



# Cambridge International AS & A Level

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**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

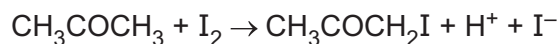
- Answer **all** questions.
- Use a black or dark blue pen. You may use an HB pencil for any diagrams or graphs.
- Write your name, centre number and candidate number in the boxes at the top of the page.
- Write your answer to each question in the space provided.
- Do **not** use an erasable pen or correction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

- 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.

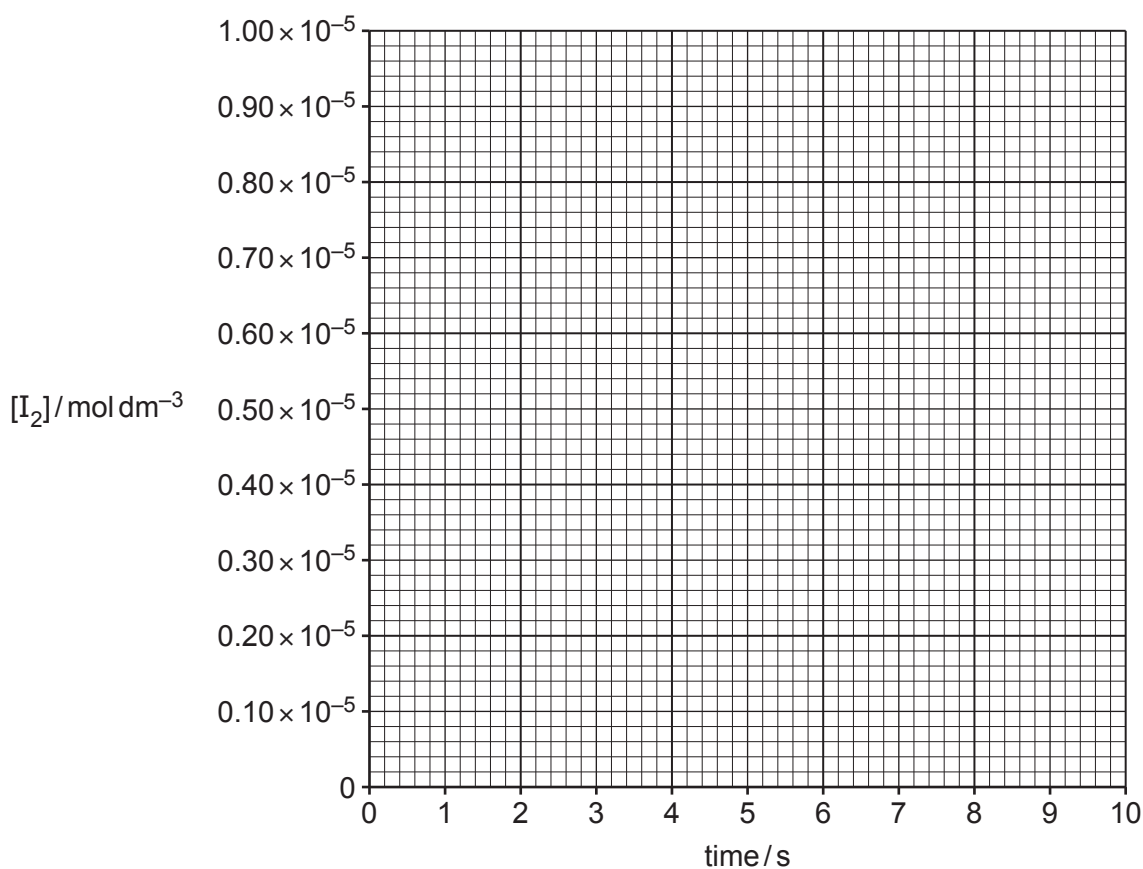
**Table 1.1**

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]

- (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]

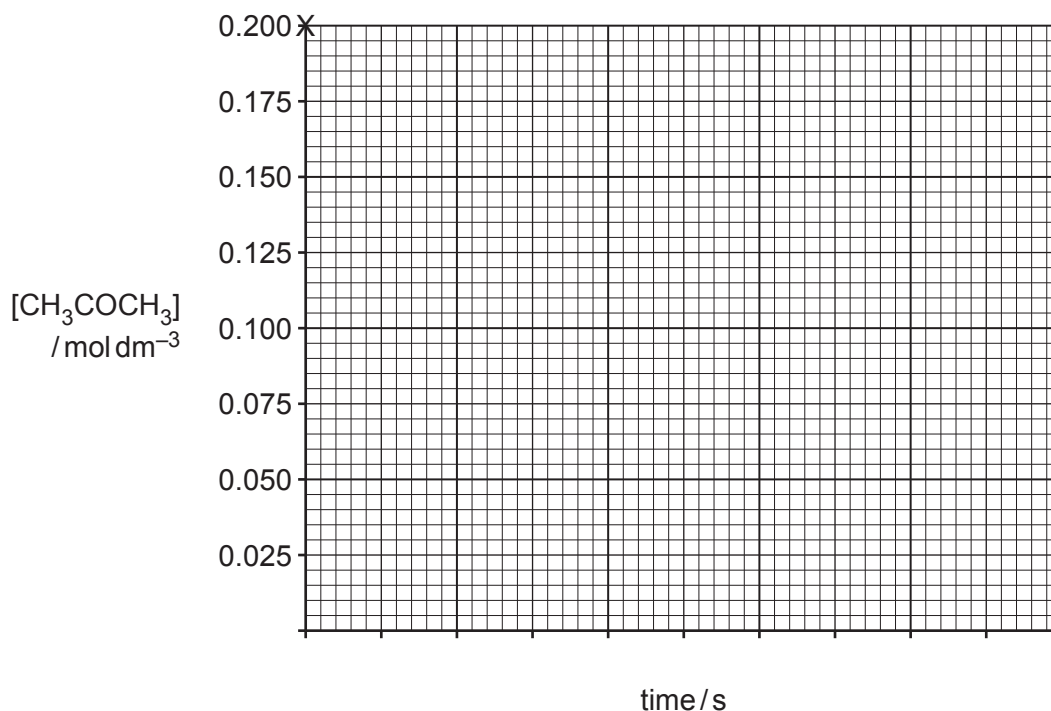
- (d) The experiment is repeated using an excess of  $\text{H}^+(\text{aq})$ . The new rate equation is shown.

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

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

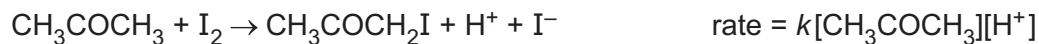
$t_{\frac{1}{2}} = \dots\dots\dots \text{ s}$  [1]

- (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  $0.0250 \text{ mol dm}^{-3}$ .

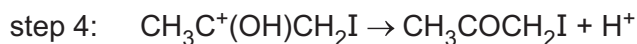
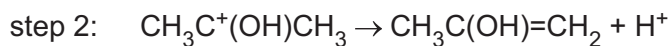
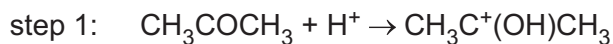


[1]

(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]



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]

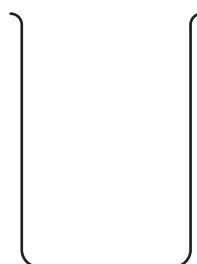
[Total: 11]

- 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.

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

- (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.

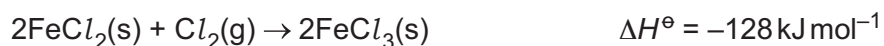
A current of 0.640 A is passed for 17.0 minutes. The mass of the cathode increases by 0.185 g.

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.

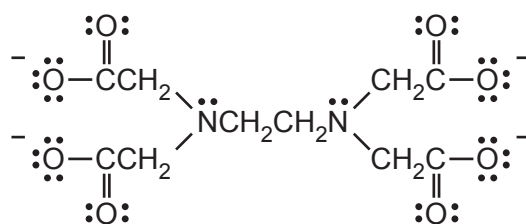


Fig. 4.1

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

Table 4.1

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

- (a) Define stability constant.

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

- (b) Calculate the oxidation states of Cu in  $[\text{Cu}(\text{EDTA})]^{2-}$  and Cr in  $[\text{Cr}(\text{EDTA})]^{-}$ .

Cu .....

Cr .....

[1]

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

..... [1]

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

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

- (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.

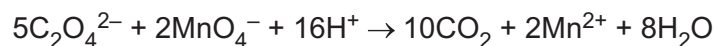
- (a) Complete the equation for the thermal decomposition of  $\text{MgC}_2\text{O}_4$ .



- (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**

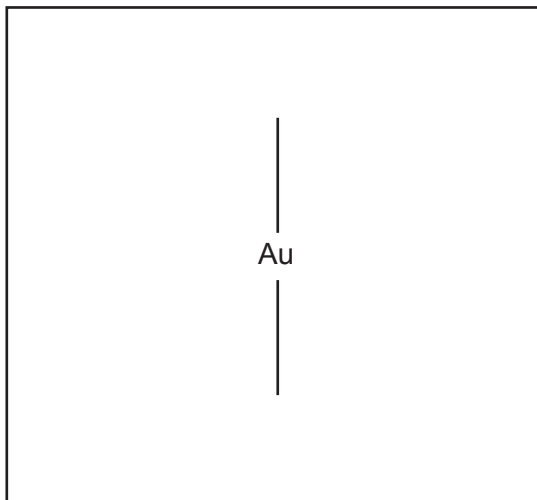
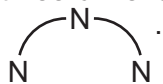
formula	isomerism shown	geometry
$[\text{Rh}(\textit{en})_2\text{Cl}_2]^+$	yes	
$[\text{Rh}(\text{CO})_2\text{Cl}_2]^+$	yes	
$[\text{Au}(\textit{dien})(\text{H}_2\text{O})_2\text{Cl}]^{2+}$		
$\text{Au}(\textit{dien})\text{Cl}_3$	no	octahedral
$\text{Ni}(\text{PH}_3)_2\text{Cl}_2$	no	
$[\text{Ni}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}$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

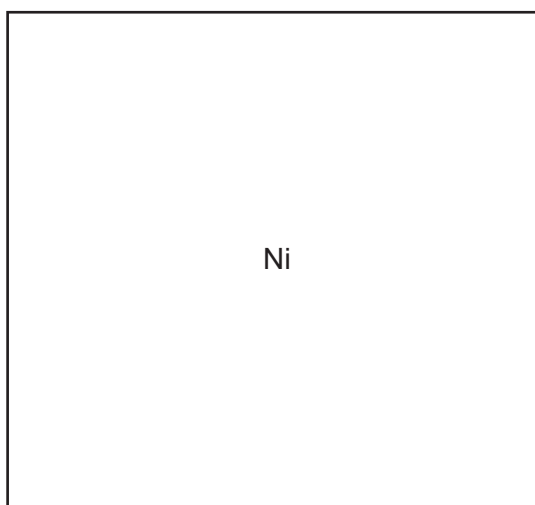
..... [1]

- (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.



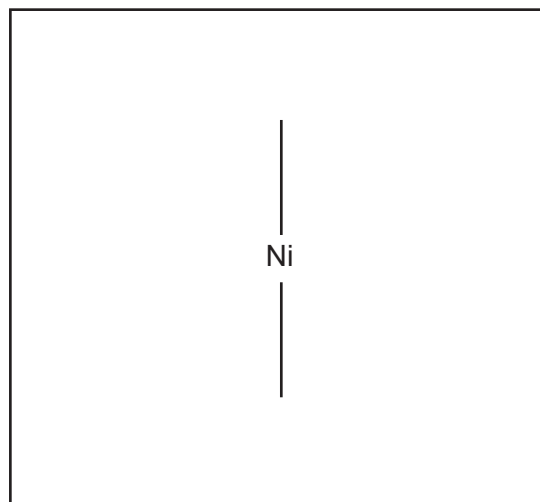
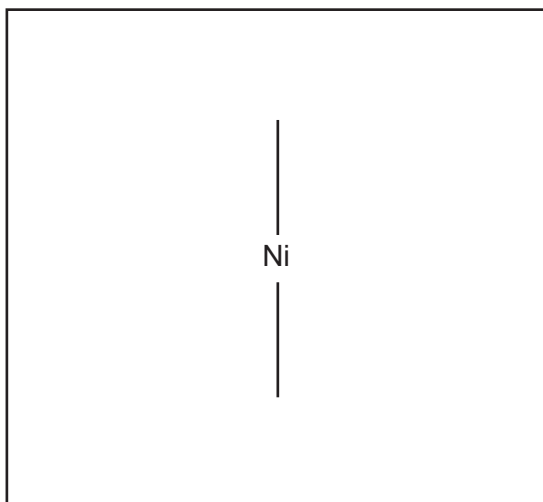
[1]

- (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]



- (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.

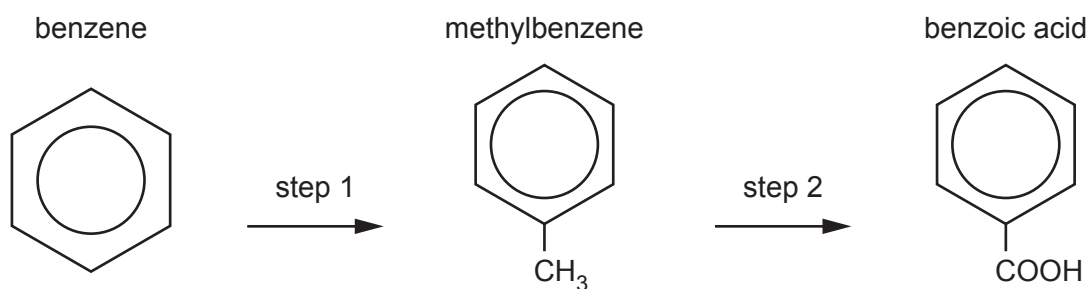


Fig. 7.1

(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:

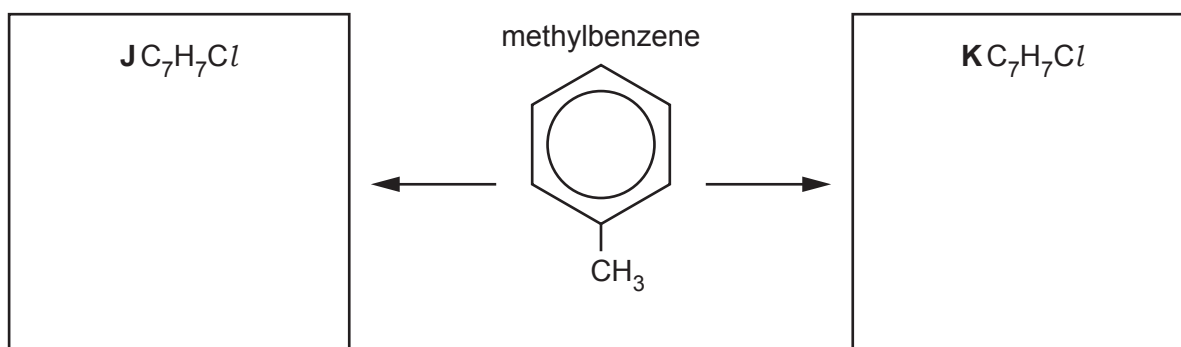
- has ..... peak(s) in the chemical shift range of ..... and
- has ..... peak(s) in the chemical shift range of .....

[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** .....

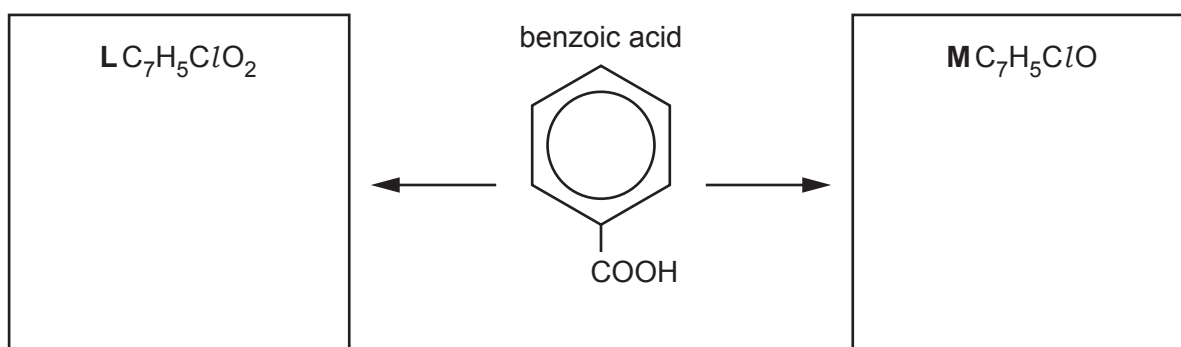
to form compound **K** .....

[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.

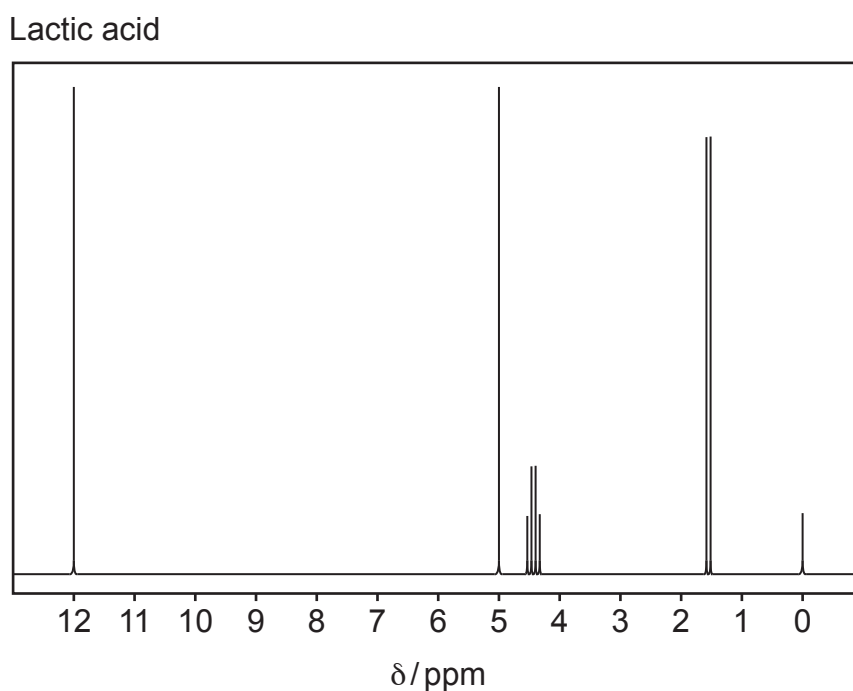


Fig. 8.1

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**.

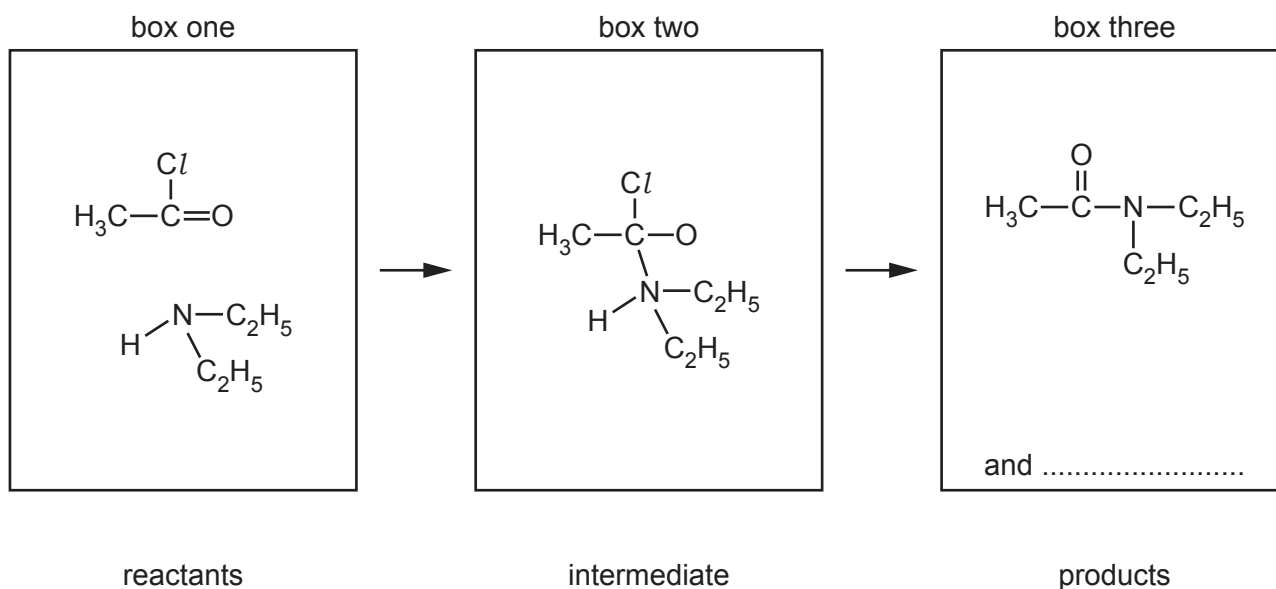
compound **Q**:

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]







**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
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">1 H hydrogen 1.0</div> <div style="border: 1px solid black; padding: 5px;">2 He helium 4.0</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">3 Li lithium 6.9</div> <div style="border: 1px solid black; padding: 5px;">4 Be beryllium 9.0</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">5 B boron 10.8</div> <div style="border: 1px solid black; padding: 5px;">6 C carbon 12.0</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">7 N nitrogen 14.0</div> <div style="border: 1px solid black; padding: 5px;">8 O oxygen 16.0</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">9 F fluorine 19.0</div> <div style="border: 1px solid black; padding: 5px;">10 Ne neon 20.2</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">11 Na sodium 23.0</div> <div style="border: 1px solid black; padding: 5px;">12 Mg magnesium 24.3</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">13 Al aluminium 27.0</div> <div style="border: 1px solid black; padding: 5px;">14 Si silicon 28.1</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">15 P phosphorus 31.0</div> <div style="border: 1px solid black; padding: 5px;">16 S sulfur 32.1</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">17 Cl chlorine 35.5</div> <div style="border: 1px solid black; padding: 5px;">18 Ar argon 39.9</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">19 K potassium 39.1</div> <div style="border: 1px solid black; padding: 5px;">20 Ca calcium 40.1</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">21 Sc scandium 45.0</div> <div style="border: 1px solid black; padding: 5px;">22 Ti titanium 47.9</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">23 V vanadium 50.9</div> <div style="border: 1px solid black; padding: 5px;">24 Cr chromium 52.0</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">25 Mn manganese 54.9</div> <div style="border: 1px solid black; padding: 5px;">26 Fe iron 55.8</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">27 Co cobalt 58.9</div> <div style="border: 1px solid black; padding: 5px;">28 Ni nickel 58.7</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">29 Cu copper 63.5</div> <div style="border: 1px solid black; padding: 5px;">30 Zn zinc 65.4</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">31 Ga gallium 69.7</div> <div style="border: 1px solid black; padding: 5px;">32 Ge germanium 72.6</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">33 As arsenic 74.9</div> <div style="border: 1px solid black; padding: 5px;">34 Se selenium 79.0</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">35 Br bromine 83.8</div> <div style="border: 1px solid black; padding: 5px;">36 Kr krypton 83.8</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">37 Rb rubidium 85.5</div> <div style="border: 1px solid black; padding: 5px;">38 Sr strontium 87.6</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">39 Y yttrium 88.9</div> <div style="border: 1px solid black; padding: 5px;">40 Zr zirconium 91.2</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">41 Nb niobium 92.9</div> <div style="border: 1px solid black; padding: 5px;">42 Mo molybdenum 95.9</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">43 Tc technetium —</div> <div style="border: 1px solid black; padding: 5px;">44 Ru ruthenium 101.1</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">45 Rh rhodium 102.9</div> <div style="border: 1px solid black; padding: 5px;">46 Pd palladium 106.4</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">47 Ag silver 107.9</div> <div style="border: 1px solid black; padding: 5px;">48 Cd cadmium 112.4</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">49 In indium 114.8</div> <div style="border: 1px solid black; padding: 5px;">50 Sn tin 118.7</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">51 Sb antimony 121.8</div> <div style="border: 1px solid black; padding: 5px;">52 Te tellurium 127.6</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">53 I iodine 126.9</div> <div style="border: 1px solid black; padding: 5px;">54 Xe xenon 131.3</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">55 Cs caesium 132.9</div> <div style="border: 1px solid black; padding: 5px;">56 Ba barium 137.3</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">57–71 lanthanoids</div> <div style="border: 1px solid black; padding: 5px;">72 Hf hafnium 178.5</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">73 Ta tantalum 180.9</div> <div style="border: 1px solid black; padding: 5px;">74 W tungsten 183.8</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">75 Re rhenium 186.2</div> <div style="border: 1px solid black; padding: 5px;">76 Os osmium 190.2</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">77 Ir iridium 192.2</div> <div style="border: 1px solid black; padding: 5px;">78 Pt platinum 195.1</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">79 Au gold 197.0</div> <div style="border: 1px solid black; padding: 5px;">80 Hg mercury 200.6</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">81 Tl thallium 204.4</div> <div style="border: 1px solid black; padding: 5px;">82 Pb lead 207.2</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">83 Bi bismuth 209.0</div> <div style="border: 1px solid black; padding: 5px;">84 Po polonium —</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">85 At astatine —</div> <div style="border: 1px solid black; padding: 5px;">86 Rn radon —</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">87 Fr francium —</div> <div style="border: 1px solid black; padding: 5px;">88 Ra radium —</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">89–103 actinoids</div> <div style="border: 1px solid black; padding: 5px;">104 Rf rutherfordium —</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">105 Db dubnium —</div> <div style="border: 1px solid black; padding: 5px;">106 Sg seaborgium —</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">107 Bh bohrium —</div> <div style="border: 1px solid black; padding: 5px;">108 Hs hassium —</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">109 Mt meitnerium —</div> <div style="border: 1px solid black; padding: 5px;">110 Ds darmstadtium —</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">111 Rg roentgenium —</div> <div style="border: 1px solid black; padding: 5px;">112 Cn copernicium —</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">113 Nh nihonium —</div> <div style="border: 1px solid black; padding: 5px;">114 Fl flerovium —</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">115 Mc moscovium —</div> <div style="border: 1px solid black; padding: 5px;">116 Lv livermorium —</div> </div>															
		<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="border: 1px solid black; padding: 5px;">117 Ts tennessine —</div> <div style="border: 1px solid black; padding: 5px;">118 Og oganeson —</div> </div>															

lanthanoids

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

actinoids