# 2.4 Kinetics and Equilibria: Test Pack

AQA 7405 · Calculator allowed · about 70 minutes

Total Marks

Name: _____ Date: ____ / ____ / _____

**Answer ALL questions. Show all your working.**

**1** This question is about the collision theory model of reaction rates.

**(a)** State two conditions that must both be met for a collision between reactant particles to result in a successful (reactive) collision. **(2)**

**(b)** Use the Maxwell-Boltzmann distribution of molecular energies to explain why increasing the temperature of a reaction mixture increases the rate of reaction. You should refer to the effect on the shape of the distribution and on the number of particles with energy greater than or equal to the activation energy. **(4)**

**(c)** Define the term activation energy, Ea. **(1)**

**(Total for Question 1 is 7 marks)**


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**2** A student investigates the rate of the reaction between excess calcium carbonate (marble chips) and dilute hydrochloric acid:

$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$

The total volume of $CO_2$ gas produced is measured at regular time intervals using a gas syringe (continuous monitoring), and plotted as a graph of gas volume against time. The total volume of the reaction mixture (acid plus chips) is 50.0 $cm^3$. This question is based on the required practical activity on measuring reaction rates.

**(a)** Suggest two reasons why the calcium carbonate is used in excess in this experiment. **(2)**

**(b)** As the reaction proceeds, the gradient of the volume-time graph continually decreases, until it becomes zero. Explain, in terms of collision theory, why the rate of reaction decreases over time. **(2)**

**(c)** A tangent drawn to the volume-time graph at t = 0 has a gradient of 0.90 $cm^3$ $s^{-1}$. Given that the molar volume of a gas is 24000 $cm^3$ $mol^{-1}$ at room temperature and pressure, and that the total volume of the reaction mixture is 50.0 $cm^3$, calculate the initial rate of this reaction in mol $dm^{-3}$ $s^{-1}$. **(4)**

**(d)** In an alternative experiment to find the initial rate of a different, colourless-to-blue-black reaction, a small, fixed volume of sodium thiosulfate solution and starch indicator are added at the start to the reaction mixture, and the time, t, taken for the blue-black colour to appear is measured (an iodine clock reaction). Explain why 1/t is taken to be directly proportional to the initial rate of the reaction being studied. **(2)**

**(e)** State one variable, other than the concentrations being investigated, that must be kept constant between repeat experiments in this type of rate investigation, and explain why it must be controlled. **(2)**

**(Total for Question 2 is 12 marks)**


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**3** A catalytic converter in a car exhaust system uses a solid platinum/palladium catalyst to catalyse the following reaction between two exhaust gases:
$2CO(g) + 2NO(g) \rightarrow 2CO_2(g) + N_2(g)$

**(a)** Describe how the reaction profile (enthalpy against reaction progress) for this reaction would differ with the catalyst present compared with the profile without the catalyst, stating clearly what changes and what stays the same. **(2)**

**(b)** Using the Maxwell-Boltzmann distribution of molecular energies, explain why lowering the activation energy increases the rate of reaction at a fixed temperature. **(2)**

**(c)** Outline the steps involved when the solid platinum catalyst increases the rate of this reaction, referring to adsorption and desorption. **(2)**

**(d)** This reaction is, in principle, reversible, with the reverse reaction having a different (higher) activation energy from the forward reaction. State and explain the effect of the platinum catalyst on the equilibrium constant, Kc, for this reaction. **(2)**

**(Total for Question 3 is 8 marks)**


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**4** This question is about determining the rate equation for the gas-phase reaction between nitrogen monoxide and bromine.

**(a)** For the reaction $2NO(g) + Br_2(g) \rightarrow 2NOBr(g)$, three experiments give: Experiment 1, [NO] = 0.10 mol/dm3, $[Br_2]$ = 0.10 mol/dm3, initial rate = $6.0 \times 10^{-3}$ mol dm-3 s-1; Experiment 2, [NO] = 0.20 mol/dm3, $[Br_2]$ = 0.10 mol/dm3, initial rate = $24 \times 10^{-3}$ mol dm-3 s-1; Experiment 3, [NO] = 0.10 mol/dm3, $[Br_2]$ = 0.20 mol/dm3, initial rate = $12 \times 10^{-3}$ mol dm-3 s-1. Deduce the order of reaction with respect to NO and with respect to $Br_2$. **(4)**

**(b)** Write the rate equation for this reaction, and state its overall order. **(2)**

**(c)** Using the data from Experiment 1, calculate the rate constant, k, including its units. **(3)**

**(d)** State the effect on the initial rate of this reaction of doubling both [NO] and $[Br_2]$ simultaneously. **(1)**

**(Total for Question 4 is 10 marks)**

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**5** This question uses an ICE table to find the equilibrium composition of the water-gas shift reaction, and explores the effect of temperature on Kc.

**(a)** Explain why the equilibrium constant expression $Kc = [H_2O][CO] / ([H_2][CO_2])$, for the equilibrium $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$, has no units. **(2)**

**(b)** 2.00 mol of $H_2$ and 2.00 mol of $CO_2$ are mixed in a sealed 2.00 dm3 container and allowed to reach equilibrium at a temperature where Kc = 4.00. Letting x be the number of moles of CO formed at equilibrium, show that x = 1.33 mol (to 3 sf), and hence calculate the equilibrium concentration of each species. **(6)**

**(c)** At a higher temperature, a new value of Kc = 9.00 is established. State whether increasing the temperature increased or decreased the equilibrium proportion of CO in the mixture, and explain this in terms of Le Chatelier's principle. **(3)**

**(Total for Question 5 is 11 marks)**


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# Mark scheme · 2.4 Kinetics and Equilibria: Test Pack

## Question 1

(a) the colliding particles must have a combined energy greater than or equal to the activation energy, Ea, of the reaction oe **B1**

(a) the particles must collide with the correct orientation (geometry) oe **B1**

**(a) Answer: Particles must collide with energy ≥ activation energy, and with the correct orientation.**

(b) at higher temperature the Maxwell-Boltzmann distribution curve becomes flatter and broader, with its peak shifted to a higher energy oe **B1**

(b) the total area under the curve stays the same (the total number of particles is unchanged) oe **B1**

(b) a greater proportion (larger area) of particles now has energy greater than or equal to the activation energy, Ea oe **B1**

(b) this means a greater proportion of collisions are successful (result in reaction), so the rate of reaction increases oe **B1**

**(b) Answer: Higher temperature flattens and broadens the Maxwell-Boltzmann distribution and shifts it to higher energy; more particles have energy ≥ Ea, so more collisions are successful and the rate increases.**

(c) the minimum energy that colliding particles must possess in order to react oe **B1**

**(c) Answer: The minimum energy required for a collision to result in a reaction.**

## Question 2

(a) ensures hydrochloric acid is the limiting reagent, so the volume of gas produced depends only on the amount (concentration) of acid used oe **B1**

(a) ensures the reaction does not stop early through the marble chips running out, so the full effect of the acid on rate can be measured oe **B1**

**(a) Answer: Excess $CaCO_3$ makes HCl the limiting reagent, so gas volume depends only on the acid, and the chips do not run out before the acid is used up.**

(b) the concentration of HCl decreases as the reaction proceeds (it is used up) oe **B1**

(b) there are fewer acid particles per unit volume, so the frequency of successful collisions between acid and carbonate particles decreases, decreasing the rate oe **B1**

**(b) Answer: As [HCl] falls, collisions between HCl and $CaCO_3$ particles become less frequent, so the rate decreases.**

(c) initial rate of gas production (mol s-1) = 0.90 / 24000 **M1**

(c) = 3.75 x $10^{-5}$ mol s-1 **A1**

(c) divides by the volume of the reaction mixture in dm3 (50.0 $cm^3$ = 0.0500 dm3) **M1**

(c) initial rate = 7.50 x $10^{-4}$ mol dm-3 s-1 cao **A1**

**(c) Answer: 7.50 x $10^{-4}$ mol dm-3 s-1**

(d) the same small, fixed amount of product (iodine) must form before all of the thiosulfate is used up and the colour change is triggered, in every repeat oe **B1**

(d) only a small/negligible extent of reaction has occurred by this point (reactant concentrations have barely changed), so t is inversely proportional to the (approximately constant) initial rate, giving rate proportional to 1/t oe **B1**

**(d) Answer: A fixed small amount of product must form to trigger the colour change each time, so t is inversely proportional to the (near-initial) rate, giving rate proportional to 1/t.**

(e) temperature **B1**

(e) temperature affects the rate constant, k (and hence the rate), so if it were not controlled it would not be possible to attribute any change in rate solely to the change in concentration oe **B1**

**(e) Answer: Temperature must be kept constant, because it affects k and therefore the rate, independently of concentration.**


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## Question 3

(a) the activation energy, Ea, is lower with the catalyst present (the peak of the profile is lower) oe **B1**

(a) the overall enthalpy change, deltaH, of the reaction (the relative energies of reactants and products) is unchanged, with or without the catalyst oe **B1**

**(a) Answer: The catalyst lowers the activation energy (lower peak); the overall enthalpy change is unchanged.**

(b) at a fixed temperature the Maxwell-Boltzmann distribution is unchanged, but because the activation energy is now lower, a greater proportion (area under the curve) of particles has energy greater than or equal to this new, lower activation energy oe **B1**

(b) a greater proportion of collisions are therefore successful (result in reaction) per unit time, increasing the rate of reaction oe **B1**

**(b) Answer: At fixed temperature, more particles now exceed the (lower) activation energy, so more collisions are successful, increasing the rate.**

(c) gas molecules of CO and NO are adsorbed onto active sites on the surface of the solid catalyst, weakening their bonds and holding the reactant molecules close together in a favourable orientation, lowering the activation energy oe **B1**

(c) the product molecules ($CO_2$ and $N_2$) then desorb from the catalyst surface, freeing up the active sites for further reactant molecules oe **B1**

**(c) Answer: CO and NO are adsorbed onto active sites (weakening bonds, favourable orientation); products desorb, freeing sites for further reaction.**

(d) the catalyst has no effect on Kc oe **B1**

(d) it lowers the activation energy of both the forward and reverse reactions by the same amount, increasing both rates equally; equilibrium is reached faster, but the equilibrium position (and hence Kc) is unchanged oe **B1**

**(d) Answer: The catalyst has no effect on Kc; it speeds up the forward and reverse reactions equally, so equilibrium is reached faster but its position (and Kc) is unaffected.**

## Question 4

(a) comparing Experiments 1 and 2: [NO] doubles ($[Br_2]$ constant) and rate increases by a factor of 4 **M1**

(a) order with respect to NO = 2 **A1**

(a) comparing Experiments 1 and 3: $[Br_2]$ doubles ([NO] constant) and rate increases by a factor of 2 **M1**

(a) order with respect to $Br_2$ = 1 **A1**

**(a) Answer: Order 2 with respect to NO; order 1 with respect to $Br_2$.**

(b) rate = $k[NO]^2[Br_2]$ **B1**

(b) overall order = 3 **B1**

**(b) Answer: rate = $k[NO]^2[Br_2]$; overall order 3.**

(c) correct substitution: $k = 6.0 \times 10^{-3} / (0.10^2 \times 0.10)$ **M1**

(c) k = 6.0, cao **A1**

(c) units: $dm^6\ mol^{-2}\ s^{-1}$ **B1**

**(c) Answer: $k = 6.0\ dm^6\ mol^{-2}\ s^{-1}$**

(d) the rate increases by a factor of 8 ($2^2 \times 2^1 = 8$), oe **B1**

**(d) Answer: Rate increases by a factor of 8.**

## Question 5

(a) there are equal total powers of concentration in the numerator and denominator (2 and 2), oe **B1**

(a) so the units of concentration cancel completely, giving Kc no units (it is dimensionless), oe **B1**

**(a) Answer: Equal powers of concentration top and bottom cancel, so Kc is dimensionless.**

(b) set up equilibrium moles: $H_2 = CO_2 = (2.00 - x)$, $H_2O = CO = x$ **M1**

(b) substitute into Kc, noting the volume cancels: $Kc = (x/(2.00-x))^2$ **M1**

(b) take the square root: x/(2.00-x) = 2.00 (since Kc = 4.00) **M1**

(b) cso: x = 1.33 mol (3 sf), as required **A1**

(b) calculate concentrations using V = 2.00 dm3: $[H_2] = [CO_2] = (2.00-1.33)/2.00$, $[H_2O] = [CO] = 1.33/2.00$ **M1**

(b) $[H_2] = [CO_2] = 0.333$ mol/dm3, $[H_2O] = [CO] = 0.667$ mol/dm3 (ft) **A1**

**(b) Answer: x = 1.33 mol; $[H_2] = [CO_2] = 0.333$ mol/dm3, $[H_2O] = [CO] = 0.667$ mol/dm3.**

(c) increasing Kc (from 4.00 to 9.00) means the equilibrium proportion of CO (and $H_2O$) increased, oe **B1**

(c) an increase in Kc with increasing temperature shows that the forward reaction is endothermic, oe **B1**

(c) by Le Chatelier's principle, increasing temperature shifts an equilibrium in the endothermic direction to oppose the change, here favouring the forward reaction (more products), consistent with the increase in Kc, oe **B1**

**(c) Answer: The proportion of CO increased; the forward reaction is endothermic, so Le Chatelier's principle predicts a shift favouring products at higher temperature.**


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