

Examiners' Report  
June 2014

IAL Chemistry WCH04 01

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June 2014

Publications Code IA038354

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## Introduction

This was the second session of the International Advanced Level Chemistry Unit 4 paper. There was a small entry for the first paper in January 2014, but there was a larger entry for the June paper. The specification and style of examination paper are exactly the same as the 6CH04 paper, so the candidates had plenty of opportunity to work through past papers to develop their examination technique.

Successful candidates:

- read the questions carefully and addressed all parts of the question in their answer;
- used scientific terminology correctly;
- completed calculations correctly;
- gave concise but detailed explanations where required;
- drew a clear mechanism for the reaction between propanal and cyanide ions;
- used the information given in the question and thought about the chemistry involved;
- wrote balanced equations;
- checked their work, particularly in calculations, to avoid careless errors such as missing or incorrect signs or units.

Less successful candidates:

- did not read the questions carefully and assumed the answer required was the same as in a past paper;
- made careless errors in calculations and did not think about the chemistry involved to realise that their answer could not be correct;
- did not express their understanding clearly when explaining concepts;
- did not use all the information given in the questions to help them in their answers;
- did not write balanced equations;
- did not relate a rate equation to the mechanism of a reaction;
- did not understand the use of curly arrows, dipoles and charges in an organic mechanism.

The majority of candidates were proficient in carrying out calculations and just made an occasional careless slip. In future, candidates need to concentrate on expressing their ideas clearly and concisely when explaining chemical concepts.

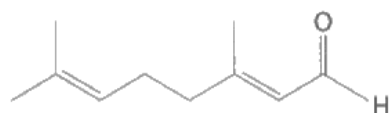
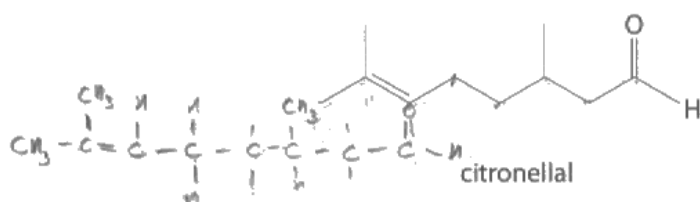
### Question 18 (a)

Although many candidates were able to work out the molecular formula for citronellal, a significant number wrote down the wrong number of hydrogen atoms. Some candidates gave a structural formula, some wrote  $C_9H_{17}CHO$  and some even tried to give a systematic name as their answer.

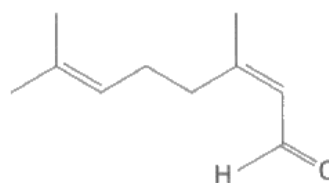
18 Citronella oil is obtained from lemongrass.

It is a source of chemicals for the perfume industry.

Three of the aldehydes found in citronella oil are shown below.



geranial



neral

(a) Give the molecular formula for citronellal.

(1)



#### ResultsPlus Examiner Comments

This candidate drew a structural formula by the skeletal formula but then used this to help work out the correct molecular formula. This response scored 1 mark.



#### ResultsPlus Examiner Tip

It is often helpful to draw a displayed or structural formula by the skeletal formula and then count the numbers of atoms from that.



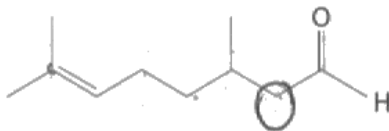
### Question 18 (b)

The majority of candidates could identify the chiral carbon atom. A small number of candidates thought that it was the carbon atom joined by the double bond to oxygen.

(b) Citronellal has one chiral carbon atom.

Draw a circle around the chiral carbon atom on the structure of citronellal below.

(1)



**ResultsPlus**  
Examiner Comments

This candidate has circled a carbon atom with two hydrogen atoms attached, so did not score a mark.



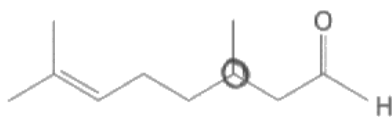
**ResultsPlus**  
Examiner Tip

Chiral carbon atoms have four different atoms or groups of atoms attached to them.

(b) Citronellal has one chiral carbon atom.

Draw a circle around the chiral carbon atom on the structure of citronellal below.

(1)



**ResultsPlus**  
Examiner Comments

This candidate has identified the correct chiral carbon atom and scored 1 mark.

### Question 18 (c) (i)

Many candidates did score both marks for this answer, but a significant number just mentioned restricted rotation, without referring to the C=C or  $\pi$  bond. Many candidates did not make it clear that there must be two different atoms or groups of atoms attached to each carbon atom in the double bond. A few candidates used a simple diagram to explain their answer. A small number of candidates thought that the C=O gives rise to *E-Z* isomerism and some described optical isomerism or the general requirements for stereoisomerism. Some candidates gave elaborate explanations of the *E-Z* system and did not answer the question. Some candidates incorrectly described different molecules attached to the carbon atoms in the C=C.

# (c) Geranial and neral are a pair of *E-Z* isomers.

(i) Explain how this type of isomerism arises.

(2)

of  
This type of isomerism arises because of there are same side  
of same side molecules that attach to a carbon atom which  
has *cis*- (same side) and *trans*- (opposite side).



#### ResultsPlus Examiner Comments

This answer did not score any marks as there is no mention of restricted rotation around the C=C and it refers to molecules attached to a carbon atom. There are different atoms or groups of atoms attached to the carbon atoms but not molecules.



#### ResultsPlus Examiner Tip

Make sure you understand the difference between an atom, a molecule and a group of atoms and use the correct terminology in answers.

(c) Geranial and neral are a pair of *E-Z* isomers.

(i) Explain how this type of isomerism arises.

(2)

This is due to the double bond ( $\pi$ ) restricting rotation around the carbon-carbon bond and so the bonded groups are fixed and not allowed to rotate and this is determined by the side which is attached / centers.



**ResultsPlus**  
Examiner Comments

This response refers to the restricted rotation around the  $\pi$  bond, but there is no mention about the requirement for two different atoms or groups of atoms attached to each carbon atom. This scored 1 mark.

(c) Geranial and neral are a pair of *E-Z* isomers.

(i) Explain how this type of isomerism arises.

(2)

#  $C=C$  restricts free rotation.  
Each double bonded carbon has 2 different groups, attached.



**ResultsPlus**  
Examiner Comments

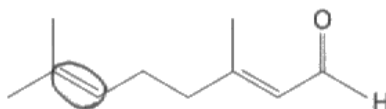
This is a good answer and it scored 2 marks.

### Question 18 (c) (ii)

The majority of candidates could circle the correct double bond. A few candidates circled both double bonds, even though one of them has two  $\text{CH}_3$  groups attached, showing they did not understand *E-Z* isomerism. A small number of candidates circled the aldehyde group.

(ii) Draw a circle around any part of the geranial structure below that causes its *E-Z* isomerism.

(1)

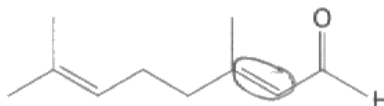


**ResultsPlus**  
Examiner Comments

This answer did not score a mark. The double bond circled here has two  $\text{CH}_3$  groups and one of the requirements for *E-Z* isomerism is that each carbon atom must be attached to two different atoms or groups of atoms.

(ii) Draw a circle around any part of the geranial structure below that causes its *E-Z* isomerism.

(1)



**ResultsPlus**  
Examiner Comments

Many candidates circled the correct double bond and scored 1 mark.

## Question 18 (d)

The majority of candidates were familiar with one of the tests for aldehydes. Common errors included: not mentioning that a red **precipitate** forms with Benedict's or Fehling's solution, omitting the use of sulfuric acid with potassium dichromate(VI) solution and mixing up the reagents and observations. Only a small number of candidates suggested using 2,4-dinitrophenylhydrazine to test for the aldehydes which on its own, is not sufficient.

(d) Describe a simple test tube reaction to show that these three carbonyl compounds are aldehydes and not ketones. State the observation you would make.

(2)

Silver mirror test. Add fehling's solution to compound and if silver mirror forms on the test tube then aldehyde is present and not a ketone.



### ResultsPlus Examiner Comments

This candidate has added a correct reagent, so scores 1 mark. However, they have given the observation for a different reagent.



### ResultsPlus Examiner Tip

Revise the reagents and observations for the tests for aldehydes so that you do not mix them up.

(d) Describe a simple test tube reaction to show that these three carbonyl compounds are aldehydes and not ketones. State the observation you would make.

(2)

Add these three carbonyl compounds to a test tube containing follen's reagent, one at a time. If the compounds are aldehydes a silver mirror is formed. If it is a ketone nothing is observed.



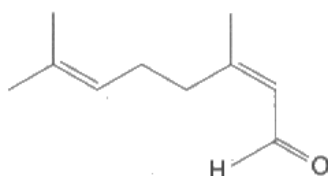
### ResultsPlus Examiner Comments

This is a correct answer and scored 2 marks.

### Question 18 (e) (i-ii)

The majority of candidates were familiar with skeletal formulae and were able to differentiate between the reducing abilities of hydrogen and lithium tetrahydridoaluminate. However, some candidates thought that hydrogen with a nickel catalyst would reduce the aldehyde group or reduce the double bonds and aldehyde group and some candidates thought that lithium tetrahydridoaluminate(III) would reduce the double bonds. Some candidates did not draw the skeletal formulae accurately and they missed out a carbon atom, particularly in part (ii) by attaching the OH group directly to the C=C, or lost a methyl group. Candidates should be aware that additional hydrogen atoms that are not part of a functional group do not need to be shown in a skeletal formula, although on this occasion, additional hydrogens were allowed alongside the OH group.

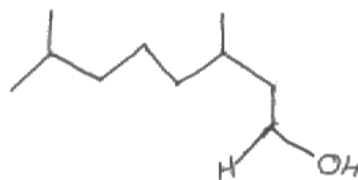
(e) The skeletal formula of neral is shown below.



Draw the **skeletal** formula for the organic product of the reaction of neral with

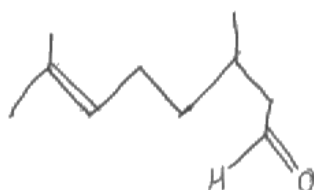
(i) excess hydrogen in the presence of a nickel catalyst.

(1)



(ii) lithium tetrahydridoaluminate(III) (lithium aluminium hydride) in dry ether.

(1)



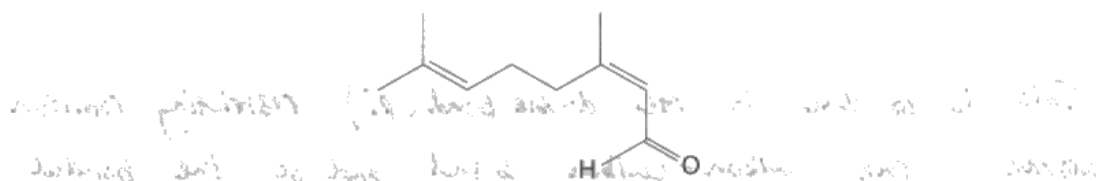


This candidate reduced the aldehyde and double bonds with hydrogen and a nickel catalyst, instead of just the double bonds. They also reduced one of the double bonds with lithium tetrahydridoaluminate(III) instead of the aldehyde. This answer did not score any marks.



Learn which groups are reduced by the different reducing agents in the specification.

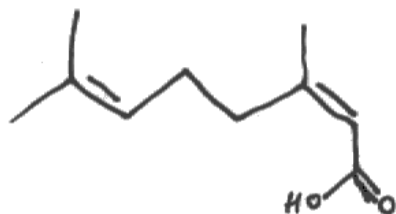
(e) The skeletal formula of neral is shown below.



Draw the skeletal formula for the organic product of the reaction of neral with

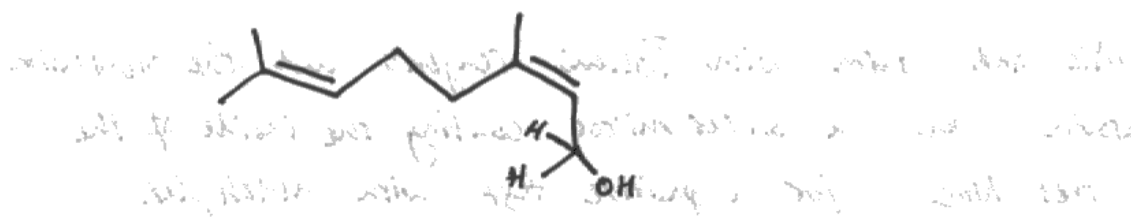
(i) excess hydrogen in the presence of a nickel catalyst.

(1)



(ii) lithium tetrahydridoaluminate(III) (lithium aluminium hydride) in dry ether.

(1)







**ResultsPlus**

**Examiner Comments**

This candidate has scored 1 mark for the correct answer to (ii). They have oxidized the aldehyde to a carboxylic acid in (i), which is incorrect. Hydrogen is a reducing agent.



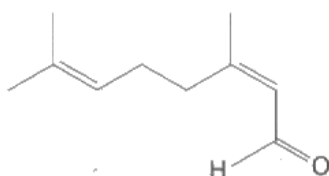
**ResultsPlus**

**Examiner Tip**

The 2 additional hydrogen atoms attached to the carbon with the OH group are not needed in a skeletal formula as they are not part of the functional group. However, they were allowed on this occasion.

Draw skeletal formulae without any additional hydrogen atoms.

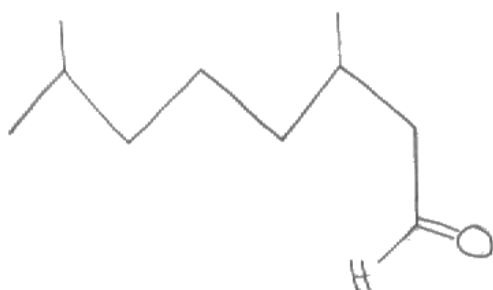
(e) The skeletal formula of neral is shown below.



Draw the **skeletal** formula for the organic product of the reaction of neral with

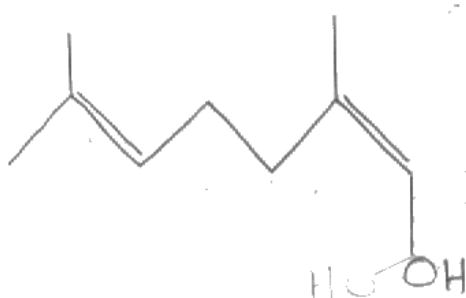
(i) excess hydrogen in the presence of a nickel catalyst.

(1)



(ii) lithium tetrahydridoaluminate(III) (lithium aluminium hydride) in dry ether.

CH<sub>3</sub>CH<sub>2</sub>OH (1)





**ResultsPlus**

**Examiner Comments**

This candidate has scored 1 mark for (i). They have left the double bonds in their answer to (ii) and reduced the aldehyde to an alcohol which is correct, but they have lost a carbon atom on the right of the chain by linking the OH group directly to the C=C.



**ResultsPlus**

**Examiner Tip**

Draw skeletal formulae carefully and check that you have the correct number of carbon atoms.

## Question 19 (a)

The majority of candidates were awarded full marks for this question.

Some candidates did not explain their reasoning for the orders in (i) and omitted need to keep the concentrations of the reactants, other than the one being changed, constant. Those who chose to use experiments 2 and 3 to deduce the order of reaction with respect to  $\text{H}^+$  ions, invariably got into difficulty. Some candidates did not understand the significance of the graph in part (ii) and thought it was zero order as it was a straight line. Candidates should look carefully at the axes for the graph. Some candidates did state that the reaction was first order with respect to iodide ions but gave an imprecise explanation such as 'the rate increases as the concentration increases'. Some candidates omitted the units in (iv).

19 (a) A student investigated the kinetics of the reaction in which an acidified, aqueous solution of hydrogen peroxide oxidizes iodide ions to iodine.



(i) The results of three experiments are shown in the table below.

Experiment number	$[\text{H}_2\text{O}_2(\text{aq})]$ / $\text{mol dm}^{-3}$	$[\text{H}^+(\text{aq})]$ / $\text{mol dm}^{-3}$	$[\text{I}^-(\text{aq})]$ / $\text{mol dm}^{-3}$	Initial rate of reaction / $\text{mol dm}^{-3}\text{s}^{-1}$
1	0.5	1.0	0.5	$7.0 \times 10^{-6}$
2	1.0	1.0	0.5	$1.4 \times 10^{-5}$
3	0.5	2.0	0.5	$7.0 \times 10^{-6}$

Determine the order with respect to hydrogen peroxide and  $\text{H}^+(\text{aq})$  ions.

Explain your reasoning.

(3)

Order with respect to  $\text{H}_2\text{O}_2(\text{aq})$

From experiment 1 and 2, the concentration of  $\text{H}_2\text{O}_2(\text{aq})$  doubles, the initial rate of reaction ~~concentration~~ doubles.

- So that the order with respect to  $\text{H}_2\text{O}_2$  is 1.

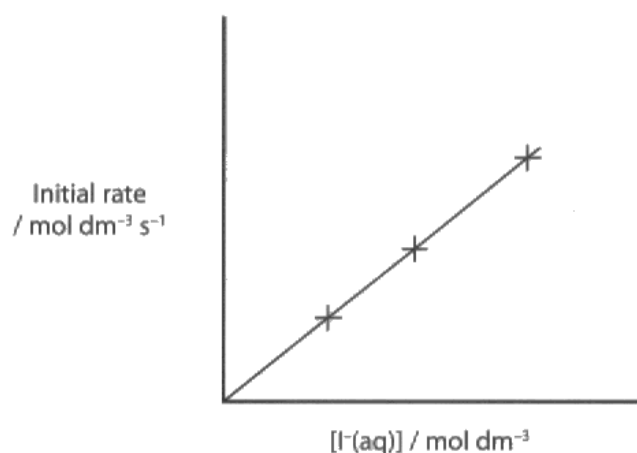
Order with respect to  $\text{H}^+(\text{aq})$

From experiment 2 and 3, the concentration of  $\text{H}^+(\text{aq})$  doubles, the initial ~~concentration~~ rate of reaction doubles.

- So that the order with respect to  $\text{H}^+(\text{aq})$  is 1.

- (ii) The student carried out three more experiments in which the initial concentrations of hydrogen peroxide and  $\text{H}^+(\text{aq})$  ions were kept constant and the initial concentration of iodide ions was changed.

A graph of the results is shown below.



State the order with respect to  $\text{I}^-(\text{aq})$  and explain your reasoning.

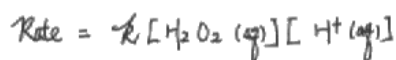
(2)

Zeroth order <sup>with</sup> respect to  $\text{I}^-(\text{aq})$

Because slope of the line is constant.

- (iii) Use your answers to (a)(i) and (a)(ii) to write the rate equation for the reaction.

(1)



- (iv) Use the data from the table and your answer to (a)(iii) to calculate the value for the rate constant. Include units in your answer.

(2)

From exp. 1,

$$\text{Rate} = k \times 0.5 \times 1.0$$

$$7.0 \times 10^{-6} = k \times 0.5$$

$$k = \underline{1.4 \times 10^{-5} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}}$$



## ResultsPlus

Examiner Comments

This candidate has explained the order with respect to hydrogen peroxide, so scored 1 mark for part (i). They have chosen experiments 2 and 3 to deduce the order with respect to hydrogen ions, but have not realised that the concentration of hydrogen peroxide is also changing.

The order with respect to iodide ions is incorrect so did not score a mark. If it was zero order, there would be a straight, horizontal line showing that the rate does not change as the concentration changes.

The rate equation and rate constant in parts (iii) and (iv) are consequentially correct and scored 1 and 2 marks respectively.

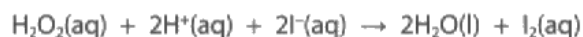


## ResultsPlus

Examiner Tip

When deducing an order of reaction, select experiments where the concentration of only one substance is changing, if possible.

- 19 (a) A student investigated the kinetics of the reaction in which an acidified, aqueous solution of hydrogen peroxide oxidizes iodide ions to iodine.



- (i) The results of three experiments are shown in the table below.

Experiment number	$[\text{H}_2\text{O}_2(\text{aq})]$ / mol dm <sup>-3</sup>	$[\text{H}^+(\text{aq})]$ / mol dm <sup>-3</sup>	$[\text{I}^-(\text{aq})]$ / mol dm <sup>-3</sup>	Initial rate of reaction / mol dm <sup>-3</sup> s <sup>-1</sup>
1	0.5	1.0	0.5	$7.0 \times 10^{-6}$
2	1.0	1.0	0.5	$1.4 \times 10^{-5}$
3	0.5	2.0	0.5	$7.0 \times 10^{-6}$

Determine the order with respect to hydrogen peroxide and H<sup>+</sup>(aq) ions.

Explain your reasoning.

(3)

Order with respect to H<sub>2</sub>O<sub>2</sub>(aq)

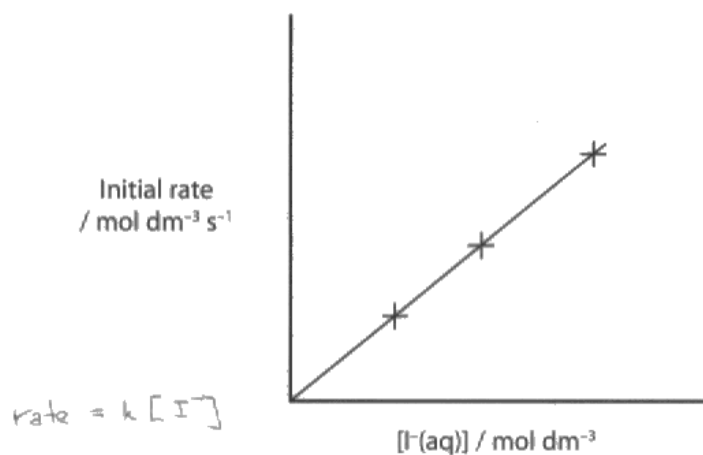
Order with respect to H<sub>2</sub>O<sub>2</sub> is 1. In experiments 1 and 2 when [H<sub>2</sub>O<sub>2</sub>] is doubled and [H<sup>+</sup>] and [I<sup>-</sup>] are kept constant, the initial rate is also doubled.

Order with respect to H<sup>+</sup>(aq)

0, when [H<sup>+</sup>] is doubled, and [H<sub>2</sub>O<sub>2</sub>] and [I<sup>-</sup>] are kept constant, the initial rate does not change.

- (ii) The student carried out three more experiments in which the initial concentrations of hydrogen peroxide and  $\text{H}^+(\text{aq})$  ions were kept constant and the initial concentration of iodide ions was changed.

A graph of the results is shown below.



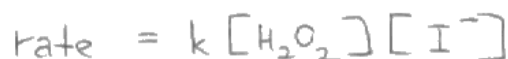
State the order with respect to  $\text{I}^-(\text{aq})$  and explain your reasoning.

(2)

The order with respect to  $\text{I}^-$  is 1 because the gradient of the graph is constant and passes through the origin. This means rate is directly proportional to  $[\text{I}^-]$

(iii) Use your answers to (a)(i) and (a)(ii) to write the rate equation for the reaction.

(1)



(iv) Use the data from the table and your answer to (a)(iii) to calculate the value for the rate constant. Include units in your answer.

(2)

$$7 \times 10^{-6} = k \times 0.5 \times 0.5$$

$$k = 2.8 \times 10^{-5} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$



**ResultsPlus**  
Examiner Comments

This candidate has answered all parts of the question correctly.

### Question 19 (b) (i)

Some candidates answered this question very well as they were able to deduce balanced equations for the mechanism. A wide variety of equations were accepted on this occasion but candidates should try to think about whether the mechanism they have suggested is one that is likely to take place. Many candidates showed that they did not understand the link between rate equations and mechanisms. Some candidates did not use the fact that the reaction is second order with respect to nitrogen dioxide and started the rate determining step with just one molecule of nitrogen dioxide or they included other species. Candidates should check that their equations are balanced in terms of atoms and charges, and that the two steps add up to the overall equation.

(b) Nitrogen dioxide reacts with carbon monoxide.



The reaction is second order with respect to nitrogen dioxide, and zero order with respect to carbon monoxide.

(i) Suggest a possible two-step mechanism for this reaction.

Write the rate determining step first.

Rate determining step

(2)



Step 2



**ResultsPlus**  
Examiner Comments

This answer scored 1 mark for a correct rate determining step.  
The equation for Step 2 is not balanced.



**ResultsPlus**  
Examiner Comments

Always check that your equations are balanced.



(b) Nitrogen dioxide reacts with carbon monoxide.



The reaction is second order with respect to nitrogen dioxide, and zero order with respect to carbon monoxide.

(i) Suggest a possible two-step mechanism for this reaction.

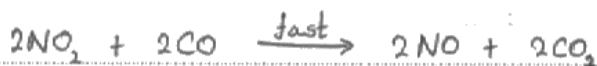
Write the rate determining step first.

(2)

Rate determining step



Step 2



### ResultsPlus Examiner Comments

These equations did not score any marks. The rate determining step does not start with  $2\text{NO}_2$  and the two equations do not add up to the overall equation.



### ResultsPlus Examiner Tip

Use the orders to work out the rate determining step. The rate determining step for this reaction must only have two molecules of nitrogen dioxide on the left of the equation as the reaction is second order with respect to nitrogen dioxide and zero order with respect to carbon monoxide. You can then deduce the equation for Step 2 as the two equations must add up to the overall equation.

(b) Nitrogen dioxide reacts with carbon monoxide.



The reaction is second order with respect to nitrogen dioxide, and zero order with respect to carbon monoxide.

(i) Suggest a possible two-step mechanism for this reaction.

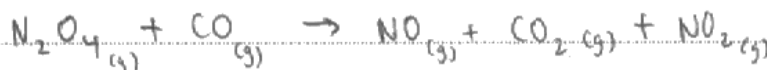
Write the rate determining step first.

(2)

Rate determining step



Step 2



**ResultsPlus**  
Examiner Comments

This is a very good answer and it scored 2 marks.





## ResultsPlus

Examiner Comments

Part (ii) is correct and scored 2 marks.

The candidate has used 266 in their working instead of 226 so the numerical value is incorrect and the sign is also incorrect so no mark was awarded in part (iii).

Part (iv) is consequentially correct and scored 2 marks.



## ResultsPlus

Examiner Tip

Check that you copy numerical data from questions carefully.

Check the sign carefully. If there are two minus signs, the final answer will be positive.

- (ii) Calculate the standard entropy change of the system,  $\Delta S_{\text{system}}^{\ominus}$  for the reaction between nitrogen dioxide and carbon monoxide at 298 K. Include a sign and units in your answer.

You will need to use the standard molar entropies on pages 20 and 27 of the Data Booklet.

$$\Delta S_{\text{system}} = [(213.6 \times 2) + 210.7] - [197.6 + 240 \times 2] \quad (2)$$
$$= \underline{\underline{-39.7 \text{ J mol}^{-1} \text{ K}^{-1}}}$$

- (iii) Given that  $\Delta H_{298}^{\ominus}$  for the reaction between nitrogen dioxide and carbon monoxide at 298 K is  $-226 \text{ kJ mol}^{-1}$ , calculate the standard entropy change of the surroundings,  $\Delta S_{\text{surroundings}}^{\ominus}$  for this reaction at 298 K. Include a sign and units in your answer.

$$\Delta S_{\text{surroundings}} = \frac{-(-226 \times 1000)}{298} \quad (2)$$
$$= \underline{\underline{+758 \text{ J mol}^{-1} \text{ K}^{-1}}}$$

(iv) Calculate the total entropy change,  $\Delta S_{\text{total}}^{\ominus}$ , for this reaction at 298 K.

State what the sign of  $\Delta S_{\text{total}}^{\ominus}$  indicates about this reaction at 298 K.

(2)

$$\begin{aligned}\Delta S_{\text{total}} &= -39.7 + 758 \\ &= \underline{\underline{+718.3}} \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

$\Delta S_{\text{total}}$  is positive hence reaction is thermodynamically feasible at 298 K.



### ResultsPlus Examiner Comments

This candidate has selected the correct entropy values from the Data Booklet but they have multiplied two of them by 2, even though there are no balancing numbers in the overall equation. They scored 1 mark for part (ii).

Part (iii) is correct and part (iv) is consequentially correct on the incorrect value from part (ii), so these both scored 2 marks.

- (ii) Calculate the standard entropy change of the system,  $\Delta S_{\text{system}}^{\ominus}$  for the reaction between nitrogen dioxide and carbon monoxide at 298 K. Include a sign and units in your answer.

You will need to use the standard molar entropies on pages 20 and 27 of the Data Booklet.

$$\begin{aligned}\Delta S_{\text{system}} &= \sum_{\text{product}} - \sum_{\text{reactant}} && (2) \\ &= (213.6 + 210.7) - (240 + 197.6) \\ &= 424.3 - 437.6 \\ &= -13.3 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

- (iii) Given that  $\Delta H_{298}^{\ominus}$  for the reaction between nitrogen dioxide and carbon monoxide at 298 K is  $-226 \text{ kJ mol}^{-1}$ , calculate the standard entropy change of the surroundings,  $\Delta S_{\text{surroundings}}^{\ominus}$  for this reaction at 298 K. Include a sign and units in your answer.

$$\begin{aligned}\Delta S_{\text{surroundings}} &= -\frac{\Delta H}{T} && (2) \\ &= -\frac{(-226000)}{298} \\ &= +758.4 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

- (iv) Calculate the total entropy change,  $\Delta S_{\text{total}}^{\ominus}$  for this reaction at 298 K.

State what the sign of  $\Delta S_{\text{total}}^{\ominus}$  indicates about this reaction at 298 K.

$$\begin{aligned}\Delta S_{\text{total}} &= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \\ &= -13.3 + 758.4 \\ &= +745.1 \text{ J K}^{-1} \text{ mol}^{-1}.\end{aligned}$$

The reaction is feasible at 298 K because  $\Delta S_{\text{total}}$  is positive.



**ResultsPlus**  
Examiner Comments

This candidate scored 2 marks for each part of the answer.

### Question 20 (a) (i)

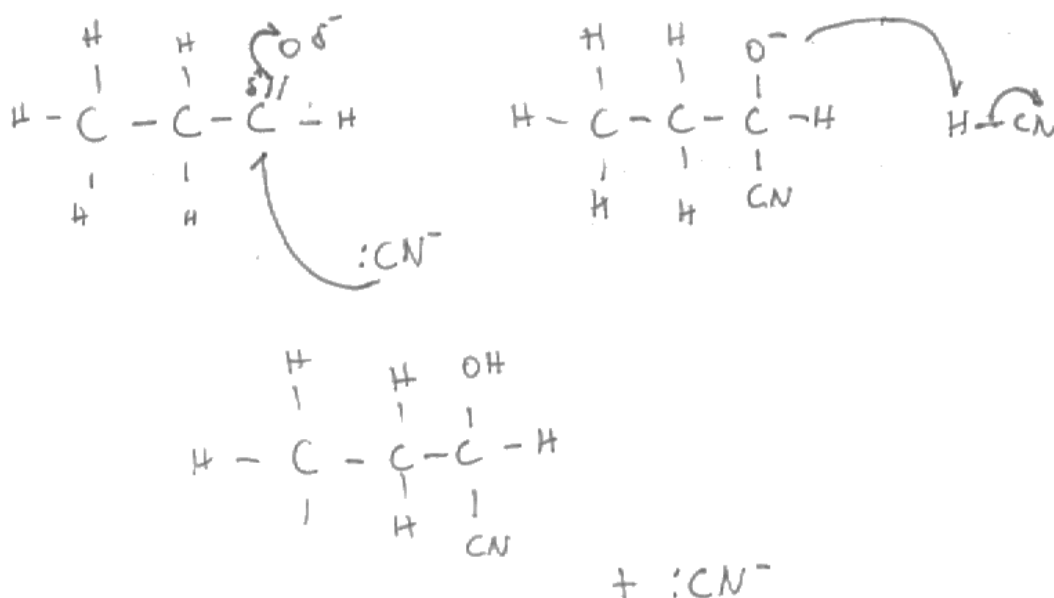
Many candidates drew clear mechanisms with a correct dipole, curly arrows and intermediate. Some candidates lost a mark as they omitted the dipole. Some candidates drew inaccurate curly arrows that seemed to start and end in space, showing that they have not understood the meaning of the curly arrows and they had just tried to memorise the mechanism. Candidates should understand that a curly arrow represents movement of electrons. Common errors included not showing the charge on the cyanide ion, starting the curly arrow at the carbon atom of the C=O instead of the bond, joining the cyanide through the nitrogen atom rather than the carbon atom and the arrow from O<sup>-</sup> to H<sup>+</sup> was frequently drawn the wrong way round. A few candidates chose to write the mechanism for propanone instead of propanal and they lost a mark for this.

20 Propanal, CH<sub>3</sub>CH<sub>2</sub>CHO, is used in the chemical industry in the manufacture of plastics, and as a disinfectant and preservative.

(a) (i) Give the mechanism for the reaction between propanal and hydrogen cyanide in the presence of potassium cyanide.

Include the dipole on the carbonyl group.

(4)



#### ResultsPlus Examiner Comments

This candidate has scored 2 marks for the correct dipole on the carbonyl group and the correct intermediate. They have drawn curly arrows with half arrow heads, which is incorrect.



#### ResultsPlus Examiner Tip

A curly arrow with a full arrow head represents the movement of a pair of electrons.

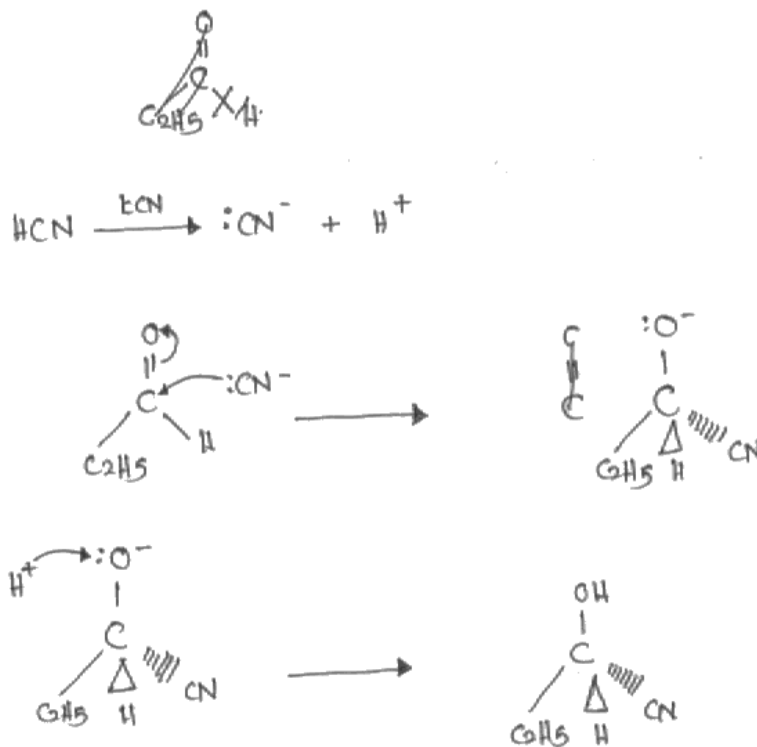
A curly arrow with a half arrow head represents the movement of a single electron. These are used in reactions that involve free radicals.

20 Propanal,  $\text{CH}_3\text{CH}_2\text{CHO}$ , is used in the chemical industry in the manufacture of plastics, and as a disinfectant and preservative.

(a) (i) Give the mechanism for the reaction between propanal and hydrogen cyanide in the presence of potassium cyanide.

Include the dipole on the carbonyl group.

(4)



### ResultsPlus Examiner Comments

This candidate has omitted the dipole on the carbonyl group. The first two curly arrows and the intermediate are correct and scored 2 marks. There is a curly arrow from the  $\text{H}^+$  ion to the lone pair of electrons on the oxygen, which is incorrect.



### ResultsPlus Examiner Tip

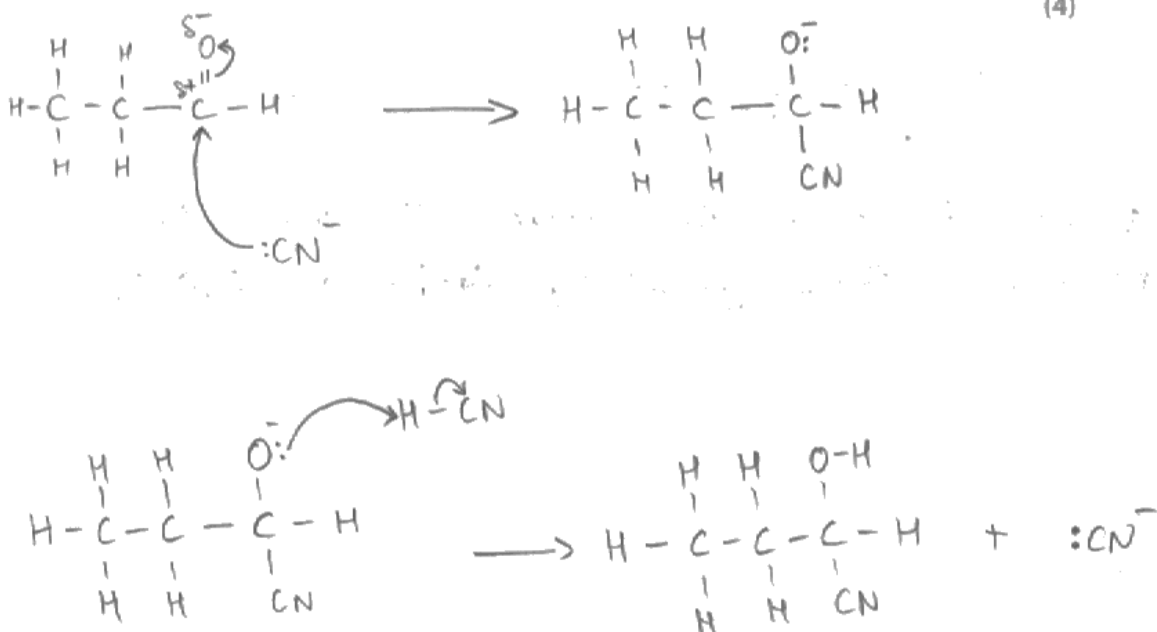
A curly arrow represents the movement of a pair of electrons so it cannot start from an  $\text{H}^+$  ion that has no electrons! Curly arrows can show the breaking of a bond by starting at a bond and moving to the atom that takes the electrons or they can show the formation of a bond by starting at a lone pair of electrons on an atom and moving towards the atom that will join to it.



20 Propanal,  $\text{CH}_3\text{CH}_2\text{CHO}$ , is used in the chemical industry in the manufacture of plastics, and as a disinfectant and preservative.

- (a) (i) Give the mechanism for the reaction between propanal and hydrogen cyanide in the presence of potassium cyanide.

Include the dipole on the carbonyl group.



**ResultsPlus**  
Examiner Comments

This is an example of a correct mechanism, scoring 4 marks.



**ResultsPlus**  
Examiner Tip

Draw mechanisms clearly, as in this example.

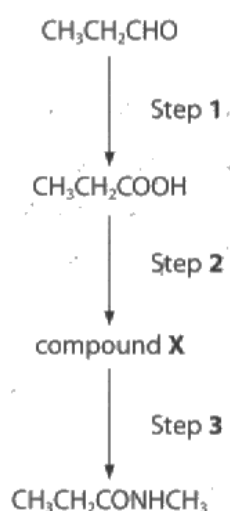
### Question 20 (a) (ii)

The majority of candidates knew that this was a nucleophilic addition reaction, although a number included  $S_N1$  or  $S_N2$  in their answer and lost a mark.

### Question 20 (b) (i)

Many candidates knew that propanoyl chloride was the required reagent for Step 1. Candidates were asked to identify the reagent by name or formula. Some candidates decided to give both name and formula, however, if one of these was incorrect, they did not score the mark. 'Propyl chloride' and 'propanyl chloride' were frequently seen as incorrect names and  $\text{CH}_3\text{CH}_2\text{COCl}$  was a common incorrect formula.

(b) Propanal can be converted into *N*-methyl propanamide,  $\text{CH}_3\text{CH}_2\text{CONHCH}_3$ , in three steps.



(i) The reagent used in Step 2 is phosphorus(V) chloride,  $\text{PCl}_5$ .  
Identify, by name or formula, compound X.

$\text{CH}_3\text{CH}_2\text{COCl}$   
ethanoyl chloride.

(1)



#### ResultsPlus Examiner Comments

This candidate gave the correct formula but the name is incorrect, so they did not score a mark



#### ResultsPlus Examiner Tip

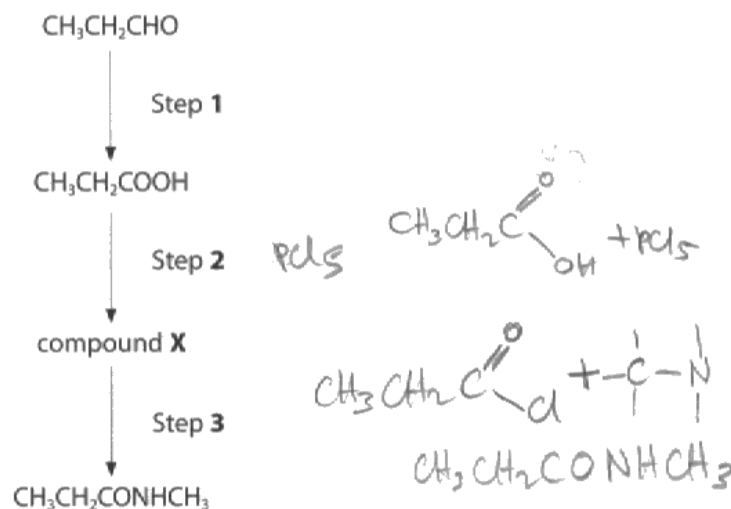
If you give a name and formula, both must be correct to score the mark. It is better to give the one you are most confident is correct.



### Question 20 (b) (ii)

This is similar to (b)(i). If the name and formula are given, both must be correct to score the mark. A number of candidates gave ammonia as the reagent for Step 3 and a few mentioned an amide.

(b) Propanal can be converted into *N*-methyl propanamide,  $\text{CH}_3\text{CH}_2\text{CONHCH}_3$ , in three steps.



(ii) Identify, by name or formula, the reagent needed for Step 3.

(1)

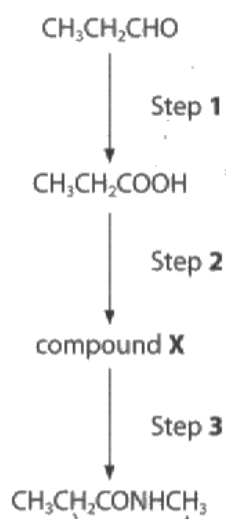
Methylamine  $\text{CH}_3\text{NH}_2$



**ResultsPlus**  
Examiner Comments

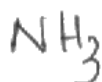
This candidate has given the correct name and formula, so scored 1 mark.

(b) Propanal can be converted into *N*-methyl propanamide,  $\text{CH}_3\text{CH}_2\text{CONHCH}_3$ , in three steps.



(ii) Identify, by name or formula, the reagent needed for Step 3.

(1)



**ResultsPlus**  
Examiner Comments

Ammonia was a common incorrect reagent.



**ResultsPlus**  
Examiner Tip

Learn the reagents required for the reactions in the specification.

### Question 20 (b) (iii)

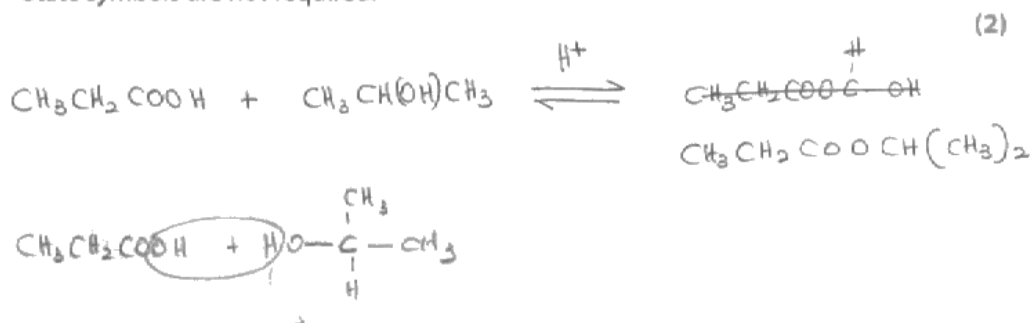
The majority of candidates could work out that there are 4 peaks in the spectrum.

### Question 20 (c)

Many candidates only scored 1 mark as they did not write a balanced equation and omitted the water that is also produced. Some candidates started with propanoic acid and propan-2-ol but drew the ester formed from propan-1-ol. A few candidates omitted the hydrogen atom from the central carbon atom of propan-2-ol in the alcohol and/or the ester, leaving a three co-ordinate carbon atom. Some candidates wrote an equation for propanoic acid reacting with propan-1-ol instead of propan-2-ol. However, they were given 1 mark if the equation, including water as a product, was completely correct.

(c) Write the equation for the reaction between propanoic acid and propan-2-ol, in the presence of an acid catalyst, showing the structure of the organic product.

State symbols are not required.



**ResultsPlus**  
Examiner Comments

This candidate has shown the correct structure for the ester and scored 1 mark. However, they have omitted water from the equation.



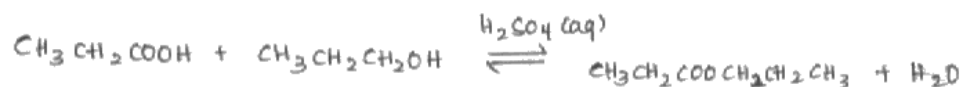
**ResultsPlus**  
Examiner Tip

Check that your equations are balanced. Remember that carboxylic acid + alcohol  $\rightarrow$  ester + water.

- (c) Write the equation for the reaction between propanoic acid and propan-2-ol, in the presence of an acid catalyst, showing the structure of the organic product.

State symbols are not required.

(2)



**ResultsPlus**

**Examiner Comments**

This candidate has underlined propan-2-ol in the question but has written an equation with propan-1-ol. The equation is correct so they were awarded 1 mark.



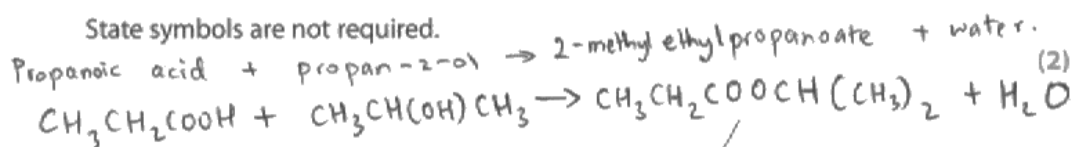
**ResultsPlus**

**Examiner Tip**

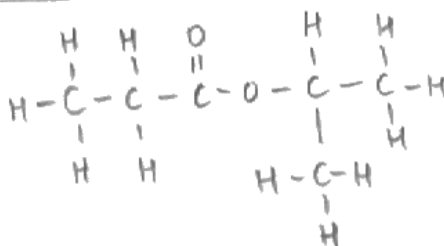
Read the question carefully and check that you have written the correct formula for the reactants.

- (c) Write the equation for the reaction between propanoic acid and propan-2-ol, in the presence of an acid catalyst, showing the structure of the organic product.

State symbols are not required.



organic product structure:



**ResultsPlus**

**Examiner Comments**

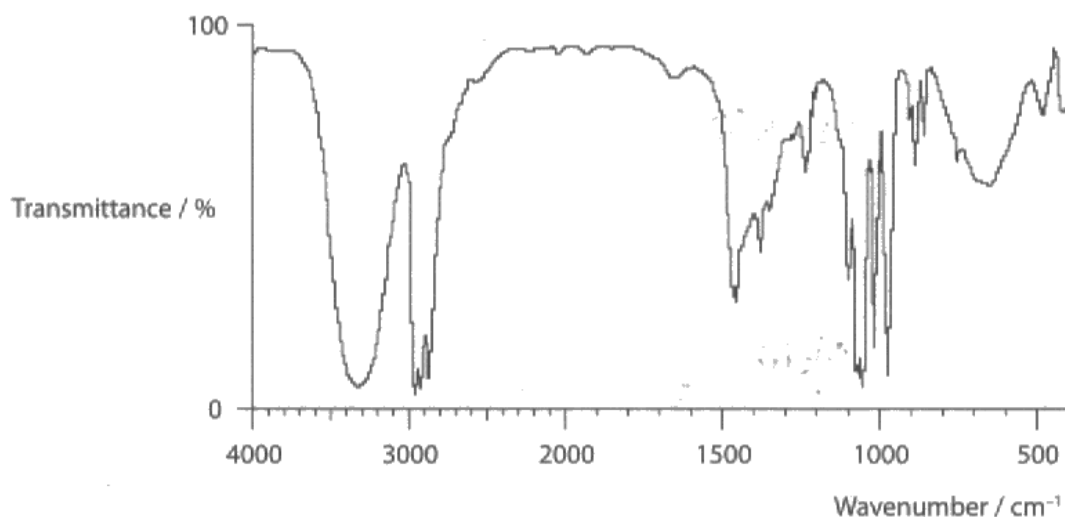
This candidate has written a correct balanced equation and scored 2 marks.

## Question 20 (d)

The majority of candidates identified compound Q as an alcohol from the absorbance of the O-H bond on the spectrum. Many candidates just stated that it was propanol. They were told that it was formed from propanoic acid, so they should have stated that it was propan-1-ol. Some candidates thought that they could identify an amine group on the spectrum. This was surprising as they were told that compound Q was formed by the reduction of propanoic acid. Candidates need to use all the information given in the question and not just try to identify a peak using the Data Booklet.

(d) A sample of propanoic acid was reduced to form compound Q.

The infrared spectrum of compound Q is shown below.



Use the infrared spectrum to identify compound Q.

Explain your reasoning, quoting suitable data.

Compound Q is propan-1-ol as there is an O-H absorption seen in the IR spectrum of compound Q. (2)



### ResultsPlus Examiner Comments

This candidate has identified propan-1-ol and stated there is an OH absorption but they have not stated which peak is caused by the OH group. This answer scored 1 mark.



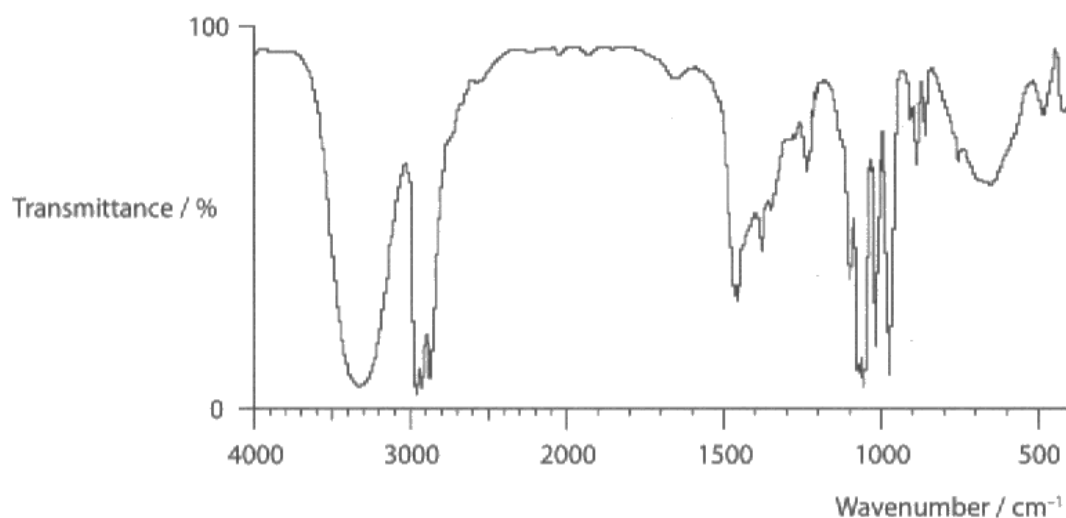
### ResultsPlus Examiner Tip

Always identify a peak by stating the **bond** that causes it and quoting the wavenumbers or indicating it on the spectrum.



(d) A sample of propanoic acid was reduced to form compound Q.

The infrared spectrum of compound Q is shown below.



Use the infrared spectrum to identify compound Q.

Explain your reasoning, quoting suitable data.

(2)

- Broad peak at around ~~30~~ 3300 cm<sup>-1</sup> corresponding to an alcohol the presence of alcohol.
- Compound Q is propanol



### ResultsPlus Examiner Comments

This is an example of a common error. The candidate has identified the alcohol group from the wavenumber, but has not stated which propanol is formed. This answer scored 1 mark.

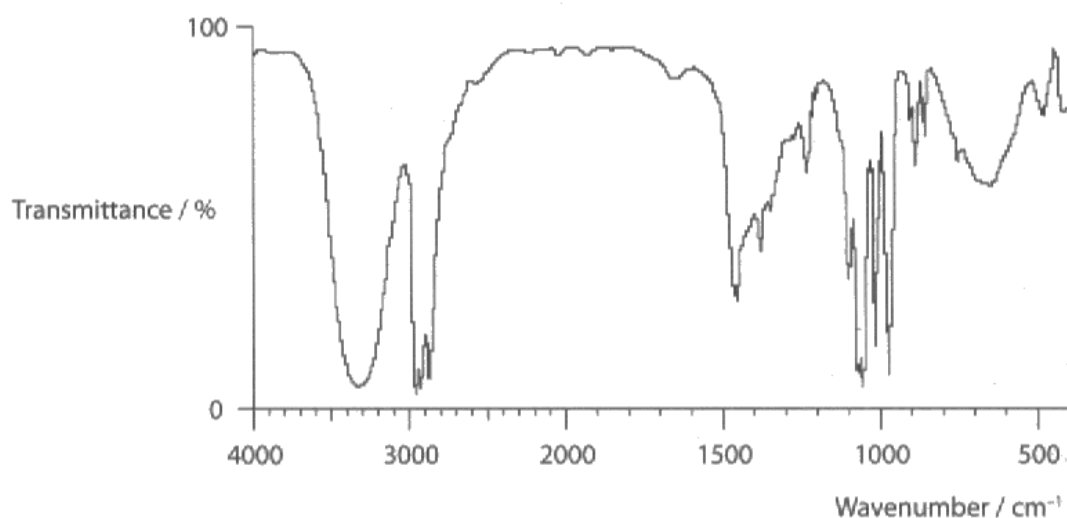


### ResultsPlus Examiner Tip

If there are two or more possible isomers, state which one is present.

(d) A sample of propanoic acid was reduced to form compound **Q**.

The infrared spectrum of compound **Q** is shown below.



Use the infrared spectrum to identify compound **Q**.

Explain your reasoning, quoting suitable data.

(2)

Propan-1-ol. Compound **Q** is propan-1-ol because we can see the presence of a broad absorption peak which results from O-H of alcohols in the range 3200-3750 cm<sup>-1</sup>.



**ResultsPlus**  
Examiner Comments

This candidate has identified the OH peak and the specific alcohol and scored 2 marks.

## Question 21 (a)

Many candidates were able to give correct expressions for  $K_p$  and to calculate its value. Some candidates omitted to show the partial pressures in the expression and some used square brackets. A small number of candidates gave the symbols of hydrogen and iodine as H and I. There were many correct calculations and many of the successful candidates set out their working clearly, using a table. Some candidates gave incorrect equilibrium moles for hydrogen and/or hydrogen iodide but they did receive consequential marks following from these errors. The majority of candidates stated that there were no units or showed them cancelling, but a few just left out this easy mark.

21 This question concerns the reaction of hydrogen with iodine to form hydrogen iodide at 700 K.



(a) (i) Write the expression for the equilibrium constant,  $K_p$ , for this reaction.

$$K_p = \frac{P(\text{HI})^2}{P(\text{H}_2)P(\text{I}_2)} \quad (1)$$

\*(ii) 1 mol of hydrogen was mixed with 1 mol of iodine in a sealed container and left to reach equilibrium at 700 K.

The total pressure was 5 atm.

At equilibrium, the amount of iodine remaining was 0.21 mol.

Calculate the partial pressure of each gas at equilibrium.

Use the partial pressures to calculate the value of  $K_p$ , stating its units, if any.

(5)

	$\text{H}_2$	+	$\text{I}_2$	$\longrightarrow$	$2 \text{HI}$
initial	1		1		0
<i>equib change amt</i>	0.21		0.21		0.42 (= 0.84)
<i>equib Mole fractions</i>	$\frac{0.21}{0.84}$		$\frac{0.21}{0.84}$		$\frac{0.42}{0.84}$
Partial pressure	$\frac{0.21}{0.84} \times 5$ = 1.25		$\frac{0.21}{0.84} \times 5$ = 1.25		$\frac{0.42}{0.84} \times 5$ = 2.5
$\therefore K_p =$	$\frac{(2.5)^2}{(1.25)^2} = 4$				

$K_p =$  4 units no units



**ResultsPlus**

**Examiner Comments**

The expression for  $K_p$  is correct and scored 1 mark.

The number of moles of hydrogen at equilibrium is correct but the number of moles of hydrogen iodide is incorrect. However, the rest of the calculation is consequentially correct, including the units, so this answer scored 4 marks.



**ResultsPlus**

**Examiner Tip**

Always show your working clearly as you can still score consequential marks, even if you make an error in a calculation.

- 21 This question concerns the reaction of hydrogen with iodine to form hydrogen iodide at 700 K.



- (a) (i) Write the expression for the equilibrium constant,  $K_p$ , for this reaction.

(1)

$$K_p = \frac{p(\text{HI})^2}{p(\text{H}_2) \cdot p(\text{I}_2)}$$

- \*(ii) 1 mol of hydrogen was mixed with 1 mol of iodine in a sealed container and left to reach equilibrium at 700 K.

The total pressure was 5 atm. →

At equilibrium, the amount of iodine remaining was 0.21 mol.

Calculate the partial pressure of each gas at equilibrium.

Use the partial pressures to calculate the value of  $K_p$ , stating its units, if any.

(5)

$\text{I}_2$	$\text{H}_2$	$2\text{HI}$
1	1	0
0.21	0.21	1.58

= 2 total.

partial pressure = mole fraction  $\times$  total pressure.

$$p(\text{I}_2) = \frac{0.21}{2} \times 5 = 0.525 \text{ atm} \quad p(\text{H}_2) = 0.525 \text{ atm}$$

$$p(\text{HI}) = \frac{1.58}{2} \times 5 = 3.95 \text{ atm}$$

$$K_p = \frac{3.95^2}{0.525 \times 0.525} =$$

$$K_p = \frac{56.60}{0.2756} \text{ units NO UNITS.}$$

56.6



### ResultsPlus

Examiner Comments

This candidate has given incorrect symbols for hydrogen and iodine so does not score the mark for part (i). The calculation in part (ii) is correct, including the units, so 5 marks were awarded.



### ResultsPlus

Examiner Tip

Use correct formulae for the reactants and products from the balanced equation.

21 This question concerns the reaction of hydrogen with iodine to form hydrogen iodide at 700 K.



(a) (i) Write the expression for the equilibrium constant,  $K_p$ , for this reaction.

(1)

$$K_p = \frac{p(\text{HI})^2}{p(\text{H}_2) \times p(\text{I}_2)}$$

\*(ii) 1 mol of hydrogen was mixed with 1 mol of iodine in a sealed container and left to reach equilibrium at 700 K.

The total pressure was 5 atm.

At equilibrium, the amount of iodine remaining was 0.21 mol.

Calculate the partial pressure of each gas at equilibrium.

Use the partial pressures to calculate the value of  $K_p$ , stating its units, if any.

(5)

Molecule	H <sub>2</sub>	I <sub>2</sub>	HI
Moles added	1	1	0
Moles at equilibrium	(1-0.79)=0.21	0.21	(2×0.79)=1.58
Mole fraction	$\frac{0.21}{2} = 0.105$	$\frac{0.21}{2} = 0.105$	$\frac{1.58}{2} = 0.79$
partial pressure	0.525	0.525	3.95

total moles at equilibrium: 2

$$K_p = \frac{p(\text{HI})^2}{p(\text{H}_2)p(\text{I}_2)} = \frac{(3.95)^2}{(0.525)^2} = 56.6$$

$$\text{units} = \frac{\text{atm}^2}{\text{atm}^2} = \text{none}$$

$$K_p = 56.6 \text{ units (no units)}$$



**ResultsPlus**  
Examiner Comments

This is an example of a completely correct answer, scoring 6 marks.



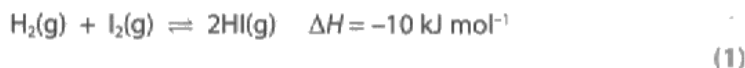
**ResultsPlus**  
Examiner Tip

Set out your working for calculations clearly, as in this answer. If you do make a mistake, the examiner can see where you have gone wrong and award consequential marks for the rest of your answer.

## Question 21 (b)

The majority of candidates realised that there were the same number of moles of gas on each side of the equation, so increasing the pressure would have no effect on the equilibrium position.

(b) State the effect of increasing the pressure on the equilibrium position. Justify your answer by using the equation:



equilibrium will move to the right. since there are less moles of gas there.  
4  
of molecules



### ResultsPlus Examiner Comments

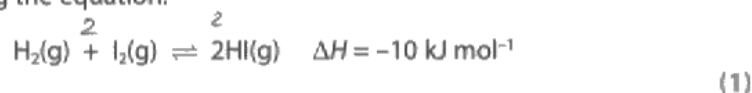
This candidate thought that there were fewer moles of gas on the right of the equation, so did not score a mark.



### ResultsPlus Examiner Tip

Count the number of gas molecules carefully. There are two moles of gas on the left and two moles of gas on the right of the equation.

(b) State the effect of increasing the pressure on the equilibrium position. Justify your answer by using the equation:



No effect. The number of moles on both sides of the reaction are the same.



### ResultsPlus Examiner Comments

The candidate should have referred to the moles of **gas** but in this equation all of the reactants and products are gases so this was awarded 1 mark.



### ResultsPlus Examiner Tip

When writing about the effect of a change of pressure on a system in equilibrium, always refer to the number of moles of **gas** molecules.

## Question 21 (c)

Many candidates did get both parts of this question correct. A small number did not look at the enthalpy change at the start of the question, so they did not realise that the reaction was exothermic and so  $\Delta S_{\text{surroundings}}$  would become less positive and  $\Delta S_{\text{total}}$  would also decrease as the temperature increases. Many candidates did state that the value for  $K_p$  would decrease and the yield of hydrogen iodide would also decrease but they explained their answer in terms of Le Chatelier's Principle instead of the relationship between  $\Delta S_{\text{total}}$  and  $\ln K_p$ . Some candidates stated that the equilibrium position would shift to the left but they omitted to state what would happen to the yield of hydrogen iodide.

- (c) (i) Explain how increasing the temperature affects the value of  $\Delta S_{\text{total}}$  of this reaction. Assume that  $\Delta S_{\text{system}}$  does not change when the temperature increases.

(2)

*Increasing the temperature decreases the value of  $\Delta S_{\text{surroundings}}$ .  
So the value of  $\Delta S_{\text{total}}$  will increase.*

- \* (ii) Use your answer to (c)(i) to explain the effect of an increase in temperature on the value of  $K_p$  and the equilibrium yield of hydrogen iodide.

(2)

*If  $\Delta S_{\text{total}}$  increases the reaction becomes more  
feasible. So the equilibrium yield of HI will increase  
so the value of  $K_p$  will also increase.*



**ResultsPlus**  
Examiner Comments

In part (i), the effect of increasing the temperature on  $\Delta S_{\text{surroundings}}$  is correct and scores 1 mark. The effect on  $\Delta S_{\text{total}}$  is incorrect.

Part (ii) scores 1 mark based on the incorrect change of  $\Delta S_{\text{total}}$  in (i).



(c) (i) Explain how increasing the temperature affects the value of  $\Delta S_{\text{total}}$  of this reaction. Assume that  $\Delta S_{\text{system}}$  does not change when the temperature increases.

(2)

The reaction is exothermic. So increasing the temperature, decreases  $\Delta S_{\text{surrounding}}$ .  $\Delta S_{\text{surrounding}} = \frac{-\Delta H}{T}$   
 $\therefore \Delta S_{\text{total}}$  will also decrease as  $\Delta S_{\text{system}}$  does not change.

\*(ii) Use your answer to (c)(i) to explain the effect of an increase in temperature on the value of  $K_p$  and the equilibrium yield of hydrogen iodide.

(2)

$K_p$  decreases. So the reactants must increase and the products decrease to remain equal as per the equation. Thus equilibrium shifts to left, and equilibrium yield of hydrogen iodide decreases.



### ResultsPlus Examiner Comments

Part (i) is correct and scores 2 marks.

Part (ii) scores 1 mark for stating the effect of increasing temperature on  $K_p$ , but the candidate has not explained the relationship between  $\Delta S_{\text{total}}$  and  $\ln K_p$ .

(c) (i) Explain how increasing the temperature affects the value of  $\Delta S_{\text{total}}$  of this reaction. Assume that  $\Delta S_{\text{system}}$  does not change when the temperature increases.

(2)

When temperature increase,  $\Delta S_{\text{surrounding}}$  becomes less positive. Since  $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$ ,  $\Delta S_{\text{total}}$  will decrease.

\*(ii) Use your answer to (c)(i) to explain the effect of an increase in temperature on the value of  $K_p$  and the equilibrium yield of hydrogen iodide.

(2)

$\Delta S_{\text{total}} = R \ln k_p$ . Since  $\Delta S_{\text{total}}$  is directly proportional to  $k_p$ , when temperature increase and  $\Delta S_{\text{total}}$  decrease,  $k_p$  will also decrease. Equilibrium tries to decrease temperature, so backward endothermic reaction is favoured. So equilibrium yield of hydrogen iodide decrease.



**ResultsPlus**  
Examiner Comments

This is an example of a correct answer, scoring 4 marks.

### Question 22 (a) (i)

The majority of candidates knew that acids are proton donors. Some candidates stated that acids release protons but did not indicate that they donate them (to another substance that acts as a base).

(a) (i) State what is meant by a Brønsted-Lowry acid.

(1)

Brønsted-Lowry acid means it has a conjugate base.



**ResultsPlus**  
Examiner Comments

The acid will have a conjugate base but the important point of the definition is missing. This answer did not score a mark.



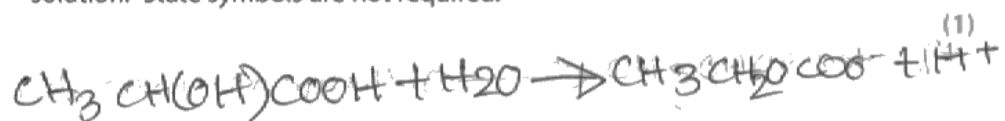
**ResultsPlus**  
Examiner Tip

Learn the Brønsted-Lowry definitions for an acid and a base.

### Question 22 (a) (ii-iii)

Many candidates were able to write the equation for lactic acid with water and the expression for  $K_a$ . Some candidates omitted some or all of the square brackets from  $K_a$ .

- (ii) Write the equation for the reaction of lactic acid with water to form an acidic solution. State symbols are not required.



- (iii) Write the expression for the acid dissociation constant,  $K_a$ , for lactic acid.

$$K_a = \frac{[\text{CH}_3\text{CH}_2\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{CH}(\text{OH})\text{COOH}][\text{H}_2\text{O}]} \quad (1)$$



#### ResultsPlus Examiner Comments

This candidate has not written a balanced equation for part (ii), so did not score the mark.

They have included water in the expression for  $K_a$ , so did not score the mark for part (iii).



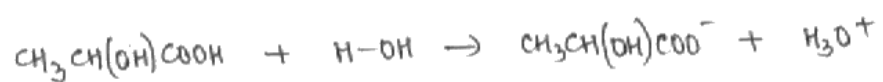
#### ResultsPlus Examiner Tip

Always check that your equations are balanced.

Do not include  $\text{H}_2\text{O}$  in expressions for  $K_a$ .

(ii) Write the equation for the reaction of lactic acid with water to form an acidic solution. State symbols are not required.

(1)



(iii) Write the expression for the acid dissociation constant,  $K_a$ , for lactic acid.

(1)

$$K_a = \frac{[\text{CH}_3\text{CH}(\text{OH})\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CH}(\text{OH})\text{COOH}]}$$



This is an example of a correct answer, scoring both marks.

### Question 22 (a) (iv)

The majority of candidates were able to calculate the correct pH. Some candidates used the  $pK_a$  value as if it were  $K_a$  and calculated a very low value of the pH of a weak acid, or they calculated an incorrect value of  $K_a$  from  $pK_a$ . Many candidates were able to give two assumptions that they made in the calculation, but some stated the same assumption twice, albeit in different words. For example, 'no hydrogen ions from water' is the same assumption as 'all the hydrogen ions are from the acid' or 'the concentration of hydrogen ions is the same as the concentration of lactate ions'.

(iv) Calculate the pH of a solution of lactic acid of concentration  $0.15 \text{ mol dm}^{-3}$  at 298 K.

The  $pK_a$  of lactic acid is 3.86 at 298 K.

State clearly any assumptions you have made.

(5)

Calculation:

$$pK_a = -\log K_a$$

$$\Rightarrow 3.86 = -\log K_a$$

$$\Rightarrow K_a = 10^{-3.86}$$

$$\approx 1.38 \times 10^{-4} \text{ mol dm}^{-3}$$

$$K_a = \frac{[H_3O^+]^2}{[CH_3CH(OH)COOH]}$$

$$\Rightarrow 1.38 \times 10^{-4} = \frac{[H_3O^+]^2}{0.15}$$

$$\Rightarrow [H_3O^+] = 0.0144 \text{ mol dm}^{-3}$$

$$pH = -\log [H_3O^+] = -\log (0.0144 \text{ mol dm}^{-3})$$

$$\approx 1.84$$

$$\therefore pH = 1.84$$

Assumptions:

$[H_3O^+] = [CH_3CH(OH)COO^-]$ . Since water provides negligible concentration of  $H_3O^+$  ions.



**ResultsPlus**  
Examiner Comments

This candidate has correctly converted  $pK_a$  into  $K_a$  at the start of their answer, but has then copied it incorrectly in the next stage. However, the rest of the working is correct. There is also one correct assumption so this answer scored 3 marks.



**ResultsPlus**  
Examiner Tip

Check that you have copied numbers correctly.

(iv) Calculate the pH of a solution of lactic acid of concentration  $0.15 \text{ mol dm}^{-3}$  at 298 K.

The  $\text{p}K_a$  of lactic acid is 3.86 at 298 K.

State clearly any assumptions you have made.

(5)

Calculation:

$$K_a = \frac{[\text{H}^+]^2}{[\text{CH}_3\text{CH}(\text{OH})\text{COOH}]}$$

$$\text{p}K_a = 3.86$$

$$\Rightarrow K_a = 10^{-3.86}$$

$$\Rightarrow K_a = 1.38 \times 10^{-4}$$

$$\therefore 1.38 \times 10^{-4} = \frac{[\text{H}^+]^2}{0.15}$$

$$\Rightarrow [\text{H}^+]^2 = 2.07 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\Rightarrow [\text{H}^+] = 4.55 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\therefore \text{pH} = -\log [\text{H}^+]$$

$$\Rightarrow \text{pH} = -\log (4.55 \times 10^{-3})$$

$$\Rightarrow \text{pH} = 2.3$$

Assumptions:

the concentration of  $\text{H}_3\text{O}^+$  from the auto-ionisation of water is negligible.



**ResultsPlus**  
Examiner Comments

This candidate has carried out a correct calculation and given one assumption, so has scored 4 marks.



(iv) Calculate the pH of a solution of lactic acid of concentration  $0.15 \text{ mol dm}^{-3}$  at 298 K.

The  $pK_a$  of lactic acid is 3.86 at 298 K.

State clearly any assumptions you have made.

(5)

Calculation:

$$\begin{aligned} pK_a &= -\log K_a \\ K_a &= 10^{-pK_a} \\ &= 10^{-3.86} \\ &= 1.38 \times 10^{-4} \end{aligned}$$

$$K_a = \frac{[\text{CH}_3\text{CH}(\text{OH})\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CH}(\text{OH})\text{COOH}]}$$

$$1.38 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+]^2}{0.15}$$

$$[\text{H}_3\text{O}^+] = \sqrt{1.38 \times 10^{-4} \times 0.15}$$

$$[\text{H}_3\text{O}^+] = 4.55 \times 10^{-3}$$

$$\begin{aligned} \text{pH} &= -\log_{10} [\text{H}_3\text{O}^+] \\ &= -\log_{10} (4.55 \times 10^{-3}) \\ &= 2.34 \end{aligned}$$

Assumptions:

$[\text{CH}_3\text{CH}(\text{OH})\text{COO}^-] = [\text{H}_3\text{O}^+]$  as self ionization of water is negligible

$[\text{CH}_3\text{CH}(\text{OH})\text{COOH}]_{\text{initial}} = [\text{CH}_3\text{CH}(\text{OH})\text{COOH}]_{\text{eqm}}$



**ResultsPlus**  
Examiner Comments

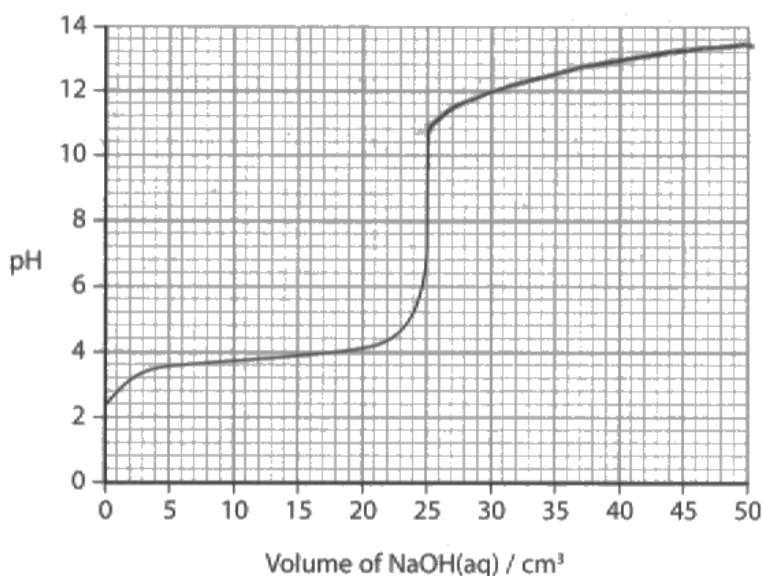
This is an example of a correct calculation with two correct assumptions and it scored 5 marks.

### Question 22 (b) (i-ii)

The majority of candidates calculated the pH of the sodium hydroxide solution correctly, but some did not read the question and did not round it to one decimal place. Many candidates were able to complete the titration curve, although many ignored the pH they had just calculated and extended the curve to above pH 13.2. Candidates should realise that the pH will never reach the value of the alkali that is being added as the excess alkali will be diluted down at the end of the titration. A few candidates did not continue the curve to show the addition of 50.0 cm<sup>3</sup> of sodium hydroxide solution and a few drew careless curves that rose to a maximum and dipped down at the end.

(b) 25 cm<sup>3</sup> of a 0.15 mol dm<sup>-3</sup> solution of lactic acid was titrated with 50 cm<sup>3</sup> of sodium hydroxide solution of the same concentration.

Part of the titration curve is shown below.



(i) Calculate the pH of 0.15 mol dm<sup>-3</sup> sodium hydroxide solution. Give your answer to one decimal place.

[ $K_w = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$  at 298 K]

$$\begin{aligned}
 K_w &= [\text{OH}^-][\text{H}_3\text{O}^+] \\
 1.0 \times 10^{-14} &= [0.15][\text{H}_3\text{O}^+] \\
 6.67 \times 10^{-14} &= [\text{H}_3\text{O}^+]
 \end{aligned}$$

(2)

$$\text{pH} = -\log\left(\frac{6.67}{10^{-14}}\right) = 13 //$$

(ii) Complete the titration curve on the diagram above to show the change in pH until 50.0 cm<sup>3</sup> of the sodium hydroxide solution has been added to the solution of lactic acid.

NaOH

(1)



**ResultsPlus**  
Examiner Comments

This candidate has scored 1 mark for part (i) as they have calculated the pH correctly, but not given their answer to one decimal place.

The titration curve is finishing at a pH higher than that of the sodium hydroxide solution, so scores no mark.

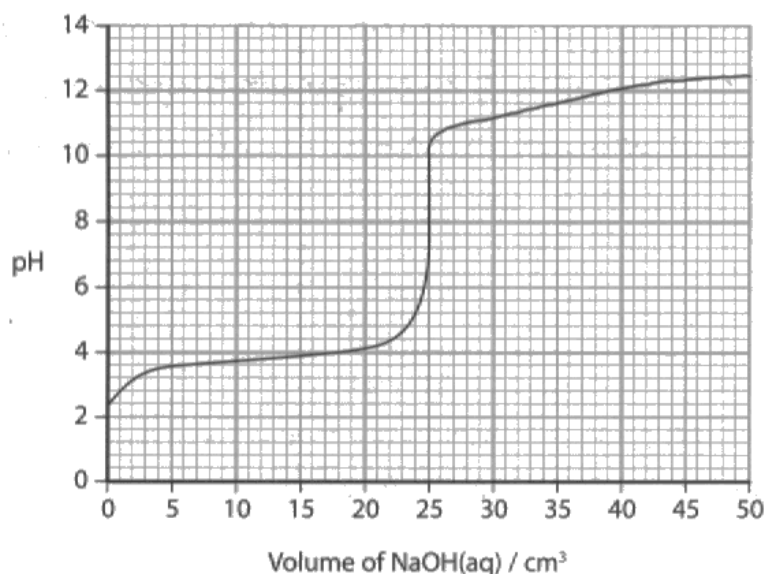


**ResultsPlus**  
Examiner Tip

Titration curves should end at a **lower** pH than the solution being added.

- (b)  $25 \text{ cm}^3$  of a  $0.15 \text{ mol dm}^{-3}$  solution of lactic acid was titrated with  $50 \text{ cm}^3$  of sodium hydroxide solution of the same concentration.

Part of the titration curve is shown below.



weak acid  
Strong base  
6 → 10

- (i) Calculate the pH of  $0.15 \text{ mol dm}^{-3}$  sodium hydroxide solution. Give your answer to one decimal place.

$$[K_w = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \text{ at } 298 \text{ K}]$$

(2)

$$\text{pOH} = -\log_{10} [0.15]$$

$$= 0.824$$

$$\text{pH} + \text{pOH} = 14$$

$$\text{pH} + 0.824 = 14$$

$$\text{pH} = 14 - 0.824$$

$$\text{pH} = 13.2 //$$

- (ii) Complete the titration curve on the diagram above to show the change in pH until  $50.0 \text{ cm}^3$  of the sodium hydroxide solution has been added to the solution of lactic acid.

(1)



**ResultsPlus**  
Examiner Comments

This candidate has scored 2 marks for part (i) as the calculation is correct (using the pOH route) and they have given the value to one decimal place.

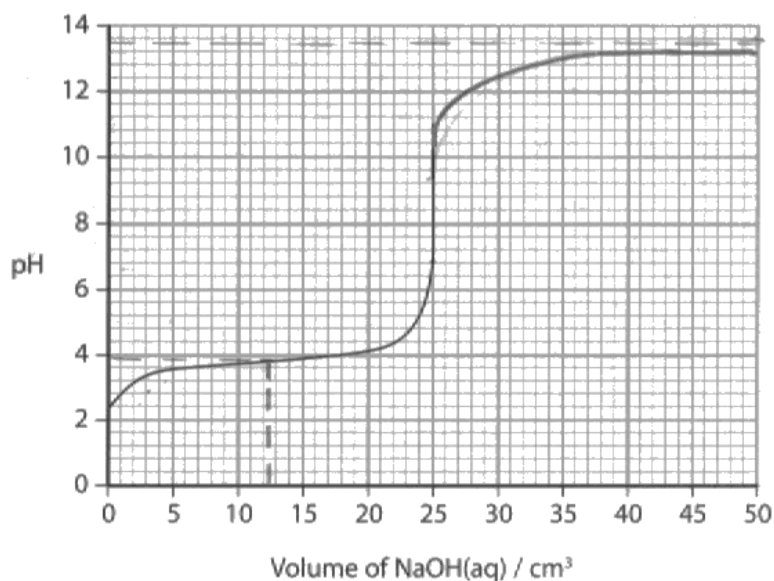
The titration curve ends at a pH lower than 13.2, so part (ii) scored 1 mark.

### Question 22 (b) (iii-iv)

Many candidates were able to select a correct indicator for the titration and justify their reason. Some candidates omitted to write the colour change of the indicator, even though these are in the Data Booklet.

Part (iv) proved very challenging for many candidates. The majority of candidates stated the pH when lactic acid is half-neutralized. However, sodium lactate is present when the acid is completely neutralized and they should have selected the pH at the mid-point of the vertical section of the titration curve.

Part of the titration curve is shown below.

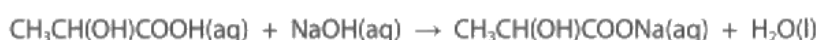


(iii) Use the information given in your Data Booklet to select a suitable indicator for this titration, giving the colour change you would expect to see.

Justify your selection.

Phenolphthalein (3)  
~~Thymol blue~~. The pH range of phenolphthalein is well within the vertical section of the graph (8.2 - 10.0) and in a weak acid - strong base titration the equivalence point is at about 9. The pH range is almost  $\pm 1$  of this point. The colour change would be from colourless  $\rightarrow$  red.

(iv) The equation for the neutralization in the titration is



Use the titration curve to suggest the pH of a  $0.075 \text{ mol dm}^{-3}$  solution of sodium lactate. Justify your answer.

$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$  (2)  
at pH of a  $0.075 \text{ mol dm}^{-3}$  solution is about 3.8 because when an acid is half neutralised  $\text{pK}_a = \text{pH}$



### ResultsPlus Examiner Comments

This candidate has chosen a suitable indicator, stated the colour change and justified their choice. This scored 3 marks for part (iii).

They have selected the pH at the half-neutralization point so scored 0 for part (iv).

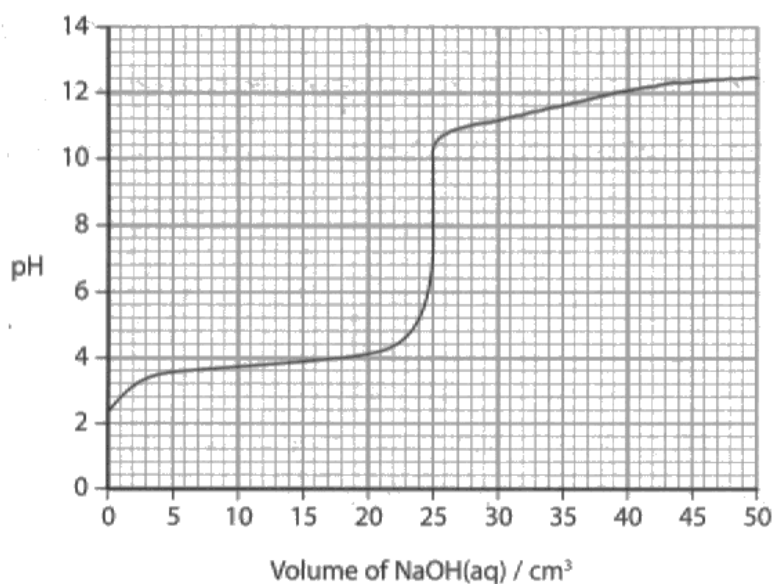


### ResultsPlus Examiner Tip

The pH of the salt formed during a titration can be found from the mid-point of the vertical section of the titration curve as there is none of the original acid left and excess alkali has not been added to it.

Part of the titration curve is shown below.

weak acid  
Strong base  
6 → 10



(iii) Use the information given in your Data Booklet to select a suitable indicator for this titration, giving the colour change you would expect to see.

Justify your selection.

(3)

The indicator will be phenolphthalein (in ethanol). The colour change will be from colourless to red. I chose phenolphthalein because it has a pH range from 8.2-10, and in this titration curve, the vertical point is from 6-10.

(iv) The equation for the neutralization in the titration is



Use the titration curve to suggest the pH of a  $0.075 \text{ mol dm}^{-3}$  solution of sodium lactate. Justify your answer.

(2)

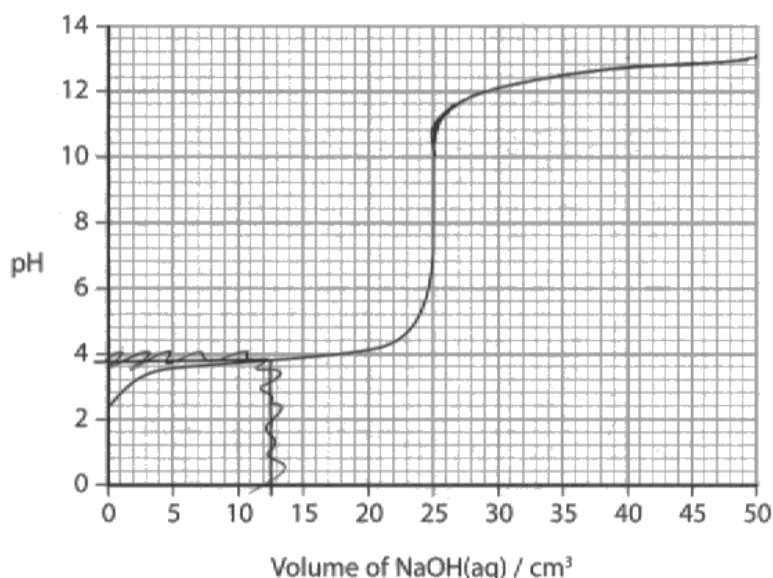
Sodium lactate would have a pH of around 9, since it's a base.



**ResultsPlus**  
Examiner Comments

This candidate has scored 3 marks for a correct answer to part (iii). They have scored 1 mark for a correct pH in part (iv), but there is not enough explanation for the second mark.

Part of the titration curve is shown below.



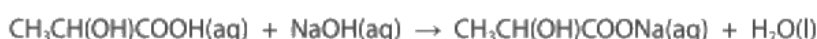
(iii) Use the information given in your Data Booklet to select a suitable indicator for this titration, giving the colour change you would expect to see.

Justify your selection.

(3)

- Phenolphthalein (in ethanol)
- pH range 8.2 - 10.0 which is within vertical region of curve (~~the pH at equivalence point~~ (pKa at 9.3 so colour change at equivalence point).
- Colour change from colourless to red.

(iv) The equation for the neutralization in the titration is



Use the titration curve to suggest the pH of a  $0.075 \text{ mol dm}^{-3}$  solution of sodium lactate. Justify your answer.

(2)

~~When half of acid neutralised  $\Rightarrow 12.5 \text{ cm}^3$  NaOH added,  
 $[\text{CH}_3\text{CH}(\text{OH})\text{COONa}]$  is  $0.075$~~

- Once  $25 \text{ cm}^3$  of NaOH added, all acid is neutralised  $\Rightarrow$  only sodium lactate  $\Rightarrow$  water left. Here pH ~~is~~ vertical from of concentration  $0.075 \text{ mol dm}^{-3}$   $\Rightarrow$  to 11 so take midpoint  $\Rightarrow$  pH is 9





**ResultsPlus**  
Examiner Comments

This is an excellent answer that scored 3 marks for part (iii) and 2 marks for part (iv).

## Question 22 (b) (v)

Many candidates started their answer with a definition of a buffer solution that was not needed here as the question asked for an explanation of how a buffer solution works. Many candidates gave good descriptions of a buffer solution and how it can work. Some candidates gave statements and ionic equations that were contradictory, for example, they stated that lactic acid only partially dissociates in water but then gave an equation to show complete dissociation. Some candidates did not include ionic equations to show how the added  $H^+$  and  $OH^-$  ions are removed.

\* (v) Explain, using ionic equations, how a solution containing lactic acid and sodium lactate can act as a buffer solution.

(4)



Sodium lactate gives an excess of  $CH_3CH(OH)COO^-$  ions, so there is a large reservoir of those ions.

From the 1<sup>st</sup> equation you get a large reservoir of  $CH_3CH(OH)COOH$ .

The increase in  $H^+$  ions by the addition of an acid is negligible because of the large reservoir of  $CH_3CH(OH)COOH$ .



**ResultsPlus**  
Examiner Comments

This candidate has described the buffer solution and given equations for how it is formed. However, they have not explained how the buffer solution reacts with added  $H^+$  or  $OH^-$  ions. This answer scored 1 mark.

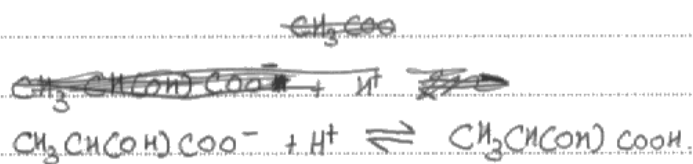


**ResultsPlus**  
Examiner Tip

Explain why the pH of the buffer solution only changes a little when small amounts of acid or alkali is added to it.

\*(v) Explain, using ionic equations, how a solution containing lactic acid and sodium lactate can act as a buffer solution.

(4)



when a small amount of  $\text{H}^+$  ion is added lactate ions reacts to form ~~lactic acid~~ undissociated lactic acid.



when a small amount of  $\text{OH}^-$  is added lactic acid reacts to form water and the salt (Lactate ions).

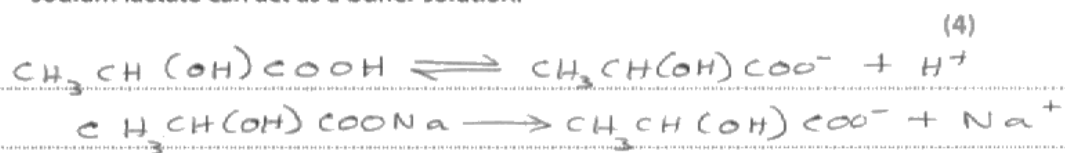
So the  $\text{pH}$  of this buffer solution ~~does not~~<sup>resists</sup> changes in  $\text{pH}$  when a ~~small~~ \* small amount of  $\text{H}^+$  ions or  $\text{OH}^-$  ions are added.



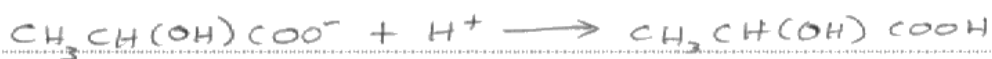
### ResultsPlus Examiner Comments

This is a good description of how a buffer solution removes the added  $\text{H}^+$  and  $\text{OH}^-$  ions. However, there is no mention that the buffer solution contains a reservoir of the weak acid and its conjugate base to react with the added ions. This answer scored 3 marks.

\*(v) Explain, using ionic equations, how a solution containing lactic acid and sodium lactate can act as a buffer solution.



- Added  $\text{H}^+$  ions are removed by a large reservoir of  $\text{CH}_3\text{CH}(\text{OH})\text{COO}^-$  from the salt



- Added  $\text{OH}^-$  ions are removed by a large reservoir of  $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$  from the acid



-  $\frac{[\text{CH}_3\text{CH}(\text{OH})\text{COO}^-]}{[\text{CH}_3\text{CH}(\text{OH})\text{COOH}]}$  remains almost constant

- Therefore, pH remains almost constant.



**ResultsPlus**  
Examiner Comments

This is an excellent answer that scored 4 marks.

### Question 22 (c)

Many candidates found this a challenging question. Many of them did not compare the  $pK_a$  values of the two acids to see that lactic acid is a stronger acid than ethanoic acid, so it donates the proton and ethanoic acid accepts the proton.

(c) Ethanoic acid,  $\text{CH}_3\text{COOH}$ , has a  $pK_a$  of 4.8 at 298 K.

Complete the equation to show the conjugate acid-base pairs that could be produced when pure samples of lactic acid and ethanoic acid are mixed.

(1)



**ResultsPlus**  
Examiner Comments

This candidate has shown ethanoic acid donating a proton to lactic acid and has not scored a mark.



**ResultsPlus**  
Examiner Tip

Use the  $pK_a$  values to find out which is the stronger acid. The stronger acid donates a proton to the weaker acid.

(c) Ethanoic acid,  $\text{CH}_3\text{COOH}$ , has a  $pK_a$  of 4.8 at 298 K.

Complete the equation to show the conjugate acid-base pairs that could be produced when pure samples of lactic acid and ethanoic acid are mixed.

(1)



**ResultsPlus**  
Examiner Comments

This candidate has realised that lactic acid is a stronger acid than ethanoic acid, so has scored the mark.

In order to improve their performance, candidates should:

- read the questions carefully and use all the information given;
- check their answers to calculations to avoid careless errors;
- explain their answers clearly and concisely;
- write balanced equations;
- understand how a rate equation relates to a mechanism;
- understand the use of dipoles, curly arrows and charges in an organic mechanism.

## **Grade Boundaries**

Grade boundaries for this, and all other papers, can be found on the website on this link:

<http://www.edexcel.com/iwantto/Pages/grade-boundaries.aspx>

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