



# Cambridge International AS & A Level

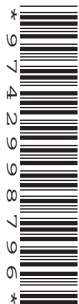
CANDIDATE  
NAME

CENTRE  
NUMBER

--	--	--	--	--

CANDIDATE  
NUMBER

--	--	--	--



**CHEMISTRY**

**9701/42**

Paper 4 A Level Structured Questions

**October/November 2023**

**2 hours**

You must answer on the question paper.

No additional materials are needed.

## INSTRUCTIONS

- Answer **all** questions.
- Use a black or dark blue pen. You may use an HB pencil for any diagrams or graphs.
- Write your name, centre number and candidate number in the boxes at the top of the page.
- Write your answer to each question in the space provided.
- Do **not** use an erasable pen or correction fluid.
- Do **not** write on any bar codes.
- You may use a calculator.
- You should show all your working and use appropriate units.

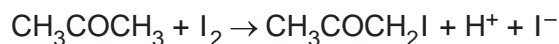
## INFORMATION

- The total mark for this paper is 100.
- The number of marks for each question or part question is shown in brackets [ ].
- The Periodic Table is printed in the question paper.
- Important values, constants and standards are printed in the question paper.

This document has **28** pages. Any blank pages are indicated.

## 2

- 1 Propanone,  $\text{CH}_3\text{COCH}_3$ , reacts with iodine,  $\text{I}_2$ , in the presence of an acid catalyst.



The rate equation for this reaction is shown.

$$\text{rate} = k[\text{CH}_3\text{COCH}_3][\text{H}^+]$$

- (a) Complete Table 1.1 to describe the order of the reaction.

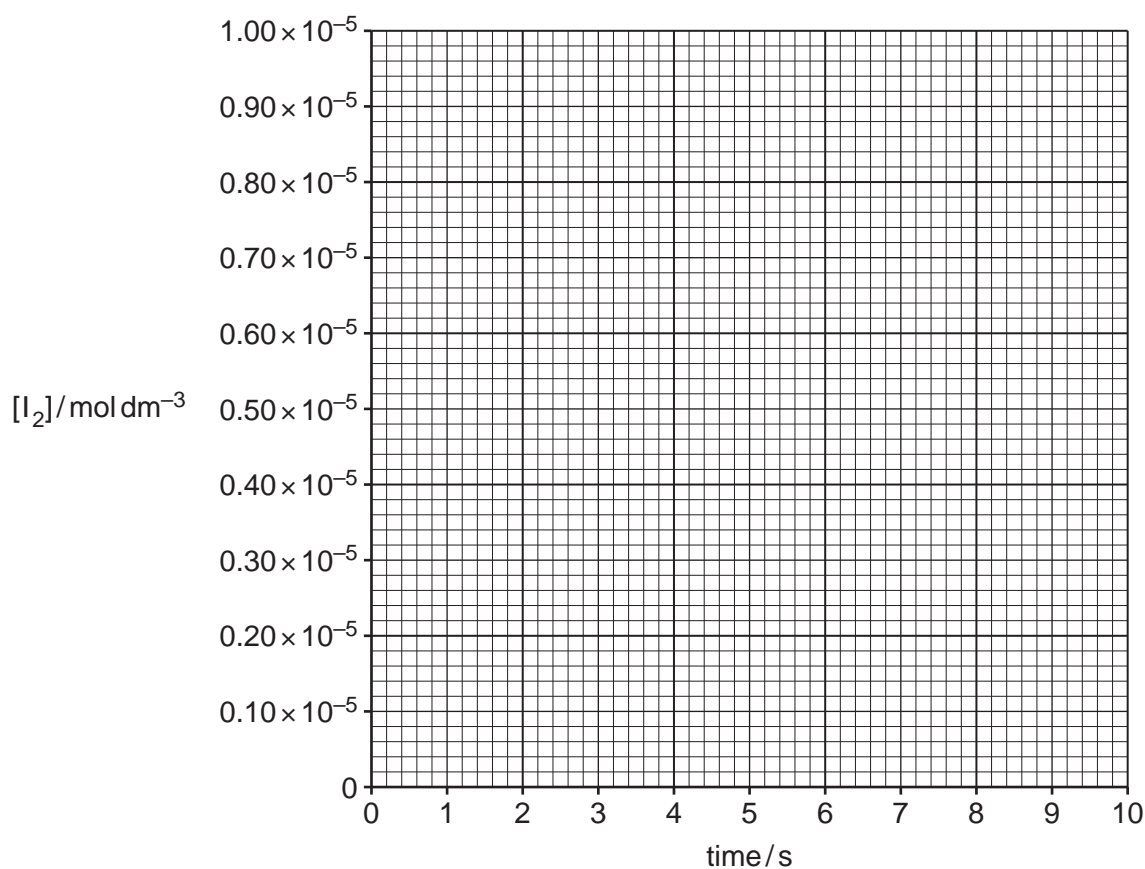
**Table 1.1**

order of the reaction with respect to $[\text{CH}_3\text{COCH}_3]$	
order of the reaction with respect to $[\text{I}_2]$	
order of the reaction with respect to $[\text{H}^+]$	
overall order of the reaction	

[2]

- (b) An experiment is performed using a large excess of  $\text{CH}_3\text{COCH}_3$  and a large excess of  $\text{H}^+(\text{aq})$ . The initial concentration of  $\text{I}_2$  is  $1.00 \times 10^{-5} \text{ mol dm}^{-3}$ . The initial rate of decrease in the  $\text{I}_2$  concentration is  $2.27 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$ .

- (i) Use the axes to draw a graph of  $[\text{I}_2]$  against time for the first 10 seconds of the reaction.



[1]

## 3

- (ii) State whether it is possible to calculate the numerical value of the rate constant,  $k$ , for this reaction from your graph. Explain your answer.

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

- (c) The experiment is repeated at a different temperature. The initial concentrations of  $\text{H}^+$  ions,  $\text{I}_2$  and  $\text{CH}_3\text{COCH}_3$  are all  $0.200 \text{ mol dm}^{-3}$ .

The value of  $k$  at this temperature is  $2.31 \times 10^{-5} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ .

Calculate the initial rate of this reaction.

rate = .....  $\text{mol dm}^{-3} \text{ s}^{-1}$  [1]

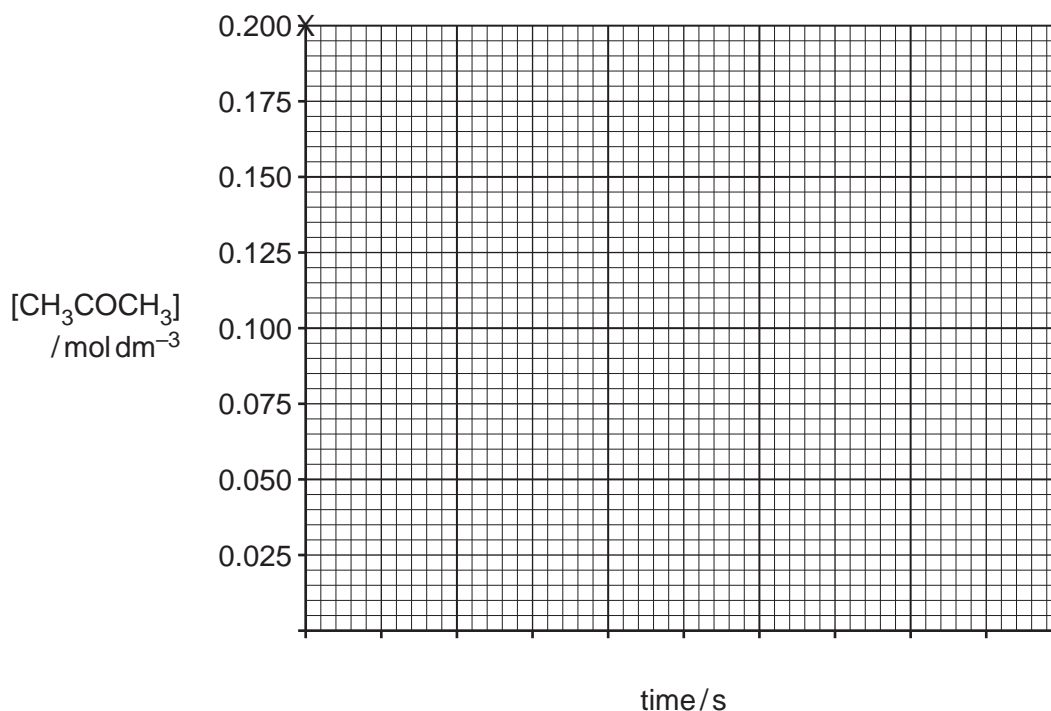
- (d) The experiment is repeated using an excess of  $\text{H}^+(\text{aq})$ . The new rate equation is shown.

$$\text{rate} = k_1[\text{CH}_3\text{COCH}_3]$$

- (i) The value of  $k_1$  is  $1.1 \times 10^{-3} \text{ s}^{-1}$ . Calculate the value of the half-life,  $t_{\frac{1}{2}}$ .

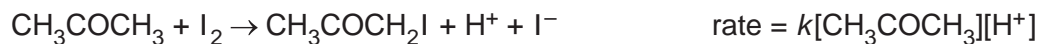
$t_{\frac{1}{2}} = \dots\dots\dots \text{ s}$  [1]

- (ii) Use your answer to (i) to draw a graph of  $[\text{CH}_3\text{COCH}_3]$  against time for this reaction. The initial value of  $[\text{CH}_3\text{COCH}_3]$  on your graph should be  $0.200 \text{ mol dm}^{-3}$ . The final value of  $[\text{CH}_3\text{COCH}_3]$  on your graph should be  $0.0250 \text{ mol dm}^{-3}$ .

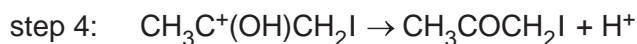
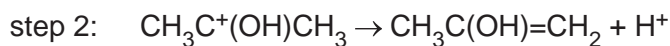
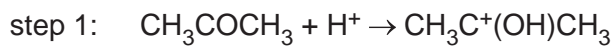


[1]

(e) A four-step mechanism is suggested for the overall reaction.



Part of this mechanism is shown.



(i) Write an equation for step 3.

..... [1]

(ii) Suggest the slowest step of the mechanism. Explain your answer.

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

(iii) Identify one conjugate acid-conjugate base pair in the mechanism.

conjugate acid ..... conjugate base ..... [1]

[Total: 10]

**BLANK PAGE**

2 Benzoic acid,  $\text{C}_6\text{H}_5\text{COOH}$ , is a weak acid. The  $K_a$  of benzoic acid is  $6.31 \times 10^{-5} \text{ mol dm}^{-3}$  at 298 K.

A  $1.00 \text{ dm}^3$  buffer solution is made at 298 K containing 1.00 g of  $\text{C}_6\text{H}_5\text{COOH}$  and a slightly greater mass of sodium benzoate,  $\text{C}_6\text{H}_5\text{COO}^- \text{Na}^+$ .

This buffer solution has a pH of 4.15.

(a) Define buffer solution.

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

(b) Write equations to show how this solution acts as a buffer solution when the named substances are added to it:

(i) dilute aqueous sodium hydroxide

..... [1]

(ii) dilute aqueous nitric acid.

..... [1]

(c) Calculate the  $\text{H}^+$  concentration and the  $\text{C}_6\text{H}_5\text{COOH}$  concentration in the buffer solution described. Use the expression for the  $K_a$  of  $\text{C}_6\text{H}_5\text{COOH}$  to calculate the concentration of  $\text{C}_6\text{H}_5\text{COO}^- \text{Na}^+$  in the buffer solution.

Show your working and give each answer to a minimum of **three** significant figures.

$$[\text{H}^+] = \dots\dots\dots \text{ mol dm}^{-3}$$

$$[\text{C}_6\text{H}_5\text{COOH}] = \dots\dots\dots \text{ mol dm}^{-3}$$

$$[\text{C}_6\text{H}_5\text{COO}^- \text{Na}^+] = \dots\dots\dots \text{ mol dm}^{-3}$$

[3]

- (d) A  $10.0\text{ cm}^3$  sample of the buffer solution is mixed with  $10.0\text{ cm}^3$  of  $1.00\text{ mol dm}^{-3}$  KOH. Both solutions are at 298 K. A reaction is allowed to occur without stirring.

Two observations are recorded:

- the temperature, after the reaction is complete, is fractionally above 298 K
- the pH, after the reaction, is greater than 13.

Explain these two observations.

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

- (e) Magnesium benzoate,  $\text{Mg}(\text{C}_6\text{H}_5\text{COO})_2$ , has a solubility in water of less than  $1.00\text{ g dm}^{-3}$  at 298 K.

$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{C}_6\text{H}_5\text{COO}^-]^2 = 1.76 \times 10^{-7} \text{ at } 298 \text{ K}$$

- (i) Calculate the solubility of  $\text{Mg}(\text{C}_6\text{H}_5\text{COO})_2$  in water at 298 K. Give your answer in  $\text{g dm}^{-3}$ .

Show your working.

[ $M_r$ :  $\text{Mg}(\text{C}_6\text{H}_5\text{COO})_2$ , 266.3]

solubility = .....  $\text{g dm}^{-3}$  [2]

- (ii) An excess of  $\text{Mg}(\text{C}_6\text{H}_5\text{COO})_2$  is added to a sample of  $0.50\text{ mol dm}^{-3}$   $\text{MgSO}_4$  at 298 K.

State whether the equilibrium concentration of  $\text{Mg}(\text{C}_6\text{H}_5\text{COO})_2$  is higher than, the same as, or lower than your answer to (i). Explain your answer.

The concentration is ..... the concentration in (i).

explanation .....

..... [1]

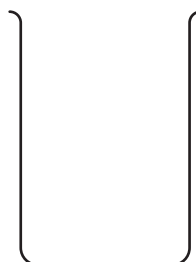
[Total: 11]

- 3 Some electrode potentials are shown in Table 3.1.

Table 3.1

electrode reaction	$E^\ominus/V$
$V^{2+} + 2e^- \rightleftharpoons V$	-1.20
$V^{3+} + e^- \rightleftharpoons V^{2+}$	-0.26
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	+0.34
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$	+1.00
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	-0.44
$Fe^{3+} + 3e^- \rightleftharpoons Fe$	-0.04
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$ClO^- + H_2O + 2e^- \rightleftharpoons Cl^- + 2OH^-$	+0.89

- (a) (i) Complete the diagram to show a standard hydrogen electrode. Label your diagram. Identify all substances. You do **not** need to state standard conditions.



[1]

- (ii) An electrochemical cell is set up using an  $Fe^{3+}/Fe^{2+}$  electrode and a standard hydrogen electrode.

Identify the positive electrode in the electrochemical cell and the direction of electron flow in the external circuit.

positive electrode .....

Electrons flow from the ..... electrode to the ..... electrode.

[1]



(b) The vanadium-containing species in the electrode reactions given in Table 3.1 are V,  $V^{2+}$ ,  $V^{3+}$ ,  $VO^{2+}$  and  $VO_2^+$ .

(i) Identify **one** vanadium-containing species that does **not** react with  $Fe^{2+}$  ions under standard conditions.

Use data from Table 3.1 to explain your answer.

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

(ii) Identify **all** the vanadium-containing species that will react with  $Fe^{2+}$  ions under standard conditions.

..... [1]

(iii) Write an equation for **one** of the possible reactions identified in (ii).

..... [1]

(c) Another electrochemical cell is set up using an  $Fe^{3+}/Fe^{2+}$  electrode and an alkaline  $ClO^-/Cl^-$  electrode.

The concentration of  $Fe^{3+}$  is 1000 times greater than the concentration of  $Fe^{2+}$  in the  $Fe^{3+}/Fe^{2+}$  electrode. All other conditions are standard.

(i) Use the Nernst equation to calculate the  $E$  value of the  $Fe^{3+}/Fe^{2+}$  electrode.

Show your working.

$E = \dots\dots\dots$  V [2]

(ii) Write an equation for the reaction that occurs in the cell, under these conditions.

..... [1]

(d) Another electrochemical cell is set up using an  $Fe^{2+}/Fe$  electrode and an alkaline  $ClO^-/Cl^-$  electrode under standard conditions.

Calculate the value of  $\Delta G^\ominus$  for the cell.

$\Delta G^\ominus = \dots\dots\dots$   $\text{kJmol}^{-1}$  [3]

## 10

- (e) A solution of iron(II) sulfate,  $\text{FeSO}_4(\text{aq})$  is electrolysed with iron electrodes. Under the conditions used, no gas is evolved at the cathode.

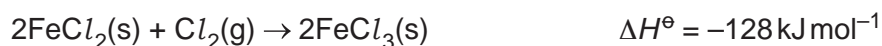
A current of  $0.640\text{A}$  is passed for  $17.0$  minutes. The mass of the cathode increases by  $0.185\text{g}$ .

Use these results to calculate an experimental value for the Avogadro constant,  $L$ .

Show your working.

$$L = \dots\dots\dots \text{mol}^{-1} \quad [3]$$

- (f) Iron(II) chloride,  $\text{FeCl}_2$ , is oxidised by chlorine to form iron(III) chloride,  $\text{FeCl}_3$ , under standard conditions.



**Table 3.2**

species	$S^\ominus/\text{JK}^{-1}\text{mol}^{-1}$
$\text{Cl}_2(\text{g})$	223
$\text{FeCl}_2(\text{s})$	120
$\text{FeCl}_3(\text{s})$	142

- (i) Use Table 3.2 and other data to calculate the Gibbs free energy change,  $\Delta G^\ominus$ , for this reaction.

Show your working.

$$\Delta G^\ominus = \dots\dots\dots \text{kJ mol}^{-1} \quad [3]$$

- (ii) Predict whether this reaction becomes more or less feasible at a higher temperature.

Explain your answer.

The reaction becomes ..... feasible.

explanation .....

.....

[1]

[Total: 18]

- 4 The structure of the polydentate ligand, EDTA<sup>4-</sup>, is shown in Fig. 4.1.

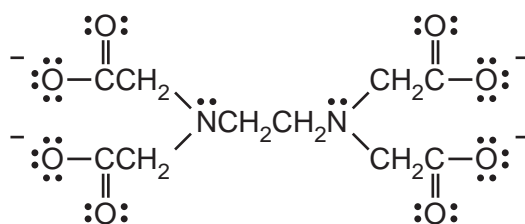


Fig. 4.1

The stability constants, at 298 K, of five octahedral complexes are given in Table 4.1.

Table 4.1

complex	$K_{\text{stab}}$
[Cu(EDTA)] <sup>2-</sup>	$6.31 \times 10^{19}$
[Cr(EDTA)] <sup>2-</sup>	$1.00 \times 10^{13}$
[Cr(EDTA)] <sup>-</sup>	$1.00 \times 10^{24}$
[Fe(EDTA)] <sup>2-</sup>	$2.00 \times 10^{14}$
[Fe(EDTA)] <sup>-</sup>	$1.26 \times 10^{25}$

- (a) Define stability constant.

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

- (b) Calculate the oxidation states of Cu in [Cu(EDTA)]<sup>2-</sup> and Cr in [Cr(EDTA)]<sup>-</sup>.

Cu .....

Cr .....

[1]

- (c) Deduce the number of lone pairs donated by each EDTA<sup>4-</sup> ligand in a single [Fe(EDTA)]<sup>2-</sup> complex ion.

..... [1]

- (d) Identify the most stable complex in Table 4.1. Explain your choice.

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

## 13

- (e) In a solution at equilibrium at 298 K,  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} = 3.00 \times 10^{-10} \text{ mol dm}^{-3}$  and  $[\text{EDTA}^{4-}] = 5.00 \times 10^{-12} \text{ mol dm}^{-3}$ .

Use the expression for  $K_{\text{stab}}$  to calculate the concentration of  $[\text{Cu}(\text{EDTA})]^{2-}$  in this solution.

Show your working.

$$[\text{Cu}(\text{EDTA})]^{2-} = \dots\dots\dots \text{ mol dm}^{-3} \quad [2]$$

- (f) A solution of  $[\text{Cu}(\text{EDTA})]^{2-}$  ions is pale blue while a solution of  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  ions is deep blue.

Explain this difference in colour.

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

[Total: 8]

- 5 Some of the ionic compounds of Group 2 elements undergo thermal decomposition.

Thermal decomposition of solid anhydrous magnesium ethanedioate,  $\text{MgC}_2\text{O}_4$ , occurs above  $650^\circ\text{C}$ . The products are magnesium oxide and a mixture of two different gases, one of which gives a white precipitate with saturated calcium hydroxide solution.

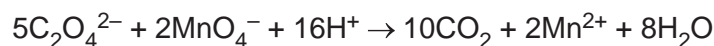
- (a) Complete the equation for the thermal decomposition of  $\text{MgC}_2\text{O}_4$ .



- (b) Suggest which of  $\text{MgC}_2\text{O}_4$  or  $\text{CaC}_2\text{O}_4$  undergoes thermal decomposition at a **lower** temperature. Explain your answer.

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

- (c) The ethanedioate ion is oxidised by acidified  $\text{KMnO}_4$ .



An experiment is performed to find the solubility of  $\text{MgC}_2\text{O}_4$  in water.

A  $40.0\text{cm}^3$  sample of saturated aqueous  $\text{MgC}_2\text{O}_4$  requires  $27.05\text{cm}^3$  of  $0.00200\text{mol dm}^{-3}$  acidified  $\text{KMnO}_4$  to oxidise all the  $\text{C}_2\text{O}_4^{2-}$  ions.

Calculate the solubility, in  $\text{mol dm}^{-3}$ , of  $\text{MgC}_2\text{O}_4$  in water. Show your working.

solubility = .....  $\text{mol dm}^{-3}$  [3]

[Total: 6]

6 (a) Phosphine,  $\text{:PH}_3$ , and carbon monoxide,  $\text{:CO}$ , are monodentate ligands found in some transition element complexes.

(i) Define monodentate ligand.

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

(ii) Define transition element complex.

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

(iii) Explain why transition elements form complexes.

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

(b) The formulae of six complexes are given in Table 6.1.

The abbreviation *en* is used for 1,2-diaminoethane.

The abbreviation *dien* is used for the tridentate ligand  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$ .

The *dien* ligand forms three bonds to the gold ion in  $[\text{Au}(\textit{dien})(\text{H}_2\text{O})_2\text{Cl}]^{2+}$  and  $\text{Au}(\textit{dien})\text{Cl}_3$ .

These three bonds all lie in the same plane.

The CO ligand coordinates through the carbon atom in  $[\text{Rh}(\text{CO})_2\text{Cl}_2]^+$ .

**Table 6.1**

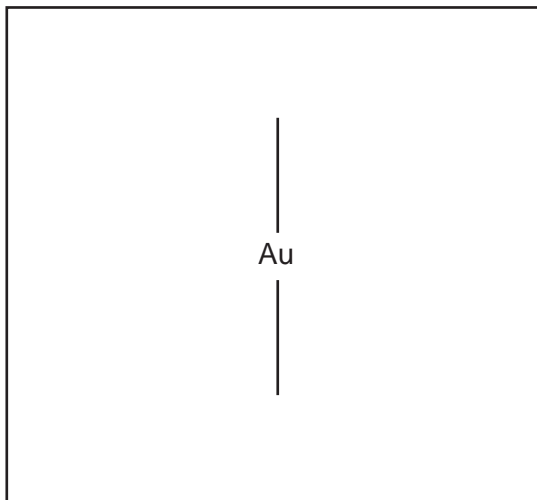
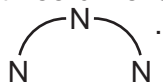
formula	isomerism shown	geometry
$[\text{Rh}(\textit{en})_2\text{Cl}_2]^+$	yes	
$[\text{Rh}(\text{CO})_2\text{Cl}_2]^+$	yes	
$[\text{Au}(\textit{dien})(\text{H}_2\text{O})_2\text{Cl}]^{2+}$		
$\text{Au}(\textit{dien})\text{Cl}_3$	no	octahedral
$\text{Ni}(\text{PH}_3)_2\text{Cl}_2$	no	
$[\text{Ni}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}$	yes	

(i) Complete Table 6.1 to state the geometry of the first three complexes. Each complex is either square planar, tetrahedral or octahedral. [1]

(ii) Use complexes  $[\text{Au}(\textit{dien})(\text{H}_2\text{O})_2\text{Cl}]^{2+}$  and  $\text{Au}(\textit{dien})\text{Cl}_3$  to write an equation showing ligand exchange.

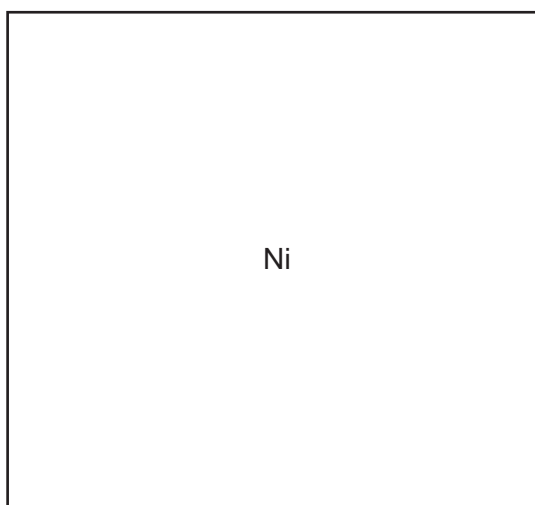
..... [1]

- (iii) Draw the three-dimensional structure of  $\text{Au}(\text{dien})\text{Cl}_3$  in the box. The *dien* ligand can be drawn as



[1]

- (iv) Draw the three-dimensional structure of  $\text{Ni}(\text{PH}_3)_2\text{Cl}_2$  in the box.



[1]

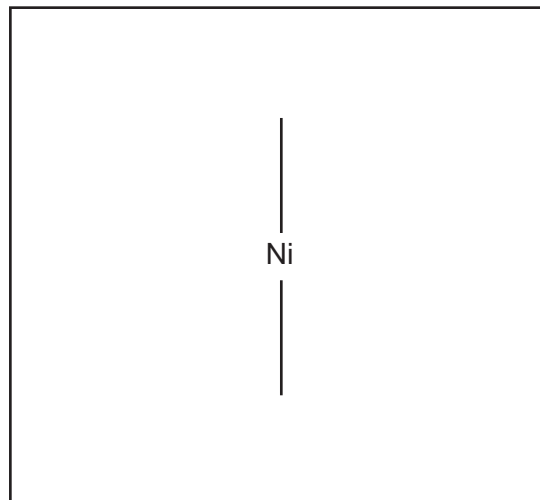
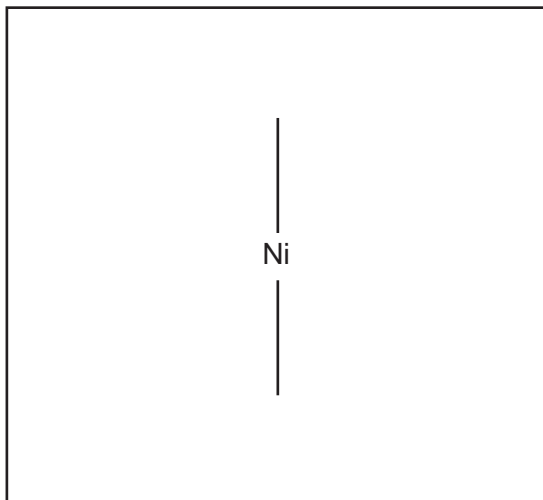
- (v) One of the complexes,  $[\text{Rh}(\text{en})_2\text{Cl}_2]^+$  or  $[\text{Rh}(\text{CO})_2\text{Cl}_2]^+$ , can exist in three isomeric forms. Identify this complex and the types of isomerism shown.

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



17

(vi) Draw the three-dimensional structures of the two isomers of  $[\text{Ni}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}$  in the boxes and identify the type of isomerism shown.



type of isomerism shown .....

[2]

[Total: 10]

7 Benzene can be used to make benzoic acid in the two-step process shown in Fig. 7.1.

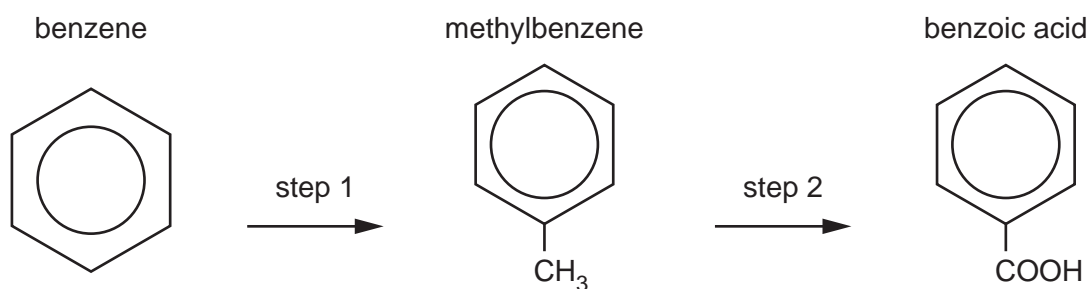


Fig. 7.1

(a) Give the reagents and conditions for step 1 and step 2.


step 1 .....

step 2 .....

[2]

(b) Methylbenzene and benzoic acid each have five different peaks in the carbon ( $^{13}\text{C}$ ) NMR spectrum.

Table 7.1

hybridisation of the carbon atom	environment of carbon atom	example	chemical shift range /ppm
$\text{sp}^3$	alkyl	$\text{CH}_3-$ , $-\text{CH}_2-$ , $-\text{CH}<$ , $>\text{C}<$	0–50
$\text{sp}^3$	next to alkene/arene	$-\text{C}-\text{C}=\text{C}$ , $-\text{C}-\text{Ar}$	25–50
$\text{sp}^3$	next to carbonyl/carboxyl	$\text{C}-\text{COR}$ , $\text{C}-\text{O}_2\text{R}$	30–65
$\text{sp}^3$	next to halogen	$\text{C}-\text{X}$	30–60
$\text{sp}^3$	next to oxygen	$\text{C}-\text{O}$	50–70
$\text{sp}^2$	alkene or arene	$>\text{C}=\text{C}<$ , 	110–160
$\text{sp}^2$	carboxyl	$\text{R}-\text{COOH}$ , $\text{R}-\text{COOR}$	160–185
$\text{sp}^2$	carbonyl	$\text{R}-\text{CHO}$ , $\text{R}-\text{CO}-\text{R}$	190–220
$\text{sp}$	nitrile	$\text{R}-\text{C}\equiv\text{N}$	100–125

Use Table 7.1 to complete the two sentences to suggest descriptions of these two spectra.

The carbon ( $^{13}\text{C}$ ) NMR spectrum of methylbenzene:

- has ..... peak(s) in the chemical shift range of ..... and
- has ..... peak(s) in the chemical shift range of .....

The carbon ( $^{13}\text{C}$ ) NMR spectrum of benzoic acid:

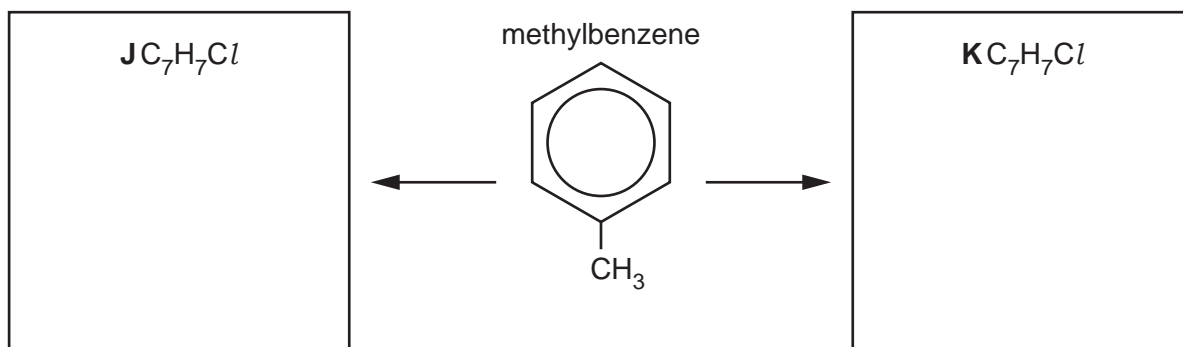
- has ..... peak(s) in the chemical shift range of ..... and
- has ..... peak(s) in the chemical shift range of .....

[2]

(c) (i) When treated with  $\text{Cl}_2$  under suitable conditions, methylbenzene forms compound **J**.

When treated with  $\text{Cl}_2$  under **different** conditions with **different** reagents, methylbenzene forms compound **K**.

Suggest and draw structures of compounds **J** and **K** in the boxes. The molecular formula of each compound is given.



State the reagents and conditions required to form each product.

to form compound **J** .....

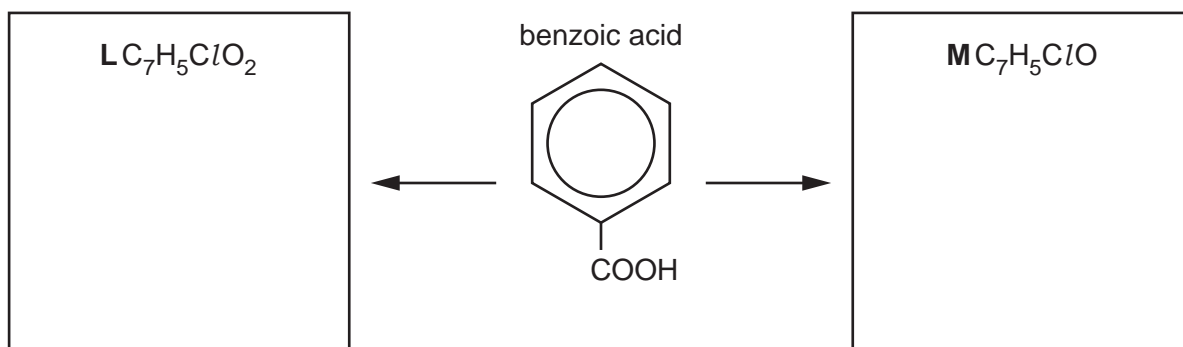
to form compound **K** .....

[4]

(ii) When treated with a chlorine-containing reagent under suitable conditions, benzoic acid forms compound **L**.

When treated with a **different** chlorine-containing reagent under **different** conditions, benzoic acid forms compound **M**.

Suggest and draw structures of compounds **L** and **M** in the boxes. The molecular formula of each product is given.



State the reagents and conditions to form compound **M** from benzoic acid.

..... [3]

8 Lactic acid,  $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ , is the only monomer needed to form the polymer polylactic acid, PLA.

- (a) (i) Draw a short length of the PLA polymer chain, including a minimum of two monomer residues. The methyl groups may be written as  $-\text{CH}_3$  but all other bonds should be shown fully displayed.

Label one repeat unit of polylactic acid on your diagram.

[2]

- (ii) Give the name of the type of polymerisation involved in the formation of PLA and the name of the functional group that forms between the monomers.

type of polymerisation .....

functional group .....

[1]

- (iii) Predict whether PLA is readily biodegradable. Explain your answer.

.....

..... [1]

- (b) The proton ( $^1\text{H}$ ) NMR spectrum of  $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$  in  $\text{CDCl}_3$  is shown in Fig. 8.1. The proton NMR chemical shift ranges are shown in Table 8.1.

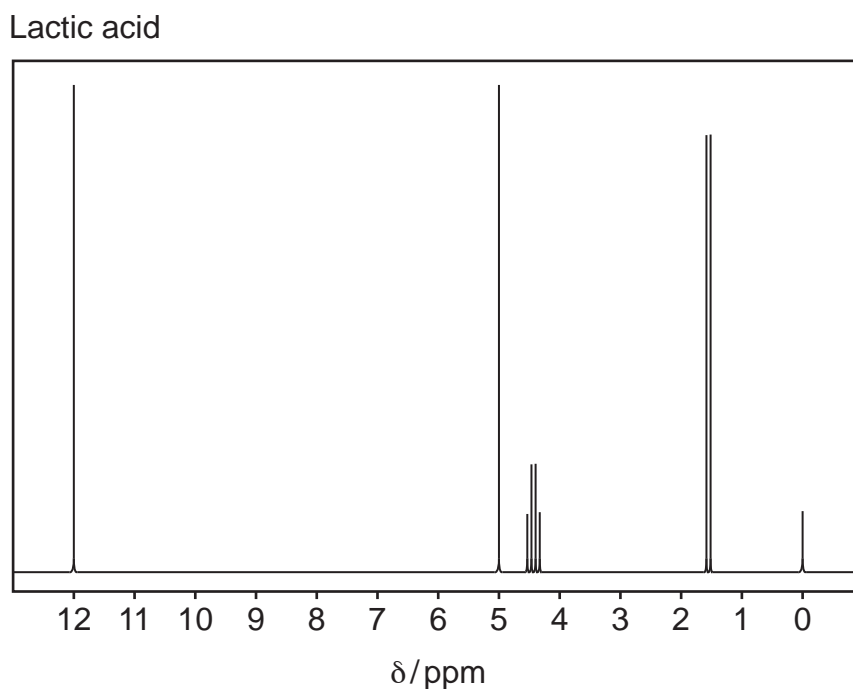


Fig. 8.1

Table 8.1

environment of proton	example	chemical shift range $\delta$ /ppm
alkane	$-\text{CH}_3$ , $-\text{CH}_2-$ , $>\text{CH}-$	0.9–1.7
alkyl next to C=O	$\text{CH}_3-\text{C}=\text{O}$ , $-\text{CH}_2-\text{C}=\text{O}$ , $>\text{CH}-\text{C}=\text{O}$	2.2–3.0
alkyl next to aromatic ring	$\text{CH}_3-\text{Ar}$ , $-\text{CH}_2-\text{Ar}$ , $>\text{CH}-\text{Ar}$	2.3–3.0
alkyl next to electronegative atom	$\text{CH}_3-\text{O}$ , $-\text{CH}_2-\text{O}$ , $-\text{CH}_2-\text{Cl}$	3.2–4.0
attached to alkene	$=\text{CHR}$	4.5–6.0
attached to aromatic ring	$\text{H}-\text{Ar}$	6.0–9.0
aldehyde	$\text{HCOR}$	9.3–10.5
alcohol	$\text{ROH}$	0.5–6.0
phenol	$\text{Ar}-\text{OH}$	4.5–7.0
carboxylic acid	$\text{RCOOH}$	9.0–13.0

(i) Use Fig. 8.1 and Table 8.1 to complete Table 8.2.

Table 8.2

proton environment	chemical shift ( $\delta$ )	name of splitting pattern
$-\text{COOH}$		
$\text{>CH}$		
$-\text{OH}$		
$-\text{CH}_3$		

[3]

(ii) Name the substance responsible for the peak at  $\delta = 0.0$ .

..... [1]

(iii) Explain why  $\text{CDCl}_3$  is a better solvent than  $\text{CHCl}_3$  for use in proton NMR.

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

(c) An impure sample of  $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$  contains pentan-3-one as the only contaminant. The mixture is analysed using gas/liquid chromatography. The pentan-3-one is found to have a longer retention time than the lactic acid.

(i) Explain what is meant by retention time.

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

(ii) Suggest suitable substances, or types of substances, that could be used as the mobile and stationary phases.

mobile phase .....

stationary phase ..... [1]

(iii) Describe how the percentage composition of the mixture can be determined from the gas/liquid chromatogram.

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

[Total: 12]

- 9 (a) State the reactants and conditions for two different types of reactions that both produce diethylamine,  $\text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_3$ .

reaction one .....

.....

reaction two .....

.....

[4]

- (b) Describe the relative basicities of diethylamine, phenylamine and ammonia in aqueous solution.

Explain your answer in terms of structure.

.....

least basic

most basic

explanation .....

.....

.....

.....

.....

[3]

- (c) Phenylamine reacts with  $\text{HNO}_2(\text{aq})$  at  $4^\circ\text{C}$  to form compound **P**. Compound **P** reacts with phenol under alkaline conditions at  $4^\circ\text{C}$ . The product of this reaction is acidified, forming azo compound **Q**.

Draw the structure of compound **Q**.

Circle the azo group on your structure.

State one use of an azo compound such as **Q**.

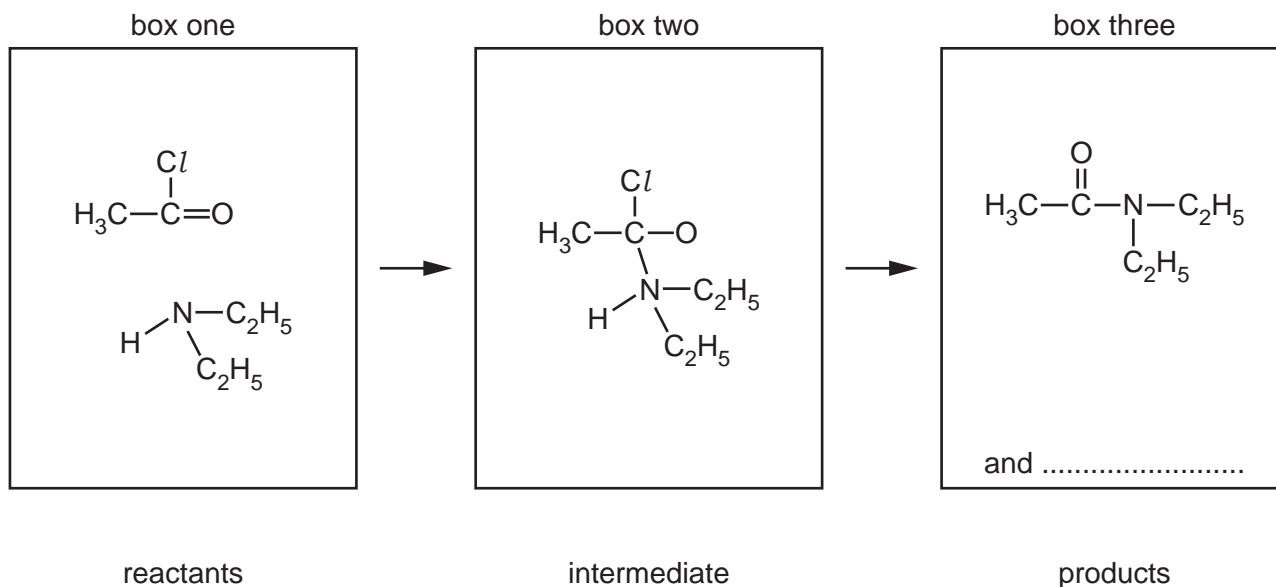
compound **Q**:

An azo compound can be used .....

[2]

- (d)  $\text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_3$  reacts with ethanoyl chloride,  $\text{CH}_3\text{COCl}$ , to give the amide N,N-diethylethanamide,  $\text{CH}_3\text{CON}(\text{C}_2\text{H}_5)_2$ .

An incomplete description of the mechanism of this reaction is shown in Fig. 9.1.



**Fig. 9.1**

- (i) Complete the mechanism in Fig. 9.1. You should include:

- all relevant dipoles ( $\delta+$  and  $\delta-$ ) and full electric charges (+ and  $-$ ) on the species in box one and in box two
- all relevant lone pairs on the species in box one and in box two
- all relevant curly arrows to show the movement of electron pairs in box one and in box two
- the formula of the second product in box three.

[4]

- (ii) Name this mechanism.

..... [1]

[Total: 14]





**BLANK PAGE**

**Important values, constants and standards**

molar gas constant	$R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$
Faraday constant	$F = 9.65 \times 10^4 \text{ C mol}^{-1}$
Avogadro constant	$L = 6.022 \times 10^{23} \text{ mol}^{-1}$
electronic charge	$e = -1.60 \times 10^{-19} \text{ C}$
molar volume of gas	$V_m = 22.4 \text{ dm}^3 \text{ mol}^{-1}$ at s.t.p. (101 kPa and 273 K) $V_m = 24.0 \text{ dm}^3 \text{ mol}^{-1}$ at room conditions
ionic product of water	$K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ (at 298 K (25 °C))
specific heat capacity of water	$c = 4.18 \text{ kJ kg}^{-1} \text{ K}^{-1}$ (4.18 $\text{J g}^{-1} \text{ K}^{-1}$ )

The Periodic Table of Elements

		Group																																																																															
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																																																																
		<table border="1"> <tr> <td style="text-align: center;">1</td> <td style="text-align: center;">H hydrogen 1.0</td> </tr> </table>																1	H hydrogen 1.0																																																														
1	H hydrogen 1.0																																																																																
		<table border="1"> <tr> <td style="text-align: center;">atomic number</td> <td style="text-align: center;">atomic symbol</td> <td style="text-align: center;">name</td> <td style="text-align: center;">relative atomic mass</td> </tr> </table>																atomic number	atomic symbol	name	relative atomic mass																																																												
atomic number	atomic symbol	name	relative atomic mass																																																																														
3	4	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89-103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
Li lithium 6.9	Be beryllium 9.0	Na sodium 23.0	Mg magnesium 24.3	Al aluminium 27.0	Si silicon 28.1	P phosphorus 31.0	S sulfur 32.1	Cl chlorine 35.5	Ar argon 39.9	K potassium 39.1	Ca calcium 40.1	Sc scandium 45.0	Ti titanium 47.9	V vanadium 50.9	Cr chromium 52.0	Mn manganese 54.9	Fe iron 55.8	Co cobalt 58.9	Ni nickel 58.7	Cu copper 63.5	Zn zinc 65.4	Ga gallium 69.7	Ge germanium 72.6	As arsenic 74.9	Se selenium 79.0	Br bromine 79.9	Kr krypton 83.8	Rb rubidium 85.5	Sr strontium 87.6	Y yttrium 88.9	Zr zirconium 91.2	Nb niobium 92.9	Mo molybdenum 95.9	Tc technetium —	Ru ruthenium 101.1	Rh rhodium 102.9	Pd palladium 106.4	Ag silver 107.9	Cd cadmium 112.4	In indium 114.8	Sn tin 118.7	Sb antimony 121.8	Te tellurium 127.6	I iodine 126.9	Xe xenon 131.3	Cs caesium 132.9	Ba barium 137.3	lanthanoids	Hf hafnium 178.5	Ta tantalum 180.9	W tungsten 183.8	Os osmium 190.2	Ir iridium 192.2	Pt platinum 195.1	Au gold 197.0	Hg mercury 200.6	Tl thallium 204.4	Pb lead 207.2	Bi bismuth 209.0	Po polonium —	At astatine —	Rn radon —	Fr francium —	Ra radium —	actinoids	Rf rutherfordium —	Db dubnium —	Sg seaborgium —	Bh bohrium —	Hs hassium —	Mt meitnerium —	Ds darmstadtium —	Rg roentgenium —	Cn copernicium —	Nh nihonium —	Fl flerovium —	Mc moscovium —	Lv livermorium —	Ts tennessine —	Og oganeson —	

lanthanoids

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La lanthanum 138.9	Ce cerium 140.1	Pr praseodymium 140.9	Nd neodymium 144.4	Pm promethium —	Sm samarium 150.4	Eu europium 152.0	Gd gadolinium 157.3	Tb terbium 158.9	Dy dysprosium 162.5	Ho holmium 164.9	Er erbium 167.3	Tm thulium 168.9	Yb ytterbium 173.1	Lu lutetium 175.0
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac actinium —	Th thorium 232.0	Pa protactinium 231.0	U uranium 238.0	Np neptunium —	Pu plutonium —	Am americium —	Cm curium —	Bk berkelium —	Cf californium —	Es einsteinium —	Fm fermium —	Md mendelevium —	No nobelium —	Lr lawrencium —

actinoids