X012/701

NATIONAL QUALIFICATIONS 2009

WEDNESDAY, 3 JUNE 9.00 AM – 11.30 AM

CHEMISTRY ADVANCED HIGHER

Reference may be made to the Chemistry Higher and Advanced Higher Data Booklet .

SECTION A – 40 marks

Instructions for completion of **SECTION A** are given on page two.

For this section of the examination you must use an **HB pencil**.

SECTION B – 60 marks

All questions should be attempted.

Answers must be written clearly and legibly in ink.

SECTION A

Read carefully

1 Check that the answer sheet provided is for **Chemistry Advanced Higher (Section A)**.

2 For this section of the examination you must use an **HB pencil** and, where necessary, an eraser.

3 Check that the answer sheet you have been given has **your name**, **date of birth**, **SCN** (Scottish Candidate Number) and **Centre Name** printed on it.

Do not change any of these details.

4 If any of this information is wrong, tell the Invigilator immediately.

5 If this information is correct, **print** your name and seat number in the boxes provided.

6 The answer to each question is **either** A, B, C or D. Decide what your answer is, then, using your pencil, put a horizontal line in the space provided (see sample question below).

7 There is **only one correct** answer to each question.

8 Any rough working should be done on the question paper or the rough working sheet, **not** on your answer sheet.

9 At the end of the exam, put the **answer sheet for Section A inside the front cover of your answer book**.

Sample Question

To show that the ink in a ball-pen consists of a mixture of dyes, the method of separation would be

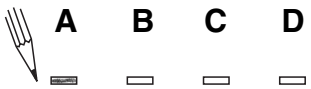
A chromatography

B fractional distillation

C fractional crystallisation

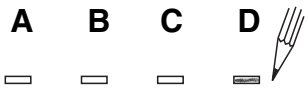
D filtration.

The correct answer is **A—**chromatography. The answer **A** has been clearly marked in **pencil** with a horizontal line (see below).

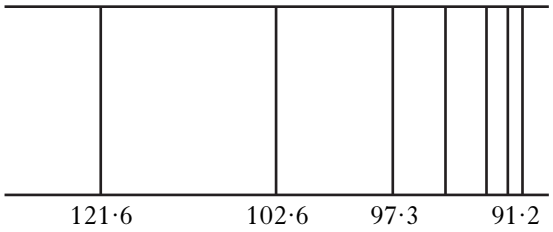


Changing an answer

If you decide to change your answer, carefully erase your first answer and using your pencil, fill in the answer you want. The answer below has been changed to **D**.



1. The diagram shows one of the series of lines in the hydrogen emission spectrum.



Each line

A represents an energy level within a hydrogen atom

B results from an electron moving to a higher energy level

C lies within the visible part of the electromagnetic spectrum

D results from an excited electron dropping to a lower energy level.

2. Which of the following compounds shows most covalent character?

A CH_4

B NaH

C NH_3

D PH_3

3. In which of the following species is a dative covalent bond present?

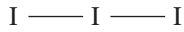
A H_3O^+

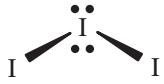
B H_2O

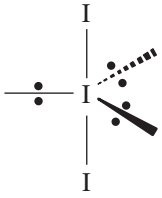
C OH^-

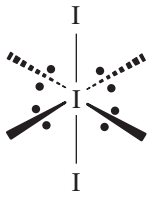
D O_2

4. Which of the following diagrams best represents the arrangement of electron pairs around the central iodine atom in the I_3^- ion?

A 

B 

C 

D 

5. When a voltage is applied to an n-type semiconductor, which of the following migrate through the lattice?

A Electrons

B Negative ions

C Positive holes

D Both electrons and positive holes

6. Which of the following compounds would produce fumes of hydrogen chloride when added to water?

A LiCl

B $MgCl_2$

C PCl_3

D CCl_4

[Turn over

7. Zinc oxide reacts as shown.

$ZnO(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2O(\ell)$

$ZnO(s) + 2NaOH(aq) + H_2O(\ell) \rightarrow Na_2Zn(OH)_4(aq)$

This shows that zinc oxide is

A basic

B acidic

C neutral

D amphoteric.

8. The correct formula for the tetraamminedichlorocopper(II) complex is

A $[Cu(NH_3)_4Cl_2]^{2-}$

B $[Cu(NH_3)_4Cl_2]$

C $[Cu(NH_3)_4Cl_2]^{2+}$

D $[Cu(NH_3)_4Cl_2]^{4+}$.

9. Which of the following aqueous solutions contains the **greatest** number of **negatively** charged ions?

A $500\,cm^3$ $0{\cdot}10$ mol l^{-1} $Na_2SO_4(aq)$

B $250\,cm^3$ $0{\cdot}12$ mol l^{-1} $BaCl_2(aq)$

C $300\,cm^3$ $0{\cdot}15$ mol l^{-1} $KI(aq)$

D $400\,cm^3$ $0{\cdot}10$ mol l^{-1} $Zn(NO_3)_2(aq)$

10. When one mole of phosphorus pentachloride was heated to 523 K in a closed vessel, 50% dissociated as shown.

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

How many moles of gas were present in the equilibrium mixture?

A $0{\cdot}5$

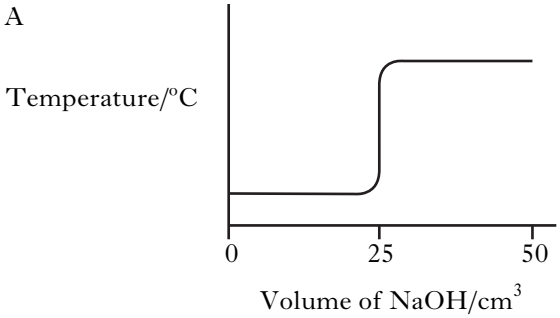
B $1{\cdot}0$

C $1{\cdot}5$

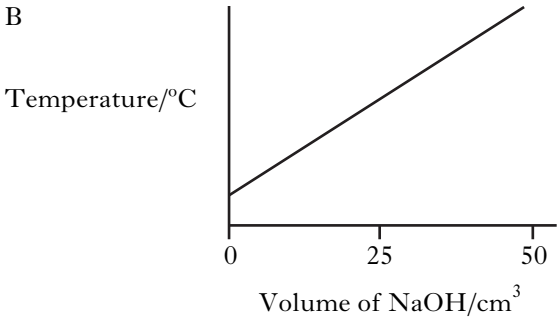
D $2{\cdot}0$

11. Which of the following graphs shows the temperature change as 2 mol l^{-1} sodium hydroxide is added to $25\,cm^3$ of 2 mol l^{-1} hydrochloric acid?

A



B



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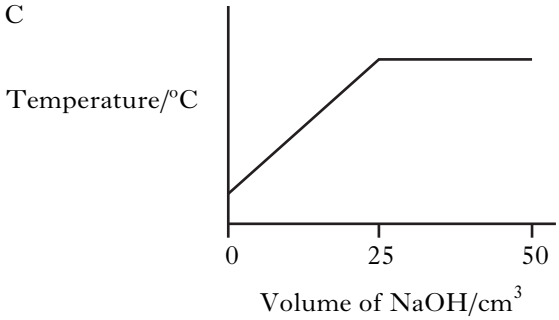
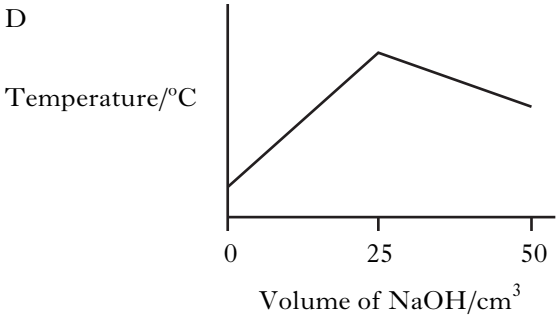


D



12. In the equilibrium $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ the forward reaction is endothermic.

Which one of the following causes an increase in the value of the equilibrium constant?

A The removal of NO_2

B An increase of pressure

C A decrease of temperature

D An increase of temperature

13. In which of the following separation techniques is partition between two separate phases **not** a part of the process?

A Recrystallisation of benzoic acid from hot water

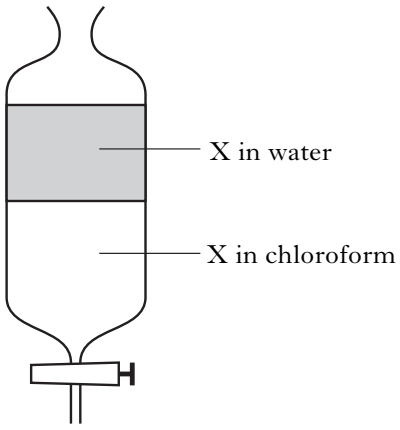
B Separation of alkanes using gas-liquid chromatography

C Separation of plant dyes using paper chromatography

D Solvent extraction of caffeine from an aqueous solution using dichloromethane

14. An aqueous solution of an organic acid, X, was shaken with chloroform until the following equilibrium was established.

X (water) $\rightleftharpoons$ X (chloroform)



$25{\cdot}0\,cm^3$ of the upper layer needed $20{\cdot}0\,cm^3$ of $0{\cdot}050$ mol l^{-1} NaOH(aq) for neutralisation.
$25{\cdot}0\,cm^3$ of the lower layer needed $13{\cdot}3\,cm^3$ of $0{\cdot}050$ mol l^{-1} NaOH(aq) for neutralisation.

The value of the partition coefficient is

A 0·67

B 1·25

C 1·50

D 1·88.

15. Which of the following would **not** be suitable to act as a buffer solution?

A Boric acid and sodium borate

B Nitric acid and sodium nitrate

C Benzoic acid and sodium benzoate

D Propanoic acid and sodium propanoate

16. Which of the following 0·01 mol l^{-1} aqueous solutions has the highest pH value?

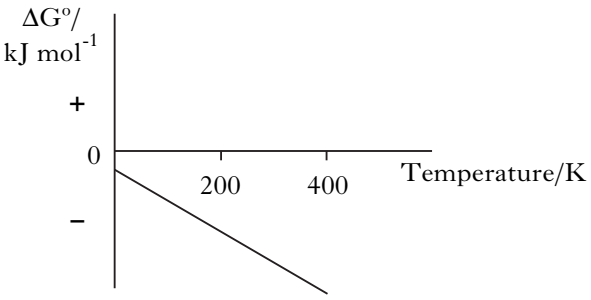
A Sodium fluoride

B Sodium benzoate

C Sodium propanoate

D Sodium methanoate

17. Which of the following graphs shows the variation in ΔG° with temperature for a reaction which is always feasible?

A


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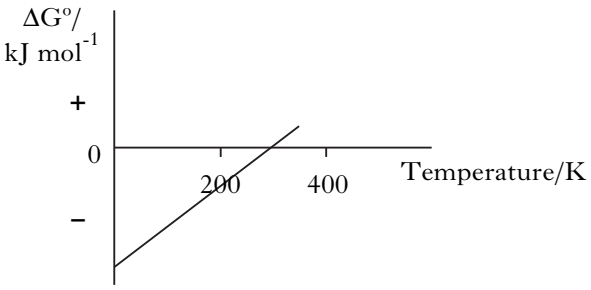

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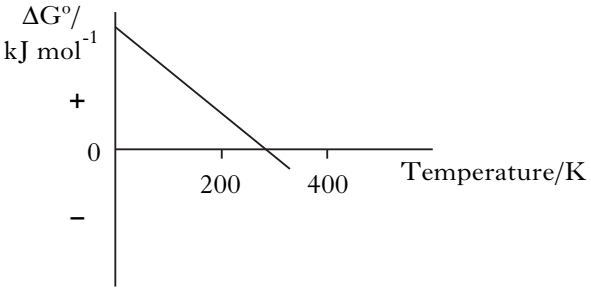

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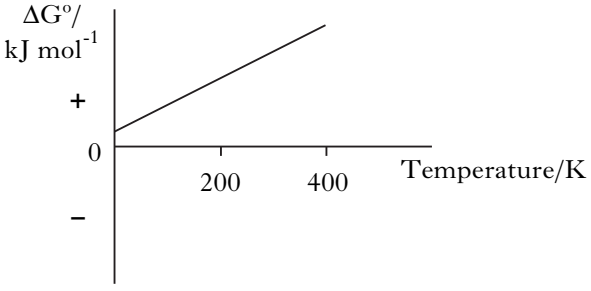


18. When water evaporates from a puddle which of the following applies?

A ΔH positive and ΔS positive

B ΔH positive and ΔS negative

C ΔH negative and ΔS positive

D ΔH negative and ΔS negative

19. For which of the following reactions would the value of $\Delta G^\circ - \Delta H^\circ$ be approximately zero?

A $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

B $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$

C $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

D $Cu^{2+}(aq) + Mg(s) \rightarrow Mg^{2+}(aq) + Cu(s)$

20. For the reaction

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$

the rate equation is

$$\text{rate} = k[NO]\,[Cl_2].$$

The overall order of this reaction is

A 1

B 2

C 3

D 5.

21. The following data refer to initial reaction rates obtained for the reaction

$$X + Y + Z \rightarrow \text{products}$$

Run	Relative concentrations			Relative initial rate
	[X]	[Y]	[Z]	
1	1·0	1·0	1·0	0·3
2	1·0	2·0	1·0	0·6
3	2·0	2·0	1·0	1·2
4	2·0	1·0	2·0	0·6

These data fit the rate equation

A Rate = k[X]

B Rate = k[X][Y]

C Rate = $k[X][Y]^2$

D Rate = k[X][Y][Z]

22. Which of the following is a propagation step in the chlorination of methane?

A $Cl_2 \rightarrow Cl^\bullet + Cl^\bullet$

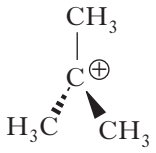
B $CH_3^\bullet + Cl^\bullet \rightarrow CH_3Cl$

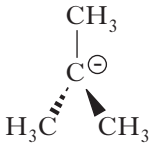
C $CH_3^\bullet + Cl_2 \rightarrow CH_3Cl + Cl^\bullet$

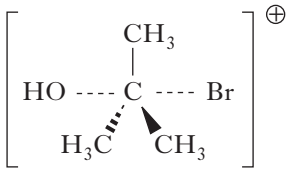
D $CH_4 + Cl^\bullet \rightarrow CH_3Cl + H^\bullet$

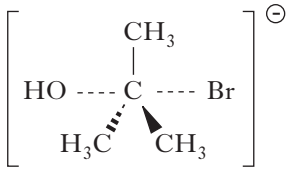
23. The hydrolysis of the halogenoalkane $(CH_3)_3CBr$ was found to take place by an S_N1 mechanism.

The rate-determining step involved the formation of

A 

B 

C 

D 

24. $OH^- + CO_2 \rightarrow HCO_3^-$

$C_2H_4 + Br_2 \rightarrow C_2H_4Br^+ + Br^-$

Which substances act as electrophiles in the above reactions?

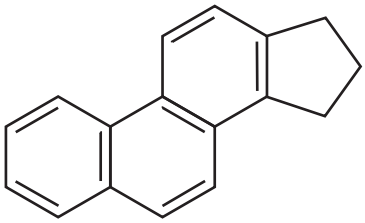
A OH^- and Br_2

B OH^- and C_2H_4

C CO_2 and Br_2

D CO_2 and C_2H_4

25.



What is the molecular formula for the above structure?

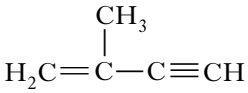
A $C_{17}H_{11}$

B $C_{17}H_{14}$

C $C_{17}H_{17}$

D $C_{17}H_{20}$

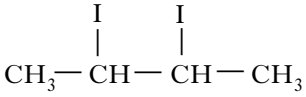
26. Which line in the table is correct for the following hydrocarbon?



	Number of σ bonds	Number of π bonds
A	4	3
B	8	5
C	10	2
D	10	3

27. When but-2-ene is shaken with an aqueous solution of chlorine in potassium iodide, the structural formula(e) of the product(s) is/are

A



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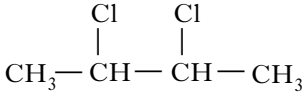
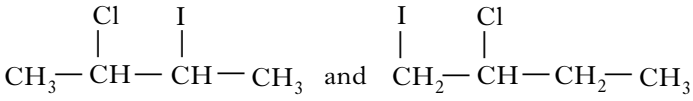


C



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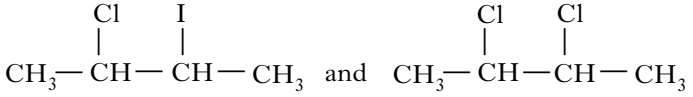


28. Which of the following reacts with ethanol to form the ethoxide ion?

A Na(s)

B $Na_2O(s)$

C NaCl(aq)

D NaOH(aq)

29. Which of the following is **not** a correct statement about ethoxyethane?

A It burns readily in air.

B It is isomeric with butan-2-ol.

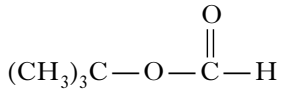
C It has a higher boiling point than butan-2-ol.

D It is a very good solvent for many organic compounds.

[Turn over

30. Which of the following esters gives a secondary alcohol when hydrolysed?

A



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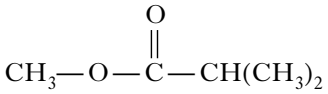

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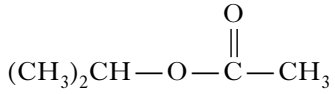
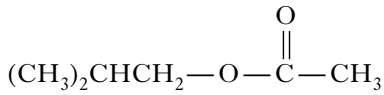


D



31. Which of the following compounds could **not** be oxidised by acidified potassium dichromate solution?

A CH_3CH_2CHO

B CH_3CH_2COOH

C $CH_3CH_2CH_2OH$

D $CH_3CH(OH)CH_3$

32. Which of the following will react with dilute sodium hydroxide solution?

A $CH_3CHOHCH_3$

B $CH_3CH{=}CH_2$

C CH_3COOCH_3

D $CH_3CH_2OCH_3$

33. Which of the following molecules is planar?

A Hexane

B Cyclohexane

C Chlorobenzene

D Methylbenzene (toluene)

34. Which of the following compounds is soluble in water and reacts with both dilute hydrochloric acid and sodium hydroxide solution?

A $C_2H_5NH_2$

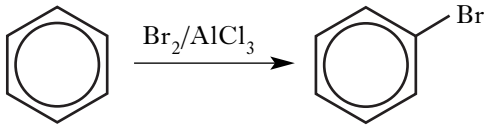
B $C_6H_5NH_2$

C $C_2H_5NH_3Cl$

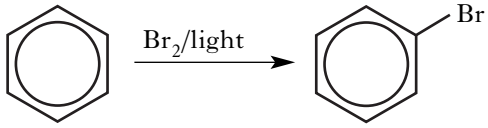
D $HOOCCH_2NH_2$

35. Which of the following reactions is least likely to take place?

A



B



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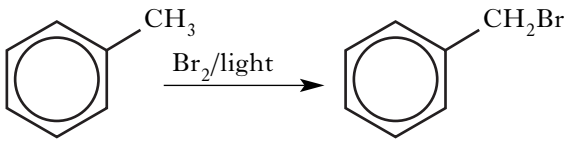
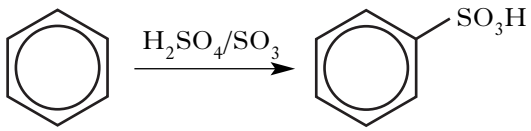
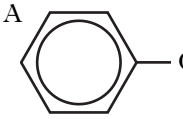
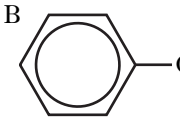


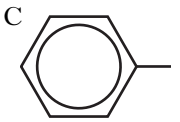
D

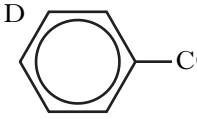


36. In which of the following pairs does an aqueous solution of the first compound have a higher pH than an aqueous solution of the second?

A  and CH_3COOH

B  and CH_3CH_2OH

C  and $HOCH_2CH_2OH$

D  and CH_3OH

37. Which of the following bases is the strongest?

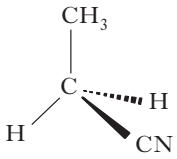
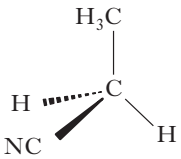
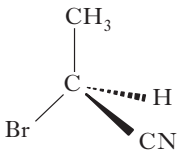
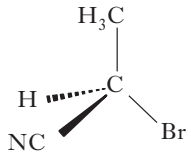
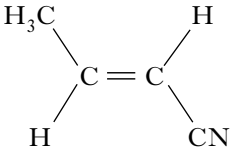
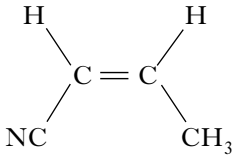
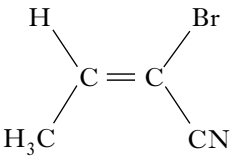
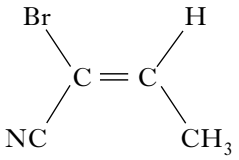
A $C_2H_5NH_2$

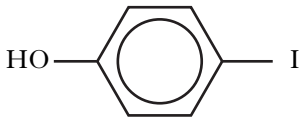
B $(C_2H_5)_2NH$

C $C_6H_5NH_2$

D $(C_6H_5)_2NH$

38. Which line in the table shows a pair of optical isomers?

A		
B		
C		
D		

39. 

Which atom in the above structure would be located **most** readily using X-ray crystallography?

A Carbon

B Hydrogen

C Iodine

D Oxygen

40. Antihistamines act by inhibiting the action of the inflammatory agent histamine in the body.

Antihistamines can be described as

A agonists

B receptors

C antagonists

D pharmacophores.

[*END OF SECTION A*]

Candidates are reminded that the answer sheet for Section A MUST be placed INSIDE the front cover of your answer book.

SECTION B

60 marks are available in this section of the paper.

All answers must be written clearly and legibly in ink.

Marks

1. A detector in a Geiger counter contains argon which ionises when nuclear radiation passes through it.

(*a*) Write the electronic configuration for argon in terms of s and p orbitals. **1**

(*b*) The first ionisation energy of argon is 1530 kJ mol^{-1}.

(i) Calculate the wavelength of the radiation, in nm, corresponding to this energy. **3**

(ii) Write the equation for the first ionisation of argon. **1**

(5)

2. Iron(III) oxide can be reduced to iron using hydrogen.

$$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(g)$$

Substance	$\Delta H_f°$/kJ mol^{-1}	$S°$/J K^{-1} mol^{-1}
$Fe_2O_3(s)$	–822	90
$H_2(g)$	0	131
Fe(s)	0	27
$H_2O(g)$	–242	189

For the reduction of iron(III) oxide with hydrogen, use the data in the table to calculate

(*a*) the standard entropy change, $\Delta S°$ **1**

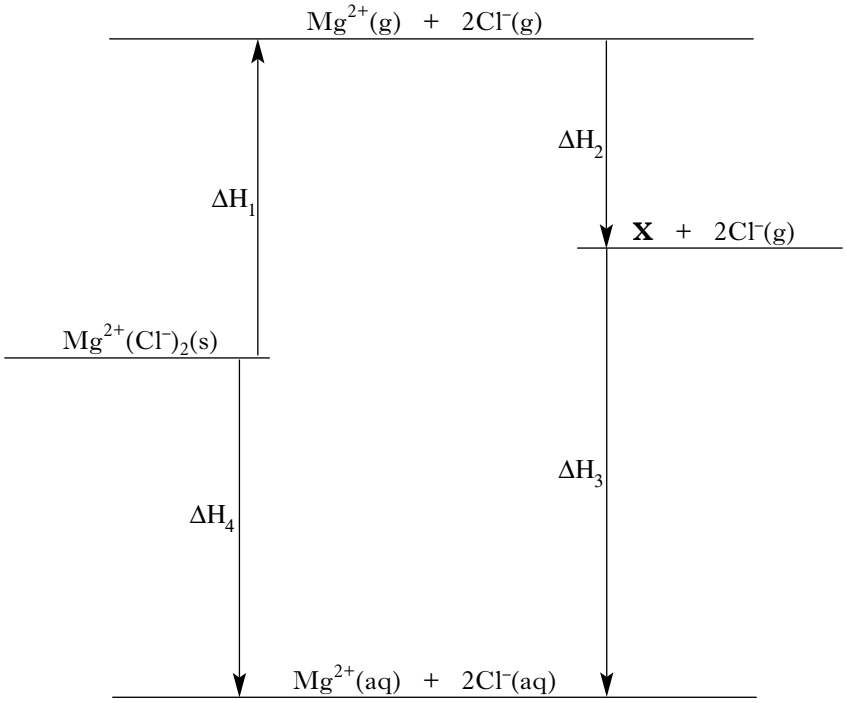
(*b*) the standard enthalpy change, $\Delta H°$ **1**

(*c*) the theoretical temperature above which the reaction becomes feasible. **2**

(4)

Marks

3. The diagram, which is not drawn to scale, represents the processes involved in a thermochemical cycle.



(*a*) What should be written in place of **X** to complete the diagram? **1**

(*b*) What name is given to the enthalpy change represented by ΔH_1? **1**

(*c*) Calculate ΔH_3 using information from the Data Booklet. **1**

(*d*) Calculate ΔH_4 using information from the Data Booklet. **1**

(4)

4. (*a*) Using the mean bond enthalpy values given in the Data Booklet, calculate the enthalpy change, in kJ mol^{-1}, for the reaction

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(g)$$ **3**

(*b*) The value given in the Data Booklet for the standard enthalpy of combustion of hydrogen is different to that calculated in part (*a*).

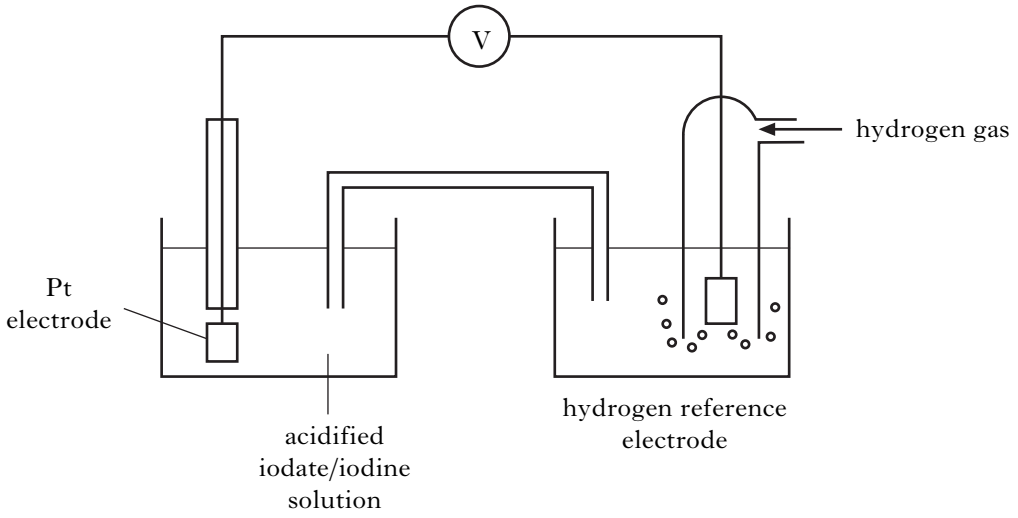
Give the main reason for this difference. **1**

(4)

[Turn over

Marks

5.



The above cell was set up under standard conditions.

(*a*) What are the three standard conditions required for the hydrogen reference electrode? **1**

(*b*) Write an ion-electron equation for the reduction of iodate ions (IO_3^-) to iodine (I_2) in acidic conditions. **1**

(*c*) If the E° value for the reduction of IO_3^- to I_2 is 1·19 V, calculate the free energy change $\Delta G°$, in kJ per mole of IO_3^-, for the cell reaction. **3**

(5)

6. When an ant bites, it injects methanoic acid (HCOOH).

(*a*) Methanoic acid is a weak acid.

$$HCOOH(aq) + H_2O(\ell) \rightleftharpoons HCOO^-(aq) + H_3O^+(aq)$$

(i) What is the conjugate base of methanoic acid? **1**

(ii) Write the expression for the dissociation constant, K_a, of methanoic acid. **1**

(*b*) (i) In a typical bite, an ant injects $3{\cdot}6 \times 10^{-3}$ g of methanoic acid.
Assuming that the methanoic acid dissolves in 1·0 cm^3 of water in the body, calculate the concentration of the methanoic acid solution in $mol\,l^{-1}$. **2**

(ii) Calculate the pH of this methanoic acid solution. **2**

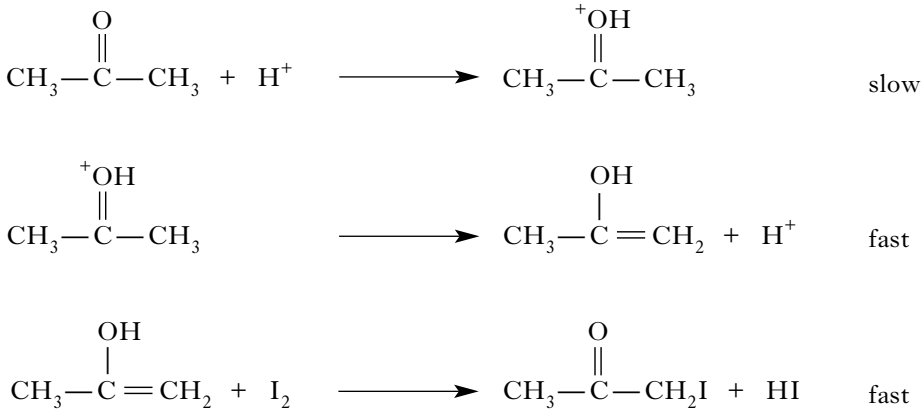
(6)

Marks

7. Iodine reacts with propanone as follows.

$$I_2 + CH_3COCH_3 \longrightarrow CH_3COCH_2I + HI$$

A possible mechanism for this reaction is



(*a*) Write a rate equation for this reaction based on the above mechanism. **1**

(*b*) What evidence indicates that the reaction is acid catalysed? **1**

(*c*) In a PPA the reaction was followed by withdrawing samples at regular intervals and adding them to sodium hydrogencarbonate solution.

The concentration of iodine in these samples was then determined by titrating with a standard solution of sodium thiosulphate.

(i) Why were the samples added to the sodium hydrogencarbonate solution? **1**

(ii) What indicator is used in the titration and what is the colour change at the end-point of the titration? **1**

(4)

[Turn over

Marks

8. Nickel can be determined quantitatively in a number of ways.

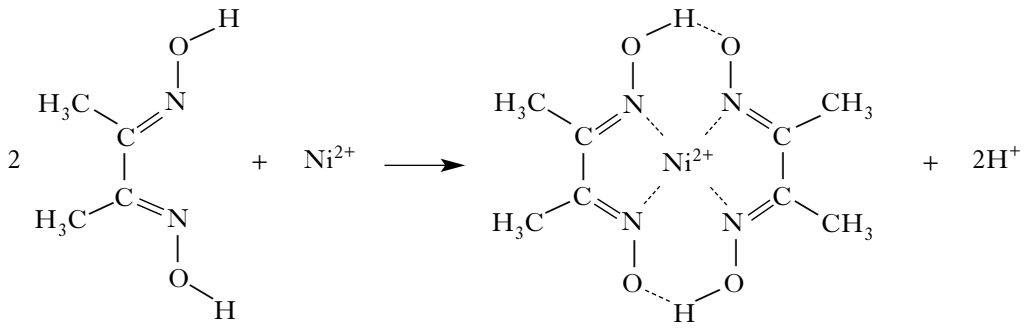
(*a*) The method used in a PPA is volumetric analysis in which a buffered solution of nickel(II) ions is titrated against a standard solution of a complexing agent.

Which complexing agent is used? **1**

(*b*) Another way of determining nickel is by colorimetric analysis.

Why would this be a suitable method of determining nickel(II) ions? **1**

(*c*) A third way of determining nickel depends on the fact that nickel(II) ions form a solid complex with butanedione dioxime.



butanedione dioxime insoluble complex

Using this method, a sample of a nickel(II) salt was accurately weighed and dissolved in water. To this solution, excess butanedione dioxime solution was added. The solid complex formed was filtered, washed and then heated in an oven to constant mass.

(i) Butanedione dioxime can act as a ligand.

What property of butanedione dioxime allows it to act as a ligand? **1**

(ii) What is the coordination number of the nickel(II) ion in the insoluble complex? **1**

(iii) Which type of quantitative analysis has been carried out using this method? **1**

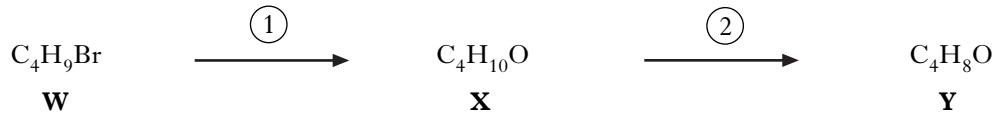
(iv) During the process of heating to constant mass, the solid complex is cooled in a desiccator.

Why is a desiccator used? **1**

(6)

Marks

9. Compound **W** reacts in two steps to form compound **Y**.



Y reacts with 2,4-dinitrophenylhydrazine solution (Brady's reagent) to form a yellow precipitate **Z**.

Y does not react with Fehling's solution, nor with Tollens' reagent.

(*a*) Identify compound **Y**. **1**

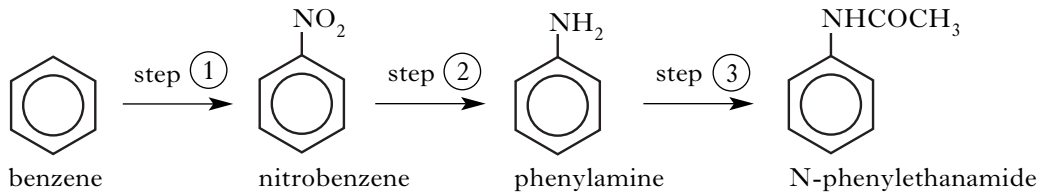
(*b*) What type of reaction is occurring in step (1)? **1**

(*c*) What property of the yellow precipitate **Z** is measured and how is this used to confirm the identity of **Y**? **1**

(*d*) Dehydration of compound **X** produces three unsaturated isomers of molecular formula C_4H_8. Two of these are **geometric** isomers.
Draw the structures of both **geometric** isomers and name each one. **2**

(5)

10. N-Phenylethanamide can be prepared from benzene in three steps.



(*a*) What chemicals are required to react with benzene to bring about step (1)? **1**

(*b*) What type of reaction occurs in step (2)? **1**

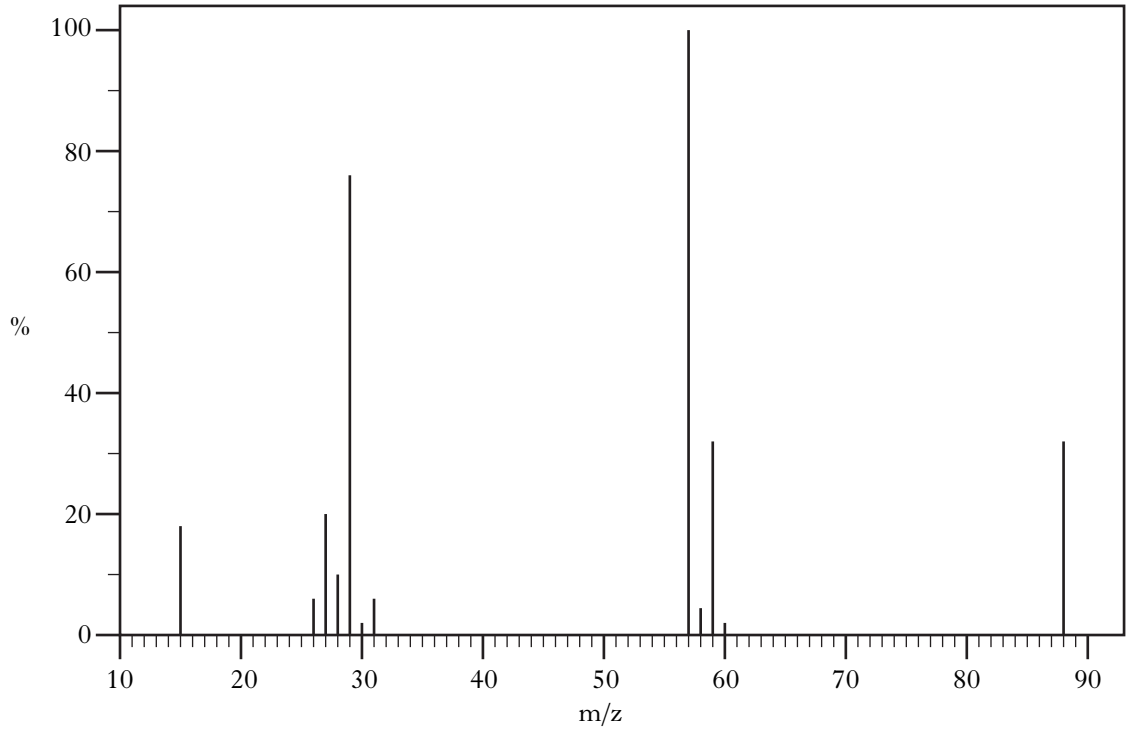
(*c*) Suggest a reagent which could be used to bring about step (3). **1**

(3)

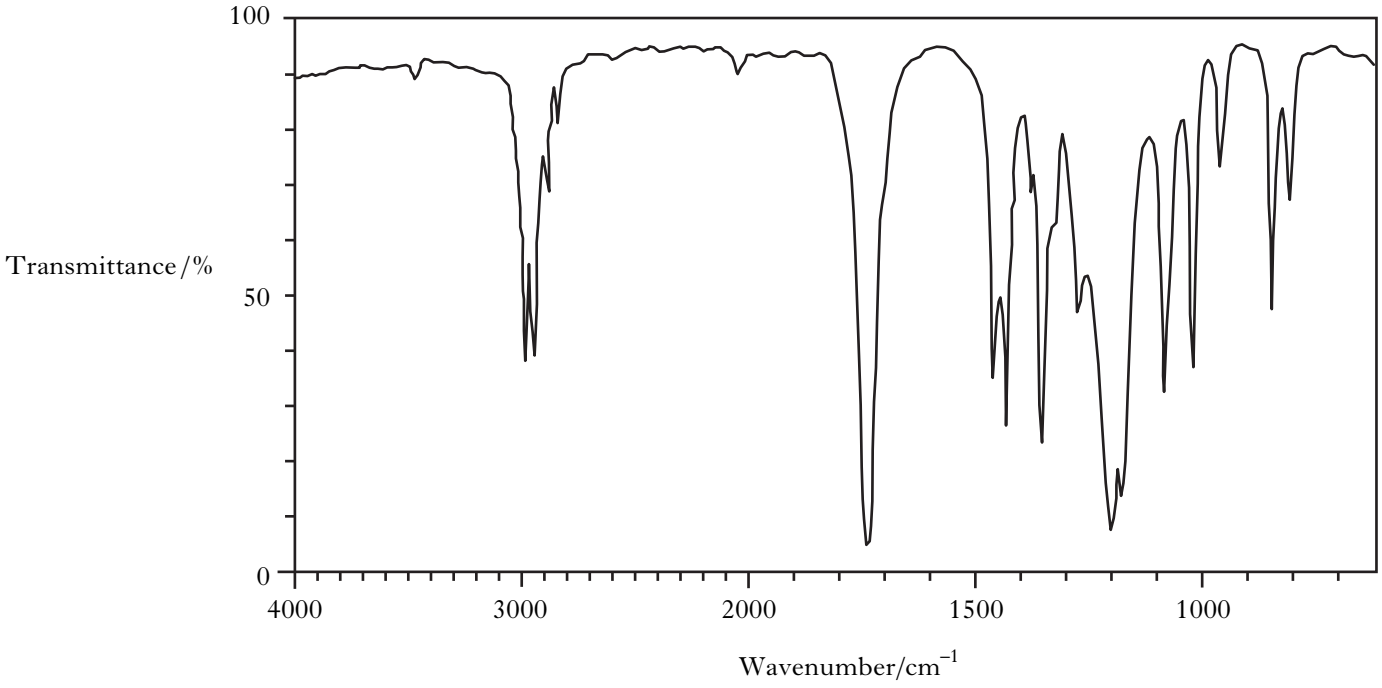
[Turn over

11. Spectra of an organic compound **A** are shown below.

Mass spectrum of compound A



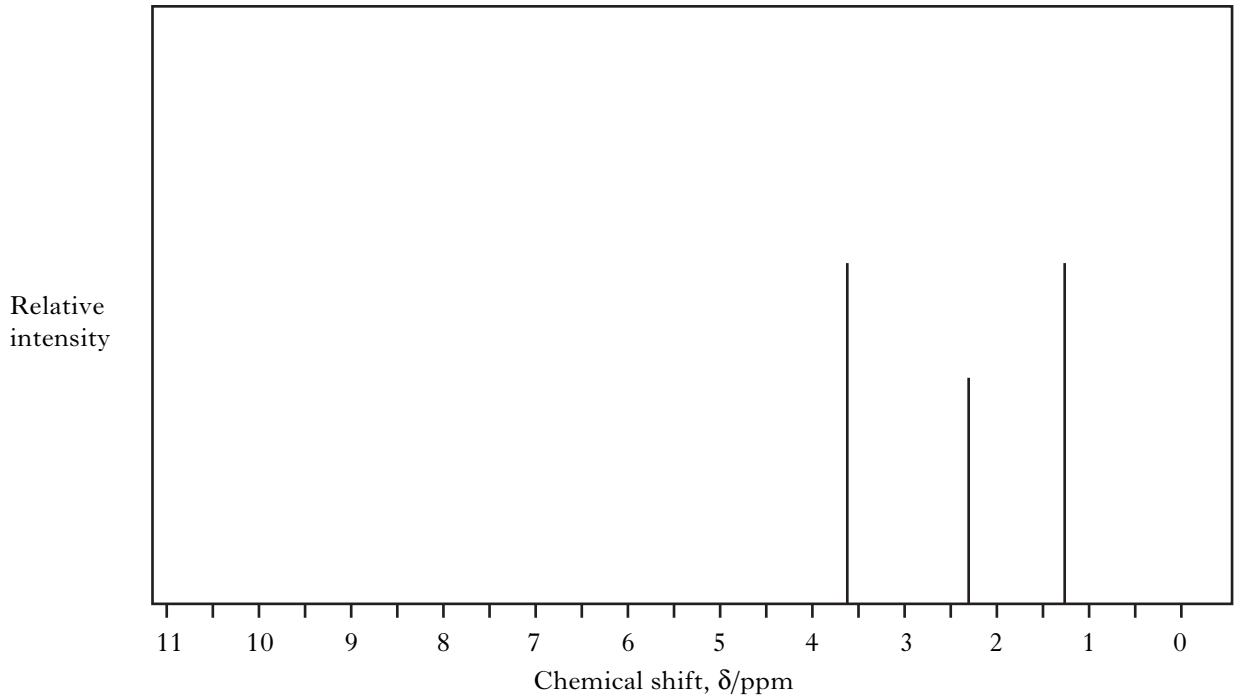
Infra-red spectrum of compound A



Marks

11. (continued)

Proton nmr spectrum of compound A



(*a*) Compound **A** has empirical formula C_2H_4O.

Using this information and the mass spectrum, deduce the molecular formula of **A**. **1**

(*b*) The absorption peak at 1745 cm^{-1} in the infra-red spectrum can be used to help identify **A**.

(i) Which bond is responsible for this absorption? **1**

(ii) Which type of compound is **A**? **1**

(*c*) Draw the structure of the ion fragment responsible for the peak at m/z 57 in the mass spectrum. **1**

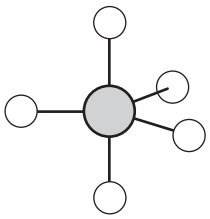
(*d*) Considering all the evidence, including the proton nmr spectrum, name compound **A**. **1**

(5)

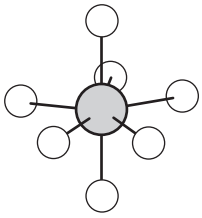
[Turn over

Marks

12. Many interhalogen compounds exist. Two of these are iodine pentafluoride and iodine heptafluoride.



IF_5



IF_7

(*a*) What are the oxidation states of iodine in iodine pentafluoride and iodine heptafluoride? **1**

(*b*) Name the shape adopted by the iodine pentafluoride molecule. **1**

(*c*) In iodine heptafluoride, there are seven I–F bonds in which iodine uses sp^3d^3 hybrid orbitals.

Suggest which hybrid orbitals iodine uses in iodine pentafluoride, in which there are five I–F bonds. **1**

(*d*) Another interhalogen compound, ClF_5, exists but ClF_7 does not.

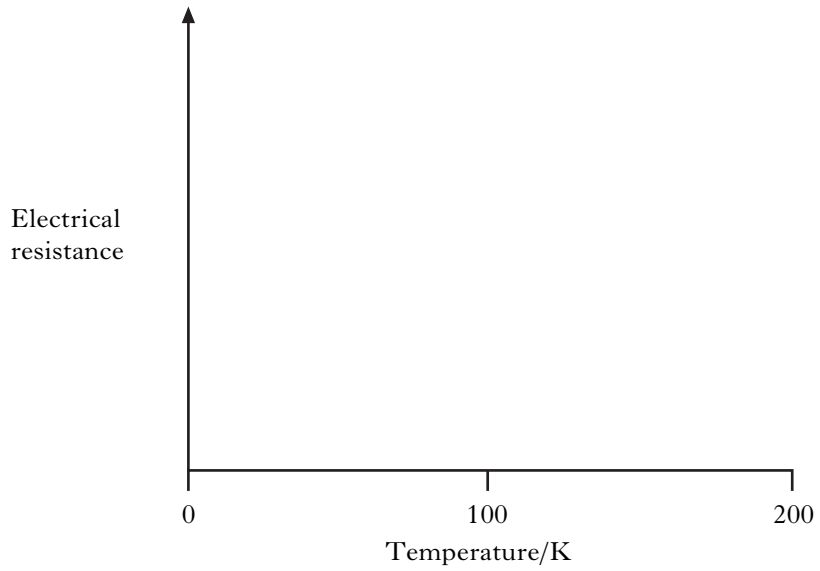
Suggest a reason why ClF_7 does not exist. **1**

(4)

Marks

13. A superconductor, **X**, with a critical temperature of 95 K, was prepared by heating yttrium oxide, barium carbonate and copper oxide at high temperatures.

(*a*) Copy the axes shown and sketch a graph to show how the **electrical resistance** of **X** varies with temperature.



1

(*b*) (i) **X** contains 13·4% yttrium, 41·2% barium, 28·6% copper and 16·8% oxygen.

Assuming that the relative atomic mass of yttrium is 88·9, show by calculation that the empirical formula for **X** is $YBa_2Cu_3O_7$. **2**

(ii) Assuming that the oxidation states of yttrium, barium and oxygen are +3, +2 and −2 respectively, calculate the **average** oxidation state of copper in **X.** **1**

(iii) When all the copper(III) initially present in **X** is reduced to copper(II), compound **Z** is produced. The oxidation states of the other three elements do not change nor does the mole ratio of the **metals**.

Suggest an empirical formula for **Z**. **1**

(5)

[*END OF QUESTION PAPER*]

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