Cambridge

AS Level

Chemistry

CODE: (9701)

Chapter 9 and Chapter 10

Rates of reaction and Periodicity

FOCUS

Chapter 09 – Rates of reaction

Reaction kinetics

The **rate of a reaction** is a crucial aspect of understanding the mechanism of a chemical reaction.

$$\text{rate} = \frac{\text{change in amount of reactants or products}}{\text{time}}$$

The rate of a reaction is determined through experiments, allowing us to measure the usage of reactants and the formation of products.

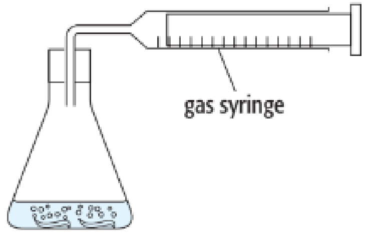


Figure 9.2 Measuring the volume of gas given off over time enables us to calculate the rate of reaction in cm^3 of gas per second.

Collision theory

Collision theory explains the impact of concentration, temperature, surface area, and catalysts on reaction rates. It states that particles must collide in the correct orientation and with sufficient energy to react. Unsuccessful collisions occur when particles lack energy, while successful collisions occur when particles have enough energy. The **activation energy** is the minimum energy required for a successful collision.

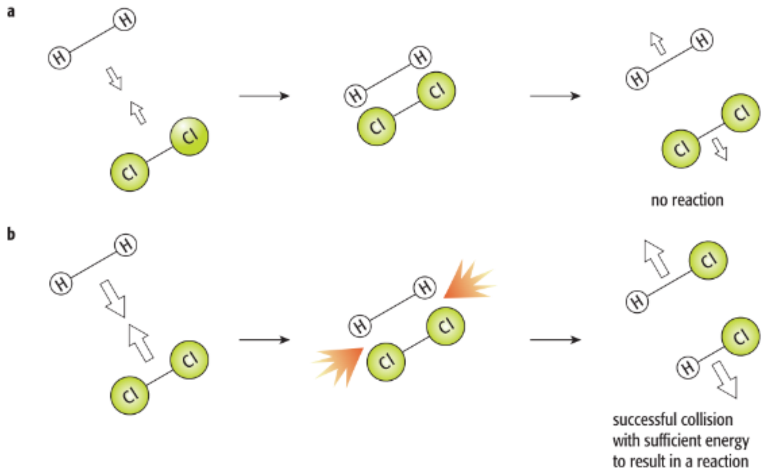


Figure 9.3 **a** Unsuccessful and **b** successful (or effective) collisions.

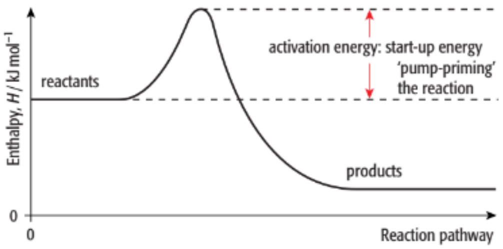


Figure 9.4 The activation energy in an exothermic reaction.

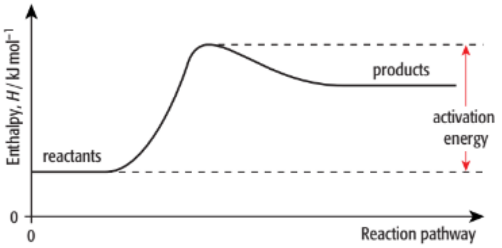


Figure 9.5 The activation energy in an endothermic reaction.

According to the collision theory, a reaction will speed up if:

- The frequency of collisions increases
- The proportion of particles with energy greater than the activation energy increases.

A **catalyst** is a substance that enhances reaction rate while maintaining chemical integrity by enabling an alternative mechanism with lower activation energy.

The effect of concentration on rate of reaction

Concentration in chemistry is measured in moles per decimetre cubed (moldm−3). More concentrated solutions have more solute particles, leading to faster reactions due to frequent collisions. Pressure also affects reactions involving gases, increasing the number of gas molecules in a volume and causing more collisions.

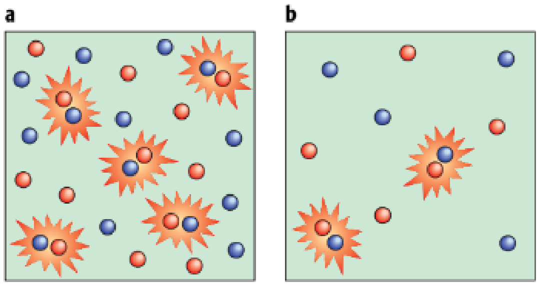


Figure 9.7 The particles in box **a** are closer together than those in box **b**. There are more particles in the same volume, so the chances and frequency of collisions between reacting particles are increased. Therefore, the rate of reaction is greater in box **a** than in box **b**.

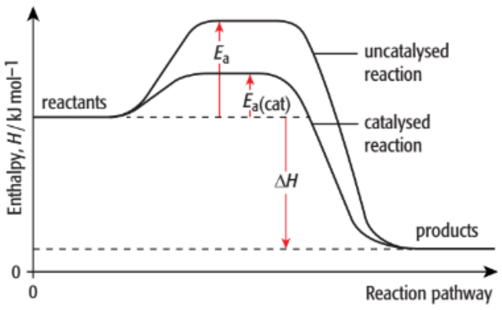


Figure 9.6 The effect of a catalyst on the activation energy in an exothermic reaction.

The effect of temperature on rate of reaction

The **Boltzmann distribution** is a graph that shows the distribution of energies at a given temperature. It shows that particles in a substance have varying amounts of energy, with some having a small amount and others having a large amount. As temperature increases, the average kinetic energy of particles increases, leading to more frequent collisions. However, experiments show that the rate of reaction cannot be entirely explained by more frequent collisions. The proportion of successful collisions increases significantly as temperature increases, affecting the molecular energies distribution.

Therefore, increasing the temperature increases the rate of reaction because:

- The increased energy results in particles moving around more quickly, which increases the frequency of collisions
- The proportion of successful collisions (i.e. those that result in a reaction) increases because the proportion of particles exceeding the activation energy increases. This is the more important factor.

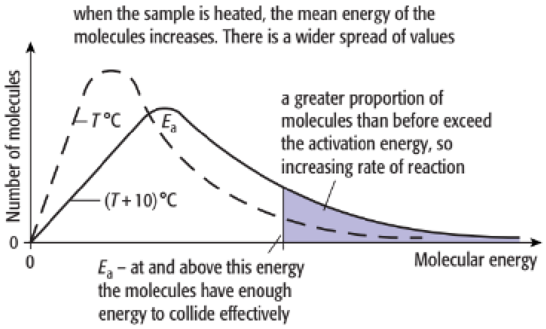


Figure 9.9 The Boltzmann distribution of molecular energies at temperatures T °C and $(T + 10)$ °C, showing the activation energy.

Catalyst

A catalyst provides an alternative mechanism with lower activation energy, allowing a greater proportion of molecules in the reaction mixture to react. This results in a higher rate of effective collisions and catalysis, as shown in Figure 9.6, which does not affect the shape of the Boltzmann distribution.

Homogeneous and heterogeneous catalysts

A catalyst is a crucial component in catalysis, either homogeneous or heterogeneous. Homogeneous catalysts are present in the same phase as reactants, like water, while heterogeneous catalysts are present in different phases, like oxygen gas production.

The reaction commonly used in the laboratory is the decomposition of hydrogen peroxide solution:

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g) \qquad \textit{slow reaction}$$

This is a very slow reaction at room temperature. However, when a little of the insoluble solid manganese (IV) oxide powder, MnO2(s), is added, oxygen is given off quickly (Figure 9.11).

$$2H_2O_2(aq) \xrightarrow{MnO_2(s)} 2H_2O(l) + O_2(g) \ \textit{fast reaction}$$

Many heterogeneous catalysts are solids that catalyse gaseous reactants. The reactions take place on the surface of the solid catalyst.

Enzymes

In common with inorganic catalysts, enzymes.

- speed up a reaction without being used up
- provide an alternative reaction pathway with a lower activation energy (Figure 9.12).

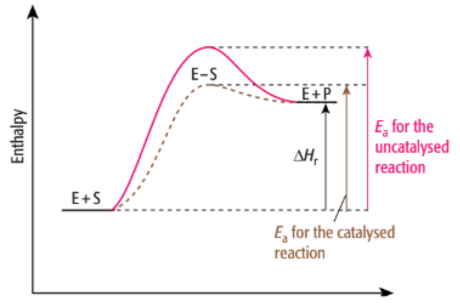


Figure 9.12 The energy profile for an enzyme-catalysed endothermic reaction, compared with the same reaction without a catalyst. As for inorganic catalysts, the enzyme provides a different reaction pathway with a lower activation energy (E_a) but the overall enthalpy change (ΔH_r) is unaffected.

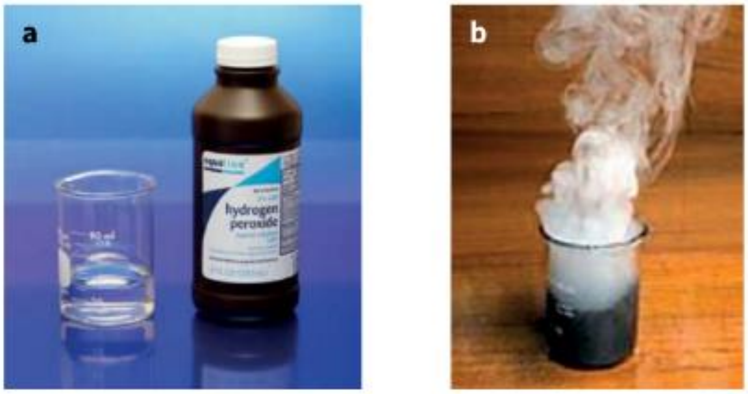


Figure 9.11 **a** A solution of hydrogen peroxide at room temperature. **b** The solution of hydrogen peroxide with a little manganese(IV) oxide added.

However, enzyme catalysis has some specific features:

- Enzymes are more efficient than inorganic catalysts; the reaction rate is often increased by a factor of 106 to 1012
- Enzymes are very specific; they usually only catalyse one reaction
- As a consequence of this specificity, enzymes do not produce byproducts
- Enzymes work under very mild conditions; for example, 35°C, pH 7, atmospheric pressure
- The amount of enzyme present in a cell can be regulated according to need.

The specific substance that fits onto the surface of the enzyme molecule and is converted to product(s) is called a **substrate**.

Chapter 10 – Periodicity

Structure of the Periodic Table

The Periodic Table, originally developed by Mendeleev, now explains the arrangement of chemical elements in atomic number order, not mass. The modern table has 18 groups, with patterns like sodium to argon appearing across periods, a concept known as **periodicity**.

Periodicity of physical properties

1. Periodic patterns of atomic radii

Atomic radii, obtained from an element's single covalent radius, provide the best data for comparison across a period. Other measures like metallic and van der Waals' radii are also available. Table 10.1 provides values for Period 3.

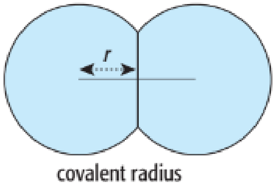
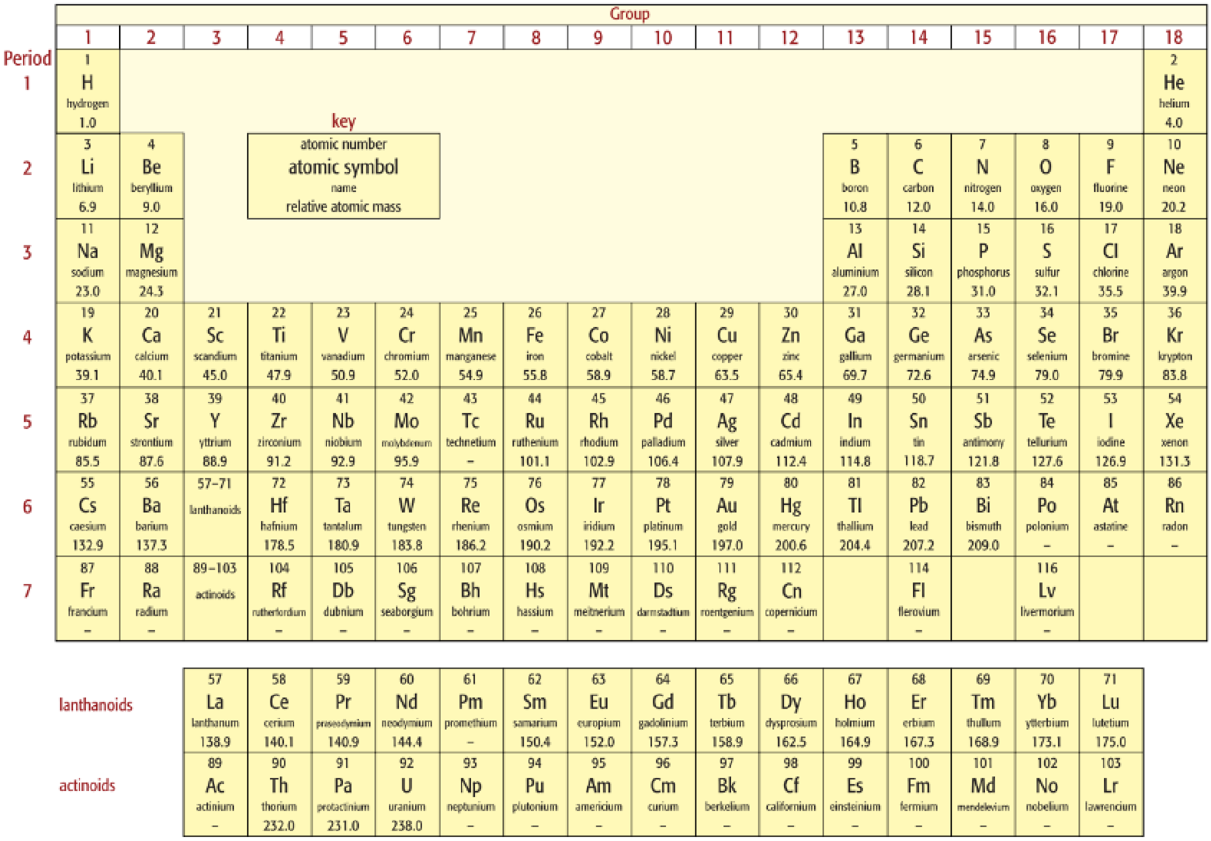


Figure 10.3 The distance between the two nuclei of the same type of atom can be determined and then divided by two to arrive at the atomic (single covalent) radius.



	Group																	
Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H hydrogen 1.0																	2 He helium 4.0
2	3 Li lithium 6.9	4 Be beryllium 9.0			key atomic number atomic symbol name relative atomic mass								5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0	10 Ne neon 20.2
3	11 Na sodium 23.0	12 Mg magnesium 24.3											13 Al aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 Cl chlorine 35.5	18 Ar argon 39.9
4	19 K potassium 39.1	20 Ca calcium 40.1	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4	31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8
5	37 Rb rubidum 85.5	38 Sr strontium 87.6	39 Y yttrium 88.9	40 Zr zirconium 91.2	41 Nb niobium 92.9	42 Mo molybdenum 95.9	43 Tc technetium –	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
6	55 Cs caesium 132.9	56 Ba barium 137.3	57–71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium –	85 At astatine –	86 Rn radon –
7	87 Fr francium –	88 Ra radium –	89–103 actinoids	104 Rf rutherfordium –	105 Db dubnium –	106 Sg seaborgium –	107 Bh bohrium –	108 Hs hassium –	109 Mt meitnerium –	110 Ds darmstadtium –	111 Rg roentgenium –	112 Cn copernicium –		114 Fl flerovium –		116 Lv livermorium –		

lanthanoids	57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.4	61 Pm promethium –	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0
actinoids	89 Ac actinium –	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium –	94 Pu plutonium –	95 Am americium –	96 Cm curium –	97 Bk berkelium –	98 Cf californium –	99 Es einsteinium –	100 Fm fermium –	101 Md mendelevium –	102 No nobelium –	103 Lr lawrencium –

Figure 10.2 The Periodic Table of the elements. A larger version of the Periodic Table can be found in Appendix 1, page 473.

Period 3 element	sodium (Na)	magnesium (Mg)	aluminium (Al)	silicon (Si)	phosphorus (P)	sulfur (S)	chlorine (Cl)	argon (Ar)
Atomic radius / nm	0.157	0.136	0.125	0.117	0.110	0.104	0.099	–

Table 10.1 The atomic (single covalent) radii of Period 3 elements (no data are available for argon). The units are nanometres, where 1 nm = 10^{-9} m.

Noble gases in Group 18, like argon in Period 3, do not form bonds, so their atomic radii are determined by their van der Waals' radius. This radius is higher than the single covalent radius of any element. The atomic radius decreases across periods due to an increase in protons and electrons, with the shielding effect remaining constant. This results in a greater attraction force on outer electrons, causing the atomic radius to decrease.

2. Periodic patterns of ionic radii

In Chapter 4, it is explained that metallic elements produce positively charged ions (cations) like Na+, while non-metallic elements form negatively charged ions (anions). The pattern in ionic radii changes across Period 3, with cations being smaller and having less shielding of outer electrons. From Na+ to Si4+, ions decrease for similar reasons. (figure 10.5)

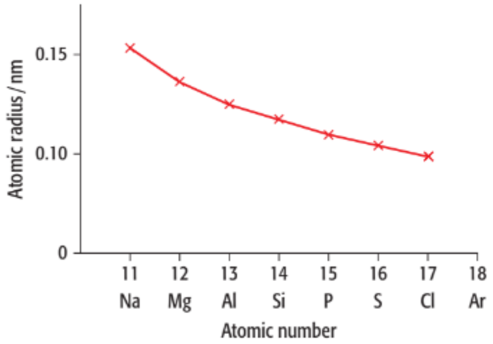


Figure 10.4 Plotting the atomic radii (single covalent radii) against atomic number for the elements in Period 3 (argon not included).

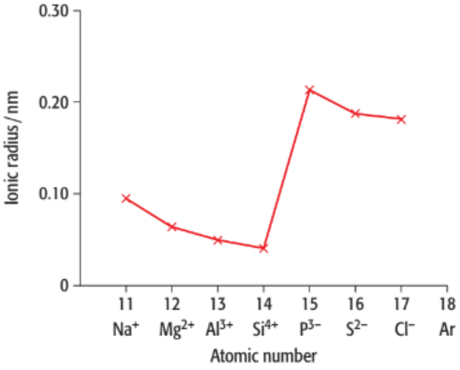


Figure 10.5 Plotting the ionic radii against atomic number for the elements in Period 3 (argon not included).

3. Periodic patterns of melting points and electrical conductivity

Physical properties like melting point and electrical conductivity show trends over time, with a significant increase in electrical conductivity across metals in Period 3. This trend is due to the bonding and structure of the elements, with a decrease in conductivity to silicon and non-metallicinsulators. The increase in melting point and electrical conductivity is due to the number of electrons each metal donates into the delocalised electron sea and the increasing charge on the metal ions in the metallic lattice.

Ions of Period 3 elements	Na^+	Mg^{2+}	Al^{3+}	Si^{4+}	P^{3-}	S^{2-}	Cl^-	Ar
Ionic radius / nm	0.095	0.065	0.050	0.041	0.212	0.184	0.181	–

Table 10.2 The ionic radii of Period 3 elements (no data are available for argon).

Aluminium's strong metallic bonding and large number of negatively charged delocalised electrons make it a better electrical conductor than sodium. Silicon, in Period 3, has the highest melting point due to its giant molecular structure. However, its electrical conductivity is lower than other metals. Non-metallic elements like sulfur, phosphorus, and chlorine exist as small molecules with weak van der Waals' forces, making them easy to break and melt. Phosphorus, sulfur, chlorine, and argon gas have low melting points at room temperature.

Period 3 element	sodium (Na)	magnesium (Mg)	aluminium (Al)	silicon (Si)	phosphorus (P)	sulfur (S)	chlorine (Cl)	argon (Ar)
Melting point / K	371	923	932	1683	317	392	172	84

Table 10.3 The melting points of Period 3 elements (measured in kelvin, K, where 0 °C = 273 K).

Period 3 element	sodium (Na)	magnesium (Mg)	aluminium (Al)	silicon (Si)	phosphorus (P)	sulfur (S)	chlorine (Cl)	argon (Ar)
Melting point / K	0.218	0.224	0.382	2×10^{-10}	10^{-17}	10^{-23}	–	–

Table 10.4 The electrical conductivity of Period 3 elements (measured in siemens per metre, $S\,m^{-1}$, where siemens are proportional to the ease with which electrons can pass through a material).

Period 3 element	sodium (Na)	magnesium (Mg)	aluminium (Al)	silicon (Si)	phosphorus (P)	sulfur (S)	chlorine (Cl)	argon (Ar)
Bonding	metallic	metallic	metallic	covalent	covalent	covalent	covalent	–
Structure	giant metallic	giant metallic	giant metallic	giant molecular	simple molecular	simple molecular	simple molecular	simple molecular

Table 10.5 The bonding and structures of Period 3 elements.

4 Periodic patterns of first ionization energies

You have looked at the pattern in first ionisation energies for the first two periods on page 41. In Period 3 the pattern is the same as in Period 2. This is shown by the data in Table 10.6 and the graph in Figure 10.7.

Period 3 element	**First ionisation energy / $kJ\,mol^{-1}$**
sodium (Na)	494
magnesium (Mg)	736
aluminium (Al)	577
silicon (Si)	786
phosphorus (P)	1060
sulfur (S)	1000
chlorine (Cl)	1260
argon (Ar)	1520

Table 10.6 The first ionisation energy ($X(g) \longrightarrow X^+(g) + e^-$) of Period 3 elements in kilojoules per mole ($kJ\,mol^{-1}$).

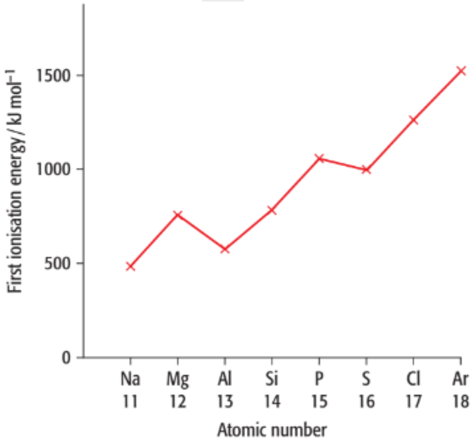


Figure 10.7 Plotting the first ionisation energy ($X(g) \longrightarrow X^+(g) + e^-$) against atomic number for the elements in Period 3.

Periodicity of chemical properties

We will now look at the chemistry of some of the elements of Period 3 and their compounds, focusing on the oxides and chlorides.

Reactions of Period 3 elements with chlorine

When sodium metal is heated then plunged into a gas jar of chlorine, there is a vigorous reaction, forming sodium chloride:

$$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$$

Magnesium and aluminium also react vigorously with chlorine gas:

$$Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$$

$$2Al(s) + 3Cl_2(g) \longrightarrow Al_2Cl_6(s)$$

Silicon reacts slowly with chlorine, as it does with oxygen, giving silicon(IV) chloride:

$$Si(s) + 2Cl_2(g) \longrightarrow SiCl_4(l)$$

Phosphorus also reacts slowly with excess chlorine gas:

$$2P(s) + 5Cl_2(g) \longrightarrow 2PCl_5(l)$$

Sulfur does form chlorides, such as SCl_2 and S_2Cl_2, but you do not need to cover these for your examination. Argon does not form a chloride.

Oxides of Period 3 elements

Oxidation numbers of oxides

Table 10.7 displays common oxide formulas of Period 3 elements. As we cross the period, the maximum oxidation number increases due to oxygen bonding, resulting in positive oxidation states.

Magnesium oxide and magnesium hydroxide are commonly used in indigestion remedies (Figure 10.11).

These basic compounds neutralise excess acid in the stomach, relieving the pain:

$$MgO(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2O(l)$$

$$Mg(OH)_2(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + 2H_2O(l)$$

Period 3 element	sodium (Na)	magnesium (Mg)	aluminium (Al)	silicon (Si)	phosphorus (P)	sulfur (S)	chlorine (Cl)	argon (Ar)
Formula of oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_2, SO_3	Cl_2O_7	–
Oxidation number of Period 3 element	+1	+2	+3	+4	+5	+4, +6	+7	–

Table 10.7 Oxidation numbers of the Period 3 elements in some common oxides. Chlorine has other oxides, such as Cl_2O, in which its oxidation number is +1, and Cl_2O_5, in which its oxidation number is +5.

Aluminium oxide does not react or dissolve in water, which is why an oxide layer can protect aluminium metal from corrosion. However, it does react and dissolve when added to acidic or alkaline solutions.

- With acid:

$$Al_2O_3(s) + 3H_2SO_4(aq) \longrightarrow Al_2(SO_4)_3(aq) + 3H_2O(l)$$

- With hot, concentrated alkali:

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \longrightarrow 2NaAl(OH)_4(aq)$$

Compounds that can act as both acids and bases, such as aluminium oxide, are called **amphoteric**.

However, it will react with and dissolve in hot, concentrated alkali:

$$SiO_2(s) + 2NaOH(aq) \longrightarrow Na_2SiO_3(aq) + H_2O(l)$$

Silicon dioxide acts as an acid when it reacts with sodium hydroxide, forming a salt (sodium silicate) plus water. It does not react with acids, so it is classed as an acidic oxide.

Phosphorus(V) oxide reacts vigorously and dissolves in water to form an acidic solution of phosphoric(V) acid (pH 2):

$$P_4O_{10}(s) + 6H_2O(l) \longrightarrow \underset{\text{phosphoric(V) acid}}{4H_3PO_4(aq)}$$

The oxides of sulfur, SO_2 and SO_3, both react and dissolve in water forming acidic solutions (pH 1):

$$SO_2(g) + H_2O(l) \longrightarrow \underset{\text{sulfurous acid (sulfuric(IV) acid)}}{H_2SO_3(aq)}$$

$$SO_3(g) + H_2O(l) \longrightarrow \underset{\text{sulfuric(VI) acid}}{H_2SO_4(aq)}$$

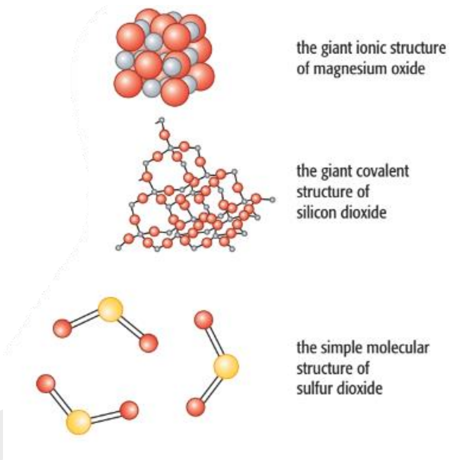


Figure 10.12 The structures of some Period 3 oxides.

Summary of the acidic/basic nature of the Period 3 oxides

Table 10.8 provides an overview of Period 3 oxides' acidic/basic nature. The oxides' behavior is explained by their structure and bonding. As the elements become more electronegative, electrons are attracted more strongly by positive nuclear charge. Oxygen's electronegativity is 3.5, indicating ionic bonding and electron transfer.

Period 3 oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_2, SO_3
Acid/base nature	basic	basic	amphoteric	acidic	acidic	acidic

Table 10.8 The acid/base nature of the Period 3 oxides.

Period 3 oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_2, SO_3
Relative melting point	high	high	very high	very high	low	low
Electrical conductivity when in liquid state	good	good	good	none	none	none
Chemical bonding	ionic	ionic	ionic (with a degree of covalent character)	covalent	covalent	covalent
Structure	giant ionic	giant ionic	giant ionic	giant covalent	simple molecular	simple molecular

Table 10.9 Some properties, chemical bonding and structure of some Period 3 oxides.

Period 3 element	sodium (Na)	magnesium (Mg)	aluminium (Al)	silicon (Si)	phosphorus (P)	sulfur (S)	chlorine (Cl)	argon (Ar)
Electronegativity	0.9	1.2	1.5	1.8	2.1	2.5	3.0	–

Table 10.10 Electronegativity values for Period 3 oxides (no data are available for argon).

Notice the high melting points of the giant ionic and giant covalent structures, leading to the use of:

- ■ Magnesium oxide to line the inside of furnaces
- ■ Aluminium oxide and silicon dioxide to make ceramics, with giant covalent structures designed to withstand high temperatures and provide electrical insulation.

The oxide ions behave as bases by accepting H+ ions from water molecules:

$$O^{2-}(aq) + H_2O(l) \longrightarrow 2OH^-(aq)$$

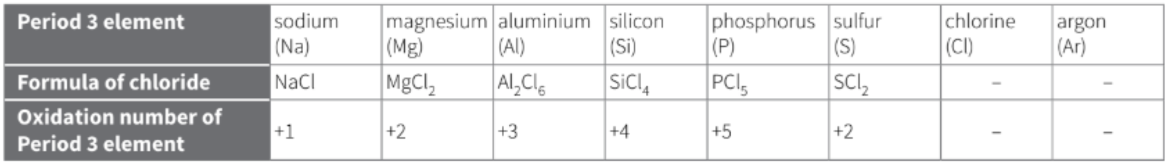
By contrast, the covalently bonded non-metal oxides of phosphorus and sulfur dissolve and react in water to form acidic solutions. The acid molecules formed donate H+ ions to water molecules, behaving as typical acids.

The insoluble oxides of aluminium and silicon exhibit acidic nature by reacting and dissolving in alkaline solutions, forming a soluble salt, while aluminium oxide exhibits ionic bonding, indicating its amphoteric nature due to its dual nature.

Chlorides of Period 3 elements

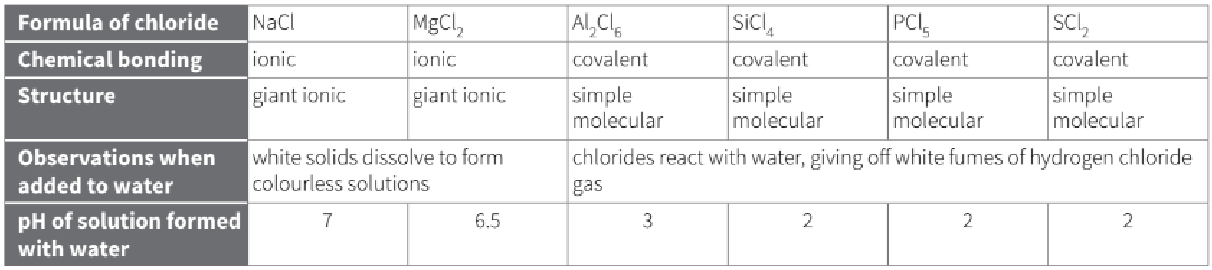
Oxidation numbers of the Period 3 elements in their chlorides

Table 10.11 outlines the formulas of common chlorides of Period 3 elements, showing that oxidation numbers increase as we cross Period 3, reaching sulfur in Group 16. This is due to chlorine's higher electrongativity.



Period 3 element	sodium (Na)	magnesium (Mg)	aluminium (Al)	silicon (Si)	phosphorus (P)	sulfur (S)	chlorine (Cl)	argon (Ar)
Formula of chloride	NaCl	$MgCl_2$	Al_2Cl_6	$SiCl_4$	PCl_5	SCl_2	–	–
Oxidation number of Period 3 element	+1	+2	+3	+4	+5	+2	–	–

Table 10.11 Oxidation numbers of the Period 3 elements in their chlorides. Phosphorus also has a chloride with the formula PCl_3, in which its oxidation number is +3. Sulfur also has a chloride S_2Cl_2, in which its oxidation number is +1.



Formula of chloride	NaCl	$MgCl_2$	Al_2Cl_6	$SiCl_4$	PCl_5	SCl_2
Chemical bonding	ionic	ionic	covalent	covalent	covalent	covalent
Structure	giant ionic	giant ionic	simple molecular	simple molecular	simple molecular	simple molecular
Observations when added to water	white solids dissolve to form colourless solutions		chlorides react with water, giving off white fumes of hydrogen chloride gas			
pH of solution formed with water	7	6.5	3	2	2	2

Table 10.12 The structure and bonding of the chlorides of Period 3 elements and the effect of water on these chlorides.

Revision questions

1. (a) A fixed mass of marble is reacted with dilute hydrochloric acid at a constant temperature. Explain why the rate of the reaction is increased if the lumps of marble are reduced in size.

(b) The initial rate of the reaction between substances **A** and **B** was measured in a series of experiments and the following rate equation was deduced.

rate = $k[\mathbf{A}][\mathbf{B}]^2$

(i) Complete the table of data below for the reaction between **A** and **B**.

Expt	Initial [**A**] /mol dm^{-3}	Initial [**B**] /mol dm^{-3}	Initial rate /mol dm^{-3} s^{-1}
1	0.020	0.020	1.2×10^{-4}
2	0.040	0.040	
3		0.040	2.4×10^{-4}
4	0.060	0.030	
5	0.040		7.2×10^{-4}

(ii) Using the data for Experiment 1, calculate a value for the rate constant, k and state its units.

2. (a) The initial rate of reaction between ester A and aqueous sodium hydroxide was measured in a series of experiments at a constant temperature. The data obtained are shown below.

Experiment	Initial concentration of NaOH / mol dm^{-3}	Initial concentration of **A** / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.040	0.030	4.0×10^{-4}
2	0.040	0.045	6.0×10^{-4}
3	0.060	0.045	9.0×10^{-4}
4	0.120	0.060	to be calculated

Use the data in the table to deduce the order of reaction with respect to A and the order of reaction with respect to NaOH. Hence calculate the initial rate of reaction in Experiment 4.

(b) In a further experiment at a different temperature, the initial rate of reaction was found to be 9.0×10^{-3} mol dm^{-3} s^{-1} when the initial concentration of **A** was 0.020 mol dm^{-3} and the initial concentration of NaOH was 2.00 mol dm^{-3}.
Under these new conditions with the much higher concentration of sodium hydroxide, the reaction is first order with respect to **A** and appears to be zero order with respect to sodium hydroxide.

(i) Write a rate equation for the reaction under these new conditions.
(ii) Calculate a value for the rate constant under these new conditions and state its units.
(iii) Suggest why the order of reaction with respect to sodium hydroxide appears to be zero under these new conditions.

3. The rate of the reaction between substance A and substance B was studied in a series of experiments carried out at the same temperature. In each experiment the initial rate was measured using different concentrations of A and B. These results were used to deduce the order of reaction with respect to A and the order of reaction with respect to B.

(a) What is meant by the term order of reaction with respect to A?

(b) When the concentrations of A and B were both doubled, the initial rate increased by a factor of 4. Deduce the overall order of the reaction.

c) In another experiment, the concentration of A was increased by a factor of three and the concentration of B was halved. This caused the initial rate to increase by a factor of nine.

(i) Deduce the order of reaction with respect to A and the order with respect to B.
(ii) Using your answers from part (c)(i), write a rate equation for the reaction and suggest suitable units for the rate constant.

4. The rate equation for a reaction between substances A, B and C is of the form:

$$\text{rate} = k[A]^x[B]^y[C]^z \text{ where } x + y + z = 4$$

The following data were obtained in a series of experiments at a constant temperature.

Experiment	Initial concentration of **A**/mol dm^{-3}	Initial concentration of **B**/mol dm^{-3}	Initial concentration of **C**/mol dm^{-3}	Initial rate/ mol dm^{-3} s^{-1}
1	0.10	0.20	0.20	8.0×10^{-5}
2	0.10	0.05	0.20	2.0×10^{-5}
3	0.05	0.10	0.20	2.0×10^{-5}
4	0.10	0.10	0.10	to be calculated

(a) Use the data in the table to deduce the order of reaction with respect to A and the order of reaction with respect to B. Hence deduce the order of reaction with respect to C.

(b) Calculate the value of the rate constant, k, stating its units and also the value of the initial rate in experiment 4.

(c) How does the value of k change when the temperature of the reaction is increased?

5. (a) A large excess of zinc was added to 100cm^3 of 0.2 M hydrochloric acid. After the reaction had ended, 240 cm3 of hydrogen had been formed. In three further experiments, extra substances were added to the original mixture as shown in the table below. Fill in the table to show the total volume of hydrogen formed in each experiment and the qualitative effect of these additions on the initial rate of reaction compared to the original experiment

Substances **added** to an excess of zinc and 100 cm^3 of 0.2 M hydrochloric acid	Volume of hydrogen/cm^3	Effect on initial rate of reaction
100cm^3 water		
10g zinc		
50 cm^3 0.2 M hydrochloric acid		

(b) The rate of reaction between compounds A and B was studied at a fixed temperature and some results obtained are shown in the table below.

Experiment	Initial concentration of **A**/mol dm^{-3}	Initial concentration of **B**/mol dm^{-3}	Initial rate/ mol dm^{-3} s^{-1}
1	0.16	0.20	5.0×10^{-5}
2	0.24	0.20	7.5×10^{-5}
3	0.32	0.10	5.0×10^{-5}
4	0.12	0.15	to be calculated

Use the data in the table to deduce the order of reaction with respect to compound A and the order of reaction with respect to compound B. Hence calculate the initial rate of reaction in experiment 4.

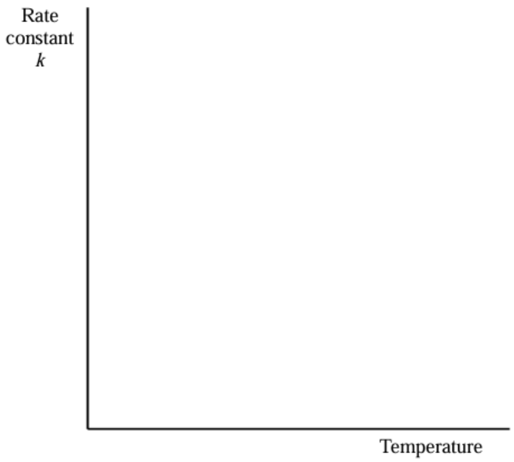
(c) The rate equation for a reaction between substances C and D is:

$$\text{rate} = k[\mathbf{C}]^2\,[\mathbf{D}]^2$$

The initial rate is found to be 7.5×10^{-3} mol dm^{-3} s^{-1} when the initial concentration of **C** is of 0.25 mol dm^{-3} and the initial concentration of **D** is 0.50 mol dm^{-3}.

(i) Calculate the value of the rate constant, k, at this temperature and deduce its units.

(ii) On the axes below sketch a graph to show how the value of k varies as temperature is increased over a considerable range.



6) Write balanced equations to show the reaction of water with:
(i) sodium
(ii) sodium oxide.

7) Write equations for the reactions of phosphorus(V) oxide and sulphur dioxide with water. In each case predict the approximate pH of a 1M aqueous solution of the product.

8) Apart from argon, the Period 3 elements all form oxides.
(i) Write an equation to represent the reaction of aluminium with oxygen.
(ii) The reaction in (b)(i) occurs very readily. Suggest why aluminium saucepans can be safely heated on a gas cooker.
(iii) Complete the following table to show information about Period 3 oxides.

	Sodium oxide	Silicon dioxide	Phosphorus(V) oxide	Sulphur dioxide
Physical state at room temperature				
Type of bonding present				

(iv) Write an equation for the reaction of sodium oxide with water.
(v) Write an equation for the reaction of sulphur dioxide with water.
(vi) Samples of silicon dioxide and phosphorus(V) oxide are added to separate samples of pure water and each mixture is stirred. State the approximate pH value of each sample after the stirring.

9) (a) Explain, with reference to the bonding in sodium oxide, why this compound reacts with water to form a solution with a pH of 14.

(b) What general type of oxide forms acidic solutions in water? Give the formula of one such oxide.

10) Describe the trend in pH of the solutions formed when the oxides of the Period 3 elements, sodium to sulphur, are added separately to water. Explain this trend by reference to the structure and bonding in the oxides and by writing equations for the reactions with water.

11) (a)The following data were obtained in a series of experiments on the rate of the reaction between compounds A and B at a constant temperature.

Experiment	Initial concentration of **A**/mol dm^{-3}	Initial concentration of **B**/mol dm^{-3}	Initial rate/mol dm^{-3} s^{-1}
1	0.12	0.15	0.32×10^{-3}
2	0.36	0.15	2.88×10^{-3}
3	0.72	0.30	11.52×10^{-3}

(i) Deduce the order of reaction with respect to A.
(ii) Deduce the order of reaction with respect to B.

(b) The following data were obtained in a series of experiments on the rate of the reaction between NO and O_2 at a constant temperature.

Experiment	Initial concentration of NO/mol dm^{-3}	Initial concentration of O_2/mol dm^{-3}	Initial rate/mol dm^{-3} s^{-1}
4	5.0×10^{-2}	2.0×10^{-2}	6.5×10^{-4}
5	6.5×10^{-2}	3.4×10^{-2}	To be calculated

The rate equation for this reaction is

$$rate = k[\mathrm{NO}]^2[\mathrm{O_2}]$$

(i) Use the data from experiment 4 to calculate a value for the rate constant, k, at this temperature, and state its units.
(ii) Calculate a value for the initial rate in experiment 5.

12) (a) The initial rate of the reaction between substances P and Q was measured in a series of experiments and the following rate equation was deduced.

$$\mathrm{rate} = k[\mathbf{P}]^2[\mathbf{Q}]$$

(i) Complete the table of data below for the reaction between P and Q.

Experiment	Initial [**P**] / mol dm^{-3}	Initial [**Q**] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.20	0.30	4.8×10^{-3}
2	0.10	0.10	
3	0.40		9.6×10^{-3}
4		0.60	19.2×10^{-3}

(ii) Using the data from experiment 1, calculate a value for the rate constant, k, and deduce its units.
(b) What change in the reaction conditions would cause the value of the rate constant to change?

12) (a) The following data were obtained in a series of experiments on the rate of the reaction between compounds A and B at a constant temperature.

Experiment	Initial concentration of **A**/mol dm^{-3}	Initial concentration of **B**/mol dm^{-3}	Initial rate/mol dm^{-3} s^{-1}
1	0.15	0.24	0.45×10^{-5}
2	0.30	0.24	0.90×10^{-5}
3	0.60	0.48	7.20×10^{-5}

(i) Show how the data in the table can be used to deduce that the reaction is first order with respect to A.

(ii) Deduce the order with respect to B.

(b) The following data were obtained in a second series of experiments on the rate of the reaction between compounds C and D at a constant temperature.

Experiment	Initial concentration of **A**/mol dm^{-3}	Initial concentration of **B**/mol dm^{-3}	Initial rate/mol dm^{-3} s^{-1}
4	0.75	1.50	9.30×10^{-5}
5	0.20	0.10	To be calculated

The rate equation for this reaction is

$$\text{rate} = k[\mathbf{C}]^2[\mathbf{D}]$$

(i) Use the data from Experiment 4 to calculate a value for the rate constant, k, at this temperature. State the units of k.

(ii) Calculate the value of the initial rate in Experiment 5.

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