4.1.1 Measured orders, rate constants and half-lives

Name: _____ Class: _____ Date: _____ **Total: 16 marks**

KEY WORDS rate equation

Objective

Infer a rate equation from controlled data and test a proposed order. Questions and marking guidance are original.

1 Key knowledge and worked examples

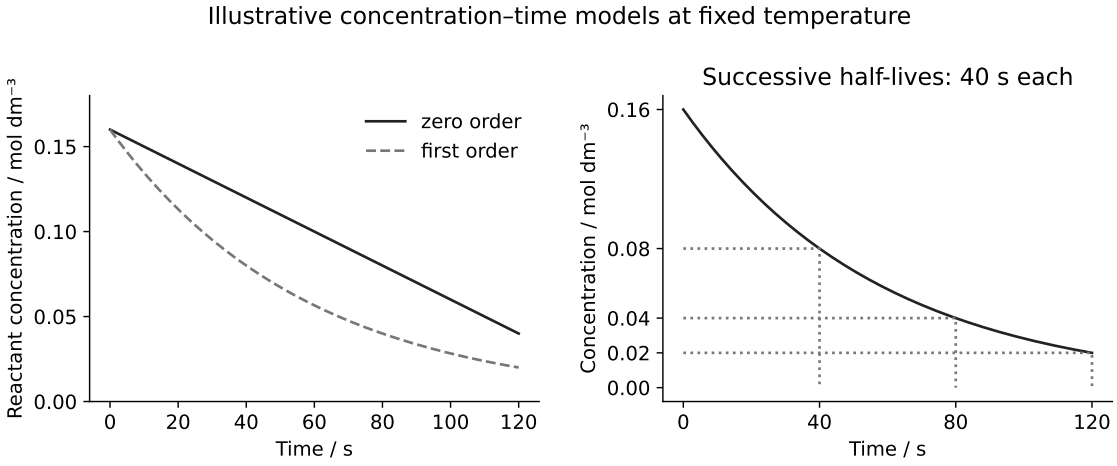
Rate is a concentration change per time. In $r = k[A]^m[B]^n$, the measured powers are orders; they need not equal equation coefficients. Change one concentration while holding the others constant. Overall order is $m + n$.

■ Worked method

Doubling [A] with fixed [B] doubles the rate, so $m = 1$. Doubling [B] with fixed [A] quadruples it, so $n = 2$. If rate is 0.00800 mol dm^{-3} s^{-1} at [A] = 0.100 and [B] = 0.200 mol dm^{-3}:

$$k = \frac{r}{[A][B]^2} = \frac{0.00800}{0.100(0.200)^2} = 2.00\ \mathrm{dm^6\,mol^{-2}\,s^{-1}}$$

An approximately constant half-life supports first-order decay under fixed conditions. A straight concentration–time line supports zero order. Use successive halvings from the same trace; a single half-life cannot distinguish every model. A concentration–time tangent gives instantaneous rate, whereas a chord gives an average.



2 Practice

2.1 At fixed [B], doubling [A] leaves rate unchanged. State the order in A and what happens when [A] is tripled. [2]

2.2 For $r = k[A]^2$, rate is 0.0120 mol dm^{-3} s^{-1} at [A] = 0.200 mol dm^{-3}. Calculate k with units. [3]

2.3 A reactant falls from 0.160 to 0.080 to 0.040 to 0.020 mol dm^{-3} at 0, 40, 80 and 120 s. State the half-life and supported order. [2]

3 Exam-style questions

3.1 Three trials have ([A], [B], rate): (0.10, 0.10, 0.0020), (0.20, 0.10, 0.0080), (0.20, 0.30, 0.0240), in mol dm^{-3} and mol dm^{-3} s^{-1}. Find the rate equation, overall order and k with units. [6]

3.2 A student uses the slope from 0 to 60 s as the rate at 60 s on a curved concentration–time trace. Explain the error and the correct graphical method. Explain why 1/time can be a rate proxy only in a controlled endpoint method. [3]

Solutions

Original marking guidance: M1 method, A1 accuracy, B1 explanation.

2.1 Zero order; rate remains unchanged at fixed other conditions.

2.2 $k = r/[A]^2 = 0.0120/(0.200)^2 = 0.300$ dm^3 mol^{-1} s^{-1}.

2.3 40 s; first order under the stated fixed conditions, because successive half-lives are constant.

3.1 First pair: doubling A quadruples rate, order 2. Last pair: tripling B triples rate, order 1. $r = k[A]^2[B]$, overall order 3. $k = 0.0020/(0.10^2 \times 0.10) = 2.0$ dm^6 mol^{-2} s^{-1}.

3.2 The chord gives an interval average; a tangent at 60 s gives instantaneous concentration gradient, and the positive disappearance rate is the negative of that gradient. Reciprocal time compares rates only when the same small conversion/endpoint and relevant conditions are controlled.