Examiners' Report

January 2010

GCE Chemistry 6CH04/01

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General

Section A of the paper contained questions that were found to be straightforward by the majority of candidates. The average mark for the multiple-choice component of the paper was just over 14/20. The structured questions in Sections B and C, however, proved to be far more demanding - such as Q26, which required candidates to use high resolution nmr spectra in order to identify the structural formulae of two unknown compounds. Examiners gave candidates every opportunity to show their knowledge and understanding in this paper. For example, when marking Q25 it was often found that the correct answer to Q25(a) was given by candidates as part of their answer to Q25(b)(v) rather than as their response to Q25(a). If so, the mark for Q25(a) was duly awarded. A similar principle was applied to the marking of Q26(a), where candidates often included answers to this part within their answer to Q26(b).

Question 21

In (a), many candidates were able to define pH and calculate the pH of a strong acid. In (b)(i), many very good answers were seen with the pH of the ethanoic acid correctly calculated and the assumption clearly stated.

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Examiner Comments

Some clear and concise answers were seen, as shown by this response which scored full marks.

(b) Ethanoic acid is a weak acid with an acid dissociation constant, K_a, of value 1.75×10^{-5} mol dm^{-3} at 25 °C.

(i) Calculate the pH of 0.0100 mol dm^{-3} ethanoic acid at 25 °C, stating any ONE assumption that you have made.

(4)

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.75 \times 10^{-5} \text{ moldm}^{-3}$$

$$= \frac{[H^+]^2}{[CH_3COOH]}$$

$$\Rightarrow [H^+] = \sqrt{K_a \times [CH_3COOH]} = 4.18 \times 10^{-4} \text{ moldm}^{-3}$$

$$pH = -\log_{10}(4.18 \times 10^{-4}) = \boxed{3.38}$$

Assumption ..The concentration of CH_3COOH after dissociation is the same as the initial concentration.

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Examiner Comments

In other answers, such as the one below, the mark for the correct assumption (here [H⁺] = [CH³COO⁻]) was awarded from what was written in the working rather than for what was written in the space provided after the calculation.

(b) Ethanoic acid is a weak acid with an acid dissociation constant, K_a, of value 1.75×10^{-5} mol dm⁻³ at 25 °C.

(i) Calculate the pH of 0.0100 mol dm⁻³ ethanoic acid at 25 °C, stating any ONE assumption that you have made.

(4)

Assume ethanoic acid partly dissociates.

$$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$$
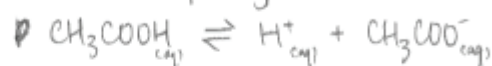
$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$\therefore [H^+] = [CH_3COO^-]$$

$$[H^+] = \sqrt{(1.75 \times 10^{-5})(0.0100)}$$

$$= 4.18 \times 10^{-4} \text{ mol dm}^{-3}$$

pH of ethanoic acid = 3.38 (to 3 s.f.)

Assumption Ethanoic acid partly dissociates.

Part (b)(ii) was found to be extremely challenging. Correct answers were few and far between. Despite this concept being clearly flagged up in the Specification (see Topic 4.7 f(ii)), many candidates were unaware that the degree of dissociation of the weak acid increases on dilution.

In the case of hydrochloric acid, dilution by a factor of 10 increases the pH by one unit. Suggest why ethanoic acid behaves differently.

(2)

Because of the following equilibrium :

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

diluting the solution by adding water will move equilibrium to the right as it would follow le Chatelier's principle. Therefore H^+ ion in the form of H_3O^+ ion would form to be produced increasing $[H^+]$ and decreasing the pH. This would counteract the increasing pH due to dilution so increase is only by 0.5 unit.

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Examiner Comments

An alternative approach to answering this question was a mathematical one as illustrated here.

Hydrochloric is a strong acid, therefore a ten-fold solution corresponds to a ten-fold change in H^+ concentration.

However, ethanoic acid is a weak acid and therefore the H^+ concentration is related to the acid concentration in the following manner: $[H^+] = \sqrt{k_a [Acid]}$. Hence dilution by a factor of 10 results in a factor of $\frac{1}{\sqrt{10}}$ for the $[H^+]$, leading to the result of a pH change of 0.5.

In (c)(ii), the definition of the term "buffer solution" was frequently given correctly. For example:-

(c) Orange marmalade usually contains sodium citrate as a preservative. Together with the fruit in the marmalade, it forms a buffer solution which, at a suitable pH, inhibits mould growth.

(i) Define the term **buffer solution**.

(2)

A solution which resists changes in pH when small quantities of acid or base are added.

Some answers, nonetheless, stated that the pH of the buffer solution remained constant, rather than **almost** constant, on addition of small amounts of acid or base.

(i) Define the term **buffer solution**.

(2)

Buffer solution maintains pH constant when small amounts of acids or bases are added.

In (c)(iii), the best answers explaining how a buffer solution works were those which contained relevant equations and concise sentences.

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Examiner Comments

This response shows an example of a well set-out answer scoring full marks.
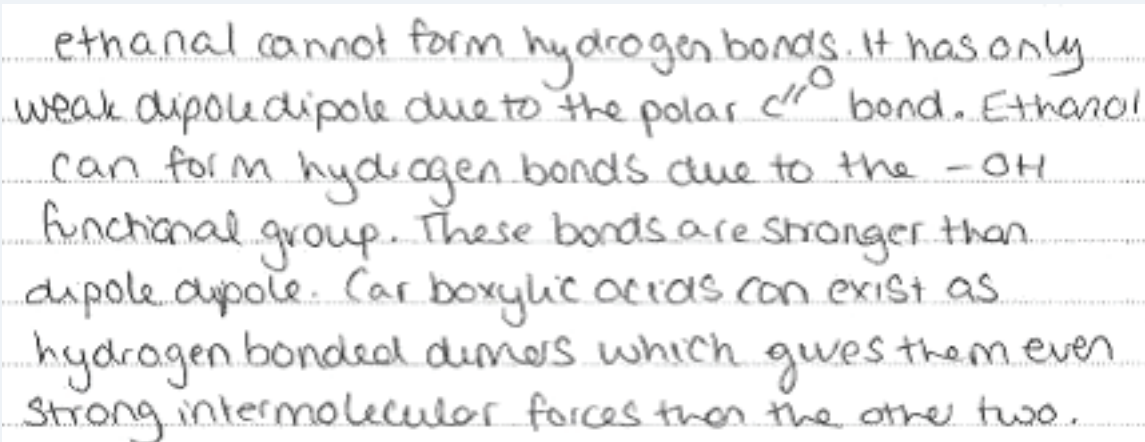
(iii) Explain how a buffer solution works using this system or any other of your choice. Support your explanation with equations.

(4)

A buffer is made of a weak acid and its salt. The salt fully dissociates and produces a reservoir of A^- ions, in the case of methanoic acid + sodium methanoate, $HCOO^-$. The acid only dissociates very slightly and produces a reservoir of $HCOOH$.

When acid is added:

$H^+ + HCOO^- \rightarrow HCOOH$

When alkali is added:

$HCOOH + OH^- \rightarrow H_2O + HCOO^-$

The changes in $HCOOH$ and $HCOO^-$ concentration are very small relative to the original concentrations.

Question 22

This question required answers exhibiting a high quality of written communication. The essential points that had to be made were that there is no hydrogen bonding in ethanal (whereas there is in ethanol and in ethanoic acid), that hydrogen bonds are the strongest of the intermolecular forces and, finally, any relevant point focusing on a reason why overall the strongest intermolecular forces exist between ethanoic acid molecules (as this substance has the highest boiling temperature of those mentioned in the question):-

> ethanal cannot form hydrogen bonds. It has only weak dipole dipole due to the polar $C=O$ bond. Ethanol can form hydrogen bonds due to the $-OH$ functional group. These bonds are stronger than dipole dipole. Carboxylic acids can exist as hydrogen bonded dimers which gives them even strong intermolecular forces than the other two.

Answers to Q22(b) showed an excellent knowledge of chemical tests encountered in the study of carbonyl chemistry. In (c)(i), many good mechanisms were seen although a lack of precision was noticeable if structural formulae were drawn too small. Inaccuracy in the position of the head and the tail of each curly arrow was more likely to occur in such cases. Many candidates remain under the impression that a curly arrow represents the movement of an atom or group of atoms to form a new linkage rather than the movement of an electron pair. In (c)(ii), the role of the potassium cyanide, KCN, in order to increase the concentration of the attacking nucleophile, CN-, was rarely known. In (c)(iii), many candidates were aware that a racemic mixture is produced, but the planar geometry around the carbon in the C=O group was often not mentioned. Confusion with other mechanisms, such as S_N1 or S_N2, was evident.
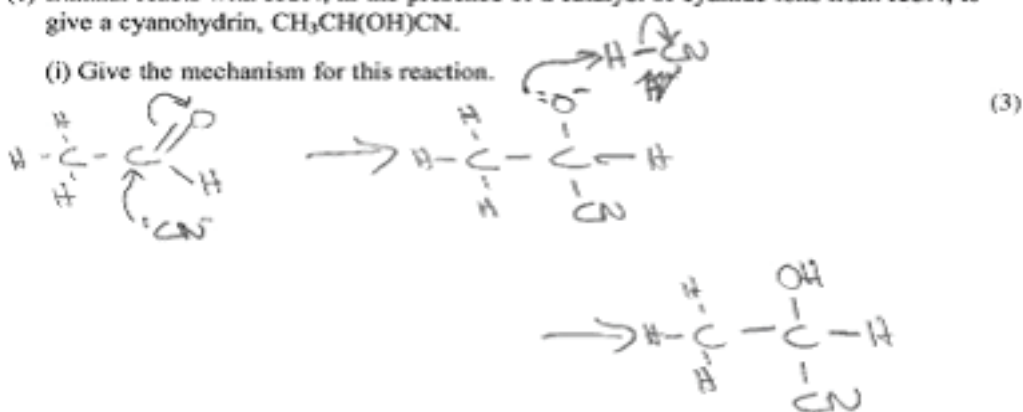
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Examiner Comments

An excellent answer to Q22(c) demonstrating clear understanding.

(c) Ethanal reacts with HCN, in the presence of a catalyst of cyanide ions from KCN, to give a cyanohydrin, CH₃CH(OH)CN.

(i) Give the mechanism for this reaction.

(3)

(ii) Explain why it is necessary to use HCN and KCN in this reaction, rather than HCN on its own.

(1)

HCN ionises very weakly and therefore does not produce sufficient CN⁻ ions. KCN ionises fully and provides these ions.

*(iii) Explain why the product mixture from this reaction is **not** optically active.

(2)

The carbonyl group in ethanal is planar and therefore can be attacked from above or below with equal probability. ~~However~~ Therefore, two enantiomers are formed in equal proportions and their effects cancel out. The product is a racemic mixture.

Question 23

This was found to be a highly demanding question. In (a)(i), the reason for keeping the concentrations of both propanone and the hydrogen ions in large excess was poorly understood. In(a)(ii), the fact that doubling the initial concentration of propanone, whilst keeping the initial concentrations of hydrogen ions and iodine constant, would double the rate of reaction was not known. Also, very few candidates realised that the gradient of the straight line of the plot of $[I_2]$ against time would be twice as steep in these circumstances. Answers to (a)(iii) were, however, more convincing.

(iii) Explain why the minimum number of steps in the mechanism for this reaction is two.

(2)

There are two species in the rate determining step, Iodine is not involved, there as seen from the rate equation. There therefore must be another step which involves Iodine.

A significant number of candidates found it difficult to write the ionic equation in (b)(i) and the equation for the iodoform reaction in (b)(ii). A mark was awarded in (b)(iii), however, for the correct formula of triiodomethane, CHI_3.

Question 24

Part (a) proved straightforward for many candidates, although K_p expressions containing square brackets appeared more often than one might expect. This showed that, in some candidates' minds, there is still confusion between K_p and K_c. In (b)(i), a common error was the misconception that, since the position of equilibrium **I** shifts to the left when the total pressure increases, it follows that "K_p decreases" under these circumstances. In (b)(ii), very few candidates were able to justify, mathematically, why an increase in total pressure lead to a decrease in yield of carbon monoxide and hydrogen in reaction **I** despite the fact that K_p **remains constant**. The vast majority of candidates applied Le Chatelier's Principle, instead, to justify the equilibrium position shifting to the left when increasing the total pressure. Few correct answers to (b)(iii) were seen, with only a minority of candidates referring to active sites. So 3/6 was a typical mark for Q24(a) and (b).

(a) Write the expression for the equilibrium constant, K_p, for reaction I.

(1)

$$K_p = \frac{p(CO) \times p(H_2)^3}{p(CH_4) \times p(H_2O)}$$

(b) Reaction I occurs at a temperature of 1000 K and a pressure of 30 atm over a nickel catalyst.

(i) State and explain the effect, if any, **on the value of K_p** of increasing the pressure on the reaction.

(1)

It has no effect on Kp because Kp only changes when temperature increases.

(ii) Explain, in terms of your answers to (a) and (b)(i), why an increase in the pressure leads to a decrease in yield in reaction I.

(2)

There are more moles of products on the right hand side of the reaction. Increase in pressure does not change Kp as Kp is a constant, but the concentration of products will lower as equilibrium shifts to the left. Therefore it leads to a decrease in yield.

Examiners saw many excellent answers to the calculation in (c). The steps were well laid out and easy to follow. However, a number of candidates were unable to deduce the molar amounts of each substance present at equilibrium. Consequential marking allowed the remaining available marks to be awarded in such cases.
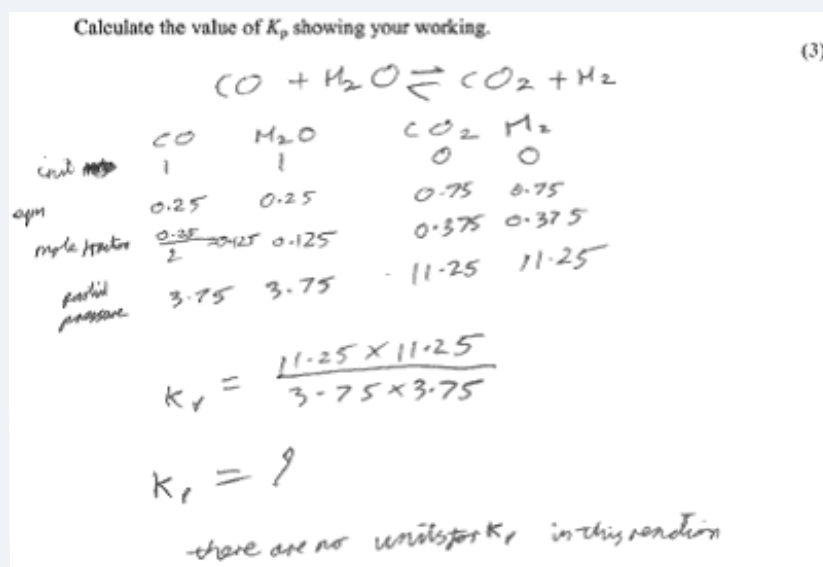
Part (d)(i) was well-answered, with 75% of all candidates scoring the mark for this question. However, in (d)(ii), a surprising number of candidates were unable to write the equation for the thermal decomposition of potassium hydrogencarbonate, $KHCO_3$, despite two of the three products being given in the stem of the question. In (e), many candidates understood that industrial processes are rarely allowed to reach equilibrium as the products are removed, although a considerable minority answered this question in terms of only "cost", without any further comment.

Question 25

Part (a) was not answered well but, as explained earlier in this report, many candidates were awarded this mark from their answer to (b)(v) when explaining why the reaction was spontaneous. For (b)(i), a substantial number of candidates were unable to look up the entropy data correctly from the data booklet.

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Examiner Tip

Candidates should be familiar with the data booklet and they should have practised looking up data prior to the examination. The value of S^θ for Fe_3O_4, rather than that for Fe_2O_3, was often quoted.

In (b)(ii), consequential marking from answers to (b)(i) enabled access to both available marks. A significant minority of candidates gave a value of S^θ for $Fe(s)$ as zero, showing that there was confusion between standard molar entropy values of an element with those of the standard enthalpy change of formation of an element.

In (b)(iii), there were many correct answers, but some candidates did not convert the standard enthalpy change for the reaction into J mol^{-1} from kJ mol^{-1} and/or convert the temperature of 25 °C into K.

In (b)(iv), the total standard entropy change for the reaction was often calculated correctly, but the + sign was then omitted from the final answer. Most candidates scored some marks on (b)(v), but many candidates did not mention that the heat energy released from the exothermic reaction would increase the movement of the molecules, hence the disorder, in the surroundings.

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Examiner Comments

This is a very good answer to this question.

(a) Explain the meaning of **spontaneous** in a thermodynamic context.

(1)

Once the activation energy has been reached, a reaction will go to completion on its own.

(b) (i) Find the values of the standard molar entropies of iron and of iron(III) oxide from your data booklet.

(1)

$Fe: \quad S^\ominus = 27.3 \ Jmol^{-1}k^{-1}$

$Fe_2O_3: \quad S^\ominus = 87.4 \ Jmol^{-1}k^{-1}$

(ii) The standard molar entropy at 298 K for oxygen molecules O_2 is +205 J mol^{-1} K^{-1}.

Calculate the standard entropy change of the system for the reaction between iron and oxygen. Include a sign and units in your answer.

(2)

$\Delta S_{sys} = \Sigma S_{product} - \Sigma S_{reactants}$

$= (2 \times 87.4) - (4 \times 27.3) - (205 \times 3)$

$= \boxed{-549.4 \ Jmol^{-1}k^{-1}}$

(iii) The standard enthalpy change for the reaction at 25 °C is −1648 kJ mol^{-1}.

Calculate $\Delta S_{surroundings}$.

(1)

$\Delta S_{surr.} = \dfrac{-\Delta H}{T}$

$= \dfrac{1648\ 000}{25 + 273}$

$= \dfrac{1648000}{298} \boxed{+5530 \ Jmol^{-1}k^{-1}}$

(iv) Use your answers to (b)(ii) and (iii) to calculate the total standard entropy change for the reaction. Include a sign and units in your answer.

(2)

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

$$= -549.4 + 5530$$

$$= +4981 \, JK^{-1}mol^{-1}$$

*(v) The reaction is thermodynamically spontaneous.

Use your answers to (b)(ii), (iii) and (iv) to explain, in terms of the physical states of the substances in the reaction and the movement of the molecules in the surroundings, why this is so.

(3)

The system itself becomes more ordered as a gas is being turned into a solid. However, the surroundings become much more disordered since a lot of heat is evolved and this excites nearby air molecules. However, Overall, the large increase in movement of the air molecules outweighs the relatively small increase in order of the products, and the reaction is spontaneous.

Question 26

This proved to be a demanding and discriminating question. In (a), many candidates earned one mark for identifying the peak at around 3400 cm⁻¹ on the IR spectrum and a second mark for this peak being due to **X** containing an –OH group or **X** being an alcohol. Candidates often then identified **Y** as being an aldehyde or a ketone. Those candidates who decided at this stage that **Y** must be butanal then ran into difficulties in (b). Many candidates found the high resolution nmr spectra in (b) challenging. There was often confusion between nmr and IR or mass spectroscopy. The peaks on both nmr spectra were frequently assigned to bonds or fragments within each molecule. The (n+1) rule, which is used to explain splitting patterns, was also applied incorrectly by many candidates. Examiners were surprised how infrequently references were made to hydrogen (or proton) environments within the molecules of **X** and **Y**. That said, some logical and well-argued responses were seen, often in cases where the displayed formulae of **X** and **Y** were drawn out and annotated.

What can be deduced about the structures of **X** and **Y** using all this information and the data booklet? Justify your answer.

(4)

Compound X — broad peak at 3400 indicating O—H group (alcohol)
— Peak at 2900-300 indicating C-H (alkane)
∴ X is an alcohol (cannot be tertiary, as it can be oxidised)
Compound Y — is produced from the oxidation of X (an alcohol)
Y must be either an aldehyde, Ketone ~~or ester~~

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Examiner Comments

This is a very well-structured answer.

Advice to candidates

- Make sure you understand data which shows how the pH of a strong acid and a weak acid changes after dilution 10, 100 and 1000 times.

- Make sure you know your way around your data booklet.

- When doing entropy calculations, always consider both the sign **and** units of your answer.

- Practise interpreting the use of high resolution nmr spectra to identify the structure of a molecule.

- Make sure you understand how the position of an equilibrium can shift even though K_p remains **constant** when the total pressure is altered.

Grade boundaries for GCE 08 Chemistry

6CH01/01

Grade	Max. Mark	A	B	C	D	E
Raw boundary mark	80	48	41	35	29	23
Uniform boundary mark	120	96	84	72	60	48

6CH02/01

Grade	Max. Mark	A	B	C	D	E
Raw boundary mark	80	51	45	39	33	27
Uniform boundary mark	120	96	84	72	60	48

6CH04/01

Grade	Max. Mark	A	B	C	D	E
Raw boundary mark	90	56	50	44	38	33
Uniform boundary mark	120	96	84	72	60	48

Maximum Mark (Raw): the mark corresponding to the sum total of the marks shown on the mark scheme.

Boundary Mark: the minimum mark required by a candidate to qualify for a given grade.

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