InkChemistry

ANSWER BOOK

Rate equations, orders of reaction and the rate constant

Rate equations · Unit C09

AQA 3.1.9.1 · OCR A 5.1.1

18 questions · 62 marks

NAVY EDITION

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SECTION A · Short, 1 to 2 marks

A1 REO-Q4

M1 the rate is multiplied by 2 for X and by $3^2 = 9$ for Y, a factor of $2 \times 9 = 18$; reject adding the factors, 2 + 9. **A1** new rate = $18 \times 2.0 \times 10^{-5} = 3.6 \times 10^{-4}$ mol dm^{-3} s^{-1}, to two significant figures. [2]

SECTION B · Standard, 3 to 5 marks

B1 REO-Q1

B1 the order with respect to a reactant is the power to which its concentration is raised in the rate equation. **B1** the overall order is the sum of the powers of all the concentration terms in the rate equation. **B1** first order overall: s^{-1}, since (mol dm^{-3} s^{-1}) ÷ (mol dm^{-3}) leaves s^{-1}. **B1** second order overall: mol^{-1} dm^3 s^{-1}; accept the units in any order, such as dm^3 mol^{-1} s^{-1}. [4]

B2 REO-Q6

M1 k = rate ÷ ([A][B]) = $4.5 \times 10^{-5} \div (0.040 \times 0.025) = 4.5 \times 10^{-5} \div 1.0 \times 10^{-3}$. **A1** k = 0.045 mol^{-1} dm^3 s^{-1}, to two significant figures. **M1** dilution halves both concentrations, so the rate is multiplied by $0.5 \times 0.5 = 0.25$. **A1** new rate = $0.25 \times 4.5 \times 10^{-5} = 1.1 \times 10^{-5}$ mol dm^{-3} s^{-1}, to two significant figures. [4]

B3 REO-Q8

B1 the zero-order reactant does not take part in the rate-determining step or in any step before it. **B1** it reacts in a fast step after the slow step, so the rate is limited by the slow step whatever its concentration. **B1** for a first-order reactant the rate is k multiplied by the concentration, so a higher concentration gives a proportionally higher rate. **B1** k is fixed at a given temperature and changes only with temperature or a catalyst; reject 'k increases with concentration'. [4]

B4 REO-Q12

B1 for rate = k[A], rate against [A] is a straight line through the origin. **B1** the gradient of that line is k. **B1** for rate = $k[A]^2$, rate against [A] is a curve with no single gradient to measure. **B1** rate against $[A]^2$ has the form y = mx, a straight line through the origin whose gradient is k. [4]

B5 REO-Q15

B1 rate against concentration: a straight line through the origin for first order, but a curve rising ever more steeply from the origin for second order. **B1** doubling the concentration doubles the rate for first order but multiplies it by four for second order. **B1** concentration against time: both are curves that fall steeply then level off, but the second-order curve has the longer tail, because its rate falls with the square of the concentration. **B1** the half-life is constant for first order, whereas each half-life is double the previous one for second order. [4]

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B6 REO-Q16 [4]

B1 for this reaction the orders do equal the coefficients, 2 for NO and 1 for O_2. **B1** but that agreement was found by experiment and could not have been predicted from the equation. **B1** a counter-example is $2N_2O_5 \rightarrow 4NO_2 + O_2$, which is first order although the coefficient of N_2O_5 is 2. **B1** so the claim is wrong: one case of agreement is a coincidence of mechanism, and orders must always be measured.

B7 REO-Q3 [3]

M1 $k = \text{rate} \div ([A]^2[B]) = 3.6 \times 10^{-4} \div (0.030^2 \times 0.020) = 3.6 \times 10^{-4} \div 1.8 \times 10^{-5}$. **M1** units: $(\text{mol dm}^{-3}\ \text{s}^{-1}) \div (\text{mol dm}^{-3})^3$ leaves two lots of mol dm^{-3} underneath. **A1** $k = 20\ \text{mol}^{-2}\ \text{dm}^6\ \text{s}^{-1}$, to two significant figures.

B8 REO-Q5 [3]

M1 halving the volume doubles the concentration of both gases. **M1** the rate is multiplied by 2^2 for NO and by 2 for O_2, a factor of 8. **A1** new rate $= 8 \times 1.5 \times 10^{-3} = 1.2 \times 10^{-2}\ \text{mol dm}^{-3}\ \text{s}^{-1}$, to two significant figures.

B9 REO-Q7 [3]

B1 the balanced equation shows only the overall amounts of each substance that react, not how the reaction happens. **B1** most reactions take place in a series of steps, and the rate depends on the slowest step and the steps before it. **B1** the particles in those steps need not match the coefficients, so the orders must be found by experiment.

B10 REO-Q9 [3]

B1 read the time for the concentration to fall to half, then to a quarter, then to an eighth of its starting value. **B1** for a first-order reactant these successive half-lives are equal. **B1** because the rate is proportional to the concentration, so halving any concentration takes the same time.

B11 REO-Q10 [3]

B1 I^- is first order in the rate equation, so tripling $[I^-]$ triples the rate: a factor of 3. **B1** the student squared the factor because I^- has a coefficient of 2 in the balanced equation. **B1** orders come from the rate equation, found by experiment, not from the coefficients; the second I^- reacts in a step after the slow one.

B12 REO-Q11 [3]

B1 (a) first order, since $2^1 = 2$. **B1** (b) second order, since $3^2 = 9$. **B1** (c) zero order, since the rate does not depend on [A].

B13 REO-Q13 [3]

B1 the reaction happens only on the surface of the tungsten, which has a fixed number of sites. **B1** at high pressure every site is occupied, so extra ammonia cannot react any faster and the rate does not depend on its concentration. **B1** at very low pressure most sites are empty, so the rate is proportional to how often ammonia molecules reach them, which is proportional to the concentration.

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B14 REO-Q14 **B1** H^+ is a catalyst: it is used in one step and regenerated in a later one, so it cancels from the overall equation. **B1** it takes part in the rate-determining step or a step before it, so its concentration affects the rate. **B1** iodine reacts only in a fast step after the rate-determining step, so it is zero order. [3]

B15 REO-Q17 **B1** raising the temperature increases k, because a larger fraction of collisions have at least the activation energy. **B1** a catalyst increases k, because it provides an alternative route with a lower activation energy. **B1** the rate rises in both cases although every concentration is unchanged, so the change must be in k. [3]

B16 REO-Q19 **M1** the mole ratio $N_2O_5 : NO_2 : O_2$ is 2 : 4 : 1, so NO_2 forms at twice the rate N_2O_5 is used and O_2 at half that rate. **A1** rate of formation of $NO_2 = 2 \times 4.0 \times 10^{-6} = 8.0 \times 10^{-6}$ mol dm^{-3} s^{-1}. **A1** rate of formation of $O_2 = 0.5 \times 4.0 \times 10^{-6} = 2.0 \times 10^{-6}$ mol dm^{-3} s^{-1}, to two significant figures. [3]

SECTION C · Long, 6 marks or more

C1 REO-Q18 **Indicative content** [6]

B1 zero order: rate against concentration is a horizontal line, because the rate does not depend on the concentration. **B1** zero order: concentration against time is a straight line with a constant negative gradient, because the reactant is used at a steady rate. **B1** first order: rate against concentration is a straight line through the origin with a gradient of k. **B1** first order: concentration against time is a curve with a constant half-life, because the rate falls in proportion to the concentration. **B1** second order: rate against concentration is a curve rising ever more steeply from the origin, rate proportional to concentration squared. **B1** second order: concentration against time is a curve whose half-lives double in turn, because the rate falls with the square of the concentration.

Levels

Level 3 (5–6 marks) all six graphs are described correctly and the shape of each concentration–time graph is explained from how the rate changes with concentration, including the constant half-life of first order and the lengthening half-lives of second order.

Level 2 (3–4 marks) the three rate–concentration graphs are right and two concentration–time graphs are explained; the third is not, or half-lives are never used.

Level 1 (1–2 marks) one or two graphs are described, often with the first-order concentration–time graph drawn as a straight line falling to zero.

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