two (i.e. the iron forms two bonds with other atoms/ions). It can also exist as iron(III), or *ferric*, iron in which the valency is three (i.e. the iron forms three bonds with other atoms/ions). Now the compounds of iron(II) are generally soluble in water while the iron(III) compounds tend to be insoluble in water. What is more, iron(II) compounds are not stable in the presence of oxygen and they will be converted into iron(III) compounds. Thus, in the environment, where oxygen is present any iron will exist as iron(III) and will be insoluble in water. On the other hand, when iron(III) compounds enter anoxic conditions the iron will be converted into iron(II) and will form water-soluble compounds. Given that living organisms absorb their nutrient from aqueous solution then iron will only be available to the biota if it is in the iron(II) form. Therefore, the nutrient iron will normally only enter food chains and webs via anaerobic organisms.

Inorganic suspended solids in water bodies are made up principally of iron(III) and manganese(III) oxides. These solid particles will have other species, for example heavy metals, adsorbed on to their surfaces. Bound as they are to these solid particles of iron and manganese oxides the heavy metals are not available to living organisms. However, should the suspended solids enter an anoxic area the iron(III) and manganese(III) oxides will be reduced to iron(II) and manganese(II) compounds which are soluble in the water. The particles dissolve so releasing the adsorbed metal ions which are now available for uptake by living organisms. Sulphur is widely distributed throughout the Earth's crust in pyritic ores, for example iron(II) pyrites, where it occurs as metal sulphides. During mining operations these ores are exposed to the air when there is a reaction between the ore and oxygen. The result is that the sulphides are oxidised to sulphur oxides which dissolve in any water passing over the rocks to form sulphuric acid. Consequently, tailings emerging from old mines are often acidic and carry with them iron(III) oxide formed as the iron(II) is oxidised as well. This is why the course of the tailings is often stained with rust.

## 2. Reduction, Oxidation and Redox Reactions

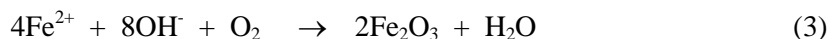
Redox reactions involve **reduction** and **oxidation**, where reduction is the gain of electrons and oxidation is the loss of electrons. Thus, in the following half reactions:



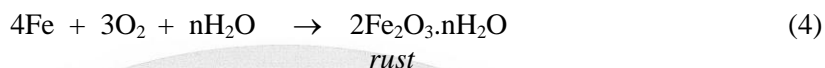
the oxygen in (1) has accepted electrons and so has been reduced to oxide. In (2) the iron(II) ions have lost electrons and so have been oxidised to iron(III) ions.

Since reduction and oxidation involve the transfer of electrons it follows that a reduction must always be accompanied by an oxidation, and *vice versa*. In other words, the electrons

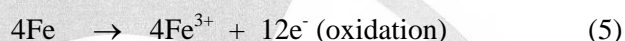
accepted by the species being reduced must have been given up by a second species which, consequently, has become oxidised. For example, in the environment reactions (1) and (2) are invariably linked. That is, iron(II) reacts with oxygen as follows:



As is well known, iron metal itself readily reacts with oxygen in exactly the same way, particularly in damp conditions, to form hydrated iron(III) oxide which is better known as rust.



The two half reactions involved in this process are:



and



Note that oxygen is such an electronegative element that when it binds to any other element (other than fluorine) it tends to pull the bonding electrons away from that element; that is it oxidises the element. Conversely, when non-metallic elements bind to hydrogen then, since they are almost invariably more electronegative than the hydrogen, they pull the bonding electrons away from it causing it to become oxidised. The non-metallic elements themselves are, therefore, reduced. For these reasons reduction is sometimes defined as loss of oxygen or gain of hydrogen while oxidation is defined as gain of oxygen or loss of hydrogen. So, consider the following transformations of sulphur:



In transforms (7) and (8) sulphur is acquiring oxygens ( $\text{SO}_2$  = sulphur dioxide;  $\text{SO}_3$  = sulphur trioxide) and so it is becoming progressively more oxidised. Conversely, in transformations (9) and (10) the sulphur is losing oxygens while in (11) it is gaining hydrogen. Therefore, reactions (9), (10) and (11) show sulphur becoming progressively more reduced.

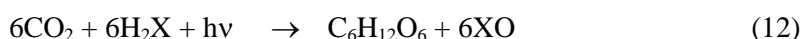
### 3. Oxygen and Life

Life is dominated by two processes, namely:

- (i) photosynthesis,
- (ii) respiration.

#### (a) Photosynthesis

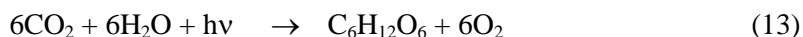
This is the process by which light energy is trapped and stored in organic compounds such as the carbohydrate glucose.



where  $\text{hv}$  represents light energy and  $\text{H}_2\text{X}$  is a source of hydrogen.

Organisms which can photosynthesise are called *producers* while those organisms which cannot photosynthesise are *consumers*. Consumers are dependent on the producers for their energy needs.

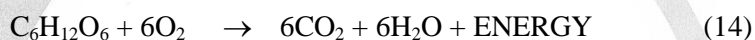
The major producers are the green plants and these use water, H<sub>2</sub>O, as the hydrogen source in the reduction of carbon dioxide:



The evolution of green plants has led to the presence of oxygen in the atmosphere and, consequently, to the evolution of aerobic organisms, which have come to dominate most habitats.

#### (b) Respiration

This is the process by which energy is released from organic matter (primarily carbohydrates). There are two forms of respiration namely *aerobic* and *anaerobic* respiration, with the anaerobic form being known also as *fermentation*. Aerobic respiration is the exact *reverse* of photosynthesis since it involves the oxidation of carbon in carbohydrates:



Note that all organisms respire, even the producers.

Examination of equation 14 shows that during aerobic respiration organisms not only utilise the energy trapped by the producers but they *consume free oxygen* as well.

### 4. Aquatic Environments

In aquatic environments most of the aerobic organisms are dependent on the oxygen which is dissolved in the water for their respiration. This dissolved oxygen is derived to a certain extent from the atmosphere, especially in turbulent aquatic systems where the surface of the river or stream is much broken and so able to entrain oxygen from the trapped bubbles of air.



However, by far the greater amount of oxygen present is the result of photosynthesis by submerged macrophytes.

Oxygen is not particularly soluble in water, having a solubility of about 7.0 μg.cm<sup>-3</sup> at 0°C. Solubility decreases as the temperature rises and increases with increasing atmospheric pressure. However, if appreciable numbers of submerged macrophytes are present and actively photosynthesising, as happens during periods of extended sunshine, or if the water flow is very turbulent, then some supersaturation by oxygen is possible and dissolved oxygen concentrations can rise to 12.0 μg.cm<sup>-3</sup> or more. With a good supply of oxygen strongly oxidising conditions prevail and aerobic communities thrive. The system is considered to be healthy all the while the rate of respiration is less than the rate of photosynthesis. Problems will arise if this balance is upset, in particular if organic or any other oxidisable material is introduced into an aquatic system in appreciable amounts.

### 5. The Healthy Aquatic System

In any healthy aquatic system there will be a thriving community of submerged macrophytes supporting a complex food web dependent on the energy and dissolved oxygen that the plants

provide. There may also be a certain number of phytoplankton, floating macrophytes (e.g. *Lemna* and *Potomageton*) and emergent vegetation which, while acting as sources of energy will contribute very little to the dissolved oxygen levels. Indeed, if the growth of phytoplankton and floating macrophytes is too vigorous then they will inhibit the growth of the submerged macrophytes with a consequent reduction in the rate of photosynthesis. This, in turn, will reduce the amount of dissolved oxygen in the water. Very often, particularly in deeper bodies of water, a concentration gradient of dissolved oxygen will exist with higher concentrations towards the surface. Anoxic conditions will prevail within the sediments at the bottom of the water body, where the anaerobic *decomposers* go to work breaking down the remains of dead organisms.

## 6. Oxygen Demand

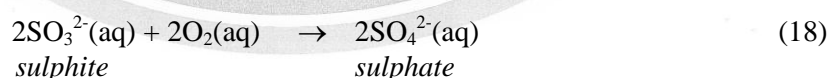
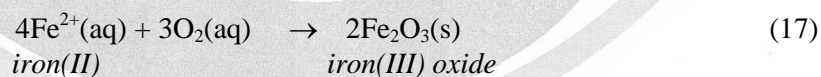
Any extraneous organic matter introduced into an aquatic environment can be divided into the biodegradable and the non-biodegradable. The first category forms an energy source for bacteria, fungi and protozoa many of which, in the first instance, require free oxygen to help them extract the energy from the organic substrate through the process of aerobic respiration. Hence, large amounts of biodegradable organic material encourage large populations of aerobic microorganisms to develop, which leads to a rapid depletion in the level of dissolved oxygen. Consequently anoxic conditions may be established, to the detriment of the aquatic system.

This increased consumption of the dissolved oxygen constitutes an *oxygen demand*. Obviously, the greater the amount of biodegradable material present the greater will be the oxygen demand. This increased demand for oxygen to fuel aerobic respiration is called *Biochemical Oxygen Demand (BOD)*.

Non-biodegradable organic matter, while immune to attack by most microorganisms, will often undergo chemical reactions with the dissolved oxygen, especially in the presence of sunlight. Therefore, with appreciable concentrations of such materials in aquatic systems the rates of oxidation reactions are increased leading to a rapid decrease in the levels of dissolved oxygen. The process can be represented as follows:



In addition to the organic matter certain types of inorganic material will react with the dissolved oxygen so contributing to any oxygen demand. Examples include readily oxidisable metal ions such as iron(II),  $Fe^{2+}$ , and manganese(II),  $Mn^{2+}$ , as well as unstable anions like sulphite,  $SO_3^{2-}$ :



It can be seen that in all these reactions dissolved oxygen is consumed. The demand for oxygen created by all the oxidisable material present, as a result of the reaction between the material and dissolved oxygen, is known as *Chemical Oxygen Demand (COD)*.

## 7. The Significance of BOD

BOD is one of the parameters used to gauge water quality. The Environment Agency stipulates that for water to be considered of high/reasonable standard BOD values must be

less than  $2.0\mu\text{g O}_2\cdot\text{cm}^{-3}$ . Any discharges into a water body must have BOD values of less than  $20\mu\text{g O}_2\cdot\text{cm}^{-3}$ .

Raw sewage commonly has values of 300 to  $600\mu\text{g O}_2\cdot\text{cm}^{-3}$ . By the time the first treatment stage has been completed this will have dropped to about  $50\mu\text{g O}_2\cdot\text{cm}^{-3}$ , while the final effluent will have a BOD of less than  $20\mu\text{g O}_2\cdot\text{cm}^{-3}$ .

## 8. Measuring BOD

In essence, the BOD of a sample is determined by measuring the dissolved oxygen concentration either of the sample itself or a diluted sub-sample, incubating for five days and measuring the dissolved oxygen concentration at the end of that time. The difference between the two concentrations is the oxygen demand.

Water samples are taken in glass BOD bottles (capacity 250 to  $300\text{cm}^3$ ) fitted with ground glass stoppers. Bottles are normally opened, filled and restoppered *under the water* being sampled in order to avoid trapping air bubbles. If the entire operation cannot be performed in this way then the bottle is filled to overflowing and the stopper inserted so that it displaces excess water without trapping any air.

In the laboratory sub-samples are diluted (e.g.  $\times 1/2$ ,  $\times 1/10$ ,  $\times 1/100$ , etc) with *dilution water*. Dilution water is simply distilled water in which nutrient ions such as iron(II), nitrate and chloride, have been dissolved, and which has been saturated with oxygen by bubbling air through it for an hour. The degree of dilution will depend on the expected BOD value. Thus raw sewage will be diluted one hundred-fold, while a river sample will probably not be diluted at all. If the approximate BOD is not known then it is sensible to prepare a series of different dilutions. The dissolved oxygen concentration of every sample/diluted sub-sample is measured, the bottles stoppered (again without trapping any air) and incubated in the dark for five days at  $25^\circ\text{C}$ . At the same time a parallel series of blanks is prepared in which distilled water takes the place of the samples. These are treated in exactly the same way as the samples.

At the end of the five days samples and blanks are removed from the incubator and their dissolved oxygen concentrations measured. The BOD of every sample is then calculated using the formula:

$$\text{BOD} = f \left[ D_0 - D_1 - \frac{(f-1)}{f} \cdot (B_0 - B_1) \right]$$

where

- $D_0$  = dissolved oxygen concentration of sample before incubation
- $D_1$  = dissolved oxygen concentration of sample after incubation
- $B_0$  = dissolved oxygen concentration of blank before incubation
- $B_1$  = dissolved oxygen concentration of blank after incubation
- $f$  = the dilution factor

In natural waters BOD and COD values are usually much the same since most of the oxidisable material present is biodegradable organic matter. However, where a water body is being polluted by industrial effluent or sewage this may not be the case. If the effluent contains non-biodegradable organic or oxidisable inorganic material then COD values will be greater than the BOD values.

---

## 9. The Measurement of Dissolved Oxygen

The determination of BOD values is obviously a time-consuming procedure and a more immediate check on the health of a body of water is the measurement of the dissolved oxygen concentration. If this has fallen to  $5.0\mu\text{g O}_2.\text{cm}^{-3}$  or less during the hours of daylight then it is possible that something is wrong and that further investigations may be necessary.

Although there are purely chemical techniques for determining dissolved oxygen concentrations they have been superseded by electrochemical techniques involving the use of ion-selective electrodes. These electrodes give an almost instantaneous reading of the dissolved oxygen levels. Most of these instruments are capable of presenting the dissolved oxygen results in two formats, one giving the concentration in  $\mu\text{g O}_2.\text{cm}^{-3}$ , the second giving the concentration as **percentage saturation**. The advantage of percentage saturation is that the degree to which oxygen dissolves in water is dependent on atmospheric pressure and since this can vary significantly in a comparatively short space of time it follows that there can be very significant variations in the values obtained when expressed as  $\mu\text{g O}_2.\text{cm}^{-3}$ ; variations which do not reflect the health of the water body.

Percentage saturation, on the other hand, refers simply to the amount of dissolved oxygen relative to the maximum solubility *at the prevailing atmospheric pressure*. Therefore, all else being equal the value will remain constant whatever the pressure. Thus if the pressure drops while taking measurements the solubility of the oxygen will drop also so that less will be required to saturate the water. However, although the actual concentration of oxygen dissolved in the water will fall, the amount remaining in solution will be the same percentage of the saturation value as that in solution at the higher pressure.

Note that because water bodies, especially lotic waters with abundant macrophyte populations, can become supersaturated with oxygen, that they dissolve greater amounts than they need for saturation, the percentage saturation can be greater than 100%.

## 10. Questions

1. Why are water samples for BOD/COD determinations taken in **glass** bottles?
2. Why is it important to exclude air from BOD bottles during sampling and during incubation?
3. Why are the samples incubated in the dark during BOD determinations?
4. The amount of oxygen required to saturate a body of water at pressure  $P_1$  is  $10\mu\text{g}.\text{cm}^{-3}$  at  $5^\circ\text{C}$ . When the actual concentration of oxygen is measured it is found to be  $8\mu\text{g}.\text{cm}^{-3}$ . what is the percentage saturation?

If the pressure drops to  $P_2$  at the same temperature then the amount of oxygen required to saturate the water falls to  $8\mu\text{g}.\text{cm}^{-3}$ . What will be the concentration of the dissolved oxygen in  $\mu\text{g}.\text{cm}^{-3}$  now?