

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 $m + n$.

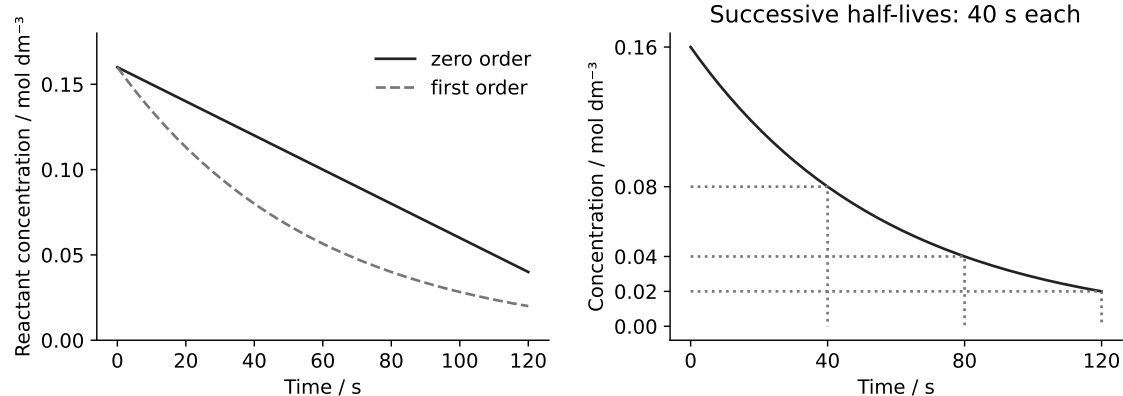
■ Worked method

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

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

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.

Illustrative concentration–time models at fixed temperature



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 $0.0120 \text{ mol dm}^{-3} \text{ s}^{-1}$ at $[A] = 0.200 \text{ mol dm}^{-3}$. Calculate k with units. [3]

2.3 A reactant falls from 0.160 to 0.080 to 0.040 to $0.020 \text{ mol dm}^{-3}$ 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 $\text{mol dm}^{-3} \text{ s}^{-1}$. 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 $1/\text{time}$ 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 $k = r/[A]^2 = 0.0120/(0.200)^2 = 0.300 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

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. $k = 0.0020/(0.10^2 \times 0.10) = 2.0 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$.

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.