Cambridge OL

Chemistry

CODE: (5070)

Chapter 07

Chemical reactions

7.1 Reactions

Physical changes alter the state of a substance, like ice melting to form water or boiling water to produce steam. Chemical changes result in the formation of something new, like frying an egg. Physical changes can be reversed, while chemical changes are permanent. Examples of slow and fast reactions include ripening apples, cheese making, and burning solid fuels. As the chemical industry becomes more complex, chemists and engineers are looking for ways to control reaction rates. They have discovered five main ways to alter the rate of a chemical reaction, which can be applied to both industry and school laboratory reactions.

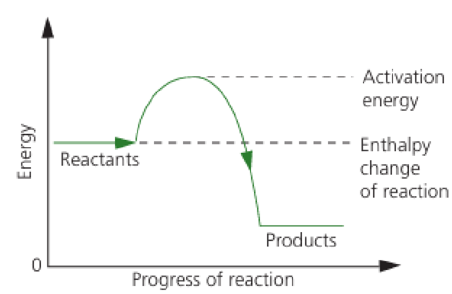
▲ **Figure 7.1** Some slow (ripening fruit and cheese making), medium (coal fire) and fast (explosion) reactions

7.2 Factors that affect the rate of a reaction

The five main ways to alter the rate of a chemical reaction are:
» Changing the concentration of solutions
» Changing the pressure of gases
» Changing the surface area of solids
» Changing the temperature » adding or removing a catalyst including enzymes.

Collision theory

Chemical reactions require particles to collide, with a minimum activation energy (E_a) required for product formation. Successful collisions have a minimum energy, while not all collisions result in product formation.



▲ **Figure 7.2** Reaction profile diagram showing activation energy

Surface area

Limestone, a substance with calcium carbonate, can neutralize soil acidity faster than lumps. This is due to the reaction between acid and limestone in the form of lumps or powder in a laboratory experiment.

hydrochloric acid + calcium carbonate → calcium chloride + carbon dioxide + water

$$2HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

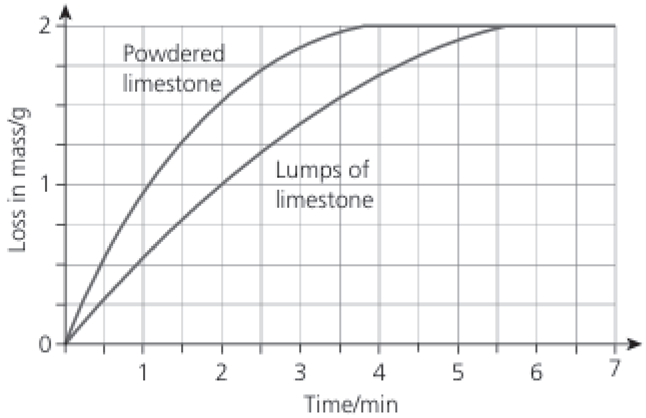
The rates at which the two reactions occur can be found by measuring either:

» The volume of the carbon dioxide gas which is produced
» The loss in mass of the reaction mixture with time.

The rate of reaction in gas formation processes is typically measured using two methods. The apparatus measures the loss in mass of the reaction mixture, plotting it against time. The reaction between hydrochloric acid and limestone is fastest in the first minute, with powdered limestone showing a higher rate than lump form.

If the surface area of a reactant is increased, more particles are exposed to the other reactant, so the rate of a chemical reaction can be raised by increasing the surface area of a solid reactant.

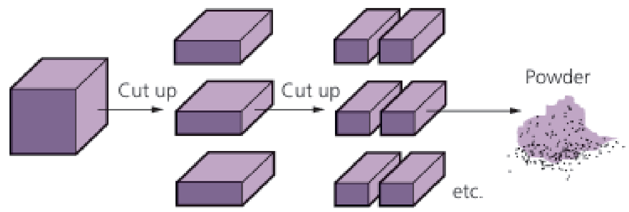
▲ **Figure 7.3** The powdered limestone (left) reacts faster with the acid than the limestone in the form of lumps



▲ **Figure 7.5** Sample results for the limestone/acid experiment

Powdering limestone increases its surface area, allowing acid particles to collide more effectively. This increases the number of collisions, leading to more successful reactions. However, the large surface area of fine powders and dusts can pose risks, such as explosions in flourmills and mines. In 1988, two silos containing wheat exploded at the Jamaica Flour Mills Plant, killing three workers.

Figure 7.4 After 60 seconds the mass has fallen by 1.24 g



▲ **Figure 7.6** A powder has a larger surface area

▲ **Figure 7.7** The dust created by this cement plant is a potential hazard

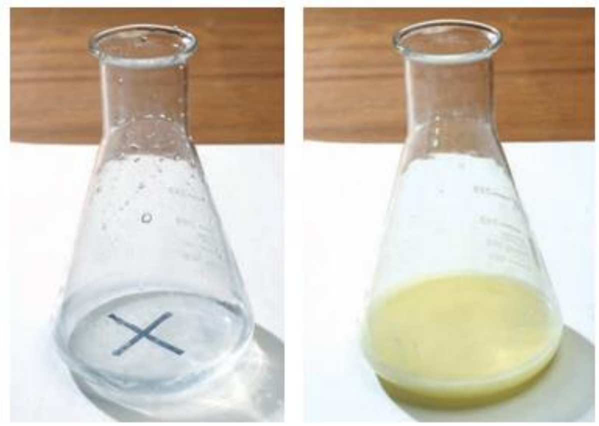
Concentration

A yellow precipitate is produced in the reaction between sodium thiosulfate and hydrochloric acid.

sodium thiosulfate + hydrochloric acid → sodium chloride + sulfur + sulfur dioxide + water

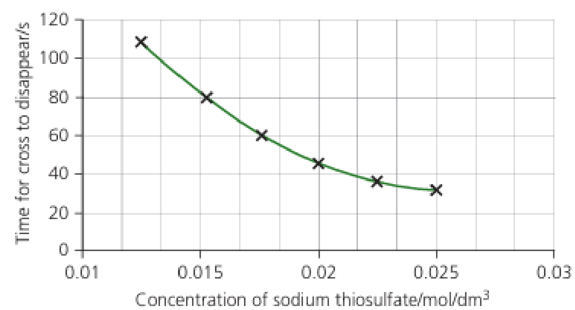
$$Na_2S_2O_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + S(s) + SO_2(g) + H_2O(l)$$

Record the time taken for yellow sulfur precipitation by placing a conical flask on a cross on paper. The time taken is a measure of the reaction rate. To understand the effect of changing reactant concentrations, conduct experiments using different concentrations of sodium thiosulfate or hydrochloric acid.



▲ **Figure 7.8** The precipitate of sulfur obscures the cross

Some sample results of experiments of this kind have been plotted in Figure 7.9.

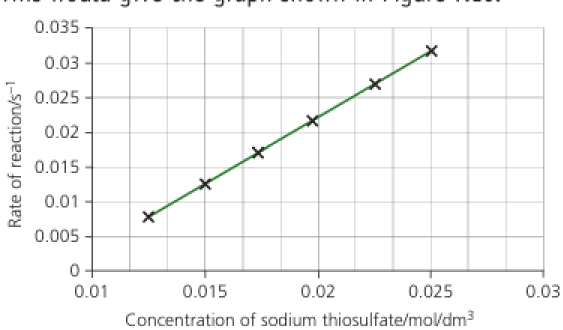


▲ **Figure 7.9** Sample data for the sodium thiosulfate/acid experiment at different concentrations of sodium thiosulfate

From the data shown in Figure 7.9 it is possible to produce a different graph which directly shows the rate of the reaction against concentration rather than the time taken for the reaction to occur against concentration. To do this, the times can be converted to a rate using:

$$\text{rate} = \frac{1}{\text{reaction time (s)}}$$

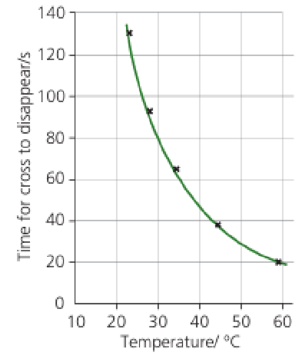
This would give the graph shown in Figure 7.10.



▲ **Figure 7.10** Graph to show the rate of reaction against concentration

Pressure of gases

Increased pressure in gas reactions boosts reaction rate by pushing gas particles closer together, increasing collision frequency and particle volume.



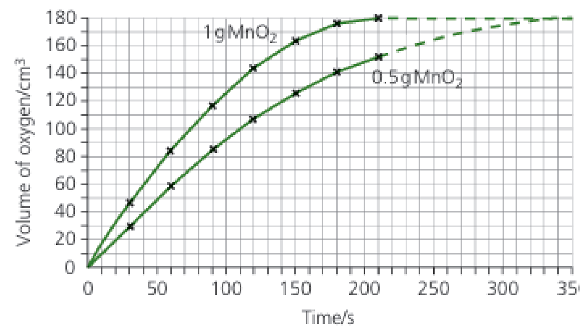
▲ **Figure 7.11** Sample data for the sodium thiosulfate/acid experiment at different temperatures

Temperature

Food is stored in a refrigerator due to slower decay rates at lower temperatures, a common feature in chemical processes. Experiments with sodium thiosulfate and hydrochloric acid show that the reaction rate is fastest at high temperatures.

Catalysts

Over 90% of industrial processes use **catalysts**. A catalyst is a substance which can alter the rate of a reaction without being chemically changed itself.



▲ **Figure 7.12** Sample data for differing amounts of MnO_2 catalyst

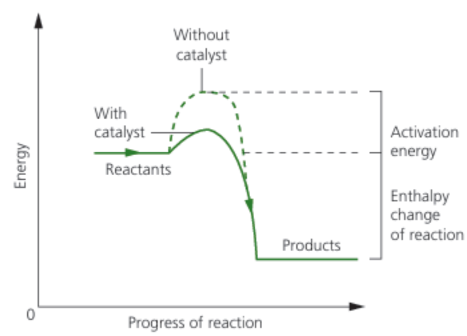
The decomposition of hydrogen peroxide at room temperature is slow, but manganese (IV) oxide can speed up the reaction. When added to hydrogen peroxide, oxygen is produced rapidly, as shown in Figure 7.12. The reaction can be faster by increasing the catalyst's surface area and amount.

Chemists have found that:

» A small amount of catalyst will produce a large amount of chemical change

» Catalysts remain unchanged chemically after a reaction has taken place, but they can change physically.

» Catalysts are specific to a particular chemical reaction.



▲ **Figure 7.13** A reaction pathway diagram showing activation energy, with and without a catalyst

A catalyst boosts chemical reaction rate by offering a lower activation energy path, causing more successful collisions. This lowers activation energy, allowing more particles to produce products at a given temperature.

Key definition

A **catalyst** is a substance which alters the rate of a chemical reaction and is unchanged at the end of the reaction. It increases the rate of a chemical reaction by providing an alternative reaction path which has a lower activation energy, E_a.

7.3 Enzymes

Enzymes, protein molecules in living cells, act as catalysts for numerous chemical reactions, with each reaction having a unique enzyme catalyst.

7.4 Reversible reactions and equilibrium

Chemical reactions typically change reactants into products, but some reversible reactions involve reactants forming products that can then be further reacted with to produce more reactants, reversing the process and regenerating the original reactants. These reactions can be altered by changing reaction conditions. Examples include the production of industrial chemicals like ammonia and sulfuric acid. For example, hydrated copper (II) sulfate can be heated to change color, while **anhydrous** copper(II) sulfate can be reformed.

This is an example of a reversible reaction:

$$\text{hydrated copper(II) sulfate} \rightleftharpoons \text{anhydrous copper(II) sulfate} + \text{water}$$

$$\text{blue solid} \rightleftharpoons \text{white solid}$$

We can show this reaction as being **reversible** by using the $\rightleftharpoons$ symbol.

Key definition

Some chemical reactions are **reversible** as shown by the $\rightleftharpoons$ symbol. This means the reaction can go both ways.

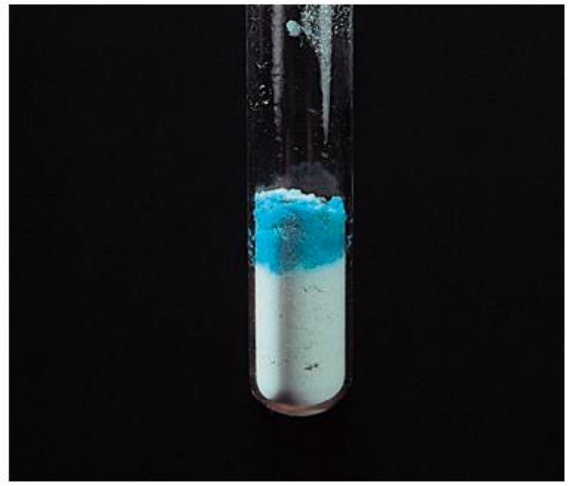


Figure 7.16 Anhydrous copper(II) sulfate changes from white to blue when water is added to it

7.5 Ammonia – an important nitrogen-containing chemical

The **Haber process**, developed by German scientist Fritz Haber in 1913, is a major method for manufacturing ammonia, a crucial bulk chemical used in explosives, nitric acid, and fertilizers like ammonium nitrate, involving the reaction of nitrogen and hydrogen.

Obtaining nitrogen

The nitrogen needed in the Haber process is obtained from the **atmosphere** by fractional distillation of liquid air

Obtaining hydrogen

The hydrogen needed in the Haber process is obtained from the reaction between methane and steam.

$$\text{methane} + \text{steam} \rightleftharpoons \text{hydrogen} + \text{carbon monoxide}$$

$$CH_4(g) + H_2O(g) \rightleftharpoons 3H_2(g) + CO(g)$$

Steam re-forming is a reversible process that produces hydrogen and carbon monoxide under specific conditions. The process is carried out at 750°C, 3000 kPa, and 30 atmospheres with a nickel catalyst, allowing maximum hydrogen production at an economic cost. Carbon monoxide reduces unreacted steam to produce more hydrogen gas.

$$\text{carbon monoxide} + \text{steam} \rightleftharpoons \text{hydrogen} + \text{carbon dioxide}$$

$$CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g)$$

Key definition

The source of hydrogen used in the **Haber process** is methane, and nitrogen gas is obtained from the air.

Making ammonia

The reaction in the Haber process is:

$$\text{nitrogen} + \text{hydrogen} \rightleftharpoons \text{ammonia}$$

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g);\ \Delta H = -92\,\text{kJ/mol}$$

The reaction is exothermic.

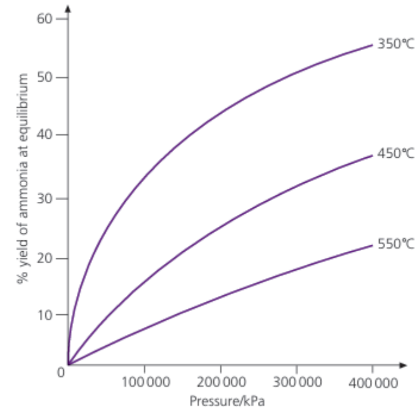
Key definition

The equation for the production of ammonia in the Haber process is $N_2 + 3H_2 \rightleftharpoons 2NH_3$.

The typical conditions used in the Haber process are 450°C, 20 000 kPa and an iron catalyst.

The 15% of ammonia produced is due to the reversible nature of the reaction, where the rate of nitrogen and hydrogen decomposition equals the rate of ammonia decomposition. This **equilibrium**, known as chemical equilibrium, remains constant in a closed system, ensuring economic production. The percentage of ammonia produced varies with temperature and pressure, demonstrating the importance of **reversible reactions** in achieving equilibrium.

> **Key definition**
> A **reversible reaction** in a closed system is at **equilibrium** when the rate of the forward reaction is equal to the rate of the reverse reaction, and the concentrations of reactants and products are no longer changing.



▲ **Figure 7.17** Yields from the Haber process

In fact, the position of equilibrium is affected by each of the following:
» Changing temperature
» Changing pressure
» Changing concentration
»Using a catalyst.

Henri Le Chatelier observed that higher pressure in gas reactions favors reactions producing the fewest molecules of gas. The Haber process, for example, is carried out at high pressures to move the equilibrium position to the right. The process also uses an iron catalyst to increase the rate of both forward and reverse reactions, resulting in faster production. The concentration of nitrogen is often increased to increase the yield of ammonia. However, the high pressure used is expensive and a safety concern, leading to the search for alternative routes involving biotechnology.

7.6 Industrial manufacture of sulfuric acid – the Contact process

The Contact process is a crucial industrial chemical production method, involving the burning of sulfur with excess oxygen in the air, resulting in millions of tonnes of sulfuric acid annually, used in the production of detergents, paints, fertilizers, and organic compounds.

$$\text{sulfur} + \text{oxygen} \rightarrow \text{sulfur dioxide}$$

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

Sulfur dioxide is produced by roasting sulfide ores in air, heating to 450°C, and then cooled to produce sulfur trioxide using a vanadium(V) oxide catalyst.

$$\text{sulfur dioxide} + \text{oxygen} \rightleftharpoons \text{sulfur trioxide}$$

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g);\quad \Delta H = -197\ \text{kJ/mol}$$

The reversible reaction can increase sulfur trioxide proportion in equilibrium mixtures. Low temperatures are ideal, with 450°C being the optimal temperature. High pressure is preferred, with 96% of sulfur dioxide and oxygen converted into sulfur trioxide. Energy is used to heat gases, saving money. The produced sulfur trioxide can be reacted with water to produce sulfuric acid.

$$\text{sulfur trioxide} + \text{water} \rightarrow \text{sulfuric acid}$$

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$$

> **Key definition**
> The equation for the production of sulfur trioxide in the **Contact process** is $2SO_2 + O_2 \rightleftharpoons 2SO_3$
> The typical conditions used in the Contact process are 450°C, 200 kPa and vanadium(V) oxide catalyst.
> Burning sulfur or sulfide ores in air is the source of sulfur dioxide and air is the source of oxygen in the Contact process.

Revision questions

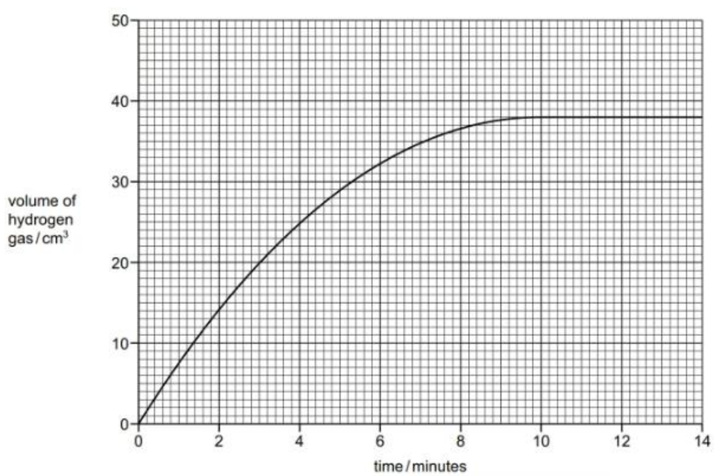
1) Biological catalysts produced by microbes cause food to deteriorate and decay.

i)What is the name of these biological catalysts?

ii) Freezing does not kill the microbes.
Suggest why freezing is still a very effective way of preserving food.

b) Describe how the pea plant makes a sugar such as glucose.

2) a) A student investigates the reaction of small pieces of zinc with dilute sulfuric acid at 20 °C. The zinc is in excess.
The graph shows the volume of hydrogen gas released as the reaction proceeds.



Suggest why the volume of hydrogen gas stays the same after 10 minutes

b) Deduce the time taken from the start of the experiment to collect 20 cm3 of hydrogen gas.

c) The student repeats the experiment at 30 °C.
All other conditions stay the same.
Draw a line on the grid in part (a) to show how the volume of hydrogen gas changes with time when the reaction is carried out at 30 °C.

d) The student repeats the experiment using zinc powder instead of small pieces of zinc.
Describe how the rate of reaction differs when zinc powder is used.
Give a reason for your answer.

3) a) Acids have characteristics properties

The rate of reaction of iron with sulfuric acid can be determined by measuring the time taken to produce 20cm3 of hydrogen.
A student measured the time taken to produce 20 cm3 of hydrogen using three different concentrations of sulfuric acid.
In each experiment the student used:

- 1g of iron powder
- The same temperature
- The same volume of sulfuric acid.

The results are shown in the table.

concentration of acid in mol / dm^3	time / s
0.1	33
0.2	17
0.5	8

Use the information in the table to describe how the rate of reaction changes with the concentration of sulfuric acid.

b) Describe the effect of each of the following on the rate of this reaction with 0.5 mol/dm3 of sulfuric acid.
- Larger pieces of iron are used.
All other conditions stay the same.
………………………………………………………………
- The temperature is increased. All other conditions stay the same.
……………………………………………….

4) Sulfur dioxide is a pollutant in the air.
Sulfur dioxide is oxidised to sulfur trioxide in the air. Oxides of nitrogen act as catalysts for this reaction.
What is meant by the term catalyst?

5) A length of magnesium ribbon was added to 50 cm^3 of sulfuric acid, concentration 1.0 mol/dm^3. The time taken for the magnesium to react was measured. The experiment was repeated with the same volume of different acids. In all these experiments, the acid was in excess, and the same length of magnesium ribbon was used.

Experiment	Acid	Concentration in mol/dm^3	Time / s
A	sulfuric acid	1.0	20
B	propanoic acid	0.5	230
C	hydrochloric acid	1.0	40
D	hydrochloric acid	0.5	80

i) Write these experiments in order of reaction speed. Give the experiment with the fastest speed first.
ii)Give reasons for the order you have given in (i).

b) Suggest two changes to experiment C which would increase the speed of the reaction and explain why the speed would increase. The volume of the acid, the concentration of the acid and the mass of magnesium used were kept the same.
change 1
explanation...............................

change 2.
explanation……………………………….

6) Sulfur dioxide, SO2, is used in the manufacture of sulfuric acid.
a) Why is a catalyst used?

b) Explain, in terms of particles, why a high temperature increases the rate of this reaction.

7) Ammonia is manufactured by the Haber process.
Explain, in terms of particles, what happens to the rate of this reaction when the temperature is increased.

8) Oxides of nitrogen are pollutants in the air.
Oxides of nitrogen act as catalysts.
What is meant by the term catalyst?

9) At present the most important method of manufacturing hydrogen is steam reforming of methane.

In the first stage of the process, methane reacts with steam at 800°C.

$$CH_4(g) + H_2O(g) \rightleftharpoons 3H_2(g) + CO(g)$$

In the second stage of the process, carbon monoxide reacts with steam at 200 °C.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

i) Explain why the position of equilibrium in the first reaction is affected by pressure but the position of equilibrium in the second reaction is not.

ii) Suggest why a high temperature is needed in the first reaction to get a high yield of products but in the second reaction a high yield is obtained at a low temperature.

Two other ways of producing hydrogen are cracking and electrolysis.

There are three products of the electrolysis of concentrated aqueous sodium chloride. Hydrogen is one of them.

i) Write an equation for the electrode reaction which forms hydrogen.

ii) Name the other two products of the electrolysis of concentrated aqueous sodium chloride and give a use of each one.

product .... use ....
product .... use ....

10)

Nitrogen dioxide is a brown gas. It can be made by heating certain metal nitrates.

$$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$$

At most temperatures, samples of nitrogen dioxide are equilibrium mixtures.

$$\underset{\text{dark brown}}{2NO_2(g)} \rightleftharpoons \underset{\text{pale yellow}}{N_2O_4(g)}$$

i) At 25 °C, the mixture contains 20 % of nitrogen dioxide. At 100 °C this has risen to 90%. Is the forward reaction exothermic or endothermic?

Give a reason for your choice.

[2]

ii) Explain why the colour of the equilibrium mixture becomes lighter when the pressure on the mixture is increased.

[2]

A 5.00 g sample of impure lead(II) nitrate was heated. The volume of oxygen formed was 0.16 dm^3 measured at r.t.p. The impurities did not decompose.

Calculate the percentage of lead(II) nitrate in the sample.

$$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$$

Number of moles of O_2 formed = ...

Number of moles of $Pb(NO_3)_2$ in the sample = ...

Mass of one mole of $Pb(NO_3)_2$ = 331 g

Mass of lead(II) nitrate in the sample = ... g

Percentage of lead(II) nitrate in sample = ...