

SECTION 4 BLOCKS 5 AND 6 (TMA 03)

Parts A and B of this Section cover important concepts and results in the area of heterogeneous catalysis (Block 5); in particular, working through the questions in Part B will give you valuable practice in analysing the kinetics of heterogeneously catalysed reactions. Part C will help you to check your understanding of some of the surface techniques discussed in Block 6.

PART A

The questions in Part A test Objectives 3, 8, 9, 10, 19, 20 and 21 of Block 5.

Q4.1 Select from the key the two statements that are correct.

KEY for Q4.1

- A The total surface area available from 2 g of metal M with a density of $8 \times 10^7 \text{ g m}^{-3}$, assuming spherical crystallites of 3 nm radius, is 25 m^2 .
- B The mode of chemical adsorption of propane gas, $\text{C}_3\text{H}_8(\text{g})$, on a suitable metal surface may be either associative or dissociative.
- C Hydrogen gas, $\text{H}_2(\text{g})$, is dissociatively adsorbed to monolayer coverage on a tin metal surface at room temperature.
- D If the enthalpy change for dissociative chemical adsorption of hydrogen on a transition metal surface is -180 kJ mol^{-1} , and the chemisorption is activated, then the enthalpy change for desorption will be greater than 180 kJ mol^{-1} .
- E If the dissociative chemisorption of a gas, A, obeys the Langmuir isotherm, the equilibrium pressure of A must be increased by a factor of 36, in order to bring about an increase in the fractional surface coverage from $\theta = 0.10$ to $\theta = 0.40$ at a fixed temperature.

Q4.2 At low coverages, the adsorption of carbon monoxide gas, CO, on a polycrystalline metal film can be described by a single-site Langmuir adsorption isotherm. In one study it was found that the ratio of the adsorption coefficients measured at 420 K and 450 K (that is, $b(420 \text{ K})/b(450 \text{ K})$) was equal to 6.75. What is the value of the enthalpy change on adsorption, according to the Langmuir model? Select from the key the value that is closest to your answer.

KEY for Q4.2

- A -100 kJ mol^{-1}
- B -40 kJ mol^{-1}
- C -15 kJ mol^{-1}
- D 15 kJ mol^{-1}
- E 40 kJ mol^{-1}
- F 100 kJ mol^{-1}

Q4.3 The surface area of 7.1 g of a particular metal catalyst was determined using nitrogen adsorption at 77 K via the BET method. Two data points taken from the physical adsorption isotherm are given in Table 4.1.

Table 4.1

$V(\text{stp})/\text{cm}^3$	p/p^*
58.3	0.13
83.6	0.28

If it is assumed that the BET plot is linear for $p/p^* < 0.30$, what is the specific surface area of the catalyst? (Take the effective area occupied by each adsorbed nitrogen molecule at 77 K to be 0.162 nm^2 .) Select from the key the value that is closest to your answer.

KEY for Q4.3

- A $20 \text{ m}^2 \text{ g}^{-1}$
- B $40 \text{ m}^2 \text{ g}^{-1}$
- C $70 \text{ m}^2 \text{ g}^{-1}$
- D $400 \text{ m}^2 \text{ g}^{-1}$
- E $700 \text{ m}^2 \text{ g}^{-1}$
- F $1000 \text{ m}^2 \text{ g}^{-1}$

PART B

The questions in Part B test Objectives 19, 22, 23 and 24 of Block 5.

Q4.4 and Q4.5 These questions are concerned with the following heterogeneously catalysed reaction:



Q4.4 If certain assumptions are made, then one possible mechanism for reaction 4.1 leads to the following theoretical rate equation:

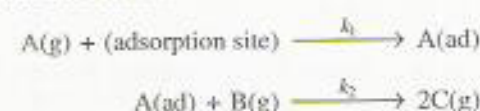
$$r = \frac{k_{\text{f}} b_{\text{A}} p_{\text{A}} b_{\text{B}} p_{\text{B}}}{(1 + b_{\text{A}} p_{\text{A}} + b_{\text{B}} p_{\text{B}})^2} \quad (4.2)$$

where the notation is similar to that used in Block 5. Select from the key those assumptions (up to three) concerning the mechanism which would be consistent with this form of rate equation.

KEY for Q4.4

- A The rate-limiting step is that between B in the gas phase and adsorbed A.
- B The rate-limiting step is that between A in the gas phase and adsorbed B.
- C The rate-limiting step is the surface reaction between adsorbed A and adsorbed B.
- D The chemical adsorption of A is a fast, reversible process.
- E The chemical adsorption of A and B on the catalyst surface is non-competitive.
- F The products of the reaction are desorbed as quickly as they are formed.
- G B must be far more strongly adsorbed on the catalyst surface than is A.

Q4.5 An alternative two-step mechanism can be proposed for reaction 4.1:



where both steps are taken to be irreversible. The fraction of the catalyst surface covered with A at any time during the reaction is denoted by θ_{A} ; all other surface intermediates are taken to be present in insignificant amounts. Examine the statements concerning this mechanism in the key and select up to three that are correct.