

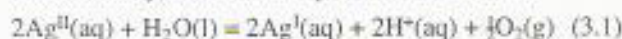
SECTION 3 BLOCKS 3 AND 4 (TMA 02)

The questions in Part A of this Section are designed to give you practice in deriving the chemical rate equation predicted by a mechanism, as discussed in Block 3. Part B covers important points in the general area of homogeneous catalysis (Block 4, Sections 2 and 3), and in the particular area of enzyme kinetics (Block 4, Section 4).

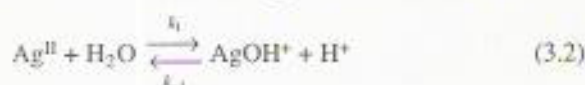
PART A

The questions in Part A test Objectives 1, 2, 4, 5, 7 and 8 of Block 3.

Q3.1 to Q3.4 The reaction between silver(II), Ag^{II} , and water in aqueous solution exhibits time-independent stoichiometry, and can be represented as follows:



One of the mechanisms proposed for this reaction involves the formation of AgOH^+ as an intermediate:



Analysis of this scheme, using the steady-state approximation, gives a chemical rate equation that reduces to an expression of the following form when either $k_{-1}[\text{H}^+]$ is much larger than $k_2[\text{Ag}^{\text{II}}]$ or $k_2[\text{Ag}^{\text{II}}]$ is much larger than $k_{-1}[\text{H}^+]$:

$$J = k_R [\text{Ag}^{\text{II}}]^\alpha [\text{H}_2\text{O}]^\beta [\text{H}^+]^\gamma [\text{Ag}^{\text{I}}]^\delta \quad (3.4)$$

Q3.1 If $k_{-1}[\text{H}^+] \gg k_2[\text{Ag}^{\text{II}}]$, what is the value of α in the reduced rate equation 3.4? Select your answer from the key for Q3.1 to Q3.3.

KEY for Q3.1 to Q3.3

- | | |
|-------|--------|
| A 2 | E -0.5 |
| B 1 | F -1 |
| C 0.5 | G -2 |
| D 0 | |

Q3.2 If $k_{-1}[\text{H}^+] \gg k_2[\text{Ag}^{\text{II}}]$, what is the value of γ in the reduced rate equation 3.4? Select your answer from the key for Q3.1 to Q3.3.

Q3.3 If $k_2[\text{Ag}^{\text{II}}] \gg k_{-1}[\text{H}^+]$, what is the value of γ in the reduced rate equation 3.4? Select your answer from the key for Q3.1 to Q3.3.

Q3.4 With reference to the proposed mechanism, select one correct statement from the key.

KEY for Q3.4

- A The rate of change of concentration of AgOH^+ arising from the back reaction of the first step (3.2) alone is given by equation 3.5:

$$\frac{d[\text{AgOH}^+]}{dt} = k_{-1}[\text{AgOH}^+][\text{H}^+] \quad (3.5)$$

- B The rate of change of concentration of O_2 arising from the second step (3.3) alone is given by equation 3.6:

$$\frac{d[\text{O}_2]}{dt} = 2k_2[\text{AgOH}^+][\text{Ag}^{\text{II}}] \quad (3.6)$$

- C If $k_{-1}[\text{H}^+] \gg k_2[\text{Ag}^{\text{II}}]$, the reduced form of the rate equation, equation 3.4, predicts that the overall order of reaction is three.
- D If $k_{-1}[\text{H}^+] \gg k_2[\text{Ag}^{\text{II}}]$, then the first step can be considered to be an established pre-equilibrium.
- E If $k_2[\text{Ag}^{\text{II}}] \gg k_{-1}[\text{H}^+]$, the mechanism reduces to two consecutive irreversible steps, the second of which is rate limiting.
- F Application of the steady-state approximation implies that the concentration of the intermediate, AgOH^+ , is zero during the course of the reaction.

PART B

The questions in Part B test Objectives 1, 2, 3, 4, 7, 8 and 10 of Block 4.

Q3.5 A possible catalytic cycle for the cobalt-catalysed hydroformylation of a terminal alkene, $\text{H}_2\text{C}=\text{CHR}$, is shown in Figure 3.1. Select from the key the two correct statements concerning the cycle.

KEY for Q3.5

- A In the overall reaction scheme, hydrogen is a non-participative ligand.
- B In step 2 the oxidation state of cobalt increases by 1.
- C Step 3 is an example of oxidative addition.
- D Step 6 is an example of reductive elimination.
- E The hydroformylation reaction is more thermodynamically favourable in the presence of the cobalt catalyst.
- F The coordination number of cobalt remains unchanged throughout the cycle.
- G In step 5 the oxidation state of cobalt increases by 2.

Q3.6 A single-substrate enzyme reaction follows Michaelis-Menten kinetics. When the initial substrate concentration, $[\text{S}]_0$, is $3.5 \times 10^{-4} \text{ mol dm}^{-3}$, the initial rate is two-thirds of its limiting value. What is the value of the Michaelis constant, K_m , for this enzyme? Select from the key the value that is closest to your answer.

KEY for Q3.6

- | | |
|--|--|
| A $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ | E $3.5 \times 10^{-4} \text{ mol dm}^{-3}$ |
| B $1.8 \times 10^{-4} \text{ mol dm}^{-3}$ | F $5.3 \times 10^{-4} \text{ mol dm}^{-3}$ |
| C $2.0 \times 10^{-4} \text{ mol dm}^{-3}$ | G $7.3 \times 10^{-4} \text{ mol dm}^{-3}$ |
| D $2.3 \times 10^{-4} \text{ mol dm}^{-3}$ | H $8.3 \times 10^{-4} \text{ mol dm}^{-3}$ |