

Equilibria

Mark Scheme 3

Level	International A Level
Subject	Chemistry
Exam Board	CIE
Topic	Equilibria
Sub-Topic	
Paper Type	Theory
Booklet	Mark Scheme 3

Time Allowed: 68 minutes

Score: /56

Percentage: /100

Grade Boundaries:

A*	A	B	C	D	E	U
>85%	77.5%	70%	62.5%	57.5%	45%	<45%

- 1 (a) (i) $\text{NH}_3 + \text{HZ} \longrightarrow \text{NH}_4^+ + \text{Z}^-$ [1]
 $\text{CH}_3\text{OH} + \text{HZ} \longrightarrow \text{CH}_3\text{OH}_2^+ + \text{Z}^-$ [1]
- (ii) $\text{NH}_3 + \text{B}^- \longrightarrow \text{NH}_2^- + \text{BH}$ [1]
 $\text{CH}_3\text{OH} + \text{B}^- \longrightarrow \text{CH}_3\text{O}^- + \text{BH}$ [1]
- [4]
- (b) (i) a reaction that can go in either direction [1]
- (ii) of forward = **rate** of backward reaction [1]
or forward/back reactions occurring but concentrations of all species do not change [1]
- [2]
- (c) (i) a solution that resists changes in pH [1]
when small quantities of acid or base/alkali are added [1]
- (ii) in the equilibrium system $\text{HZ} + \text{H}_2\text{O} \rightleftharpoons \text{Z}^- + \text{H}_3\text{O}^+$ [1]
addition of acid: reaction moves to the left
or H^+ combines with Z^- **and** forms HZ [1]
addition of base: the reaction moves to the right
or H^+ combines with OH^- **and** more Z^- formed [1]
- [5 max 4]
- (d) (i) $[\text{H}^+] = \sqrt{0.5 \times 1.34 \times 10^{-5}} = 2.59 \times 10^{-3} \text{ (mol dm}^{-3}\text{)}$ [1]
 $\text{pH} = 2.59/2.6$ (min 1 d.p) ecf [1]
- (ii) $\text{CH}_3\text{CH}_2\text{CO}_2\text{H} + \text{NaOH} \longrightarrow \text{CH}_3\text{CH}_2\text{CO}_2\text{Na} + \text{H}_2\text{O}$ [1]
- (iii) $n(\text{acid}) \text{ in } 100 \text{ cm}^3 = 0.5 \times 100/1000 = 0.05 \text{ mol}$
 $n(\text{acid}) \text{ remaining} = 0.05 - 0.03 = 0.02 \text{ mol}$
 $[\text{acid remaining}] = 0.2 \text{ (mol dm}^{-3}\text{)}$ [1]
likewise, $n(\text{salt}) = 0.03 \text{ mol}$
 $[\text{salt}] = 0.3 \text{ (mol dm}^{-3}\text{)}$ [1]
- (iv) $\text{pH} = 4.87 + \log(0.3/0.2) = 5.04\text{--}5.05$ ecf [1]
- [6]
- (e) **G** is $\text{CH}_3\text{CH}_2\text{COCl}$
H is SOCl_2 or PCl_5
J is NaCl [2]
(or corresponding Br compounds for **G**, **H** and **J**; $\text{CH}_3\text{CH}_2\text{COBr}$, SOBr_2 , NaBr)

- 2 (a) $K_c = \frac{[\text{CH}_3\text{CH}_2\text{R}][\text{H}_2\text{O}]}{[\text{CH}_3\text{CH}_2\text{H}][\text{ROH}]}$ (1)
 no units (1) [2]
- (b) (i) $n(\text{NaOH}) = \frac{22.5 \times 2.00}{1000} = 0.045$ (1)
- (ii) $n(\text{NaOH}) = n(\text{HCl}) = 0.005$ (1)
- (iii) $\text{CH}_3\text{CO}_2\text{H} + \text{NaOH} \rightarrow \text{CH}_3\text{CO}_2\text{Na} + \text{H}_2\text{O}$ (1)
- (iv) $n(\text{NaOH}) = 0.045 - 0.005 = 0.04$ (1) [4]
 allow ecf on (i) and/or (ii)
- (c) (i) $n(\text{NaOH})$ and $n(\text{CH}_3\text{CO}_2\text{H}) = 0.04$ (1)
 $n(\text{CH}_3\text{CO}_2\text{R})$ and $n(\text{H}_2\text{O}) = 0.06$ (1)
- (ii) $K_c = \frac{0.06 \times 0.06}{0.04 \times 0.04} = 2.25$
 allow ecf on wrong values in (b)(i)
 allow ecf on wrong expression in (a) (1)
- (d) E_a for reaction with ester is high or
 E_a for reaction with acid is low
 or
 reaction with ester is slow or
 reaction with acid is fast (1) [1]
- (e) equilibrium moves to RHS/more ester would be formed (1)
 to maintain value of K_c or
 to restore system to equilibrium (1) [2]

[Total: 12]

- 3 (a) (i) One that can go in either direction. [1]
- (ii) both forward & reverse reactions are going on at the same time, but the concentrations of all species do not change (owtte)
or rate of forward = rate of backward reaction [1]
- (b) (i) $K_c = \frac{[H^+][OH^-]}{[H_2O]}$ [1]
- (ii) $K_w = [H^+][OH^-]$ [1]
rearrangement of equation in (i) gives $K_c[H_2O] = [H^+][OH^-]$ & $K_w = K_c[H_2O]$ (owtte)
or the $[H_2O]$ is contained within K_w [1]
- (iii) K_w will be higher in hot water **because** reaction is endothermic [1]
- (c) (i) $[OH^-] = 5 \times 10^{-2}$; $[H^+] = (1 \times 10^{-14}) / 5 \times 10^{-2} = 2 \times 10^{-13}$ [1]
 $pH = -\log_{10}[H^+] = 12.7$ (correct ans = [2]) ecf [1]
- (ii) $[NH_4^+] = [OH^-] (= x)$ [1]
 $x^2 = 1.8 \times 10^{-5} \times 0.05 \Rightarrow x (= [OH^-]) = 9.49 \times 10^{-4} \text{ (mol dm}^{-3}\text{)}$ (correct ans = [2]) [1]
- (iii) $[H^+] = K_w/[OH^-] = (1 \times 10^{-14}) / 9.49 \times 10^{-4} = 1.05 \times 10^{-11} \text{ (mol dm}^{-3}\text{)}$ ecf [1]
- (iv) $pH = 11.0$ ecf [1]

[Total: 12 max 11]

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- 4 (a) (i) Order w.r.t. $[\text{CH}_3\text{CHO}] = 1$ [1]
 Order w.r.t. $[\text{CH}_3\text{OH}] = 1$ [1]
 Order w.r.t. $[\text{H}^+] = 1$ [1]
- (ii) $\text{rate} = k[\text{CH}_3\text{CHO}][\text{CH}_3\text{OH}][\text{H}^+]$ [1]
- (iii) $\text{units} = \text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$ [1]
- (iv) rate will be $2 \times 4 = 8$ times as fast as reaction 1 (relative rate = 8) [1]
[6]

(b)

	$[\text{CH}_3\text{CHO}]$ /mol dm ⁻³	$[\text{CH}_3\text{OH}]$ /mol dm ⁻³	$[\text{H}^+]$ /mol dm ⁻³	[acetal A] /mol dm ⁻³	$[\text{H}_2\text{O}]$ /mol dm ⁻³
at start	0.20			0.00	
at equilibrium	$(0.20 - x)$	$(0.10 - 2x)$	0.05	x	x
at equilibrium	0.175		0.05	0.025	0.025

- (i) 3 values in second row 3 x [1]
- (ii) 4 values in third row 4 x [1]
- (iii) $K_c = \frac{[\text{acetal A}][\text{H}_2\text{O}]}{[\text{CH}_3\text{CHO}][\text{CH}_3\text{OH}]^2}$ [1]
 units = mol⁻¹dm³ [1]
- (iv) $K_c = 0.025^2 / (0.175 \times 0.05^2) = \mathbf{1.4(3)}$ (mol⁻¹ dm³) [1]
[max 9]

[Total: 15]

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