

Module 4: Energy

Supplementary material

1. Meaning of rate of reaction

The average rate of reaction over a small interval of time is defined on page 290. Although the HSC exam will probably ask only qualitative questions about reaction rates (such as deciding which of two graphs of concentration versus time has the greater rate), a quantitative calculation of a reaction rate may help understanding of the concept. Hence the following example.

For the experiment shown in Figure 10.5(a) on page 290 for the reaction of NO with O₂ (Equation 10.6), calculate the average rate of reaction over the time intervals

(a) 0 to 10 s

(b) 30 to 40 s

(c) 60 to 70 s

Then use Figure 10.5(b) to calculate the average rate over the time interval 30 to 40 s. Is your answer what you would have expected from (b)?

To calculate the average rate over the time interval 0 to 10 s we use the equation on page 290,

$$\text{average rate of reaction} = \frac{c_2 - c_1}{t_2 - t_1}$$

We note from the graph that at $t_1 = 0$, $c_1 = 0$ and that at $t_2 = 10$ s, $c_2 = 1.1 \times 10^{-4}$ mol/L. Hence $c_2 - c_1 = 1.1 \times 10^{-4}$ mol/L and $t_2 - t_1 = 10$ s. Therefore between 0 and 10 s

$$\begin{aligned} \text{average rate of reaction} &= \frac{1.1 \times 10^{-4} \text{ mol/L}}{10 \text{ s}} \\ &= \mathbf{1.1 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}} \end{aligned}$$

Note how the units for rate of reaction become moles per litre per second which we always write as $\text{mol L}^{-1} \text{ s}^{-1}$ and not as mol/L/s because the latter is ambiguous.

We have seen that moles per litre is a common unit for concentration of solutes in solution (Section 8.9). However it can equally well be used for concentration of gases: it gives moles of gas per litre of space occupied by the gas. A pressure of 100.0 kPa at 25°C corresponds to a concentration of 0.040 mol/L.

To calculate the average rate over the time interval, 30 to 40 s, we again read concentrations from the graph:

$$\begin{aligned} c_2 - c_1 &= (2.7 - 2.4) \times 10^{-4} = 0.3 \times 10^{-4} \text{ mol/L} \\ \text{and } t_2 - t_1 &= 40 - 30 = 10 \text{ s} \end{aligned}$$

Therefore

$$\left(\begin{array}{l} \text{average rate of reaction} \\ \text{over this time interval} \end{array} \right) = \frac{0.3 \times 10^{-4}}{10} = \mathbf{3 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}}$$

Similarly over the time interval 60 to 70 s, reading from the graph,

$$\text{average rate of reaction} = \frac{(3.4 - 3.2) \times 10^{-4}}{10} = \mathbf{2 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}}$$

The average rate of reaction has decreased quite significantly as reaction has proceeded – from 1.1×10^{-5} to 3×10^{-6} to 2×10^{-6} $\text{mol L}^{-1} \text{ s}^{-1}$ for time intervals 0 to 10, 30 to 40 and 60 to 70 s respectively. These calculations confirm the qualitative conclusion on page 291 that the rate of reaction rate decreases as reaction proceeds.

To calculate the average rate between 30 and 40 s using graph (b), we note that at $t_1 = 30$ s, $c_1 = 2.6 \times 10^{-4}$ mol/L, and at $t_2 = 40$ s, $c_2 = 2.3 \times 10^{-4}$ mol/L so

$$\frac{c_2 - c_1}{t_2 - t_1} = \frac{(2.3 - 2.6) \times 10^{-4}}{10} = -3 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$$

As noted on page 291 rates of reaction are always positive, being the magnitude of the slope (gradient) if the curve has a negative slope. Hence

$$\left(\begin{array}{l} \text{average rate of reaction over} \\ \text{the time interval 30 to 40 s} \end{array} \right) = \mathbf{3 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}}$$

This is the same as calculated above from graph (a) as is to be expected since the same reaction and the same time interval are involved.

Exercises L1 and L4 below involve quantitative calculation of rates of reaction along the lines described here.

2. Catalysts and crude oil

Catalysts are involved in three important aspects of the refining and use of oil products:

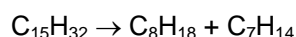
- balancing supply to demand
- improving the quality of gasoline (petrol)
- minimising pollution from automobiles.

(i) Balancing supply to demand

Oil refineries need to balance their outputs of various products (petrol, diesel, fuel oil etc) to match the demands of the marketplace. As was mentioned in *CCPC* Section 9.8 pages 257–8, generally more petrol is required than is obtained from fractional distillation. Hence oil refineries increase the proportion of gasoline by converting some of the lower demand fractions into gasoline. The process is called *catalytic cracking*.

Catalytic cracking is the process in which high molecular weight (high boiling point) fractions from crude oil are broken into lower molecular weight (lower boiling point) substances in order to increase the output of high-demand products.

The column in which this occurs is called a **cat cracker** (catalytic cracker). Hydrocarbons, with 15 to 20 carbon atoms per molecule, are broken into ones with 6 to 8 carbon atoms; for example:



(pentadecane → octane + heptene)

Cracking of a large alkane molecule produces a smaller alkane molecule and an alkene molecule.

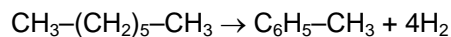
Catalytic cracking is discussed on page 6 of *CCHSC* 4th edition.

(ii) Improving the quality of gasoline (petrol)

Gasoline consisting of straight chain alkanes as obtained from fractional distillation of crude oil does not perform very well in modern petrol engines: it has the tendency to ignite before the piston reaches the top of its stroke. This causes the engine to run roughly and lose power. It is called **pre-ignition** or sometimes 'knocking' or 'pinging'.

The performance of petrol in motor cars is measured by its **octane rating**. The octane rating of petrol obtained by straight distillation or catalytic cracking is too low for most car engines. Originally octane rating was improved by adding a compound called **tetraethyl lead**, $(\text{C}_2\text{H}_5)_4\text{Pb}$. Two problems with this are first emitting lead to the atmosphere through the exhaust of motor cars is undesirable because lead is a poison and secondly lead 'poisons' the catalysts used to remove other pollutants from car exhausts (next sub-section).

An alternative approach to using lead to boost octane rating is **catalytic reforming**. This is a process in which straight-chain alkanes are converted into branched-chain alkanes or into aromatic compounds (Figure 9.8 on page 258). The catalyst used is metallic platinum. An example of catalytic reforming is the conversion of heptane to toluene:



(heptane → toluene + hydrogen)

By using catalytic reforming it is possible to produce petrol with a sufficiently high octane rating without adding any lead compound, though this so-called unleaded petrol is more expensive to produce than lead-containing petrol of the same octane rating. Petrol containing lead is no longer available in NSW.

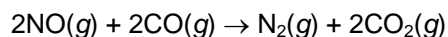
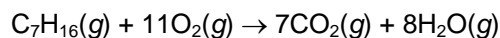
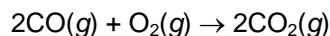
(iii) Minimising pollution from automobiles (catalytic exhausts)

In Section 10.8 it was stated that the major pollutants from burning fossil fuels were carbon monoxide and soot, sulfur dioxide, oxides of nitrogen and particulates. Automobiles produce negligible amounts of sulfur dioxide, because virtually all sulfur is removed from petrol and diesel during refining. Petrol engines produce very little soot, but they do produce significant amounts of unburnt hydrocarbon. The main pollutants from motor cars are then

- carbon monoxide
- hydrocarbons
- oxides of nitrogen.

In Australia today, as in most developed countries, there are legal restrictions on the amount of these pollutants that cars are allowed emit. Most car makers meet these restrictions by fitting catalytic converters into the exhaust pipes of their cars. A typical one is shown in Figure 10.7 on page 297. It consists of a ceramic honeycomb block about 30 cm long with a cross-sectional area of about 50 to 100 cm² inside a metal canister that looks like an extra muffler in the exhaust pipe. The hexagonal or square holes pass right through the block. A thin layer of a mixture of platinum and rhodium metals which are the actual catalysts is deposited on all surfaces of the block. The aims are (1) to provide a large surface area of metal while using the smallest possible mass of these very expensive metals, and (2) to allow all the exhaust gas to come into contact with the catalytic metal film while providing only minimum resistance to flow through the catalyst. The structure has to be sufficiently robust to last at least 80000 km.

The platinum catalyses the conversion of carbon monoxide to carbon dioxide and of unburnt hydrocarbons to carbon dioxide and water, while the rhodium catalyses the reaction of NO with CO to form N₂ and CO₂:



The formation of photochemical smog and the operation of catalytic converters are discussed further in *CCHSC*, pages 239–41.