Cambridge Assessment
International Education

Cambridge International AS & A Level

CANDIDATE NAME			
CENTRE NUMBER		CANDIDATE NUMBER	

5961197939

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **October/November 2024**

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 **24** pages. Any blank pages are indicated.

DC (DE/JG) 336276/3

1 **(a)** The equation for reaction 1 is shown.

reaction 1 $X \rightarrow 2Y$

Reaction 1 is first order with respect to the concentration of X. The half-life of the reaction, $t_{\frac{1}{2}}$, is 900 s at 20 °C.

(i) A solution of X with a concentration of 0.180 mol dm^{-3} is prepared at 20 °C. Calculate the average rate of reaction 1 over the first 1800 s.

average rate of reaction 1 = ... [2]

(ii) Complete the rate equation for reaction 1.

rate = ... [1]

(iii) Show that the rate constant, k, is $7.70 \times 10^{-4}\,s^{-1}$ at 20 °C.

[1]

(iv) Calculate the initial rate of reaction 1 when the concentration of X is 0.150 mol dm^{-3}.

Include units.

rate = ... units .... [2]

(b) Catalysts may be homogeneous or heterogeneous.

(i) Platinum is a transition element. Explain why transition elements behave as catalysts.

....

....

.... [1]

(ii) Name the metal catalyst in the Haber process and explain why it is a **heterogeneous** catalyst.

metal ....

.... [1]

(iii) Platinum acts as a heterogeneous catalyst in the removal of nitrogen dioxide, NO_2, from the exhaust gases of car engines.

Describe the mode of action of a platinum catalyst in this process.

....

....

....

.... [2]

(iv) NO_2 acts as a homogeneous catalyst in the oxidation of atmospheric sulfur dioxide, SO_2.

Write equations for the **two** reactions that occur.

equation 1 ....

equation 2 ....
[1]

(c) SO_2 dissolves in water, forming H_2SO_3.

H_2SO_3 can be oxidised under acidic conditions.

The relevant electrode reaction and its $E^\ominus$ value are shown.

$$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons H_2SO_3 + H_2O \qquad E^\ominus = +0.17\,V$$

Four more half-equations for reactions occurring under acidic conditions, and their $E^\ominus$ values, are shown.

$$H_3BO_3 + 3H^+ + 3e^- \rightleftharpoons B + 3H_2O \qquad E^\ominus = -0.73\,V$$
$$BiO^+ + 2H^+ + 3e^- \rightleftharpoons Bi + H_2O \qquad E^\ominus = +0.28\,V$$
$$S + 2H^+ + 2e^- \rightleftharpoons H_2S \qquad E^\ominus = +0.14\,V$$
$$Sb + 3H^+ + 3e^- \rightleftharpoons SbH_3 \qquad E^\ominus = -0.51\,V$$

Select the oxidising agent that could oxidise H_2SO_3 to SO_4^{2-} ions under acidic conditions.

Write an equation, and give the $E^\ominus_{cell}$ value, for the reaction that occurs.

oxidising agent ....

equation ....

$E^\ominus_{cell}$ = ... V

[3]

[Total: 14]

2 **(a)** Predict and explain the variation in enthalpy change of hydration for the ions Na^+, Mg^{2+} and Al^{3+}.

....

....

....

....

.... [3]

(b) Fig. 2.1 shows an incomplete energy cycle.

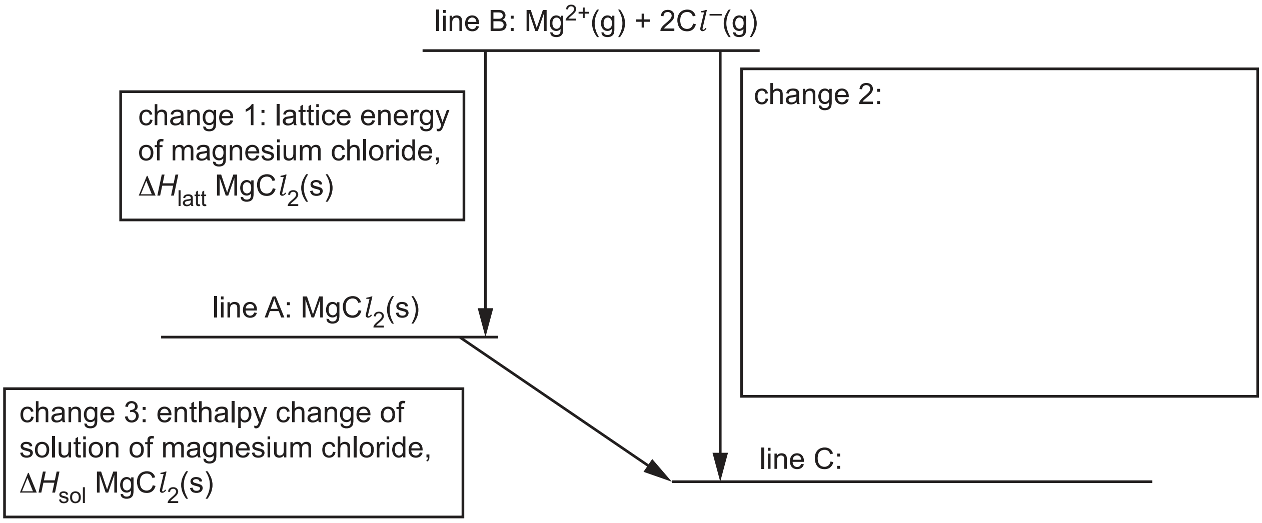

Fig. 2.1

(i) Complete line C on Fig. 2.1. Include state symbols. [1]

(ii) Use **both** words **and** symbols to identify change 2 on Fig. 2.1.

Use changes 1 and 3 as examples of how this should be done.

[2]

(iii) Calculate a value for the lattice energy of magnesium chloride, ΔH_{latt} $MgCl_2(s)$, by selecting and using appropriate data from Table 2.1.

Table 2.1

energy change	value / kJ mol^{-1}
enthalpy change of solution of magnesium chloride	–155
enthalpy change of formation of magnesium chloride	–642
first ionisation energy of magnesium	+736
second ionisation energy of magnesium	+1450
electron affinity of chlorine	–349
enthalpy change of hydration of Mg^{2+}	–1920
enthalpy change of hydration of Cl^-	–364

ΔH_{latt} $MgCl_2(s)$ = ... kJ mol^{-1} [3]

(c) Define entropy.

....

.... [1]

(d) At 25 °C the enthalpy change of solution of compound **Z** is +26 kJ mol^{-1}. The entropy change of solution of **Z** at the same temperature is +52 J K^{-1} mol^{-1}.

Calculate the value of the Gibbs free energy change, ΔG, for the solution of **Z** at 25 °C.

ΔG = ... kJ mol^{-1} [2]

(e) **(i)** Use your answer to **(d)** to predict whether or not **Z** is soluble in water at 25 °C. Explain your answer.

....

.... [1]

(ii) Predict whether **Z** becomes more or less soluble as the water is heated from 25 °C to 95 °C. Explain your answer.

....

.... [1]

[Total: 14]

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[Turn over

3 **(a)** The pH of a saturated solution of calcium hydroxide is 12.35 at 298 K.

(i) Show that the concentration of hydroxide ions in a saturated solution of calcium hydroxide is 0.0224 mol dm^{-3} at 298 K.

[2]

(ii) Use data given in **(i)** to calculate the solubility product, K_{sp}, of calcium hydroxide at 298 K.

Include the units of K_{sp} in your answer.

K_{sp} = ... units .... [3]

(iii) A spatula measure of solid calcium chloride is stirred into a sample of saturated calcium hydroxide solution. All of the calcium chloride dissolves.

Describe **one** other observation that would be made and give an estimated value of the pH of the solution obtained.

Explain **both** your answers.

observation ....

pH of solution ....

explanation ....

....

[3]

(iv) Calcium hydroxide reacts with dilute sulfuric acid to form calcium sulfate. Barium hydroxide behaves in a similar way, forming barium sulfate.

Explain why calcium sulfate is more soluble in water than barium sulfate.

....

....

....

....

.... [3]

(b) Some solid calcium is added to an excess of aqueous ethanoic acid, CH_3COOH, and left until all the calcium has reacted. The resulting mixture, mixture **D**, contains no undissolved solids.

(i) Write an equation for the reaction of calcium with CH_3COOH.

.... [1]

(ii) Use formulae of molecules and ions to identify **two** conjugate acid–base pairs present in mixture **D**.

Pair 1 should consist of organic species.

pair 1: ....
conjugate acid conjugate base

pair 2: ....
conjugate acid conjugate base

[2]

(iii) Write the expression for the K_a of CH_3COOH.

K_a =

[1]

(iv) The concentration of calcium ethanoate, $(CH_3COO)_2Ca$, in mixture **D** is $0.394\,mol\,dm^{-3}$. The concentration of CH_3COOH in mixture **D** is $0.270\,mol\,dm^{-3}$.

The K_a of CH_3COOH is $1.74 \times 10^{-5}\,mol\,dm^{-3}$ at 298 K.

Calculate the pH of mixture **D**.

pH = ... [2]

(v) Write **two** equations to show how mixture **D** can act as a buffer solution.

equation 1 ....

equation 2 ....

[2]

[Total: 19]

4 Transition metal atoms and transition metal ions form complexes by combining with species called ligands.

(a) When NaOH(aq) is added to an aqueous solution containing $[Co(H_2O)_6]^{2+}$ a precipitation reaction occurs accompanied by a colour change.

In this reaction two of the water ligands each lose one H^+ ion. The H^+ ions are gained by OH^- ions from the NaOH(aq).

(i) State the colour change seen in this precipitation reaction.

from .... to .... [1]

(ii) Complete the ionic equation for this precipitation reaction.

$[Co(H_2O)_6]^{2+}$ + ... → .... + ...

[1]

(iii) This precipitation reaction can also be described as a **different** type of reaction.

Name this type of reaction.

.... [1]

(b) **L** is an uncharged tridentate ligand. **L** donates three lone pairs to a metal atom or ion.

Cobalt forms an octahedral complex ion, **E**, with **L**. Complex ion **E** has a 2+ charge.

(i) Give the formula of **E**.

.... [1]

(ii) Identify the oxidation state of cobalt in **E**.

.... [1]

(iii) The d-orbitals of the cobalt atom or ion present in **E** are split in energy.

State the number of d-orbitals that are at a higher energy level and the number of d-orbitals that are at a lower energy level.

number of d-orbitals at a higher energy level	
number of d-orbitals at a lower energy level	

[1]

(iv) Define the term non-degenerate d-orbitals.

....

.... [1]

(c) The mineral chromite contains a compound which has the formula $FeCr_nO_4$. The oxidation state of iron in $FeCr_nO_4$ is +2.

A sample of 4.18 g of $FeCr_nO_4$ is dissolved in an excess of sulfuric acid. The resulting solution is made up to $250\,cm^3$. This is solution **F**.

All the Fe^{2+} ions in $25.0\,cm^3$ of solution **F** are oxidised to Fe^{3+} ions by exactly $18.7\,cm^3$ of $0.0200\,mol\,dm^{-3}$ $KMnO_4$.

One MnO_4^- ion reacts with five Fe^{2+} ions. Assume no other oxidation reaction occurs.

(i) Write an equation for the reaction of Fe^{2+} ions with MnO_4^- ions in acid solution.

.... [1]

(ii) Calculate the number of moles of Fe^{2+} ions in $25.0\,cm^3$ of solution **F**.

number of moles of Fe^{2+} ions = ... [2]

(iii) Calculate the M_r of $FeCr_nO_4$ and use your answer to deduce the value of n.

M_r of $FeCr_nO_4$ = ...

value of n = ...

[2]

[Total: 12]

5 Ni^{2+} ions form a number of different complex ions, including $[Ni(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$ and $[Ni(en)_3]^{2+}$.

The abbreviation *en* represents 1,2-diaminoethane. The numerical values of two stability constants, K_{stab}, are given in Table 5.1.

Table 5.1

complex	K_{stab}
$[Ni(NH_3)_6]^{2+}$	4.8×10^7
$[Ni(en)_3]^{2+}$	2.0×10^{18}

(a) Complete the expression for the K_{stab} of $[Ni(en)_3]^{2+}$.

K_{stab} =

[1]

(b) A solution of $[Ni(H_2O)_6]^{2+}$ is added to a solution that contains 0.10 mol dm^{-3} NH_3 and 0.10 mol dm^{-3} *en*.

(i) Predict which complex ion, $[Ni(NH_3)_6]^{2+}$ or $[Ni(en)_3]^{2+}$, is present in the resulting mixture in the highest concentration. Explain your answer.

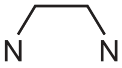
complex ion present in largest concentration = ...

explanation ....
[1]

(ii) Complete the equation for the ligand exchange reaction occurring in **(i)**.

$[Ni(H_2O)_6]^{2+}$ + ... → .... + ...
[1]

(c) Complete Fig. 5.1 to show the three-dimensional structures of the two isomers of $[\mathrm{Ni}(en)_3]^{2+}$.

Use  to represent the *en* ligand.

Name the type of isomerism shown.

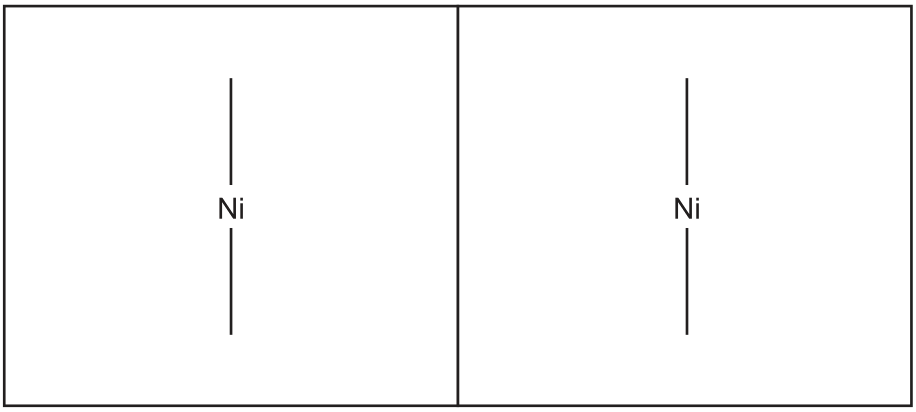


Fig. 5.1

type of isomerism shown ....

[3]

[Total: 6]

6 Fig. 6.1 shows two reactions of ethanedioic acid, HOOCCOOH.

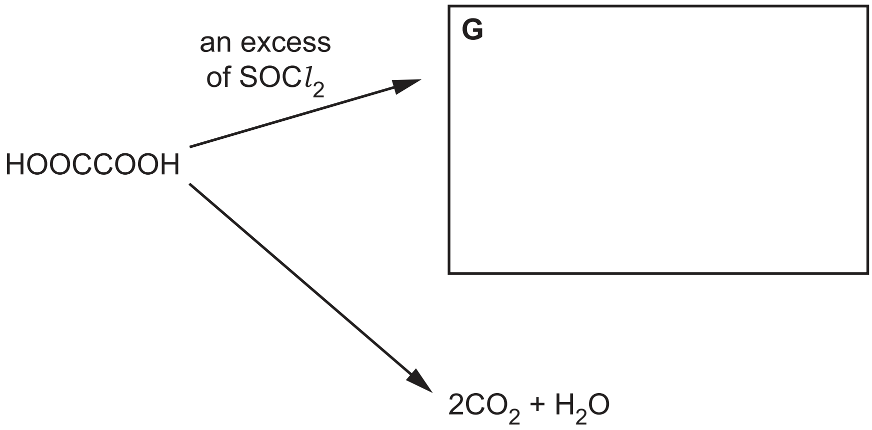


Fig. 6.1

(a) **(i)** Draw the organic product **G** in the box in Fig. 6.1.

[1]

(ii) In Fig. 6.1, $SOCl_2$ is given as the reagent that reacts with HOOCCOOH to produce **G**.

Identify a different reagent that also reacts with HOOCCOOH to produce **G**.

.... [1]

(b) Identify **two** different reagents that oxidise HOOCCOOH to form carbon dioxide and water.

....

.... [2]

(c) HOOCCOOH ionises as shown.

$$\text{HOOCCOOH} \rightleftharpoons \text{HOOCCOO}^- + \text{H}^+$$

HOOCCOOH is a much stronger acid than methanoic acid, HCOOH.

Suggest an explanation for this difference in acidity.

....

....

.... [2]

(d) Benzene-1,4-dicarboxylic acid, $HOOCC_6H_4COOH$, can be made from benzene, C_6H_6, in two steps as shown in Fig. 6.2.

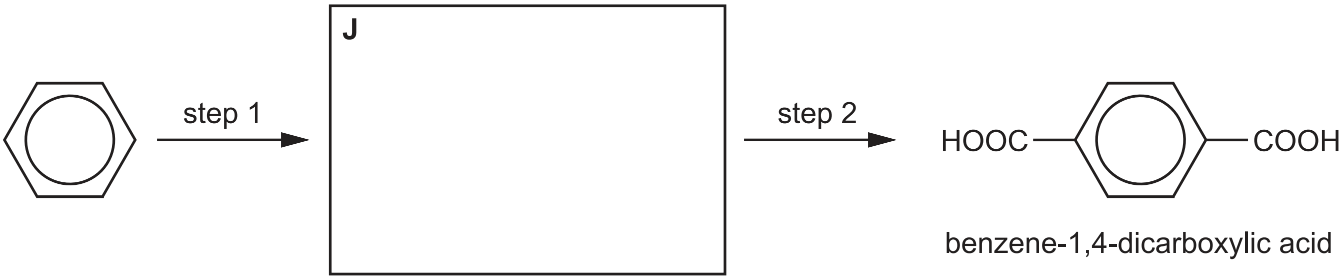


Fig. 6.2

(i) Suggest the identity of **J** by drawing its structure in the box in Fig. 6.2.

[1]

(ii) Identify the reagents and conditions for step 1 and step 2.

step 1 ....

step 2 ....

[2]

(iii) Draw the structure of exactly **one** repeat unit of the polymer formed when benzene-1,4-dicarboxylic acid reacts with ethane-1,2-diol, $HOCH_2CH_2OH$. The linkage formed between the monomers should be shown fully displayed.

[2]

(iv) State the type of polymerisation that occurs when benzene-1,4-dicarboxylic acid reacts with ethane-1,2-diol and name the linkage formed between the monomers.

type of polymerisation ....

linkage ....

[1]

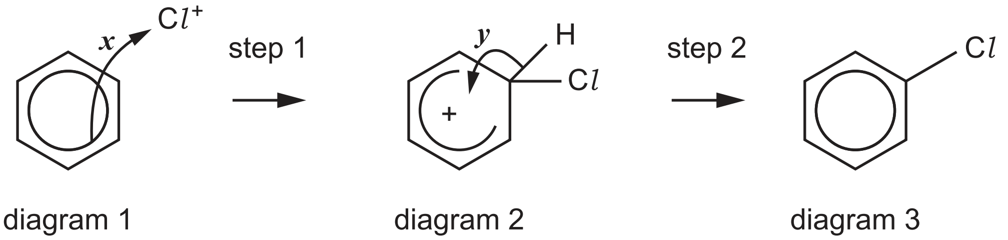
[Total: 12]

7 Benzene reacts with chlorine gas to form chlorobenzene. This reaction can be described as the reaction between benzene molecules and Cl^+ ions. The Cl^+ ions are formed by adding a suitable catalyst to the chlorine gas.

(a) Give the name or formula of a catalyst that can be used for this reaction.

.... [1]

(b) The mechanism for this reaction is shown.



(i) The movement of a pair of electrons is represented by x in diagram 1.

- State where this pair of electrons is **before** step 1 takes place.

....

- State where this pair of electrons is **after** step 1 has taken place.

....

[2]

(ii) The movement of another pair of electrons is represented by y in diagram 2.

- State where this pair of electrons is **before** step 2 takes place.

....

- State where this pair of electrons is **after** step 2 has taken place.

....

[2]

(c) There are six carbon atoms in diagram 2.

State how many of these carbon atoms are sp hybridised, sp^2 hybridised, and sp^3 hybridised.

sp hybridised ....

sp^2 hybridised ....

sp^3 hybridised ....

[1]

(d) Complete the equation for this reaction between benzene and chlorine.

C_6H_6 + ... → .... + ...

[1]

(e) The mechanism for this reaction is electrophilic substitution.

Complete the following sentence. Write formulae in the gaps provided.

During this reaction, the electrophile is .... and a .... atom

in benzene is substituted by a .... atom.

[1]

(f) Chloroethane reacts with NaOH(aq). Chlorobenzene does not.

(i) Name the mechanism of the reaction that chloroethane undergoes with NaOH(aq), and identify the major organic product that is formed.

mechanism ....

major organic product ....

[1]

(ii) Explain the difference in reactivity of chloroethane and chlorobenzene when treated with NaOH(aq).

....

....

.... [2]

[Total: 11]

8 The amino acid serine, $HOCH_2CH(NH_2)COOH$, exists in two optically active forms. These optical isomers, isomer **P** and isomer **Q**, are shown in Fig. 8.1.

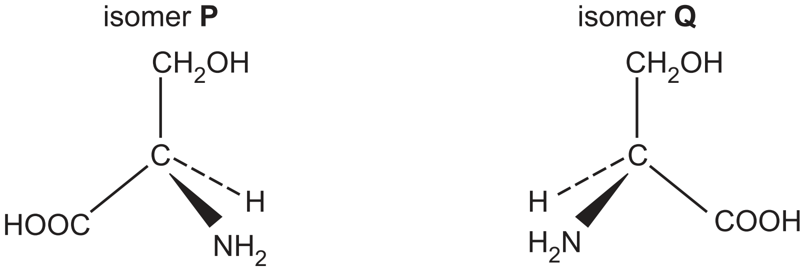


Fig. 8.1

(a) Isomer **P** and isomer **Q** have identical physical and chemical properties, with the exception of two specific properties. One of these two properties is their differing effect on plane polarised light.

State the other property by which they differ.

....

.... [1]

(b) A solution of pure isomer **P** of a particular concentration rotates plane polarised light by 5.0° in a clockwise direction.

Describe how a solution of pure isomer **Q** of the same concentration affects plane polarised light.

....

.... [1]

(c) State another term, in addition to stereoisomers, optical isomers and non-superimposable mirror images, which can be used to describe this pair of chiral compounds, isomer **P** and isomer **Q**.

.... [1]

(d) Give the term used to describe a mixture containing equal amounts of isomer **P** and isomer **Q**.

.... [1]

(e) Describe **one** way in which a single pure optical isomer of serine can be produced, instead of making a mixture of isomer **P** and isomer **Q**.

.... [1]

(f) Complete Table 8.1 to describe the peaks seen in the proton (^1H) NMR spectrum of $HOCH_2CH(NH_2)COOH$ dissolved in D_2O.

Use as many rows in Table 8.1 as you need to, leaving the other rows blank.

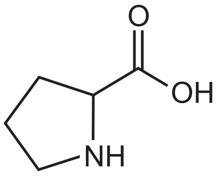
Table 8.1

group responsible for peak	name of splitting pattern shown by peak	explanation for splitting pattern

[3]

(g) Proline is a naturally occurring amino acid. The skeletal formula of proline is shown.

proline



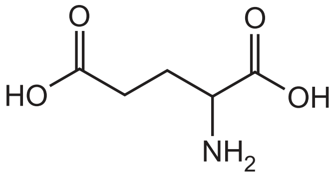
State the number of peaks in the carbon-13 (^{13}C) NMR spectrum of proline.

.... [1]

(h) Glutamic acid is a naturally occurring amino acid.

The skeletal formula of glutamic acid is shown.

glutamic acid



The isoelectric point of glutamic acid is pH 3.

A sample of glutamic acid is dissolved in a solution of pH 1. A strong alkali is then added until the pH of the mixture reaches pH 14. During this process **all** possible ionised forms of glutamic acid are present at different times, depending on the pH of the solution.

Complete the boxes below to show four **different** ionised forms of glutamic acid that are present at the stated pH values.

at pH 1

at pH 3

at pH 9

at pH 14

[3]

[Total: 12]

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Important values, constants and standards

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

The Periodic Table of Elements

Key

atomic number
atomic symbol
name
relative atomic mass

Group																	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
							1 H hydrogen 1.0										2 He helium 4.0
3 Li lithium 6.9	4 Be beryllium 9.0											5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0	10 Ne neon 20.2
11 Na sodium 23.0	12 Mg magnesium 24.3											13 A*l* aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 C*l* chlorine 35.5	18 Ar argon 39.9
19 K potassium 39.1	20 Ca calcium 40.1	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4	31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8
37 Rb rubidium 85.5	38 Sr strontium 87.6	39 Y yttrium 88.9	40 Zr zirconium 91.2	41 Nb niobium 92.9	42 Mo molybdenum 95.9	43 Tc technetium –	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57–71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 T*l* thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium –	85 At astatine –	86 Rn radon –
87 Fr francium –	88 Ra radium –	89–103 actinoids	104 Rf rutherfordium –	105 Db dubnium –	106 Sg seaborgium –	107 Bh bohrium –	108 Hs hassium –	109 Mt meitnerium –	110 Ds darmstadtium –	111 Rg roentgenium –	112 Cn copernicium –	113 Nh nihonium –	114 F*l* flerovium –	115 Mc moscovium –	116 Lv livermorium –	117 Ts tennessine –	118 Og oganesson –

lanthanoids	57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium –	62 Sm samarium 150.4	63 Eu europium 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
actinoids	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 mendelevium –	102 No nobelium –	103 Lr lawrencium –