

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 | | | | | | | | | | | | |
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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

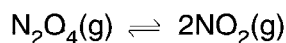
- The number of marks is given in brackets [] at the end of each question or part question.
- You will be awarded marks for the quality of written communication where this is indicated in the question.
- You may use a scientific calculator.
- You may use the *Data Sheet for Chemistry*.
- You are advised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

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 .



The equilibrium concentrations were: $\text{N}_2\text{O}_4(\text{g})$, $0.0390 \text{ mol dm}^{-3}$; $\text{NO}_2(\text{g})$, $0.0150 \text{ mol dm}^{-3}$.

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

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

[2]

- (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.



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

[3]

[Total : 11]

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

$$\text{rate} = k[\text{H}_2(\text{g})][\text{NO}(\text{g})]^2$$

- (a) Using $6.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ H}_2(\text{g})$ and $3.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ NO}(\text{g})$, the initial rate of this reaction was $4.5 \times 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$.

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 $\text{H}_2(\text{g})$ is doubled.

effect on rate

reason

.....[2]

- (ii) The concentration of $\text{NO}(\text{g})$ is halved.

effect on rate

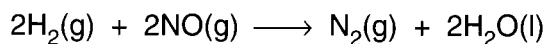
reason

.....[2]

- (iii) The concentrations of $\text{H}_2(\text{g})$ and $\text{NO}(\text{g})$ are both tripled.

effect on rate[1]

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



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

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

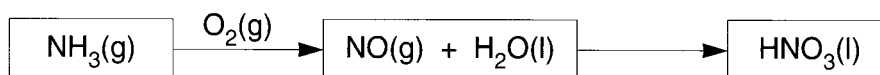
.....
[1]

- (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.



[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 .



- (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 $\text{NO}(\text{g})$ from $\text{NH}_3(\text{g})$.

.....[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]

- 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 $1.2 \times 10^{-5} \text{ mol dm}^{-3}$. 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*.

.....
.....[1]

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

.....[1]

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

.....
.....
.....
.....[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]



RECOGNISING ACHIEVEMENT

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) $K_c = \frac{[\text{NO}_2(\text{g})]^2}{[\text{N}_2\text{O}_4(\text{g})]}$ ✓ [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: $\frac{[\text{N}_2\text{O}_4(\text{g})]}{[\text{NO}_2(\text{g})]^2}$, then ans = 173 ✓ dm³ mol⁻¹ ✓ accept 173.33333.....to 170

if no square in (i): $\frac{[\text{NO}_2(\text{g})]}{[\text{N}_2\text{O}_4(\text{g})]}$, then ans = 0.384615.. ✓ no units ✓ (must be stated)

if no square in (i) and inverse: $\frac{[\text{N}_2\text{O}_4(\text{g})]}{[\text{NO}_2(\text{g})]}$, 2.6 ✓ no units ✓ (must be stated)

(b) $\Delta H = (2 \times 33) - (9)$ ✓ = (+)57 kJ mol⁻¹ ✓ [2]

common errors: -57 ✓ x +24 ✓ x +75 ✓ x -24 x x [2]

(c) *change* more NO₂ / less N₂O₄ ✓

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.

(d) 1 mol N₂O₄ reacts with 2 mol NaOH ✓ [3]

amount of NaOH required = 0.00930 mol ✓

volume NaOH = 1000 × 0.0093 / 0.300 = 31.0 cm³ / 0.0310 dm³ ✓

Common errors

3.1 × 10^x (where x is incorrect) ✓ ✓ x

15.5 cm³ / 0.0155 dm³ ✓ ✓ x

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

62 cm³ / 0.062 dm³ ✓ ✓ x

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

[Total: 11]

2. (a) $k = \frac{\text{rate}}{[\text{H}_2(\text{g})][\text{NO}(\text{g})]^2}$ ✓
 $k = 8.3 \times 10^4$ ✓ $\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$ ✓ calculator value: $8.33333\dots \times 10^4$

If [NO] is not squared: $\frac{\text{rate}}{[\text{H}_2(\text{g})][\text{NO}(\text{g})]}$ ×, ans = 250 ✓ units: $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ✓

If the expression is upside down: $\frac{[\text{H}_2(\text{g})][\text{NO}(\text{g})]^2}{\text{rate}}$ ×, ans = 1.2×10^{-5} ✓ units: $\text{mol}^2 \text{s dm}^{-6}$ ✓

upside down and not squared: $\frac{[\text{H}_2(\text{g})][\text{NO}(\text{g})]}{\text{rate}}$ × ×, ans = $0.004 \text{ mol s dm}^{-3}$ ✓ [3]

(b) (i) effect on rate × 2 ✓
 reason 1st order wrt $\text{H}_2(\text{g})$ ✓ [2]

(ii) effect on rate × 1/4 ✓
 reason 2nd order wrt $\text{NO}(\text{g})$ ✓ [2]

(iii) effect on rate × 27 ✓ [1]

(c) (i) slowest step ✓ [1]

(ii) step 1 (RDS) $\text{H}_2(\text{g}) + 2 \text{NO}(\text{g}) \longrightarrow \text{N}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{l})$ ✓
 step 2 $\text{H}_2(\text{g}) + \text{N}_2\text{O}(\text{g}) \longrightarrow \text{N}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$ rest of equations ✓ [2]

(d) (i) NH_3 , -3 ✓
 NO , +2 ✓
 HNO_3 , +5 ✓ [3]

(ii) $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \longrightarrow 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{l})$
 products + reactants → 1 mark; balancing → 1 mark ✓ ✓ [2]

(iii) molar masses $\text{NH}_3 = 17$; $\text{HNO}_3 = 63$ ✓
 mass = $700\,000 \times 17/63 = 1.89 \times 10^5$ tonnes ✓ calc value $1.888888\dots \times 10^5$
 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 ✓
= CH₂O ✓

mass CH₂O = 30; M_r = 90 ∴ molecular formula = C₃H₆O₃ ✓

[3]

(b)

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

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

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

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

4 marks: K_a expression ✓;

[H⁺] ✓;

pH expression ✓;

calculation of pH from [H⁺] (ecf) ✓

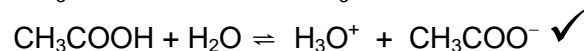
Common error: Without square root, answer is 4.7/ 4.7447... ✓✓✓x

[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) CH₃COOH ⇌ H⁺ + CH₃COO⁻ /



[1]

(iii) The weak acid or CH₃COOH reacts with added alkali / added alkali reacts with H⁺ ✓

The base or CH₃COO⁻ 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 CH₃COO⁻ ✓

[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 / H₂O accepts H⁺/behaves as a base ✓

equation: $\text{H}_3\text{A} + 3\text{H}_2\text{O} \longrightarrow 3\text{H}_3\text{O}^+ + \text{A}^{3-}$
 or $\text{H}_3\text{A} \longrightarrow 3\text{H}^+ + \text{A}^{3-}$
 or $\text{H}_3\text{A} + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+ + \text{H}_2\text{A}^-$
 or $\text{H}_3\text{A} \longrightarrow \text{H}^+ + \text{H}_2\text{A}^-$ ✓ (or other intermediate dissociation)

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

how H⁺ reacts: H⁺ now reacts with HCO₃⁻ ions/NaHCO₃ ✓

equation: $\text{H}^+ + \text{HCO}_3^- \longrightarrow \text{H}_2\text{O} + \text{CO}_2$ ✓

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

5 marks → [4] max

(ii) Molar mass of NaHCO₃ = 84.0 ✓

amount of NaHCO₃ = 0.5/84.0 = 5.95 x 10⁻³ mol ✓

3 mol NaHCO₃ 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 → ✓✓✓✓ x

[5]

[Total: 16]