InkChemistry

ANSWER BOOK

Finding orders from initial rates, half-lives and graphs

Rate equations · Unit C09

AQA 3.1.9.2, RP7 · OCR A 5.1.1 (b) to (e); PAG 9, PAG 10

14 questions · 42 marks

NAVY EDITION

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SECTION A · Short, 1 to 2 marks

A1 FOI-Q8

B1 sodium hydrogencarbonate neutralises the H^+ catalyst, which stops the reaction in the sample. **B1** so the titre gives the iodine concentration at the moment the sample was taken, not some time later. [2]

A2 FOI-Q12

B1 the rate constant depends on temperature, so a warmer afternoon gives a larger k. **B1** carry out every run in a thermostatted water bath at the same temperature and check it with a thermometer. [2]

A3 FOI-Q17

B1 colorimetry, measuring the absorbance of a coloured reactant or product. **B1** gas collection in a syringe, measuring the volume of gas produced; or titration of quenched samples, or mass loss on a balance, or pH. [2]

A4 FOI-Q19

B1 measure the electrical conductivity, or the pH, of the mixture at regular time intervals. **B1** the reaction makes H^+ and Cl^- ions from neutral molecules, so the conductivity rises, or the pH falls, as the reaction proceeds. [2]

SECTION B · Standard, 3 to 5 marks

B1 FOI-Q14

B1 the colorimeter gives many readings without disturbing the mixture, whereas titration removes samples and gives only a few points. **B1** the colorimeter reading is almost instant, whereas each titration sample must be quenched and any delay adds a timing error. **B1** titration needs no calibration, whereas the colorimeter needs a calibration graph to turn absorbance into concentration. **B1** titration end points are judged by eye with starch, whereas the colorimeter gives an objective reading. [4]

B2 FOI-Q2

M1 $k = \ln 2 \div t_{½} = 0.693 \div 34$. **A1** $k = 0.020\ s^{-1}$, to two significant figures. **A1** one eighth is three half-lives, $3 \times 34 = 102$ s, so 1.0×10^2 s to two significant figures. [3]

B3 FOI-Q6

B1 the colour appears when a fixed amount of product has formed, the same amount in every run. **B1** rate is amount formed ÷ time, so with a fixed amount the rate is proportional to 1/t. **B1** the amount is small, so little reactant has been used and the rate over that time is close to the initial rate. [3]

B4 FOI-Q7

B1 with both in large excess their concentrations hardly change during the run. **B1** the only concentration that changes is that of iodine, which is the coloured species the colorimeter measures. **B1** so any change in rate during the run is due to iodine alone, and the graph shows the order with respect to iodine. [3]

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B5 FOI-Q9 **B1** an equal fall in every minute is a constant rate (a straight line of constant gradient on a concentration–time graph), so the rate is the same throughout the run. **B1** the iodine concentration falls during the run while the rate stays constant. **B1** so the rate does not depend on the iodine concentration, which is zero order. [3]

B6 FOI-Q11 **B1** collect the oxygen in a gas syringe and record its volume at regular time intervals. **B1** the volume still to be released is proportional to the hydrogen peroxide remaining, so a graph of it against time is a concentration–time graph. **B1** read successive half-lives from the graph: if they are constant, the reaction is first order in hydrogen peroxide. [3]

B7 FOI-Q13 **B1** the change in rate is the product of the effects of both changes, so it cannot be split between A and B. **B1** a factor of 4, for example, could be second order in one and zero in the other, or first order in each. **B1** a further run changing only one of the two concentrations, the other kept as in the first run, separates the two effects. [3]

B8 FOI-Q18 **M1** iodine is zero order and the excess reactants hardly change, so the measured rate equals $k[CH_3COCH_3][H^+]$ throughout the run. **M1** $k = 2.5 \times 10^{-5} \div (1.00 \times 0.500)$, with units $(\text{mol dm}^{-3}\ \text{s}^{-1}) \div (\text{mol dm}^{-3})^2$. **A1** $k = 5.0 \times 10^{-5}\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$, to two significant figures. [3]

B9 FOI-Q20 **B1** with B in large excess, [B] hardly changes while all of A is used up. **B1** so $k[B]$ is effectively constant and the rate equation behaves as rate = $k'[A]$, where $k' = k[B]$. **B1** the run is pseudo-first-order in A, so its half-life is constant, and only the order with respect to A has been found. [3]

SECTION C · Long, 6 marks or more

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C1 FOI-Q10 **Indicative content** [6]

B1 calibrate: measure the absorbance of iodine solutions of known concentration with a blue filter and plot a calibration graph. **B1** bring the propanone, acid and water mixture and the iodine solution to the same temperature in a water bath before mixing. **B1** mix, start the timer at the moment of mixing, and record the absorbance at regular intervals such as every 30 s. **B1** convert absorbance to iodine concentration, plot it against time and find the gradient, which is the rate. **B1** repeat with a different volume of propanone, made up with water to the same total volume so that the other concentrations and the temperature are unchanged. **B1** compare the factor on the propanone concentration with the factor on the rate: halving propanone halves the rate, so it is first order.

Levels

Level 3 (5–6 marks) the calibration graph, the temperature control before mixing, the timing and regular absorbance readings, the conversion to concentration and the rate from the gradient, and the repeat with a different propanone concentration at the same total volume are all present, with the order deduced from the factors on concentration and rate.

Level 2 (3–4 marks) the colorimeter follows the iodine concentration with time and the run is repeated with a different propanone concentration; the calibration, the constant concentrations of iodine and acid, or the step from rates to order is not there.

Level 1 (1–2 marks) the colorimeter is said to measure the colour of iodine; the propanone concentration is often changed along with the total volume, so two things vary at once.

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