## 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


## 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 |  |

## Answer all questions.

1 A chemist set up an equilibrium system between dinitrogen tetroxide, $\mathrm{N}_{2} \mathrm{O}_{4}$, and nitrogen dioxide, $\mathrm{NO}_{2}$, at $25^{\circ} \mathrm{C}$.

$$
\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NO}_{2}(\mathrm{~g})
$$

The equilibrium concentrations were: $\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g}), 0.0390 \mathrm{~mol} \mathrm{dm}^{-3} ; \mathrm{NO}_{2}(\mathrm{~g}), 0.0150 \mathrm{~mol} \mathrm{dm}^{-3}$.
(a) (i) Write the expression for $K_{c}$ in this equilibrium system.
(ii) Calculate $K_{c}$ for this equilibrium. State the units.
(b) The standard enthalpy changes of formation of $\mathrm{N}_{2} \mathrm{O}_{4}$ and $\mathrm{NO}_{2}$ are given below.

| compound | $\Delta H_{f}^{\ominus} / \mathrm{kJ} \mathrm{mol}^{-1}$ |
| :---: | :---: |
| $\mathrm{~N}_{2} \mathrm{O}_{4}$ | +9 |
| $\mathrm{NO}_{2}$ | +33 |

Calculate the standard enthalpy change for the forward reaction in this equilibrium.
(c) This equilibrium system was heated at constant pressure. How would you expect the relative proportions of $\mathrm{N}_{2} \mathrm{O}_{4}$ and $\mathrm{NO}_{2}$ to change? Explain your answer.
change
explanation $\qquad$
$\qquad$
$\qquad$
(d) $\mathrm{NO}_{2}$ and $\mathrm{N}_{2} \mathrm{O}_{4}$ are both poisonous. After this investigation, the chemist needed to dispose of $0.00465 \mathrm{~mol}_{2} \mathrm{O}_{4}$ safely. The chemist decided to do this by reacting the $\mathrm{N}_{2} \mathrm{O}_{4}$ with an alkali and chose aqueous sodium hydroxide.

$$
\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g})+2 \mathrm{NaOH}(\mathrm{aq}) \longrightarrow \mathrm{NaNO}_{3}(\mathrm{aq})+\mathrm{NaNO}_{2}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

Calculate the minimum volume of $0.300 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{NaOH}(\mathrm{aq})$ required to dispose of this amount of $\mathrm{N}_{2} \mathrm{O}_{4}$.

2 The reaction between hydrogen, $\mathrm{H}_{2}$, and nitrogen monoxide, NO , has the following rate equation.

$$
\text { rate }=k\left[\mathrm{H}_{2}(\mathrm{~g})\right][\mathrm{NO}(\mathrm{~g})]^{2}
$$

(a) Using $6.0 \times 10^{-3} \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{H}_{2}(\mathrm{~g})$ and $3.0 \times 10^{-3} \mathrm{moldm}^{-3} \mathrm{NO}(\mathrm{g})$, the initial rate of this reaction was $4.5 \times 10^{-3} \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{~s}^{-1}$.

Calculate the rate constant, $k$, for this reaction and state its units.
(b) Predict what would happen to the reaction rate after the following changes in concentrations. Show your reasoning.
(i) The concentration of $\mathrm{H}_{2}(\mathrm{~g})$ is doubled.
effect on rate
reason $\qquad$
$\qquad$
(ii) The concentration of $\mathrm{NO}(\mathrm{g})$ is halved.
effect on rate $\qquad$
reason $\qquad$
(iii) The concentrations of $\mathrm{H}_{2}(\mathrm{~g})$ and $\mathrm{NO}(\mathrm{g})$ are both tripled. effect on rate
(c) The overall equation for the reaction between hydrogen and nitrogen monoxide is shown below.

$$
2 \mathrm{H}_{2}(\mathrm{~g})+2 \mathrm{NO}(\mathrm{~g}) \longrightarrow \mathrm{N}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{I})
$$

This reaction takes place by a two step mechanism with the rate-determining step taking place first.
(i) Explain the term rate-determining step.
$\qquad$
$\qquad$
(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) $\qquad$ $+2$. $\qquad$ $\longrightarrow$ $\qquad$ $+\mathrm{H}_{2} \mathrm{O}(\mathrm{I})$
step 2
$+$ $\qquad$

$$
\longrightarrow \mathrm{N}_{2}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I})
$$

(d) Each year in the UK, 700000 tonnes of nitric acid, $\mathrm{HNO}_{3}$, 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, $\mathrm{NH}_{3}$.

(i) What is the oxidation state of nitrogen in the following?
$\mathrm{NH}_{3}$ $\qquad$
NO
$\mathrm{HNO}_{3}$
(ii) Construct a balanced equation for the formation of $\mathrm{NO}(\mathrm{g})$ from $\mathrm{NH}_{3}(\mathrm{~g})$.
$\qquad$
(iii) Assuming that $1 \mathrm{~mol} \mathrm{NH}_{3}$ produces $1 \mathrm{~mol}_{\mathrm{HNO}_{3}}$, calculate the mass of $\mathrm{NH}_{3}$ that is required to meet the annual demand for $\mathrm{HNO}_{3}$ in the UK.

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 $1.5 \mathrm{~mol} \mathrm{dm}^{-3}$ ) are used to remove dead skin.
(a) An AHA was analysed and had the percentage composition by mass:

$$
\mathrm{C}, 40.0 \% ; \mathrm{H}, 6.7 \% ; \mathrm{O}, 53.3 \% . M_{\mathrm{r}}=90 .
$$

Calculate the molecular formula of this AHA.
(b) Calculate the pH of a $1.5 \mathrm{moldm}^{-3}$ solution of an AHA with an acid dissociation constant, $K_{\mathrm{a}}$, of $1.2 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3}$. Show your working.
(c) Beauty treatments often contain buffers. An example of a buffer is a mixture of ethanoic acid, $\mathrm{CH}_{3} \mathrm{COOH}$, and an ethanoate salt such as sodium ethanoate, $\mathrm{CH}_{3} \mathrm{COONa}$.
(i) Explain what is meant by a buffer solution.
$\qquad$
$\qquad$
(ii) Write the chemical equation for the equilibrium in this buffer system.
(iii) Explain how this buffer solution works. Use equations where appropriate.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
(d) A buffer solution was prepared using equal concentrations of $\mathrm{CH}_{3} \mathrm{COOH}$ and $\mathrm{CH}_{3} \mathrm{COONa}$.

What would be the effect on the pH of this buffer solution of adding some solid $\mathrm{CH}_{3} \mathrm{COONa}$ ? Explain your answer.
effect on pH
explanation $\qquad$
$\qquad$
$\qquad$

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.

$$
\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g}) \Delta H=-92 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

Explain why the conditions of temperature and pressure used in the Haber process $\left(450^{\circ} \mathrm{C}, 15000 \mathrm{kPa}\right.$ ) are a compromise.
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(b) An Alka-Seltzer tablet contains about 0.5 g sodium hydrogencarbonate, $\mathrm{NaHCO}_{3}$, 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 $\mathrm{H}_{3} A$.

$$
3 \mathrm{NaHCO}_{3}+\mathrm{H}_{3} \mathrm{~A} \longrightarrow \mathrm{Na}_{3} \mathrm{~A}+3 \mathrm{CO}_{2}+3 \mathrm{H}_{2} \mathrm{O}
$$

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