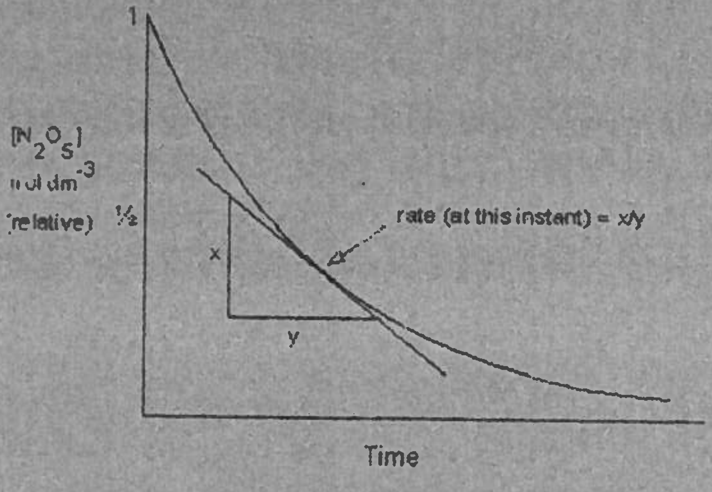
5.1.1 & 5.1.2

Kinetics & Equilibrium Exam Questions



gChemistry

Name ANSWERS

Unifying Concepts in Chemistry

June 2005

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Question			Expected Answers	Marks
1	(a)	(i)	constant half-life ✓	[1]
		(ii)	rate = k [N_2O_5] ✓ Common error will be to use '2' from equation.	[1]
		(iii)	curve downwards getting less steep ✓ curve goes through 1200,0.30; 2400,0.15; 3600,0.075 ✓	[2]
		(iv)	tangent shown on graph at t = 1200 s ✓	[1]
		(v)	3.7(2) x 10^{4} ✓ mol dm^{-3} s^{-1} ✓ ecf possible from (ii) using [N_2O_5]^x (2nd order answer: 2.2(3) x 10^{4})	[2]
	(b)	(i)	slow step ✓	[1]
		(ii)	$(CH_3)_2C{=}CH_2$ + H_2O ---→ $(CH_3)_3COH$ ✓	[1]
		(iii)	H^+ is a catalyst ✓ H^+ used in first step and formed in second step/ regenerated/ not used up ✓	[2]
		(iv)	rate = k [$(CH_3)_2C{=}CH_2$] [H^+] ✓ common error will be use of H_2O instead of H^+	[1]
				Total: 12

2. **(a)** $k = \frac{\text{rate}}{[H_2(g)][NO(g)]^2}$ ✓

$k = 8.3 \times 10^4$ ✓ $dm^6\ mol^{-2}\ s^{-1}$ ✓ calculator value: $8.33333.... \times 10^4$

If [NO] is not squared: $\frac{\text{rate}}{[H_2(g)][NO(g)]}$ ×, ans = 250 ✓ units: $dm^3\ mol^{-1}\ s^{-1}$ ✓

If the expression is upside down: $\frac{[H_2(g)][NO(g)]^2}{\text{rate}}$ ×, ans = 1.2×10^{-5} ✓ units: $mol^2\ s\ dm^{-6}$ ✓

upside down and not squared: $\frac{[H_2(g)][NO(g)]}{\text{rate}}$ ××, ans = 0.004 $mol\ s\ dm^{-3}$ ✓ [3]

(b) **(i)** *effect on rate* x 2 ✓

reason 1st order wrt $H_2(g)$ ✓

[2]

(ii) *effect on rate* x 1/4 ✓

reason 2nd order wrt $NO(g)$ ✓

[2]

(iii) *effect on rate* x 27 ✓

[1]

(c) **(i)** slowest step ✓

[1]

(ii) step 1 (RDS) $H_2(g) + 2\,NO(g)$ ✓ $\longrightarrow N_2O(g) + H_2O(l)$

step 2 $H_2(g) + N_2O(g) \longrightarrow N_2(g) + H_2O(l)$ rest of equations ✓

[2]

(d) **(i)** NH_3, −3 ✓

NO, +2 ✓

HNO_3 +5 ✓

[3]

(ii) $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(l)$

products + reactants ⟶ 1 mark; balancing ⟶ 1 mark ✓ ✓

[2]

(iii) molar masses $NH_3 = 17$; $HNO_3 = 63$ ✓

mass = 700 000 x 17/63 = 1.89×10^5 tonnes ✓ calc value $1.888888.... \times 10^5$

ans: mark could be consequential on incorrect molar masses.

[2]

[Total: 18]

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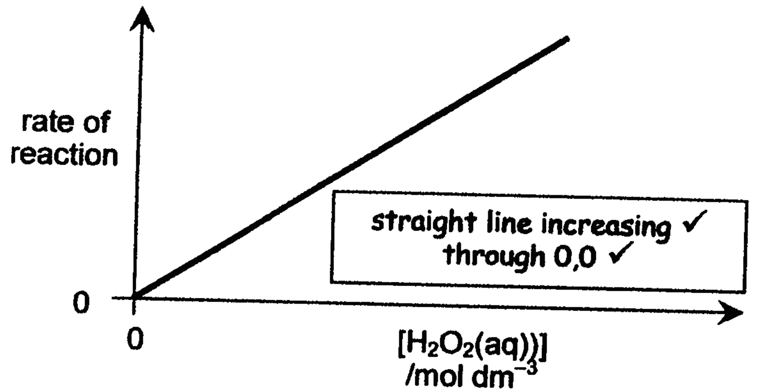
Question	**Expected Answers**	**Marks**
3 (a)	$H_2O_2 + 2I^- + 2H^+ \longrightarrow I_2 + 2H_2O$ equation includes H_2O, I^-, H^+ as reactants and I_2 as product ✓ equation balanced ✓	[2]
(b) (i)	Exp 2 has twice $[I^-]$ as Exp 1 and rate has quadrupled ✓, so order = 2 with respect to I^- ✓ Exp 3 has twice $[H^+]$ as 2 and rate is unchanged ✓, so order = 0 with respect to H^+ ✓..............AW	[4]
(ii)	rate = $k[H_2O_2][I^-]^2$ ✓✓ 1 mark for: rate = k x concs (ecf from (i))	[2]
(iii)	k = rate/$[H_2O_2][I^-]^2$ ✓(ecf from (ii)) From one of expts, e.g. Exp 1: $k = 1.15 \times 10^{-6}/(0.01)(0.01)^2$ $= 1.15$ ✓ $dm^6\ mol^{-2}\ s^{-1}$ ✓ (ecf from (ii))	[3]
(c)	 straight line increasing ✓ through 0,0 ✓	[2]
(d) (i)	$2H_2O_2 \longrightarrow 2H_2O + O_2$ ✓	[1]
(ii)	1 dm^3 $H_2O_2 \longrightarrow$ 20 dm^3 O_2 ✓ amount of O_2 = 20/24 mol ✓ concentration of H_2O_2 = 2 x 20/24 = 1.67 mol dm^{-3} ✓	[3]
		Total: 17

4 (a) (i) What is meant by the *half-life* of a reaction, $t_{½}$?

Time for half a reactant to react ✓

[1]

(ii) $t_{½}$ = 460 ± 10 s ✓

constant half life ✓

evidence on graph to support constant half life (at least two half-lifes shown) ✓

[3]

(iii) no change ✓

[1]

(b) $k = 0.693 / t_{½} = 0.693/460 = 1.51 \times 10^{-3}$ ✓ s^{-1} ✓

*for consequential marking: answer should be: 0.693/ans to **(a)(ii)***

[2]

(c) Rate = $k[C_6H_5N_2Cl(aq)]$ ✓

[1]

(d) (i) After 800s, $[C_6H_5N_2Cl(aq)] = 1.8 \times 10^{-4}$ mol dm^{-3} ✓

(*allow any value from 1.7×10^{-4} to 1.8×10^{-4}*)

[1]

(ii) *Rate* = $k[C_6H_5N_2Cl(aq)] = (1.51 \times 10^{-3}) \times (1.8 \times 10^{-4})$

$= 2.7 \times 10^{-7}$ ✓ mol dm^{-3} s^{-1} ✓

[2]

(iii) measure gradient at t = 800 s ✓

[1]

[Total: 12]

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Question	**Expected Answers**	**Marks**
5 (a) (i)	O_3: 1 and C_2H_4 ✓	[1]
(ii)	2 ✓	[1]
(iii)	rate = $k[O_3][C_2H_4]$ ✓	[1]
(b) (i)	measure gradient/tangent ✓ at t = 0/start of reaction ✓	[2]
(ii)	$k = \frac{\text{rate}}{[O_3][C_2H_4]}$ ✓ $k = \frac{1.0 \times 10^{-12}}{0.5 \times 10^{-7} \times 1.0 \times 10^{-8}} = 2 \times 10^3$ ✓ $dm^3\ mol^{-1}\ s^{-1}$ ✓	[3]
(iii)	2 mol CH_2O forms for every 0.5 mol O_2 / stoichiometry of $CH_2O : O_2$ is not 1:1 ✓	[1]
(iv)	rate increases ✓ k increases ✓	[2]
(c) (i)	each atom has two unpaired electrons ✓	[1]
(ii)	2 oxygen atoms bonded by double bond ✓ third oxygen bonded by a covalent bond and outer shells correct ✓ For 2nd mark, all O atoms must have an octet. A triangular molecule would have 3 single covalent bonds for 1st mark but the origin of each electron must be clear for 2nd mark	[2]
(iii)	amount of O_3 in 150 kg = $150 \times 10^3/48 = 3.13 \times 10^3$ mol ✓ amount of Cl radicals in 1 g = $1/35.5 = 2.82 \times 10^{-2}$ mol ✓ 1 mol Cl destroys $3.13 \times 10^3/2.82 \times 10^{-2} = 1.11 \times 10^5$ mol O_3 1 Cl radical destroys 1.11×10^5 O_3 molecules ✓ (calculator: 110937)	[3]
		Total: 17

6 (a)(i)	**H^+(aq)**: Exp 3 has 2 x [H^+(aq)] as Exp 1 and rate has increased by 4✓ so order = 2 with respect to H^+(aq) ✓	[2]
	BrO_3^-(aq): Exp 2 has 2 x [BrO_3^-] as Exp 1 and rate increases by 2 ✓ so order = 1 with respect to BrO_3^-(aq) ✓	[2]
	Br^-(aq): Exp 4 has 3 x [BrO_3^-(aq)] as Exp 1 which increases rate by 3 and Exp 4 has 2 x [Br^-(aq)] as Exp 1 rate has increased by 6 so doubling [Br^-(aq)] doubles rate ✓ so order = 1 with respect to Br^-(aq) ✓	[2]
(ii)	rate = $k\,[H^+]^2\,[BrO_3^-]\,[Br^-]$ ✓	[1]
(iii)	$k = \frac{\text{rate}}{[H^+]^2\,[BrO_3^-]\,[Br^-]}$ / $\frac{1.68 \times 10^{-5}}{0.30^2 \times 0.05 \times 0.25}$ ✓ = 0.0149/0.015 ✓ units: $dm^9\ mol^{-3}\ s^{-1}$ ✓ answer to 2 or 3 sig figs ✓ (calculator: 0.0149333333) **mark consequentially from (a)(ii)** common ecfs: From expt 1: rate = $k\,[H^+]^2\,[BrO_3^-] \longrightarrow 0.00373\ dm^6\ mol^{-2}\ s^{-1}$	[4]
(b)	gradient at t=0/start ✓	[1]
(c)	Overall equation has different stoichiometry/number of moles to rate equation ✓	[1]
		13

7. From graph, constant half-life **(1)**
Therefore 1st order w.r.t. $[CH_3COCH_3]$ **(1)** 2

From table, rate doubles when $[H^+]$ doubles **(1)**
Therefore 1st order w.r.t. $[H^+]$ **(1)** 2

From table, rate stays same when $[I_2]$ doubles **(1)**
Therefore zero order w.r.t. $[I_2]$ **(1)**
Order with no justification does **not** score. 2

rate = $k[H^+][CH_3COCH_3]$ **(1)**
(from all three pieces of evidence)

$$k = \frac{\text{rate}}{[H^+][CH_3COCH_3]} / \frac{2.1 \times 10^{-9}}{0.02 \times 1.5 \times 10^{-3}} \ \textbf{(1)}$$

$= 7.0 \times 10^{-5}$ **(1)** $dm^3\ mol^{-1}\ s^{-1}$ **(1)** 4

accept 7×10^{-5}

rate determining step involves species in rate equation **(1)**

two steps that add up to give the overall equation **(1)**

The left hand side of a step that contains the species in rate-determining step **(1)**
i.e., for marking points 2 and 3:
$CH_3COCH_3 + H^+ \rightarrow [CH_3COHCH_3]^+$
$[CH_3COHCH_3^+] + I_2 \rightarrow CH_3COCH_2I + HI + H^+$ 3

organises relevant information clearly and coherently,
using specialist vocabulary where appropriate
Use of the following four words/phrases:
constant, half-life, order, doubles/x2 **(1)** 1

[14]

Question	**Expected Answers**	**Marks**
1 (a)	$K_c = \dfrac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]}$ ✓✓ *award 1 mark if upside down*	**[2]**
(b) (i)	$\underbrace{\begin{array}{\|c\|c\|}\hline CH_3COOH & C_2H_5OH \\ \hline 6.0 & 12.5 \\ \hline 1 & 7.5 \\ \hline\end{array}}_{\checkmark}\underbrace{\begin{array}{\|c\|c\|}\hline CH_3COOC_2H_5 & H_2O \\ \hline 0 & 0 \\ \hline 5 & 5 \\ \hline\end{array}}_{\checkmark}$	**[2]**
(ii)	$K_c = \dfrac{5 \times 5}{1 \times 7.5} = 3.3$ ✓ no units ✓ (or ecf based on answers to (i) and/or (a))	**[2]**
(c)	leave experiment longer ✓ monitor compositions and repeat until constant value ✓	**[2]**
(d) (i)	more $CH_3COOC_2H_5$ & H_2O / less CH_3COOH & C_2H_5OH ✓ equilibrium ⟶ right ✓ AW	**[2]**
(ii)	K_c stays same ✓	**[1]**
(e)	stays the same/ catalyst does not shift equilibrium position ✓ forward & reverse reactions altered by same amount/ equilibrium achieved in less time ✓	**[2]**
(f) (i)	equilibrium ⟶ left ✓ more reactants / less products ✓	**[2]**
(ii)	forward reaction is exothermic ✓	**[1]**
		Total: 16

Question	Expected Answers	Marks
2 (a) (i)	$K_c = \frac{[NO]^2}{[N_2]\,[O_2]}$ ✓✓ *award 1 mark if upside down* *K_p expression worth 1 mark*	[2]
(ii)	Equil ⟶ left because K_c is very small	[1]
(iii)	$[O_2(g)] = \frac{[NO]^2}{[N_2] \times K_c} = \frac{(4.0 \times 10^{-16})^2}{1.1 \times 4.8 \times 10^{-31}}$ ✓ = 0.30 mol dm^{-3} ✓ (calculator: 0.303030303) answer given to 2 sig figs ✓ 3.3 ✓✓ (upside down) calc: 3.3 7.6×10^{14} ✓✓ (missing out ^{2}) calc: 7.5757..... 0.37 ✓✓ (1.1 on top) calc: 0.366666.. 5.2×10^{-46} ✓✓ ('4' values swapped) calc: $5.236363. \times 10^{-46}$	[3]
(b) (i) (ii)	ΔH is +ve ✓ equilibrium moves to the right to compensate for increase in temperature/to lower the temperature / to minimise the change ✓ increase in proportion of NO ✓ because K_c increases *Can be linked to either increased proportion of NO or enthalpy change* ✓	[4]
(iii)	$2NO + O_2 \longrightarrow 2NO_2$ ✓✓ *species correct for 1st mark* *'simplest' balanced equation for 2nd mark* $NO + {}^1/_2O_2 \longrightarrow NO_2$ also gets both marks *N_2O_4 is fine* *NO_2 for 1st mark*	[2]

(c)	Optimum Pressure low pressure ✓ fewer gaseous moles on left ✓ Optimum Temperature optimum: low temperature ✓ forward reaction is exothermic ✓ Reason mark can only be awarded if the condition mark is correct. Condition mark is independent 1000°C used to increase rate with more energetic collisions *OR* so that a greater proportion of molecules exceed activation energy ✓ 10 atm used to increase rate by increasing concentration *OR* increasing collisons ✓ Catalyst used to increase rate by lowering the activation energy/providing a lower energy route ✓ *NOT increase equilibrium yield*	[7]
	Quality of written communication: Recognition of a compromise between rate and equilibrium amount ✓	[1]
		Total: 20

3 **(a)** Forward and reverse reactions at same rate ✓

Achievable from either direction ✓, requires closed system ✓

concentrations of reactants and products are constant ✓

max: [2]

(b) **(i)**

$$K_c = \frac{[\,CH_3OH(g)\,]}{[\,CO(g)\,]\,[\,H_2(g)\,]^2}$$ ✓✓ *1 mark for top; 1 mark for bottom*

[2]

(ii)

$$K_c = \frac{(2.6 \times 10^{-5})}{(3.1 \times 10^{-3})\,(2.4 \times 10^{-2})^2}$$ ✓ = 14.6 ✓ ($dm^6\ mol^{-2}$)

[2]

(c) (i) *Why did the equilibrium move to the right*

fewer molecules on right ✓

reaction relieves increase in pressure ✓

[2]

(ii) *What is the effect, if any, on K_c*

K_c stays same ✓

[1]

(iii) *Rate changes*

Rate increases ✓

Increased collisions/more concentrated ✓

Rates initially forward faster than reverse ✓

At equil, rates same ✓

[4]

(d) **(i)** K_c decreases so products decrease/reactants increase ✓

Therefore equilibrium moves to the left/to endothermic side ✓

2nd mark dependent on first.

[2]

(ii) Δ*H* is negative because of equilibrium change in **(i)** ✓

Mark consequential on (i)

[1]

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4. **(a)** **(i)** $K_c = \frac{[NO_2(g)]^2}{[N_2O_4(g)]}$ ✓ [1]

(ii) $K_c = \frac{(0.0150)^2}{(0.0390)} = 5.77 \times 10^{-3}$ ✓ mol dm^{-3} ✓ accept 5.76923 to 5.8×10^{-3}

If (i) is upside down: $\frac{[N_2O_4(g)]}{[NO_2(g)]^2}$, then ans = 173 ✓ dm^3 mol^{-1} ✓ accept 173.33333.....to 170

if no square in (i): $\frac{[NO_2(g)]}{[N_2O_4(g)]}$, then ans = 0.384615..✓ no units ✓ (must be stated)

if no square in (i) and inverse: $\frac{[N_2O_4(g)]}{[NO_2(g)]}$, 2.6 ✓ no units ✓ (must be stated) [2]

(b) $\Delta H = (2 \times 33) - (9)$ ✓ = (+)57 kJ mol^{-1} ✓

common errors: −57 ✓✗ +24 ✓✗ +75 ✓✗ −24 ✗✗ [2]

(c) *change* more NO_2 / less N_2O_4 ✓

explanation equilibrium position ⟶ right or forwards / K_c increases ✓

reaction is endothermic ✓

THIS ANSWER IS CONSEQUENTIAL ON SIGN OF THE ANSWER TO (i)

BUT, a candidate interpreting a '+' enthalpy change as 'exothermic' (or vice versa) will lose the 3rd mark but the 2 'logic marks' before are still consequentially available. [3]

(d) 1 mol N_2O_4 reacts with 2 mol NaOH ✓

amount of NaOH required = 0.00930 mol ✓

volume NaOH = 1000 x 0.0093/0.300 = 31.0 cm^3 / 0.0310 dm^3 ✓

Common errors

3.1 x 10^x (where x is incorrect) ✓✓✗

15.5 cm^3 / 0.0155 dm^3 ✓✓✗

62 cm^3 / 0.062 dm^3 ✓✓✗

1.55 x 10^x (where x is incorrect) ✓✗✗

6.2 x 10^x (where x is incorrect) ✓✗✗ [3]

[Total: 11]