

OXFORD CAMBRIDGE AND RSA EXAMINATIONS

Advanced GCE

CHEMISTRY

Unifying Concepts in Chemistry

2816/01

Friday

24 JANUARY 2003

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 | | | | | | | | | | |
| | <table border="1" style="display: inline-table; border-collapse: collapse;"> <tr> <td style="width: 15px; height: 20px;"></td> <td style="width: 15px; height: 20px;"></td> <td style="width: 15px; height: 20px;"></td> <td style="width: 15px; height: 20px;"></td> <td style="width: 15px; height: 20px;"></td> </tr> </table> | | | | | | <table border="1" style="display: inline-table; border-collapse: collapse;"> <tr> <td style="width: 15px; height: 20px;"></td> <td style="width: 15px; height: 20px;"></td> <td style="width: 15px; height: 20px;"></td> <td style="width: 15px; height: 20px;"></td> <td style="width: 15px; height: 20px;"></td> </tr> </table> | | | | | |
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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 provided 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.

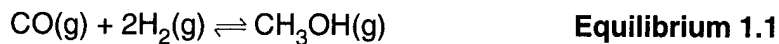
| FOR EXAMINER'S USE | | |
|---------------------------|-------------|-------------|
| Qu. | Max. | Mark |
| 1 | 17 | |
| 2 | 17 | |
| 3 | 12 | |
| 4 | 14 | |
| TOTAL | 60 | |

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

Answer **all** the questions.

- 1 *Syngas* is a mixture of carbon monoxide and hydrogen gases, used as a feedstock for the manufacture of methanol.

A dynamic equilibrium was set up between carbon monoxide, CO, hydrogen, H₂, and methanol, CH₃OH. The equilibrium system is shown by Equilibrium 1.1 below.



The equilibrium concentrations of the three components of this equilibrium are shown below.

| component | CO(g) | H ₂ (g) | CH ₃ OH(g) |
|---|------------------------|------------------------|------------------------|
| equilibrium concentration /mol dm ⁻³ | 3.1 × 10 ⁻³ | 2.4 × 10 ⁻² | 2.6 × 10 ⁻⁵ |

- (a) State **two** features of a system that is in *dynamic equilibrium*.

.....

[2]

- (b) (i) Write the expression for K_c for this equilibrium system.

[2]

- (ii) Calculate the numerical value of K_c for this equilibrium.

[2]

- (c) The pressure was increased whilst keeping the temperature constant. The system was left to reach equilibrium. The equilibrium position of Equilibrium 1.1 shifted to the right.

- (i) Explain why the equilibrium moved to the right.

.....
[2]

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

.....[1]

(iii) State and explain the effect on the rates of the forward and reverse reactions

- when the pressure was first changed
- when the system reached equilibrium.

.....
.....
.....
.....
.....[4]

(d) The temperature was increased whilst keeping the pressure constant. The system was left to reach equilibrium. The value of K_c for Equilibrium 1.1 decreased.

(i) Explain what happens to the equilibrium position of Equilibrium 1.1.

.....
.....
.....
.....
.....[2]

(ii) Deduce the sign of the enthalpy change for the forward reaction shown in Equilibrium 1.1. Explain your reasoning.

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

(iii) Explain how the partial pressure of $\text{CH}_3\text{OH}(\text{g})$ would change as the system moves towards equilibrium.

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

[Total: 17]

- 2 Nitrous oxide, N_2O , is a colourless gas with a mild, pleasing odour and sweet taste. It is widely used as a propellant in aerosol cans of whipped cream.

- (a) Nitrous oxide is formed when ammonium nitrate, NH_4NO_3 , is gently heated.



- (i) What mass of N_2O is formed by heating 100 g of NH_4NO_3 ?

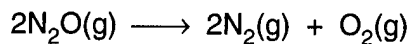
[3]

- (ii) What happens to the oxidation number of each nitrogen from NH_4NO_3 in this reaction?

.....

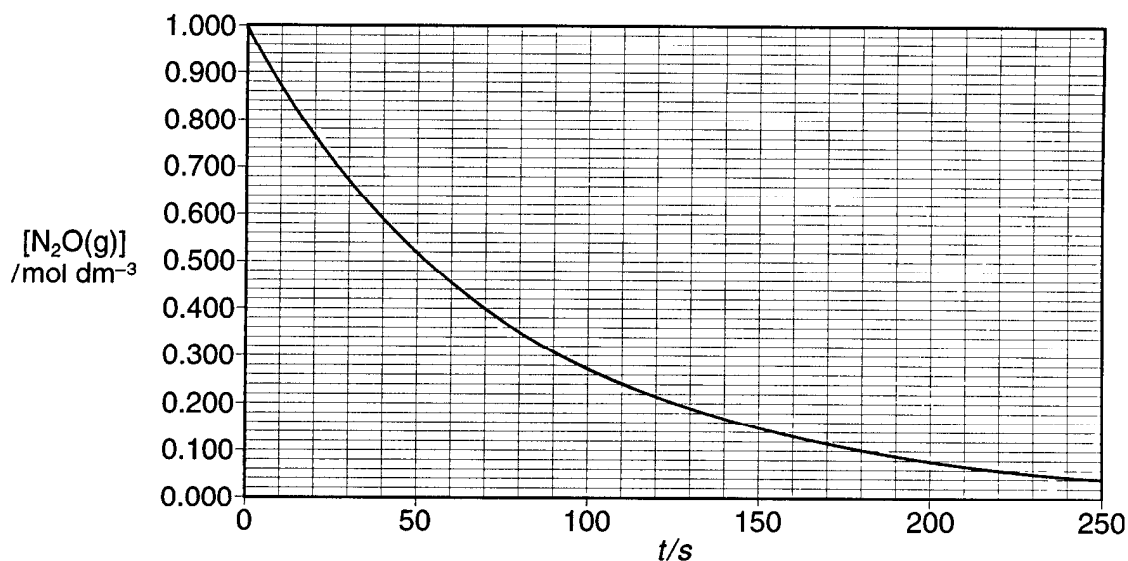
[2]

- (b) When heated strongly, nitrous oxide decomposes into its elements.



This reaction is first order with respect to N_2O .

The graph below shows how nitrous oxide decomposes with time at constant temperature.



(i) Explain how the graph confirms that this reaction is first order with respect to N₂O.

.....
.....
.....
.....[3]

(ii) Write the expression for the rate equation of this reaction.

[1]

(iii) Use the graph to work out the rate of reaction, in mol dm⁻³s⁻¹, at 70 seconds. Show clearly your working on the graph.

rate =mol dm⁻³s⁻¹ [2]

(iv) Calculate the rate constant for this reaction. State the units.

k = units [2]

(v) What evidence is there that the mechanism of this reaction takes place in more than a single step?

.....
.....
.....[2]

(c) N₂O is occasionally injected into the engines of racing cars to give more power and exceptional acceleration. The N₂O decomposes exothermically to N₂ and O₂.

Suggest **two** reasons why this reaction provides an extra boost to the engine.

.....
.....
.....[2]

[Total: 17]

(b) The acid dissociation constant K_a of hydrocyanic acid, HCN, is $4.9 \times 10^{-10} \text{ mol dm}^{-3}$.

(i) Write an expression for the acid dissociation constant of HCN.

[1]

(ii) Calculate the pH of a $0.010 \text{ mol dm}^{-3}$ solution of hydrocyanic acid.

[3]

[Total: 12]

4 Organic acids occur widely in nature.

- (a) Butanoic acid, $\text{CH}_3(\text{CH}_2)_2\text{COOH}$, is a straight-chain organic acid, largely responsible for the odour of rancid butter.

Caprylic acid is another straight-chain organic acid. It is produced in the body in small amounts as an antifungal agent in human sweat.

- (i) Some caprylic acid was isolated from human sweat and analysed. The sample of caprylic acid had the percentage composition by mass:

C, 66.7%; H, 11.1%; O, 22.2%. $M_r = 144$.

Calculate the molecular formula of caprylic acid and suggest its structural formula.

[4]

- (ii) Tracker dogs are trained to follow odours such as the characteristic blend of organic acids in the sweat from a person's feet. A dog is able to detect extremely small quantities of these acids.

Sweat containing equal amounts of butanoic and caprylic acids produces more butanoic acid vapour than caprylic acid vapour.

Suggest a reason for this. Explain your answer.

.....
.....
.....
.....[2]

Subject: Unifying Concepts
Code: 2816/1

Session: January
Year: 2003

Final Mark Scheme

25/1/2003

| | |
|---------------------|-----------|
| MAXIMUM MARK | 60 |
|---------------------|-----------|

1. (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)

$$K_c = \frac{[\text{CH}_3\text{OH}(\text{g})]}{[\text{CO}(\text{g})][\text{H}_2(\text{g})]^2} \checkmark\checkmark \text{ 1 mark for top; 1 mark for bottom}$$

[2]

(ii)

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

[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) ΔH is negative because of equilibrium change in (i) ✓

Mark consequential on (i)

[1]

(iii) Partial pressure decreases because less CH_3OH is now present ✓

[1]

[Total: 17]

2. (a) (i) $m(\text{NH}_4\text{NO}_3) = 80$ ✓
moles $\text{N}_2\text{O} = \text{moles } \text{NH}_4\text{NO}_3 = 100/80 = 1.25 \text{ mol}$ ✓
mass $\text{N}_2\text{O} = 1.25 \times (28 + 16) = 55 \text{ g}$ ✓

[3]

(ii) nitrogen in NH_4^+ : $-3 \longrightarrow +1$ / increases by 4 ✓
nitrogen in NO_3^- : $+5 \longrightarrow +1$ / decreases by 4 ✓

[2]

(b) (i) 1st order has a constant half life ✓
Evidence from graph, either drawn or stated below with 2 half lives ✓
half life approx 52 s ✓

[3]

(ii) rate = $k[\text{N}_2\text{O}(\text{g})]$ ✓

[1]

(iii) evidence of tangent on graph ✓
rate = $0.00524 \text{ mol dm}^{-3} \text{ s}^{-1}$ ✓
(allow ± 0.005 : i.e. values in range $0.00475 - 0.00575 \text{ mol dm}^{-3} \text{ s}^{-1}$)

[2]

(iv) 0.00524 (ans to (ii)) = $k \times 0.400$
 $k = 0.0131 \text{ s}^{-1}$ ✓

[2]

(v) rate determining step involves 1 molecule of N_2O ✓
equation shows 2 mol N_2O reacting ✓

[2]

(c) Increases the pressure/rate increases ✓
Gives out heat ✓
Forms oxygen \longrightarrow more efficient combustion ✓
moles of products > moles of reactants ✓

[2 max]

[Total: 17]

3. (a)

Acid is a proton/H⁺ donor ✓

Base is a proton/H⁺ acceptor ✓

Conjugate acid has H⁺ more than conjugate base ✓

Equation showing acid-base pairs ✓

2 acid-base pairs labelled correctly ✓

Dilute acid has small number of moles dissolved per volume ✓

Weak acid has partial dissociation ✓

[7]

Quality of Written Communication

At least **two** complete sentences that are legible and where the spelling, punctuation and grammar allow the meaning to be clear. At least one equation shown. ✓

[1]

(b) (i)

$$K_a = \frac{[\text{H}^+(\text{aq})][\text{CN}^-(\text{aq})]}{[\text{HCN}(\text{aq})]} \quad \checkmark$$

[1]

(ii)

$$K_a = \frac{[\text{H}^+(\text{aq})]^2}{[\text{HCN}(\text{aq})]} \quad \therefore 4.9 \times 10^{-10} = \frac{[\text{H}^+(\text{aq})]^2}{0.010} \quad \checkmark$$

$$[\text{H}^+(\text{aq})] = \sqrt{\{ (4.9 \times 10^{-10}) \times (0.010) \}} = 2.2 \times 10^{-6} \text{ mol dm}^{-3} \quad \checkmark$$

$$\text{pH} = -\log[\text{H}^+(\text{aq})] = -\log 2.2 \times 10^{-6} = 5.65/5.66/5.7 \quad \checkmark$$

(accept calculator value)

[3]

[Total: 12]

4. (a) (i)

$$\begin{array}{rcccc} & \text{C} & : & \text{H} & : & \text{O} \\ = & 66.7/12 & : & 11.1/1 & : & 22.2/16 \quad \checkmark \\ = & 5.56 & : & 11.1 & : & 1.39 \\ = & 4 & : & 8 & : & 1 \end{array}$$

empirical formula = $\text{C}_4\text{H}_8\text{O}$ ✓

$48 + 8 + 16 = 72$ which is half of M_r

Therefore molecular formula = $\text{C}_8\text{H}_{16}\text{O}_2$ ✓

Structural formula = $\text{CH}_3(\text{CH}_2)_6\text{COOH}$ ✓

[4]

(ii) caprylic acid is a longer molecule/contains more electrons ✓

caprylic acid has more van der Waals forces between molecules ✓

caprylic acid has a higher boiling point / is less volatile ✓

[2 max]

(b)

$$[\text{H}^+(\text{aq})] = K_w / [\text{OH}^-(\text{aq})] \quad \checkmark = 1.00 \times 10^{-14} / 0.500 = 2.00 \times 10^{-14} \text{ mol dm}^{-3} \quad \checkmark$$

$$\text{pH} = -\log[\text{H}^+(\text{aq})] = -\log 2 \times 10^{-14} = 13.699 / 13.7 \quad \checkmark \quad (\text{calculator value: } 13.69897)$$

[3]

$$\text{moles NaOH in } 25.00 \text{ cm}^3 = \text{moles NaOH} = 0.0125 \text{ mol} \quad \checkmark$$

$$\text{moles A in } 21.40 \text{ cm}^3 = \text{moles NaOH} = 0.0125 \text{ mol} \quad \checkmark$$

$$\text{moles A in } 250 \text{ cm}^3 = 0.0125 \times 250/21.40 = 0.146 \text{ mol} / [\text{A}] = 0.584 \text{ mol dm}^{-3} \quad \checkmark$$

0.146 mol **A** has a mass of 10.8 g

$$\text{molar mass of A} = 10.8/0.146 = 74 \text{ g mol}^{-1} \quad \checkmark$$

Therefore **A** is propanoic acid / $\text{CH}_3\text{CH}_2\text{COOH}$ ✓

[5]

[Total: 14]