OCR RECOGNISING ACHIEVEMENT

OXFORD CAMBRIDGE AND RSA EXAMINATIONS

Advanced GCE

CHEMISTRY **2816/01**

Unifying Concepts in Chemistry

Wednesday **19 JUNE 2002** Afternoon 1 hour 15 minutes

Candidates answer on the question paper
Additional materials
Data Sheet for Chemistry
Scientific calculator

Candidate Name	Centre Number	Candidate Number

TIME 1 hour 15 minutes

INSTRUCTIONS TO CANDIDATES

- Write your name in the space above.
- Write your Centre number and Candidate number in the boxes above.
- Answer **all** the questions.
- Write your answers in the spaces on the question paper.
- Read each question carefully and make sure you know what you have to do before starting your answer.

INFORMATION FOR CANDIDATES

- The number of marks is given in brackets [ ] at the end of each question or part question.
- You will be awarded marks for the quality of written communication where this is indicated in the question.
- You may use a scientific calculator.
- You may use the *Data Sheet for Chemistry*.
- You are advised to show all the steps in any calculations.

FOR EXAMINER'S USE		
Qu.	**Max.**	**Mark**
1	**11**	
2	**18**	
3	**15**	
4	**16**	
TOTAL	**60**	

This question paper consists of 10 printed pages and 2 blank pages.

(NH) S10968/4

[Turn over

For Examiner's Use

Answer **all** questions.

1 A chemist set up an equilibrium system between dinitrogen tetroxide, N_2O_4, and nitrogen dioxide, NO_2, at 25 °C.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

The equilibrium concentrations were: $N_2O_4(g)$, 0.0390 mol dm^{-3}; $NO_2(g)$, 0.0150 mol dm^{-3}.

(a) **(i)** Write the expression for K_c in this equilibrium system.

[1]

(ii) Calculate K_c for this equilibrium State the units.

[2]

(b) The standard enthalpy changes of formation of N_2O_4 and NO_2 are given below.

compound	$\Delta H_f^\ominus$/kJ mol^{-1}
N_2O_4	+9
NO_2	+33

Calculate the standard enthalpy change for the forward reaction in this equilibrium.

[2]

For Examiner's Use

(c) This equilibrium system was heated at constant pressure. How would you expect the relative proportions of N_2O_4 and NO_2 to change? Explain your answer.

change ....

explanation ....

....

....[3]

(d) NO_2 and N_2O_4 are both poisonous. After this investigation, the chemist needed to dispose of 0.00465 mol N_2O_4 safely. The chemist decided to do this by reacting the N_2O_4 with an alkali and chose aqueous sodium hydroxide.

$$N_2O_4(g) + 2NaOH(aq) \longrightarrow NaNO_3(aq) + NaNO_2(aq) + H_2O(l)$$

Calculate the minimum volume of 0.300 mol dm^{-3} NaOH(aq) required to dispose of this amount of N_2O_4.

[3]

[Total : 11]

[Turn over

For Examiner's Use

2 The reaction between hydrogen, H_2, and nitrogen monoxide, NO, has the following rate equation.

$$\text{rate} = k[H_2(g)][NO(g)]^2$$

(a) Using $6.0 \times 10^{-3}\,mol\,dm^{-3}$ $H_2(g)$ and $3.0 \times 10^{-3}\,mol\,dm^{-3}$ NO(g), the initial rate of this reaction was $4.5 \times 10^{-3}\,mol\,dm^{-3}\,s^{-1}$.

Calculate the rate constant, *k*, for this reaction and state its units.

[3]

(b) Predict what would happen to the reaction rate after the following changes in concentrations. Show your reasoning.

(i) The concentration of $H_2(g)$ is doubled.

effect on rate ....

reason ....

....[2]

(ii) The concentration of NO(g) is halved.

effect on rate ....

reason ....

....[2]

(iii) The concentrations of $H_2(g)$ and NO(g) are both tripled.

effect on rate ....[1]

For Examiner's Use

(c) The overall equation for the reaction between hydrogen and nitrogen monoxide is shown below.

$$2H_2(g) + 2NO(g) \longrightarrow N_2(g) + 2H_2O(l)$$

This reaction takes place by a two step mechanism with the rate-determining step taking place first.

(i) Explain the term *rate-determining step.*

....

....[1]

(ii) Suggest the two steps for this reaction and write their equations below. The equation for the rate-determining step (RDS) has been partly completed.

step 1 (RDS) .... + 2.............. $\longrightarrow$ .... + $H_2O(l)$

step 2 .... + ... $\longrightarrow$ $N_2(g) + H_2O(l)$

[2]

(d) Each year in the UK, 700 000 tonnes of nitric acid, HNO_3, are manufactured for the production of fertilisers, dyes, explosives, etc. Nitrogen monoxide, NO, is prepared as an intermediate in the production of nitric acid from ammonia, NH_3.

$$NH_3(g) \xrightarrow{O_2(g)} NO(g) + H_2O(l) \longrightarrow HNO_3(l)$$

(i) What is the oxidation state of nitrogen in the following?

NH_3 ....

NO ....

HNO_3 ....[3]

(ii) Construct a balanced equation for the formation of NO(g) from $NH_3(g)$.

....[2]

(iii) Assuming that 1 mol NH_3 produces 1 mol HNO_3, calculate the mass of NH_3 that is required to meet the annual demand for HNO_3 in the UK.

[2]

[Total : 18]

[Turn over

3 Alpha hydroxy acids (AHAs) are monobasic organic acids, used in skin creams to combat the appearance of ageing. Approximately 1% solutions of AHAs remove wrinkles as the low pH aggravates the skin, causing it to swell. More concentrated solutions (approximately 12% or 1.5 mol dm^{-3}) are used to remove dead skin.

(a) An AHA was analysed and had the percentage composition by mass:

C, 40.0%; H, 6.7%; O, 53.3%. $M_r = 90$.

Calculate the molecular formula of this AHA.

[3]

(b) Calculate the pH of a 1.5 mol dm^{-3} solution of an AHA with an acid dissociation constant, K_a, of 1.2×10^{-5} mol dm^{-3}. Show your working.

[4]

(c) Beauty treatments often contain buffers. An example of a buffer is a mixture of ethanoic acid, CH_3COOH, and an ethanoate salt such as sodium ethanoate, CH_3COONa.

(i) Explain what is meant by a *buffer solution*.

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....[1]

(ii) Write the chemical equation for the equilibrium in this buffer system.

....[1]

For Examiner's Use

(iii) Explain how this buffer solution works. Use equations where appropriate.

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....

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....[3]

(d) A buffer solution was prepared using equal concentrations of CH_3COOH and CH_3COONa.

What would be the effect on the pH of this buffer solution of adding some solid CH_3COONa? Explain your answer.

effect on pH ....

explanation ....

....

....[3]

[Total : 15]

[Turn over

For Examiner's Use

4 In this question, you should use knowledge, principles and concepts from different areas of chemistry. *(In this question, 1 mark is available for the quality of written communication.)*

(a) The equation for the production of ammonia in the Haber process is shown below.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92\,kJ\,mol^{-1}$$

Explain why the conditions of temperature and pressure used in the Haber process (450 °C, 15 000 kPa) are a **compromise**.

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....[7]

For Examiner's Use

(b) An *Alka-Seltzer* tablet contains about 0.5 g sodium hydrogencarbonate, $NaHCO_3$, and an excess of citric acid. When water is added to an *Alka-Seltzer* tablet, carbon dioxide gas is released.

The equation for the reaction that takes place is shown below. The formula of citric acid has been simplified as H_3A.

$$3NaHCO_3 + H_3A \longrightarrow Na_3A + 3CO_2 + 3H_2O$$

(i) Explain, using ionic equations, how the addition of water allows the release of carbon dioxide from an *Alka-Seltzer* tablet.

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....[4]

(ii) Calculate the minimum mass of citric acid that needs to be in an *Alka-Seltzer* tablet to ensure that all the sodium hydrogencarbonate reacts. (M_r citric acid: 192)

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....[5]

[Total : 16]

Subject: Unifying Concepts
Code: 2816/1

Session: June
Year: 2002

Final Mark Scheme

22/6/2002

MAXIMUM MARK	60

Abbreviations, annotations and conventions used in the Mark Scheme	/	=	alternative and acceptable answers for the same marking point
	;	=	separates marking points
	NOT	=	answers which are not worthy of credit
	( )	=	words which are not essential to gain credit
	___	=	(underlining) key words which **must** be used to gain credit
	ecf	=	error carried forward
	AW	=	alternative wording
	ora	=	or reverse argument

1. (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) ΔH = (2 x 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 ✓✓✗ *1.55 x 10^x (where x is incorrect)* ✓✗✗

62 cm^3 / 0.062 dm^3 ✓✓✗ 6.2 x 10^x (where x is incorrect) ✓✗✗ [3]

[Total: 11]

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]

3. **(a)** Empirical formula = C : H : O = 40.0/12 : 6.7/1 : 53.3/16 = 3.33 : 6.7 : 3.33 ✓

= CH_2O ✓

mass CH_2O = 30; M_r = 90 ∴ molecular formula = $C_3H_6O_3$ ✓

[3]

(b)

$$K_a = \frac{[H^+(aq)]\,[A^-(aq)]}{[HA(aq)]} \; / \; \frac{[H^+(aq)]^2}{[HA(aq)]}$$ ✓

$$\therefore 1.2 \times 10^{-5} = \frac{[H^+(aq)]^2}{1.5}$$

$[H^+(aq)] = \sqrt{\{(1.2 \times 10^{-5}) \times (1.5)\}} = 4.2 \times 10^{-3}$ mol dm^{-3} ✓

pH = $-\log[H^+(aq)]$ ✓ = $-\log 4.2 \times 10^{-3}$ = 2.4 / 2.37 ✓

***4 marks**:* K_a expression✓;

$[H^+]$✓;

pH expression✓;

calculation of pH from $[H^+]$ (ecf) ✓

Common error: Without square root, answer is 4.7/ 4.7447... ✓✓✓✗

[4]

(c) **(i)** A solution that minimises changes/resists change in pH after addition of acid/alkali ✓
NOT 'maintains constant pH' or 'cancel out'

[1]

(ii) $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$ /
$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$ ✓ [1]

(iii) The weak acid or CH_3COOH reacts with added alkali / added alkali reacts with H^+ ✓

The base or CH_3COO^- reacts with added acid ✓
Direction of movement indicated for one change / indication of the products formed for one change ✓

[3]

(d) *effect on pH* increases ✓

explanation equilibrium ⟶ left ✓
H^+ removed by CH_3COO^- ✓

[3]
[Total: 15]

4. (a)

Pressure: 3 marks

high pressure ✓ fewer gaseous moles on right ✓

Compromise: pressure used but too much is requires too much energy/high costs/causes safety issues/thick pipes ✓

Temperature: 4 marks

low temperature ✓ reaction is exothermic ✓

Increased temperature needed to increase the rate/low temperature gives a slow rate ✓

Compromise: idea of a compromise between rate and equilibrium amount ✓

7 marking points ⟶ 6 max

Clear, well-organised, using specialist terms ✓

[7]

(b) (i)

***what citric acid does*:** citric acid dissociates ✓

H^+ released / H_2O accepts H^+/behaves as a base ✓

equation: $H_3A + 3H_2O \longrightarrow 3H_3O^+ + A^{3-}$
or $H_3A \longrightarrow 3H^+ + A^{3-}$
or $H_3A + H_2O \longrightarrow H_3O^+ + H_2A^-$
or $H_3A \longrightarrow H^+ + H_2A^-$ ✓ (or other intermediate dissociation)

The equation alone will also score the 2 'what citric acid does' marks.

how H^+ reacts: H^+ now reacts with HCO_3^- ions/$NaHCO_3$ ✓

equation: $H^+ + HCO_3^- \longrightarrow H_2O + CO_2$ ✓

The equation alone will also score the 'how H^+ reacts' mark.

5 marks ⟶[4] max

(ii) Molar mass of $NaHCO_3$ = 84.0 ✓

amount of $NaHCO_3$ = 0.5/84.0 = 5.95 x 10^{-3} mol ✓

3 mol $NaHCO_3$ reacts with 1 mol citric acid ✓

amount of citric acid = 5.95 x 10^{-3}/3 = 1.98 x 10^{-3} mol ✓

mass of citric acid required = 1.98 x 10^{-3} x 192 = 0.380 g ✓
(allow 0.4 g)

Answer of 0.127g / 0.12698 g from dividing by 3 twice ⟶ ✓✓✓✓✗

[5]

[Total: 16]