

- A1. Which variable relating to the hydrolysis reaction of methyl ethanoate needs to be controlled?
- A2. What equipment should be used to remove the sample of reaction mixture for titration? Explain your answer.
- A3. Suggest a suitable alkali for titrating the samples of reaction mixture.
- A4. Plot a graph of ester concentration against time.
- A5 a. By drawing tangents to the curve, calculate the rate of reaction at these ester concentrations (mol dm^{-3}):
- 0.200
 - 0.125
 - 0.100
- b. Plot a graph of rate of hydrolysis against ester concentration against time. What does this tell you about the order of reaction?
- c. Calculate the gradient of the line of best fit. This gives the rate constant k for the hydrolysis of methyl ethanoate.

Second-order reactions

The rate equation where the reaction is second order for a given reactant is:

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

where A is a given reactant.

Second-order reactions are relatively common. Examples include dimerisation reactions, where two monomers add together to form a dimer, and the decomposition of nitrogen dioxide to give nitrogen monoxide and oxygen:



Second-order reactions can also be identified by:

- Measuring the concentration of reactant over time
- Plotting this data
- Calculating the rate of reaction at given concentrations
- Plotting rate against concentration.

The patterns shown in Figure 26.6 will be seen for any second-order reaction.

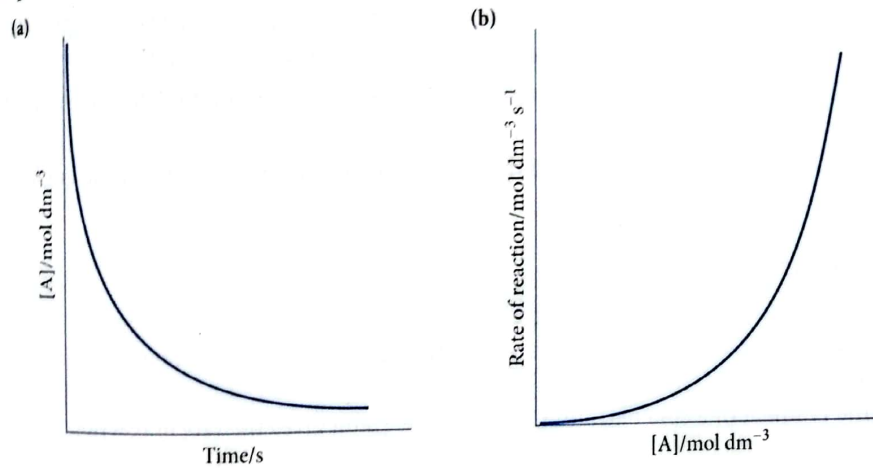


Figure 26.6 (a) The pattern for concentration against time for a second-order reaction. (b) The pattern for rate against concentration.

You cannot assume that, just because a curve is produced when rate is plotted against concentration, the reaction is indeed second order. You can only be certain it is *not* zero or first order (Table 26.3). To determine whether the curve is second order, you could plot a further graph of rate against $[A]^2$. In this case a straight line is produced for a second-order reaction.

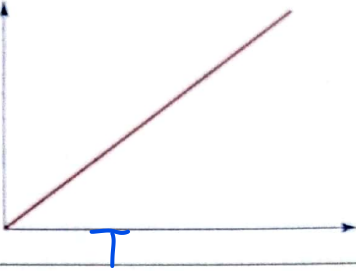
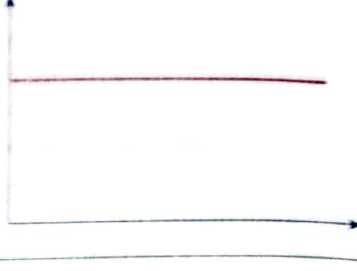
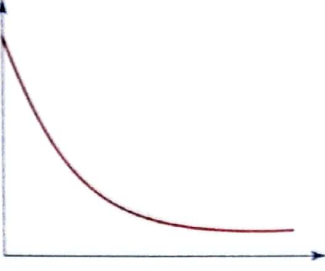
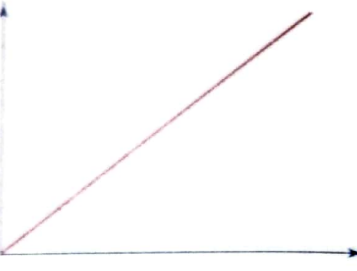
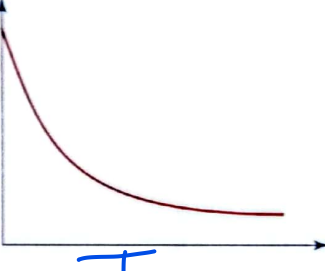
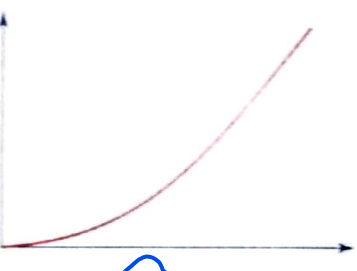
Order of reaction	Concentration against time graph	Rate against concentration graph
zero		
first		
second		

Table 26.3 These sketches summarise the expected patterns for different orders of reaction for different graphs.

3. Which statement is true?

- A For a first-order reaction, a graph of concentration against time is a straight line.
- B The gradient of a concentration-time gradient is always constant.
- C There is no need to draw a rate against concentration graph to determine a second-order reaction.
- D The gradient of the tangent to the curve of a concentration against time graph gives the rate of reaction.

Key ideas

- An order of reaction can be determined by monitoring the concentration of a reactant over time. Plot a graph of concentration against time and then rate against concentration.
- The gradient of a concentration against time graph gives the rate of reaction.

FINDING ORDERS OF REACTIONS USING THE HALF-LIFE METHOD

It is difficult to tell apart the curves of concentration against time for first-order and second-order reactions. However, we can use the half-life to prove that a reaction is first order. The half-life is the time it takes for the concentration of a substance to fall by half. In all first-order reactions the half-life is always constant, irrespective of the starting concentration.