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About A LEVEL CHEMISTRY

(TOPICAL)

About Learning Corner

This section reveals the extra/relevant information that are not required as part of the model answers but to expand the student's knowledge in the respective fields. At the same time, it induces eagerness and interest into their learning process.

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contents	June & November, P4, Worked Solutions
form	Topic By Topic
compiled for	A Level
special features	Learning Corner

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☞ ***A LEVEL***

Topic 1

Chemical Energetics

1.1 Lattice energy and Born-Haber cycles

Learning outcomes

Candidates should be able to:

1 define and use the terms:
   (a) enthalpy change of atomisation, ΔH_{at}
   (b) lattice energy, ΔH_{latt} (the change from gas phase ions to solid lattice)

2 (a) define and use the term first electron affinity, EA
   (b) explain the factors affecting the electron affinities of elements
   (c) describe and explain the trends in the electron affinities of the Group 16 and Group 17 elements

3 construct and use Born–Haber cycles for ionic solids
   (limited to +1 and +2 cations, −1 and −2 anions)

4 carry out calculations involving Born–Haber cycles

5 explain, in qualitative terms, the effect of ionic charge and of ionic radius on the numerical magnitude of a lattice energy

1.2 Enthalpies of solution and hydration

Learning outcomes

Candidates should be able to:

1 define and use the term enthalpy change with reference to hydration, ΔH_{hyd}, and solution, ΔH_{sol}

2 construct and use an energy cycle involving enthalpy change of solution, lattice energy and enthalpy change of hydration

3 carry out calculations involving the energy cycles in 23.2.2

4 explain, in qualitative terms, the effect of ionic charge and of ionic radius on the numerical magnitude of an enthalpy change of hydration

1.3 Entropy change, ΔS

Learning outcomes

Candidates should be able to:

1 define the term entropy, S, as the number of possible arrangements of the particles and their energy in a given system

2 predict and explain the sign of the entropy changes that occur:

(a) during a change in state, e.g. melting, boiling and dissolving (and their reverse)

(b) during a temperature change

(c) during a reaction in which there is a change in the number of gaseous molecules

3 calculate the entropy change for a reaction, ΔS, given the standard entropies, $S^{\ominus}$, of the reactants and products, $\Delta S^{\ominus} = \sum S^{\ominus}(\text{products}) - \sum S^{\ominus}(\text{reactants})$

(use of $\Delta S^{\ominus} = \Delta S\text{surr}^{\ominus} + \Delta S\text{sys}^{\ominus}$ is not required)

1.4 Gibbs free energy change, ΔG

Learning outcomes

Candidates should be able to:

1 state and use the Gibbs equation $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

2 perform calculations using the equation $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

3 state whether a reaction or process will be feasible by using the sign of ΔG

4 predict the effect of temperature change on the feasibility of a reaction, given standard enthalpy and entropy changes

learning CORNER

TOPIC *opening .....*

Question 1

(a) What is meant by the term *bond energy*? [2]

(b) Describe and explain what is observed when a red-hot wire is plunged into separate samples of the gaseous hydrogen halides HC*l* and HI.
How are bond energy values useful in interpreting these observations? [3]

(c) The following reaction occurs in the gas phase.

$$3F_2(g) + Cl_2(g) \longrightarrow 2ClF_3(g), \qquad \Delta H_r^{\ominus} = -328 \text{ kJ mol}^{-1}$$

Use these and other data from the *Data Booklet* to calculate the average bond energy of the C*l*-F bond in ClF_3. [2]

[N09/P4/Q4]

Suggested Solution:

(a) The energy required to break one mole of bonds in the gas phase.

(b) With HC*l*, no change with HI purple fumes of iodine are produced.

H — C*l* bond being strong does not break whereas H — I bond being weaker breaks into its elements.

$$2HI \rightarrow H_2 + I_2$$

(c) Bonds broken − Bonds formed = −328

$$\Rightarrow \quad 3BE(F-F) + BE(Cl-Cl) - 6BE(Cl-F) = -328$$
$$(3\times 158) + 244 - 6BE(Cl-F) = -328$$
$$718 - 6BE(Cl-F) = -328$$
$$6BE(Cl-F) = 1046$$
$$BE(Cl-F) = 174.3 \approx 174$$

Question 2

(a) (i) What is meant by the term *enthalpy change of hydration*, $\Delta H_{hyd}^{\ominus}$?

(ii) Write an equation that represents the $\Delta H_{hyd}^{\ominus}$ of the Mg^{2+} ion.

(iii) Suggest a reason why $\Delta H_{hyd}^{\ominus}$ of the Mg^{2+} ion is greater than $\Delta H_{hyd}^{\ominus}$ of the Ca^{2+} ion.

(iv) Suggest why it is impossible to determine the enthalpy change of hydration of the oxide ion, O^{2-}. [5]

(b) The enthalpy change of solution for $MgCl_2$, $\Delta H_{sol}^{\ominus}(MgCl_2(s))$, is represented by the following equation.

$$MgCl_2(s) + aq \longrightarrow Mg^{2+}(aq) + 2Cl^{-}(aq)$$

Describe the simple apparatus you could use, and the measurements you would make, in order to determine a value for $\Delta H_{sol}^{\ominus}(MgCl_2(s))$ in the laboratory. [4]

(c) The table below lists data relevant to the formation of $MgCl_2(aq)$.

enthalpy change	value / kJ mol^{-1}
$\Delta H_f^{\ominus}(MgCl_2(s))$	–641
$\Delta H_f^{\ominus}(MgCl_2(aq))$	–801
lattice energy of $MgCl_2(s)$	–2526
$\Delta H_{hyd}^{\ominus}(Mg^{2+}(g))$	–1890

By constructing relevant thermochemical cycles, use the above data to calculate a value for

(i) $\Delta H_{sol}^{\ominus}(MgCl_2(s))$,

(ii) $\Delta H_{hyd}^{\ominus}(Cl^-(g))$. [3]

(d) Describe and explain how the solubility of magnesium sulfate compares to that of barium sulfate. [4]

[J12/P4/Q1]

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Suggested Solution:

(a) (i) The enthalpy change when 1 mol of gaseous ions dissolve in sufficient water to give an infinitely dilute solution.

(ii) $Mg^{2+}(g) + aq \longrightarrow Mg^{2+}(aq)$

(iii) Mg^{2+} has greater charge density than Ca^{2+}.

(iv) This is because the oxide ion reacts with water to give OH^-.

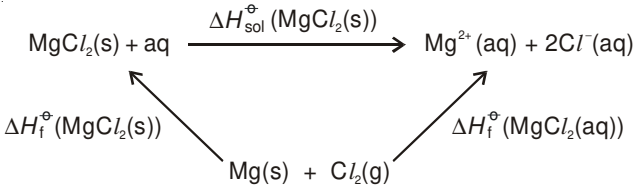
$O^{2-} + H_2O \longrightarrow 2OH^-$

(a) (iii) Although the charge on the Mg^{2+} and Ca^{2+} ion is the same, Mg^{2+} has a smaller ionic radius than Ca^{2+}. Hence, Mg^{2+} has a greater charge density than Ca^{2+}.

(b) Apparatus: Insulated Calorimeter, Water, Thermometer.

Pour a known volume of water into the calorimeter. Record the temperature of the water. Add a known mass of $MgCl_2$ into the water, and record the highest temperature change of the solution. These measurements would be sufficient for determining a value for $\Delta H_{sol}^{\ominus}(MgCl_2(s))$.

(c) (i)



$$\Delta H_f^{\ominus}(MgCl_2(s)) + \Delta H_{sol}^{\ominus}(MgCl_2(s)) = \Delta H_f^{\ominus}(MgCl_2(aq))$$

$$-641 + \Delta H_{sol}^{\ominus}(MgCl_2(s)) = -801$$

$$\Delta H_{sol}^{\ominus}(MgCl_2(s)) = -801 + 641$$

$$= -160 \text{ kJ/mol}$$

(ii) $\Delta H_{hyd}^{\ominus}(Mg^{2+}(g)) + 2\Delta H_{hyd}^{\ominus}(Cl^{-}(g)) = \Delta H_{sol}^{\ominus}(MgCl_2(s)) + \text{L.E of } MgCl_2(s)$

$$-1890 + 2\Delta H_{hyd}^{\ominus}(Cl^{-}(g)) = -160 - 2526$$

$$2\Delta H_{hyd}^{\ominus}(Cl^{-}(g)) = -160 - 2526 + 1890$$

$$2\Delta H_{hyd}^{\ominus}(Cl^{-}(g)) = -796$$

$$\Delta H_{hyd}^{\ominus}(Cl^{-}(g)) = -\frac{796}{2} = -398 \text{ kJ/mol}$$

(d) Magnesium sulfate is more soluble than barium sulfate because ΔH_{sol} is more exothermic for magnesium sulfate than barium sulfate. Increasing the ionic radius, leads to a smaller lattice and hydration enthalpy. Therefore, as Ba^{+2} has a larger ionic radius, the lattice enthalpy of barium sulfate is smaller than magnesium sulfate and the hydration enthalpy of Ba^{+2} is lesser than Mg^{+2}. However, the change in hydration enthalpy is more dominant and hydration enthalpy decreases more than L.E, causing magnesium sulfate to be more soluble than barium sulfate.

Question 3

(a) Write down what you would see, and write equations for the reactions that occur, when silicon(IV) chloride and phosphorus(V) chloride are separately mixed with water. [4]

(c) When $SiCl_4$ vapour is passed over Si at red heat, Si_2Cl_6 is formed. Si_2Cl_6 contains a Si-Si bond.
The reaction of Si_2Cl_6 and Cl_2 re-forms $SiCl_4$.

$$Si_2Cl_6(g) + Cl_2(g) \rightarrow 2SiCl_4(g)$$

Use bond energy data from the *Data Booklet* to calculate $\Delta H^{\ominus}$ for this reaction. [2]

(d) Calcium forms three calcium silicides, Ca_2Si, CaSi and $CaSi_2$. The first of these reacts with water as follows.

$$.....Ca_2Si + ...H_2O \rightarrow .....Ca(OH)_2 + ...SiO_2 + ...H_2$$

(i) Balance this equation. You may find the use of oxidation numbers helpful.

(ii) During this reaction, state
which element(s) have been oxidised,
which element(s) have been reduced. [2]

[N12/P4/Q1 a,c,d]

Suggested Solution:

(a) $SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$

observation: White / steamy fumes of HCl are produced.

$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$

observation: Fizzing occurs and white / steamy fumes are produced.

(c) Bond energy of Si-Si Bond = 222 kJ / mol
Bond energy of Si-C*l* Bond = 359 kJ / mol
Bond energy of C*l*-C*l* Bond = 244 kJ / mol

$$\text{bonds broken} = (\text{Si-Si}) + 6(\text{Si-C}l) + (\text{C}l\text{-C}l)$$
$$= 222 + 6(359) + 244 = 2620$$
$$\text{bonds formed} = 2 \times (4 \times \text{Si-C}l)$$
$$= 8\ (\text{Si-C}l) = 2872$$
$$\therefore\ \Delta H^{\ominus} = 2620 - 2872$$
$$= -252\ \text{kJ / mol}$$

(d) (i) $Ca_2Si + 6H_2O \rightarrow 2Ca(OH)_2 + SiO_2 + 4H_2$

(ii) Silicon is oxidized
Hydrogen has been reduced

Question 4

(a) Calcium has atomic number 20.
Complete the electronic structures for a

calcium atom, $1s^2 2s^2 2p^6$.....

calcium ion in the +2 oxidation state. $1s^2 2s^2 2p^6$..... [1]

(b) Calcium nitrate, $Ca(NO_3)_2$, is used in fertilisers and can be prepared by an acid-base reaction.
Write an equation for the preparation of calcium nitrate by an acid-base reaction. [1]

(c) (i) When anhydrous calcium nitrate is heated strongly, it decomposes to leave a white solid.
Identify this white solid and suggest **another** observation for this reaction. [1]

(ii) The ease of thermal decomposition of the Group II nitrates **decreases** down the group.
Explain this trend. [2]

(d) (i) What is meant by the term *standard enthalpy change of hydration*, $\Delta H^{\ominus}_{hyd}$? [2]

(ii) Use the following data to calculate the lattice energy, $\Delta H^{\ominus}_{latt}$, of calcium nitrate, $Ca(NO_3)_2(s)$. You may find it helpful to construct an energy cycle.

enthalpy change	value
$\Delta H^{\ominus}_{hyd}\ (Ca^{2+}(g))$	$-1650\ \text{kJ mol}^{-1}$
$\Delta H^{\ominus}_{hyd}\ (NO_3^-(g))$	$-314\ \text{kJ mol}^{-1}$
enthalpy change of solution for $Ca(NO_3)_2(s)$	$-19\ \text{kJ mol}^{-1}$

[3]

(e) The standard enthalpy change of hydration for Ba^{2+}, $\Delta H^{\ominus}_{hyd}\ (Ba^{2+}(g))$, is $-1305\ \text{kJ mol}^{-1}$.
Suggest an explanation for why the $\Delta H^{\ominus}_{hyd}$ of the Ba^{2+} ion is **less** exothermic than the $\Delta H^{\ominus}_{hyd}$ of the Ca^{2+} ion. [2]

[N15/P4/Q1]

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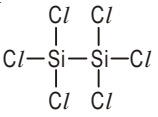
(c) The structure of Si_2Cl_6 is



From here it can be seen that 1 Si-Si and 6 Si-C*l* bonds are broken.

(d) Let oxidation state of Si in Ca_2Si be x
$\therefore\ 2(+2) + x = 0$
$\therefore\ x = -4$
Let oxidation state of Si in SiO_2 be y
$\therefore\ y + 2(-2) = 0$
$\therefore\ y = +4$
Hence Si is oxidized. Similarly, oxidation state of H in H_2O = +1 and oxidation state of H in H_2 = 0. Hence Hydrogen is reduced.

Suggested Solution:

(a) calcium atom: $1s^2 2s^2 2p^6$ **$3s^2 3p^6 4s^2$**

calcium ion in the +2 oxidation state: $1s^2 2s^2 2p^6$ **$3s^2 3p^6$**

(b) $CaO + 2HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O$

(c) (i) CaO is the white solid formed. Brown fumes of NO_2 gas are produced.

(ii) Down the group cationic radius increase and charge density decreases. Therefore polarising power of cation decreases and N—O bonds are less polarised down the group.

(d) (i) It is the enthalpy change when 1 mol of gaseous ion is dissolved in water to form infinite dilute solution under standard conditions.

(ii) $\Delta H_{sol}^{\ominus} = \Delta H_{hyd}^{\ominus} - \Delta H_{L.E}^{\ominus}$

$-19 = [-1650 + 2(-314)] - \Delta H_{latt}^{\ominus}$

$\Delta H_{latt} = -2259\ kJ\,mol^{-1}$

(e) Ca^{2+} ion is a smaller ion with higher charge density than Ba^{2+}, therefore Ca^{2+} has a stronger attraction to H_2O.

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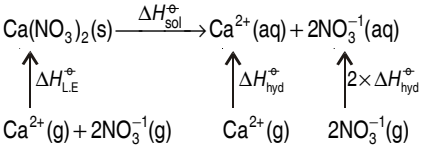
(b) Alternatively:

$Ca(OH)_2 + 2HNO_3 \rightarrow Ca(NO_3)_2 + 2H_2O$

(c) (i) $Ca(NO_3)_2 \rightarrow CaO + 2NO_2 + \frac{1}{2}O_2$

(d) (ii)



(e) $\Delta H_{hyd} \propto \left|\frac{q^+}{r^+}\right|$

Smaller the radius, greater is the charge i.e. larger the change density, more exothermic is ΔH_{hyd}.

Question 5

(a) Describe and explain the trend in the solubility of the hydroxides down Group 2. [3]

(b) Calcium reacts vigorously with HC*l*(aq) producing $H_2(g)$.

$$Ca(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2(g)$$

(i) How would you expect the enthalpy change for this reaction to compare with the enthalpy change for the reaction where $HNO_3(aq)$ is used in place of HC*l* but all other conditions are the same? Explain your answer. [1]

(ii) The ionic equation for this reaction is shown.

$$Ca(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2(g) \qquad \Delta H^{\ominus} = \mathbf{x}\ kJ\,mol^{-1}$$

Construct a **fully labelled** Hess' Law cycle to connect each side of this equation to the relevant gas phase ions.

Use your cycle, the following data, **and** data from the *Data Booklet*, to calculate a value for **x**.

standard enthalpy of atomisation of Ca(s), $\Delta H_{at}^{\ominus}(Ca)$	+178 kJ mol^{-1}
standard enthalpy of hydration of $Ca^{2+}(g)$, $\Delta H_{hyd}^{\ominus}(Ca^{2+})$	–1576 kJ mol^{-1}
standard enthalpy of hydration of $H^+(g)$, $\Delta H_{hyd}^{\ominus}(H^+)$	–1090 kJ mol^{-1}

[4]

(c) The standard enthalpy change for the reaction between Ca(s) and $CH_3CO_2H(aq)$ is **less negative** than **x** by 2 kJ mol^{-1}.

Suggest an explanation for this. [2]

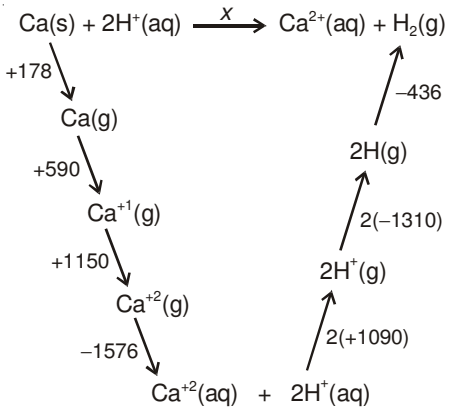
[J16/P4/Q8]

Suggested Solution:

(a) Solubility of hydroxides increases down the group. Down the group charge density of cation decreases, therefore, $\Delta H_{C\text{-}E}$ and ΔH_{hyd} decrease but $\Delta H_{C\text{-}E}$ decreases more than ΔH_{hyd} thereby making ΔH_{sol} more exothermic down the group.

(b) (i) Enthalpy change will be similar as both are strong acids and have fully ionised.

(ii)



$$x = 178 + 590 + 1150 + (-1576) + 2(1090) + 2(-1310) + (-436)$$
$$= -534 \text{ kJmol}^{-1}$$

(c) CH_3COOH is a weak acid which partially dissociates. Therefore some energy will be utilised to dissociate acid to release more H^+ for the complete reaction.

Question 6

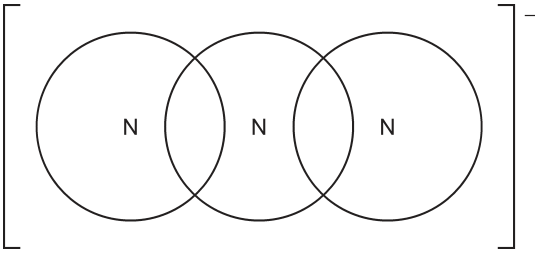
Most car air bags contain a capsule of sodium azide, NaN_3. In a crash, the NaN_3 decomposes into its elements.

(a) Write an equation for the decomposition of NaN_3. [1]

(b) Complete the 'dot-and-cross' diagram for the azide ion, N_3^-.

Use the following key for the electrons.

- ● electrons from central nitrogen atom
- × electrons from the other two nitrogen atoms
- □ added electron(s) responsible for the overall negative charge



[3]

(c) Lattice energies are always negative showing that they represent exothermic changes.

(i) Explain what is meant by the term *lattice energy*. [2]

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(a) More exothermic ΔH_{Sol}, More soluble the compound is!

(b) (i) $Ca + CH_3COOH$ will have leser enthalpy as some energy is required to dissociate the acid.

(c)

$$CH_3COOH \rightarrow CH_3COO^- + H^+$$

$$Ca + 2H^+ \rightarrow Ca^{2+} + H_2$$

As Ca reacts with H^+, H^+ decrease in concentration thereby shifting equilibrium towards product side. This dissociation of acid requires O – H bond breakage which utilizes energy.

(ii) Explain why lattice energy represents an exothermic change. [1]

(iii) Use the following data and any relevant data from the *Data Booklet* to calculate the standard enthalpy change of formation, $\Delta H_f^{\ominus}$, of $NaN_3(s)$. Include a sign in your answer. Show all your working.

lattice energy, $\Delta H_{latt}^{\ominus}$, of $NaN_3(s)$	$-732\ kJ\ mol^{-1}$
standard enthalpy change of atomisation, $\Delta H_{at}^{\ominus}$, of Na(g)	$+107\ kJ\ mol^{-1}$
standard enthalpy change, $\Delta H^{\ominus}$, for $1\frac{1}{2}N_2(g) + e^- \rightarrow N_3^-(g)$	$+142\ kJ\ mol^{-1}$

[3]

(iv) The lattice energy, $\Delta H_{latt}^{\ominus}$, of $RbN_3(s)$ is $-636\ kJ\ mol^{-1}$.

Suggest why the lattice energy of $NaN_3(s)$, $-732\ kJ\ mol^{-1}$, is more exothermic than that of $RbN_3(s)$. [1]

[N16/P4/Q2]

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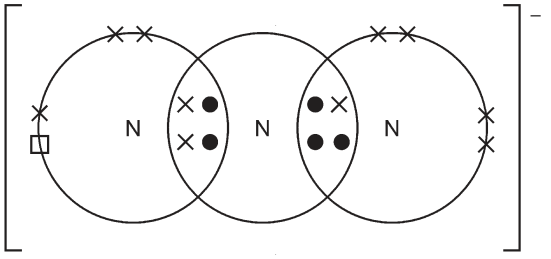
Suggested Solution:

(a) $NaN_3 \longrightarrow Na + 1.5N_2$

(b)



(c) (i) It is the enthalpy change when one mole of an ionic compound (solid/ lattice) is formed from its gaseous ions.

(ii) An ionic bond is formed and so electrostatic attractions are developed that causes release of energy.

(iii) $\Delta H_f^{\ominus} = 107 + 494 + 142 + (-732)$

$= +11\ kJ\ mol^{-1}$

(iv) Rb^{1+} forms a larger cation and less attractions as lattice energy is inversely proportional to the size of ions.

(c) (ii) Bond formation is exothermic and bond breaking is endothermic.

(iii) $\Delta H_{E.A}$ is a negative value if one e^- is gained, it will be positive value if more e^- gained.

Question 7

Iron has atomic number 26.

(a) Complete the electronic configuration for the iron atom and the iron ion in the +3 oxidation state.

- iron atom [Ar] .....
- iron ion in the +3 oxidation state [Ar] ..... [2]

(b) Fe^{3+} can act as a homogeneous catalyst in the reaction between peroxodisulfate ions ($S_2O_8^{2-}$) and iodide ions.

(i) What is meant by a *homogeneous* catalyst? [1]

(ii) Write an equation for the overall reaction between $S_2O_8^{2-}$(aq) and I^-(aq). [1]

(iii) Suggest why, in the absence of a catalyst, the activation energy for this reaction is high. [1]

(iv) Write two equations to show how Fe^{3+}(aq) ions can catalyse the reaction between $S_2O_8^{2-}$(aq) ions and I^-(aq) ions. [2]

(c) Iron(III) oxide can be reduced to iron metal using carbon monoxide at a temperature of 1000 °C.

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g) \qquad \Delta H^{\ominus} = -43.6\,kJ\,mol^{-1}$$

Some relevant standard entropies are given in the table.

substance	$Fe_2O_3(s)$	CO(g)	Fe(s)	$CO_2(g)$
$S^{\ominus}$ / $JK^{-1}\,mol^{-1}$	+90	+198	+27	+214

(i) What is meant by the term *entropy* ? [1]

(ii) Calculate the standard entropy change, $\Delta S^{\ominus}$, for this reaction. [2]

(iii) Calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for this reaction at 25 °C. [2]

(iv) Suggest why a temperature of 1000 °C is usually used for this reaction, even though the reaction is spontaneous (feasible) at 25 °C. Explain your answer. [1]

[N16/P4/Q3]

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Suggested Solution:

(a) Iron atom: [Ar] **$3d^6\,4s^2$**

Iron ion in the +3 oxidation state: [Ar] **$3d^5$**

(b) (i) Catalyst is present in the same physical state as the reactants.

(ii) $S_2O_8^{2-} + 2I^{1-} \longrightarrow 2SO_4^{2-} + I_2$

(iii) Both reactants are negatively charged ions which repel each other.

(iv) equation 1: $2Fe^{3+} + 2I^{1-} \longrightarrow 2Fe^{2+} + I_2$

equation 2: $S_2O_8^{2-} + 2Fe^{2+} \longrightarrow 2SO_4^{2-} + 2Fe^{3+}$

(b) (ii) Use of data booklet and $E^{\ominus}$ values.

(iv) Homogenous catalyst used up in one reaction step and regenerated in the other reaction step.

(c) (i) It is the measure (degree) of disorder of a substance.

(ii) $\Delta S^{\ominus} = \sum S_P^{\ominus} - \sum S_R^{\ominus}$

$= [2\times(+27) + 3(+214)] - [(+90) + 3(+198)]$

$= 696 - 684$

$= +12\ JK^{-1}\,mol^{-1}$

(iii) $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

$= -43.6 - \left(298\times\frac{12}{1000}\right)$

$= -47.2\ kJ\,mol^{-1}$

(c) (iii) Temperature is in K. $S^{\ominus}$ is divided by 1000 to convert in kJ mol^{-1}.

(iv) The reaction has high E_a and high temperature. This will speed up the rate of reaction.

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Question 22

(a) Complete Table 3.1 by placing **one** tick (✓) in each row to indicate the sign of each type of energy change under standard conditions.

Table 3.1

energy change	always positive	always negative	can be either negative or positive
bond energy			
enthalpy change of atomisation			
enthalpy change of formation			

[1]

(b) Define standard enthalpy change of atomisation. [2]

(c) Table 3.2 shows some energy changes.

Table 3.2

energy change	value / kJ mol^{-1}
standard enthalpy change of atomisation of silver	+285
first ionisation energy of silver	+731
second ionisation energy of silver	+2074
bond energy of O=O	+496
bond energy of O–O	+150
first electron affinity of oxygen	–141
second electron affinity of oxygen	+798
first ionisation energy of oxygen	+1314
standard enthalpy change of formation of silver oxide, $Ag_2O(s)$	–31

Calculate the lattice energy, $\Delta H^{\ominus}_{latt}$, of $Ag_2O(s)$ using relevant data from Table 3.2.

It may be helpful to draw a labelled energy cycle.

Show your working. [3]

(d) Suggest the trend in the magnitude of the lattice energies of the silver compounds Ag_2S, Ag_2O and Ag_2Se.

Explain your answer.

....
least exothermic most exothermic

[2]

(e) Silver sulfite, $Ag_2SO_3(s)$, is sparingly soluble in water.

(i) Give an expression for the solubility product, K_{sp}, of Ag_2SO_3. [1]

Learning CORNER

(ii) Calculate the equilibrium concentration of Ag^+ in a saturated solution of Ag_2SO_3 at 298 K.

[K_{sp} : Ag_2SO_3, 1.50×10^{-14} mol^3 dm^{-9} at 298 K] [1]

(f) The standard enthalpy change of solution, $\Delta H^{\ominus}_{sol}$, of $AgNO_3(s)$ in water is +22.6 kJ mol^{-1}.

Suggest how the feasibility of dissolving $AgNO_3(s)$ in water changes with temperature.

Explain your answer. [2]

[J23/P4/Q3]

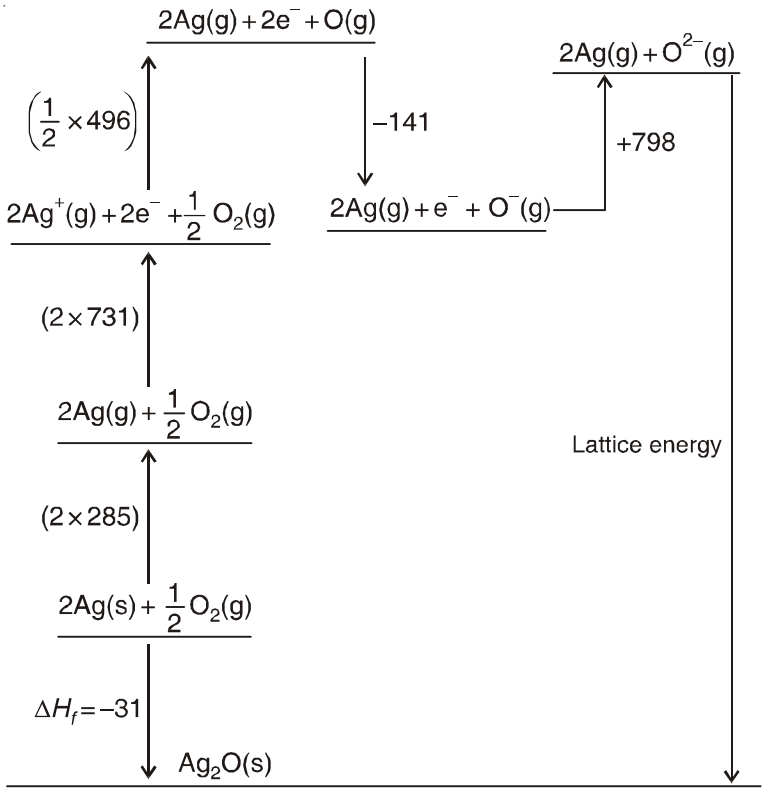
Suggested Solution:

(a)

energy change	always positive	always negative	can be either negative or positive
bond energy	✓		
enthalpy change of atomisation	✓		
enthalpy change of formation			✓

(b) The Enthalpy change when one mole of a gaseous atom is produced from its elements under standard states and conditions of 298 K and 1 atm.

(c)



$$-31 = 2(285) + 2(731) + (\tfrac{1}{2} \times 496) + (-141) + 798 + x$$

$$-31 = 2937 + x$$

$$x = -2968$$

$\therefore$ Lattice energy, $\Delta H^{\ominus}_{latt}$ of $Ag_2O(s) = -2968$ kJ mol^{-1}

(d)

AgSe	Ag_2S	Ag_2O
least exothermic		most exothermic

The radius of the anion increases down the group,thus, Se^{2-} has the largest radius while O^{2-} has the smallest radius. As the radius increases, the charge density decreases over the anion which weakens the ionic bond and the lattice energy becomes less exothermic.

(e) (i) $K_{sp} = [Ag^+]^2[SO_3{}^{2-}]$

(ii) $K_{sp} = [Ag^+]^2[SO_3{}^{2-}]$

$[Ag^+] = [SO_3{}^{2-}]$. Let, $Ag^+ = x$

$$\Rightarrow K_{sp} = x^3$$

$$\Rightarrow x^3 = \frac{1.5 \times 10^{-14}}{4}$$

$$\Rightarrow x = \sqrt[3]{\frac{1.5 \times 10^{-14}}{4}} = 1.55 \times 10^{-5}$$

$\therefore [Ag^+] = (1.55 \times 10^{-5}) \times 2 = 3.11 \times 10^{-5}$ mol dm^{-3}

(f) On increasing the temperature, the feasibility of dissolving $AgNO_3(s)$ in water increases. This is because the $T\Delta S$ term becomes more negative as the temperature increases and ΔS becomes more positive. As ΔH is already positive, increasing the temperature makes the ΔG more negative, increasing the feasibility.

learning CORNER

Question 23

(a) Define lattice energy, ΔH_{latt}. [2]

(b) State and explain the main factors that affect the magnitude of lattice energies. [2]

(c) Table 1.1 shows some energy changes.

Table 1.1

energy change	value / kJ mol^{-1}
standard enthalpy change of atomisation of potassium	+89
first ionisation energy of potassium	+419
second ionisation energy of potassium	+3070
standard enthalpy change of atomisation of sulfur	+279
S–S bond energy	+265
first ionisation energy of sulfur	+1000
second ionisation energy of sulfur	+2260
first electron affinity of sulfur	–200
second electron affinity of sulfur	+640
standard enthalpy change of formation of potassium sulfide, $K_2S(s)$	–381

(i) Born–Haber cycles can be used to determine the lattice energies of ionic compounds.
Complete the Born–Haber cycle in Fig. 1.1 for potassium sulfide, $K_2S(s)$.
Include state symbols for all of the species. [3]

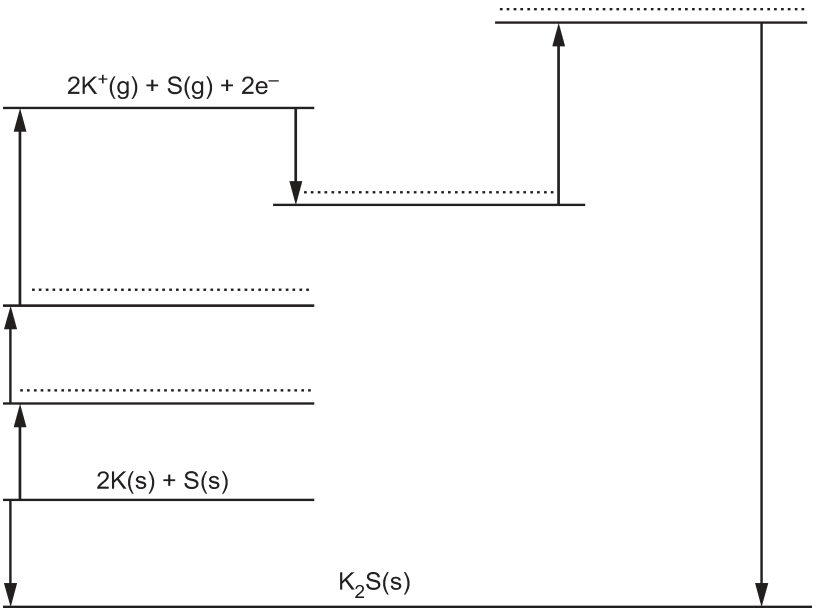


Fig. 1.1

(ii) Calculate the lattice energy, $\Delta H^{\ominus}_{latt}$, of $K_2S(s)$ using relevant data from Table 1.1. Show your working. [2]

[J24/P4/Q1 b,c,d]

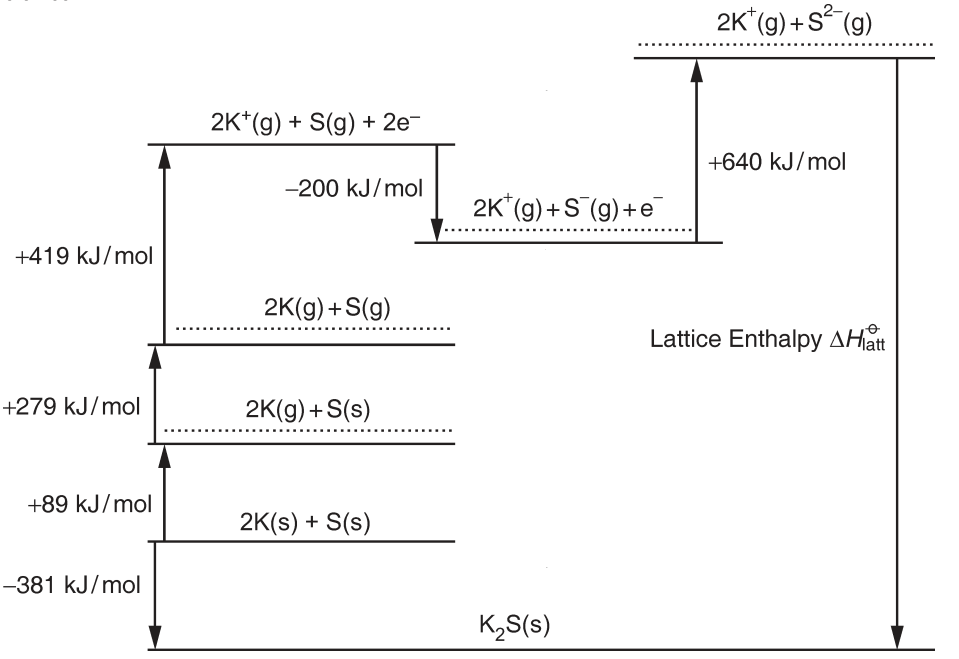
Suggested Solution:

Learning CORNER

(a) Lattice enthalpy is the energy change when 1 mol of a solid ionic compound is formed from its gaseous ions under standard conditions.

(b) The two main factors that influence the magnitude of lattice energies are ionic charge and ionic radius. With increasing ionic radius, the distance between oppositely charged ions increases, making the lattice energy less exothermic. With higher ionic charge, the electrostatic forces between ions increases, making the lattice energy more exothermic.

(c) (i)



(ii) Using the values labelled on the haber-cycle:

$$-381 = (2 \times 89) + 279 + (2 \times 419) + (-200) + 640 + \Delta H^{\ominus}_{latt}$$

$$\Delta H^{\ominus}_{latt} = -2116 \text{ kJ mol}^{-1}$$

Question 24

(a) Carbon disulfide, CS_2, is flammable and reacts readily with oxygen, as shown in reaction 1.

reaction 1 $\quad CS_2(g) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g)$

Table 3.1 shows the standard enthalpy of formation, $\Delta H^{\ominus}_f$, and the standard entropy, $S^{\ominus}$, for some substances.

Table 3.1

	$CS_2(g)$	$O_2(g)$	$CO_2(g)$	$SO_2(g)$
$\Delta H^{\ominus}_f$ / kJ mol^{-1}	116.7	0.0	–393.5	–296.8
$S^{\ominus}$ / J K^{-1} mol^{-1}	237.8	205.2	213.8	248.2

Learning CORNER

Calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, in kJ mol^{-1}, for reaction 1 at 25 °C. [3]

(b) Carbon disulfide reacts with chlorine to form tetrachloromethane, as shown in reaction 2.

reaction 2 $CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2$ $\Delta H^{\ominus} = -261.6$ kJ mol^{-1}

$\Delta S^{\ominus} = -365.5$ J K^{-1} mol^{-1}

Calculate the maximum temperature, in K, for reaction 2 to be feasible. [2]

[J24/P4/Q3]

Suggested Solution:

(a) Change in Entropy = Entropy of products – Entropy of reactants

$\Delta S^{\ominus} = (213.8 + (2 \times 248.2)) - (237.8 + (3 \times 205.2))$

$= -143.2$ J K^{-1} mol^{-1}

Change in Enthalpy

= Enthalpy of formation of products – Enthalpy of formation of reactants

$\Delta H_f^{\ominus} = (-393.5 + (2 \times -296.8)) - (116.7) = -1103.8$ kJ mol^{-1}

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

$$\Delta G^{\ominus} = -1103.8 - \left((25 + 273) \times \frac{-143.2}{1000} \right)$$

$= -1061.2$ kJ mol^{-1}

(b) For the reaction 2 to be feasible the change in gibbs free energy needs to be ≤ 0

$\Delta G^{\ominus} = \Delta H^{\ominus} + T\Delta S^{\ominus}$

$$0 = -261.6 + T\left(\frac{-365.5}{1000} \right) \quad \Rightarrow \quad T = 715.7 \text{ K}$$

learning CORNER

Question 25

(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.

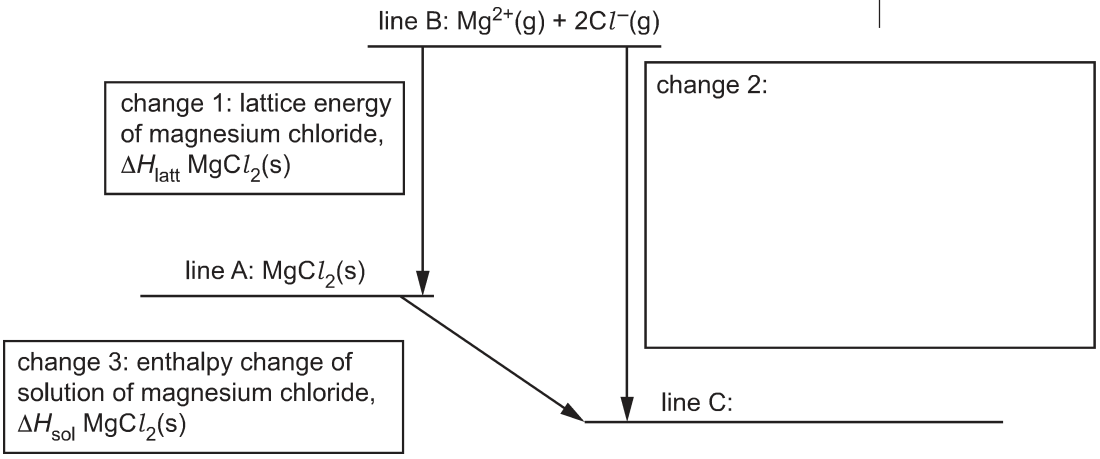


Fig. 2.1

(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

[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 JK^{-1} mol^{-1}.

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

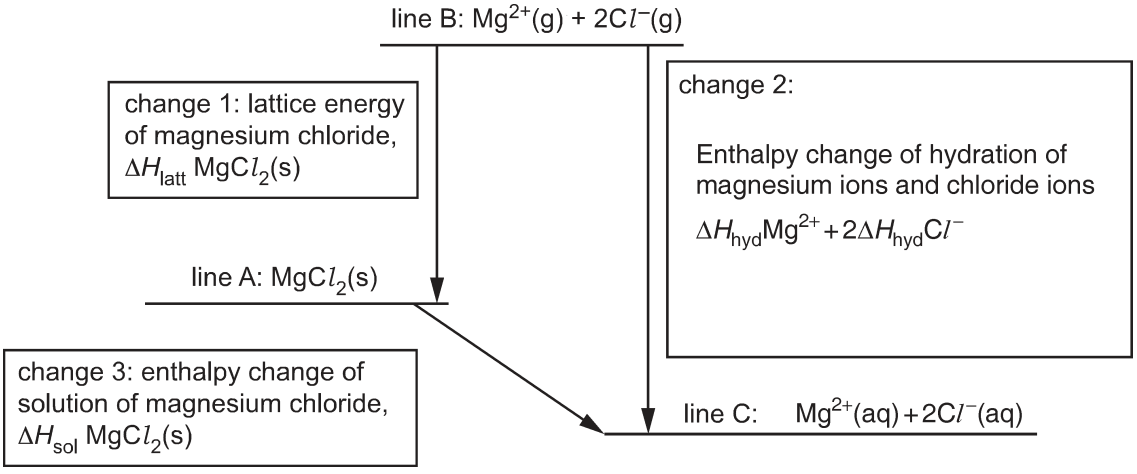
[N24/P4/Q2]

Learning CORNER

Suggested Solution:

(a) The enthalpy change of hydration becomes more exothermic from Na^+ to Mg^{2+} to Al^{3+} because as the ionic charge increases and the ionic radius decreases, the ions attract water molecules more strongly.

(b) (i) & (ii)



(iii) $\Delta H_{sol} + \Delta H_{latt} = \Delta H_{hyd}\ Mg^{2+} + 2\Delta H_{hyd}\ Cl^-$

$-155 + \Delta H_{latt} = (-1920) + (2 \times -364)$

$\Delta H_{latt} = -2493\ kJ\ mol^{-1}$

(c) Entropy is the number of arrangements of particles and the energy distribution of the system.

(d) $\Delta G = \Delta H - T\Delta S$

$= 26000 - (25 + 273)(52) = 10504\ J\ mol^{-1}$

$= 10.5\ kJ\ mol^{-1}$

(e) (i) As the value of the Gibbs free energy change is positive, **Z** is not soluble in water.

(ii) With increased temperature, the Gibbs free energy change will become less positive and so it will become more soluble.

(e) (ii) At 95 °C,

$\Delta G = 26000 - (95 + 273)(52)$

$= 6864\ J\ mol^{-1}$

Topic 11

Nitrogen Compounds

11.1 Primary and secondary amines

Learning outcomes

Candidates should be able to:

1 recall the reactions (reagents and conditions) by which primary and secondary amines are produced:
   (a) reaction of halogenoalkanes with NH_3 in ethanol heated under pressure
   (b) reaction of halogenoalkanes with primary amines in ethanol, heated in a sealed tube / under pressure
   (c) the reduction of amides with LiA*l*H_4
   (d) the reduction of nitriles with LiA*l*H_4 or H_2 / Ni

2 describe the condensation reaction of ammonia or an amine with an acyl chloride at room temperature to give an amide

3 describe and explain the basicity of aqueous solutions of amines

11.2 Phenylamine and azo compounds

Learning outcomes

Candidates should be able to:

1 describe the preparation of phenylamine via the nitration of benzene to form nitrobenzene followed by reduction with hot Sn/concentrated HC*l*, followed by NaOH(aq)

2 describe:
   (a) the reaction of phenylamine with Br_2(aq) at room temperature
   (b) the reaction of phenylamine with HNO_2 or $NaNO_2$ and dilute acid below 10 °C to produce the diazonium salt; further warming of the diazonium salt with H_2O to give phenol

3 describe and explain the relative basicities of aqueous ammonia, ethylamine and phenylamine

4 recall the following about azo compounds:
   (a) describe the coupling of benzenediazonium chloride with phenol in NaOH(aq) to form an azo compound
   (b) identify the azo group
   (c) state that azo compounds are often used as dyes
   (d) that other azo dyes can be formed via a similar route

11.3 Amides

Learning outcomes

Candidates should be able to:

1 recall the reactions (reagents and conditions) by which amides are produced:
   (a) the reaction between ammonia and an acyl chloride at room temperature
   (b) the reaction between a primary amine and an acyl chloride at room temperature

2 describe the reactions of amides:
   (a) hydrolysis with aqueous alkali or aqueous acid
   (b) the reduction of the CO group in amides with $LiAlH_4$ to form an amine

3 state and explain why amides are much weaker bases than amines

11.4 Amino acids

Learning outcomes

Candidates should be able to:

1 describe the acid / base properties of amino acids and the formation of zwitterions, to include the isoelectric point

2 describe the formation of amide (peptide) bonds between amino acids to give di- and tripeptides

3 interpret and predict the results of electrophoresis on mixtures of amino acids and dipeptides at varying pHs (the assembling of the apparatus will not be tested)

TOPIC opening .....

Question 1

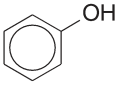
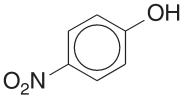
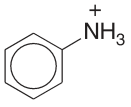
(a) (i) Write the equation for a reaction in which ethylamine, $C_2H_5NH_2$, acts as a Brønsted-Lowry base.

(ii) Ammonia, ethylamine and phenylamine, $C_6H_5NH_2$, are three nitrogen-containing bases.
Place these three compounds in order of basicity, with the most basic first.

most basic		least basic

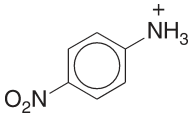
(iii) Explain why you have placed the three compounds in this order. [4]

(b) (i) Write an equation for a reaction in which phenol, C_6H_5OH, acts as a Brønsted-Lowry acid.
The pK_a values for phenol, 4-nitrophenol and the phenylammonium ion are given in the table.

compound	pK_a
	10.0
	7.2
	4.6

(ii) Suggest an explanation for the difference in the pK_a values of phenol and nitrophenol.

(iii) Using the information in the table opposite, predict which of the following pK_a values is the most likely for the 4-nitrophenylammonium ion.

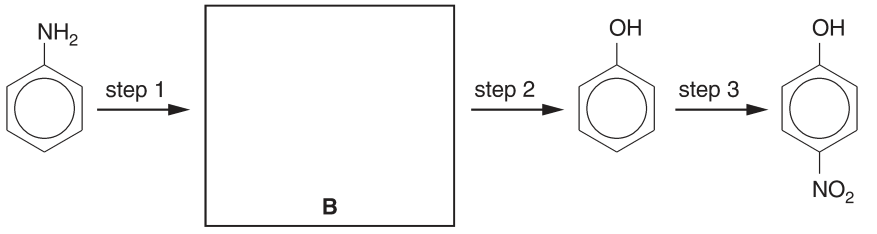


Place a tick (✓) in the box beside the value you have chosen.

pK_a	
1.0	
4.5	
7.0	
10.0	

(iv) Explain your answer to part **(iii)**. [5]

(c) Phenylamine can be converted to 4-nitrophenol by the following steps.



(i) Suggest the identity of intermediate **B** by drawing its structure in the box above.

(ii) Suggest reagents and conditions for the three steps in the above scheme.

	reagent(s)	conditions
step 1		
step 2		
step 3		

[5]

[N11/P4/Q4]

Learning CORNER

Suggested Solution:

(a) (i) $C_2H_5NH_2 + HA \rightarrow C_2H_5NH_3^+ + A^-$

(ii)

most basic		least basic
Ethylamine	**Ammonia**	**Phenylamine**

(iii) Ethylamine is more basic than Ammonia due to the electron donating ethyl group. Phenylamine is less basic than Ammonia due to delocalisation of lone pair of nitrogen over ring.

(b) (i) $C_6H_5OH + OH^- \rightarrow C_6H_5O^- + H_2O$

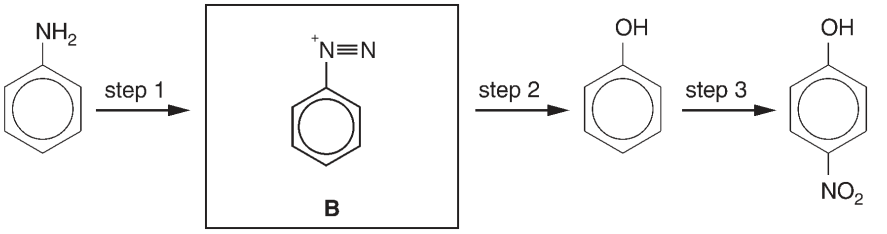
(ii) pK_a of nitrophenol is smaller than phenol as nitrophenol is a stronger acid and dissociates more than phenol. This is because the anionic charge is spread out more over the NO_2 group.

(iii)

pK_a	
1.0	✓
4.5	
7.0	
10.0	

(iv) The Nitro group, which is an electron withdrawing group, will increase the acidity of the 4-nitrophenylammonium ion, due to which the value of K_a will increase. Increasing the K_a value will decrease the pK_a value.

(c) (i)



(ii)

	reagent(s)	conditions
step 1	**HNO_2**	**temperature < 10°C**
step 2	**H_2O**	**heat at temperature > 10°C**
step 3	**HNO_3**	**dilute**

Question 2

One of the key areas of investigation in understanding the structures of polypeptides and proteins is the sequence of amino acids that make up the polypeptide chains.

(a) One of the methods used to determine the amino acids present in a polypeptide chain is electrophoresis.
Sketch and label the apparatus used to carry out electrophoresis. [4]

(b) In electrophoresis, different amino acids move in different directions and at different speeds.

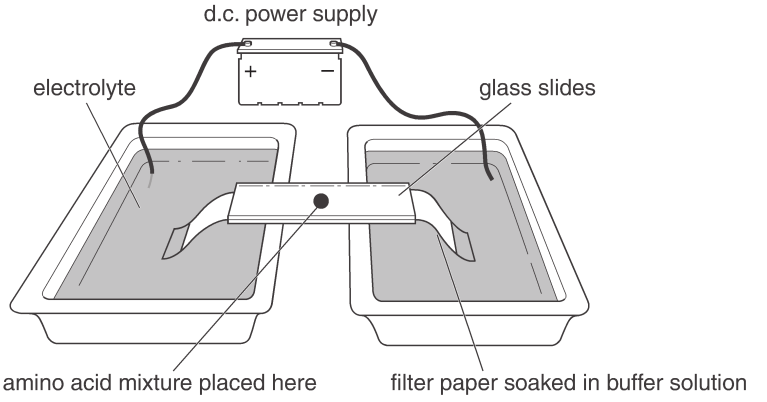
(i) What factors determine the *direction of travel* of an amino acid?

(ii) What factors determine the *speed of movement* of an amino acid? [3]

[N11/P4/Q7]

Suggested Solution:

(a)



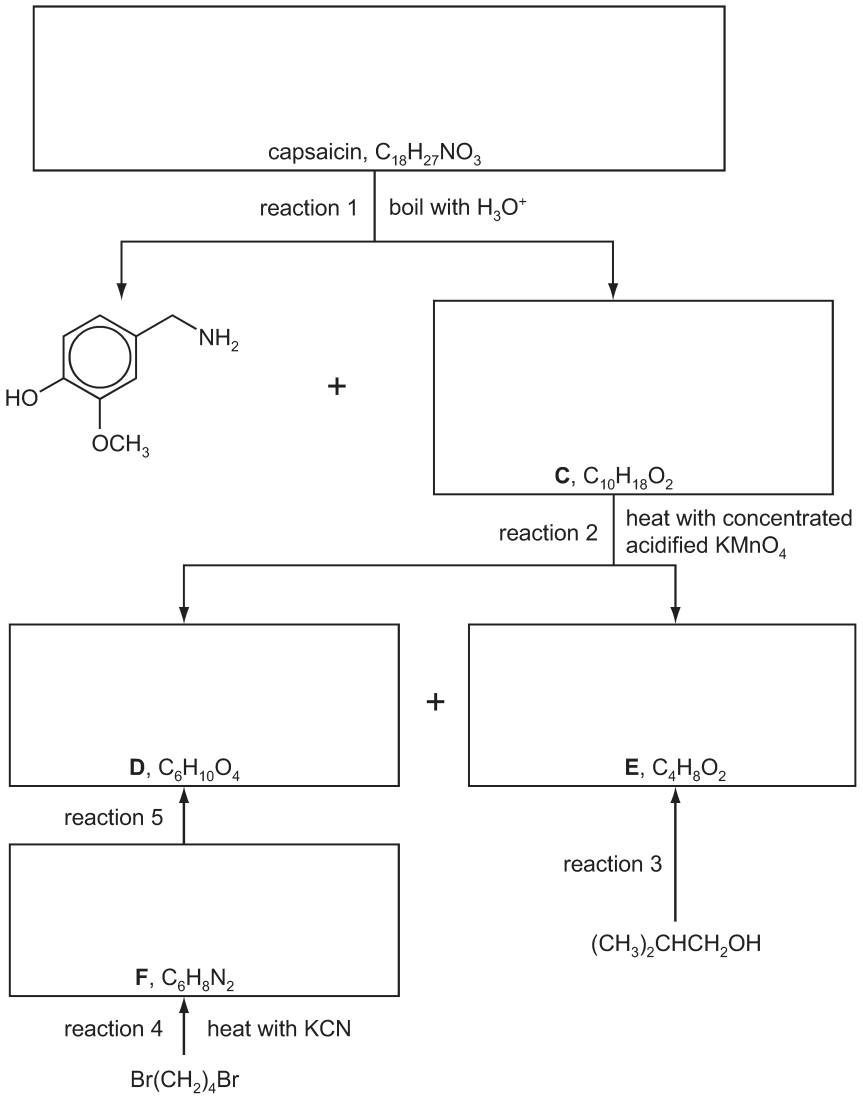
(b) (i) The pH of the buffer and the charge on the amino acid species determines the direction of travel of an amino acid.

(ii) The magnitude of charge of the amino acid species, the size of the amino acid species, the voltage applied, and the temperature determine the speed of movement of the amino acid.

learning CORNER

Question 3

The compound responsible for the hot taste of chilli peppers is capsaicin. Its molecular structure can be deduced by the following reaction scheme.



Compounds **C**, **D** and **E** all react with Na_2CO_3(aq).

Answer the following questions.

(a) Suggest reagents and conditions for reaction 3. [1]

(b) What *type of reaction* is reaction 4? [1]

(c) Suggest reagents and conditions for reaction 5. [1]

(d) Name the functional group in **C** that has reacted with hot concentrated acidified $KMnO_4$. [1]

(e) Suggest the name of the functional group in capsaicin that has reacted in reaction 1. [1]

(f) Work out structures for compounds **C**–**F** and capsaicin, and draw their structural formulae in the boxes opposite. [5]

[N12/P4/Q4]

Learning CORNER

Suggested Solution:

(a) $K_2Cr_2O_7$ / H^+ + heat under reflux.

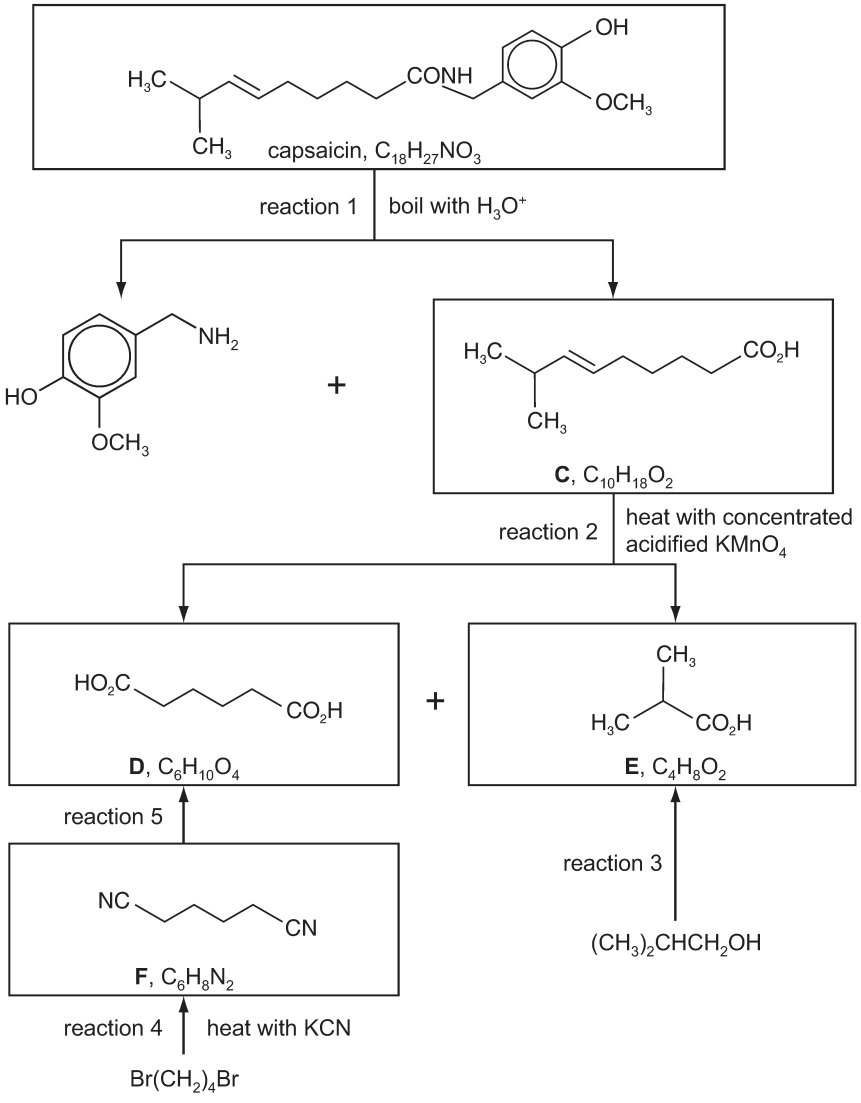
(b) Nucleophilic substitution

(c) Heat under reflux + aqueous HCl

(d) Alkene

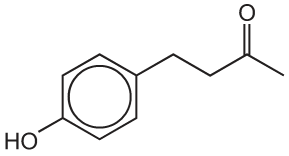
(e) Amide

(f)



Question 4

Compound **G** is a naturally occurring aromatic compound that is present in raspberries.



compound **G**

Learning CORNER

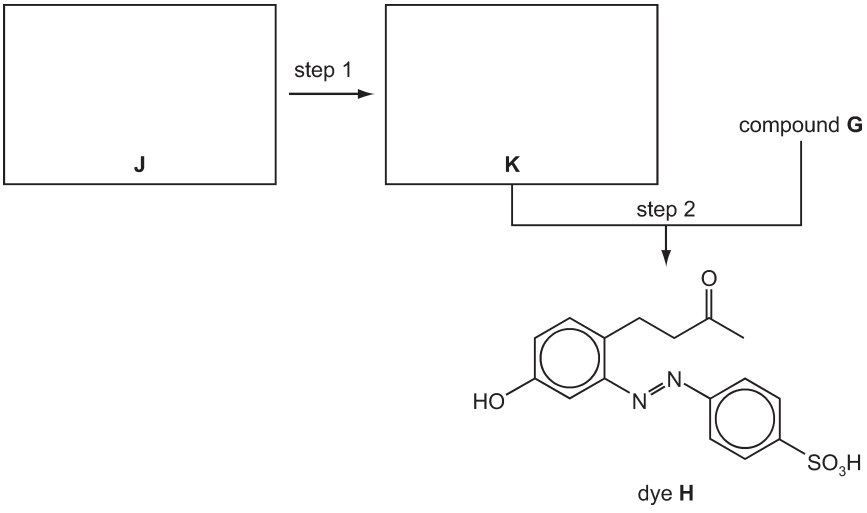
(a) Identify the functional groups present in compound **G**. [2]

(b) Complete the following table with information about the reactions of the three stated reagents with compound **G**.

reagent	observation	structure of organic product	type of reaction
sodium metal			
aqueous bromine			
aqueous alkaline iodine			

[8]

(c) The dye **H** can be made from compound **G** by the route shown below.



dye **H**

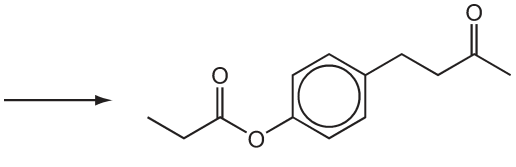
(i) Draw the structures of the amine **J** and the intermediate **K** in the boxes above.

(ii) Suggest reagents and conditions for

step 1,

step 2. [5]

(d) Suggest a reaction scheme by which compound **G** and propanoic acid could be converted into compound **L**.



compound **L** [3]

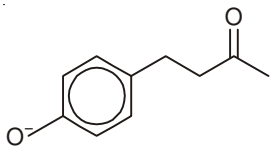
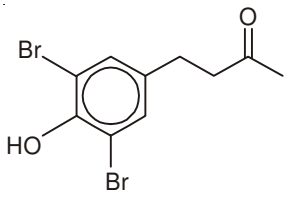
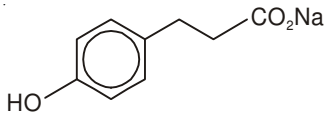
[N12/P4/Q5]

Suggested Solution:

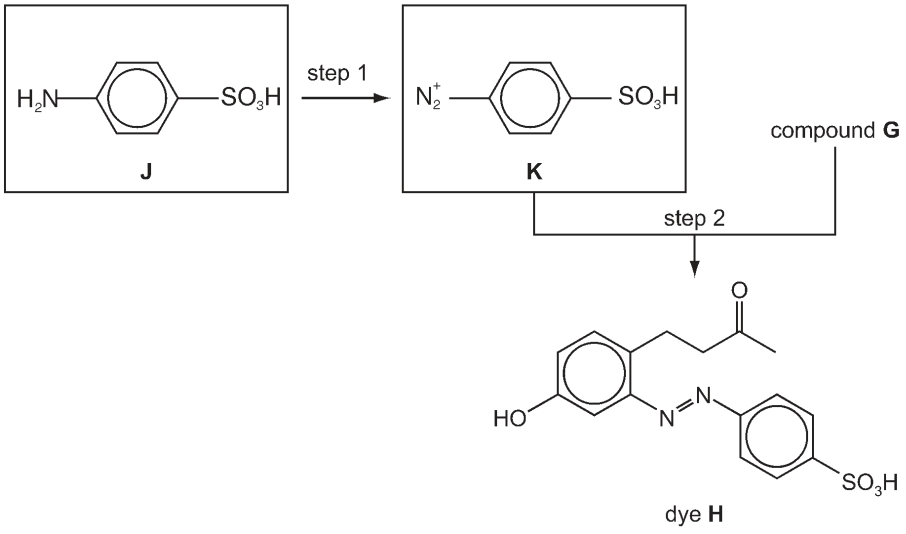
Learning CORNER

(a) Phenol and Ketone

(b)

reagent	observation	structure of organic product	type of reaction
sodium metal	**effervescence occurs**		**redox**
aqueous bromine	**aqueous bromine decolourises**		**electrophilic substitution**
Aqueous alkaline iodine	**yellow precipitate is produced**		**oxidation**

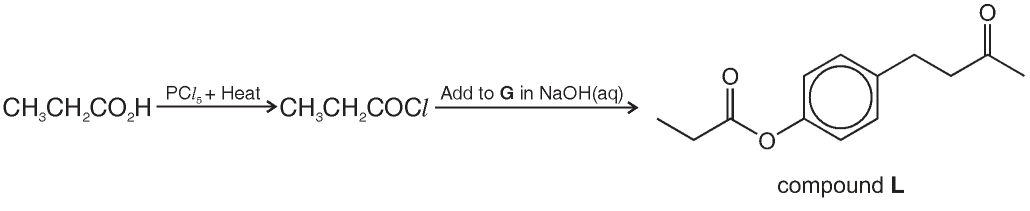
(c) (i)



(ii) Step 1: reagents: $NaNO_2$ + HC*l*
condition: at a temperature lesser than 10 °C

Step 2: reagents: K and G
conditions: aqueous NaOH

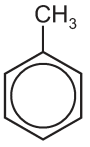
(d)



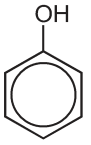
Learning CORNER

Question 5

(a) Describe the reagents and conditions required to form a nitro compound from the following.

(i) methylbenzene 

.....

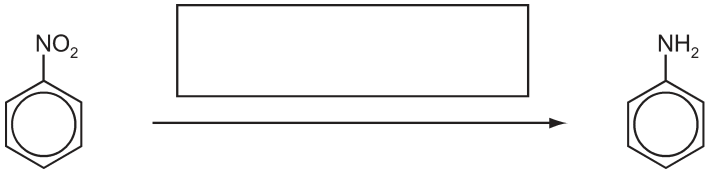
(ii) phenol 

.....

[3]

(b) Draw the structure of the intermediate organic ion formed during the nitration of benzene. [1]

(c) In the box over the arrow below, write the reagents needed to convert nitrobenzene into phenylamine.

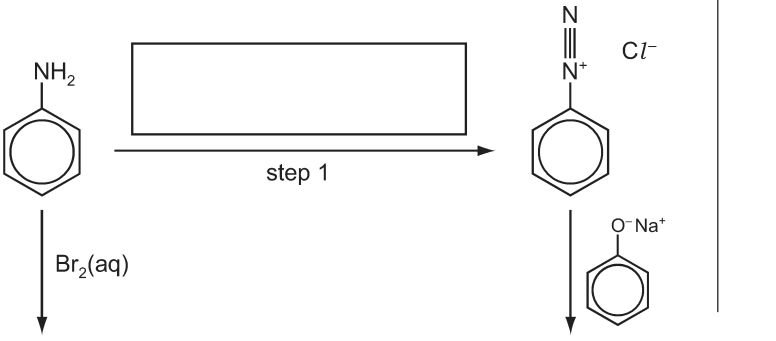


[1]

(d) Phenylamine can be converted into the organic compounds **A** and **B**.

(i) Suggest the structural formulae of **A** and **B** in the boxes below.

(ii) Suggest suitable reagents and conditions for step 1, and write them in the box over the arrow.



A **B**

[3]

learning CORNER

(e) When phenylamine is treated with propanoyl chloride a white crystalline compound, **C**, $C_9H_{11}NO$, is formed.

(i) Name the functional group formed in this reaction.

(ii) Calculate the percentage by mass of nitrogen in **C**.

(iii) Draw the structural formula of **C**. [3]

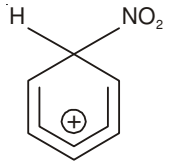
[J13/P4/Q3]

Suggested Solution:

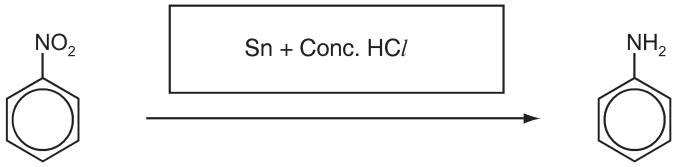
(a) (i) methylbenzene: Conc. HNO_3 , Conc. H_2SO_4 and warm.

(ii) phenol: HNO_3(aq), room temperature.

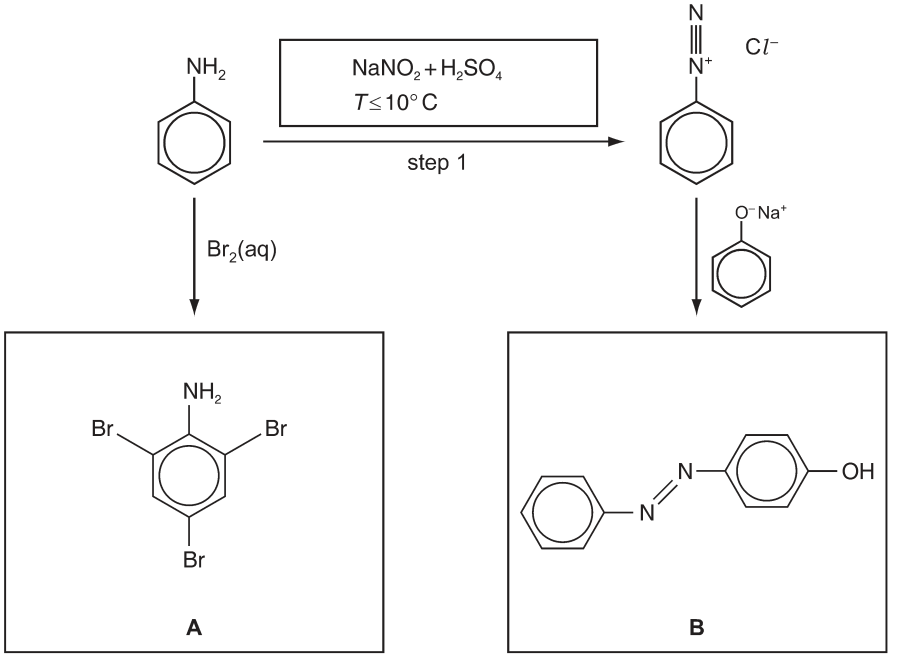
(b)



(c)



(d) (i) & (ii)

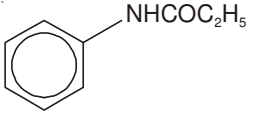


(e) (i) amide

(ii) M_r of $C_9H_{11}NO = (12\times9)+(1\times11)+14+16 = 149$

percentage by mass of nitrogen in $C_9H_{11}NO = \frac{14}{149}\times100 = 9.4\%$

(iii)



Learning CORNER

Question 6

Electrophoresis is a technique which can be used to separate amino acids or peptide fragments present in a mixture.

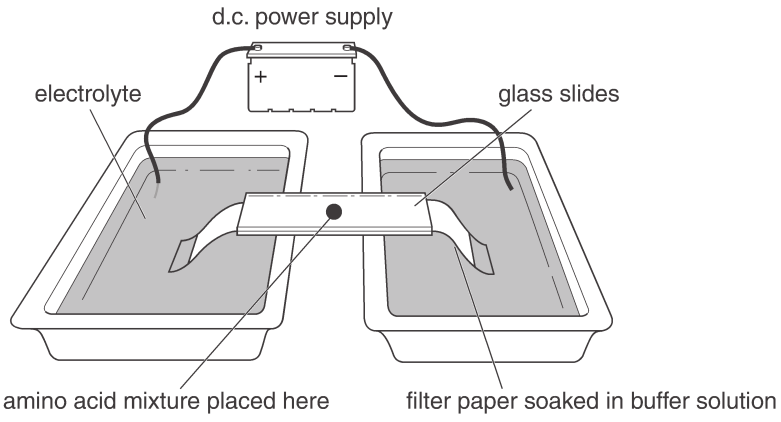
(a) Draw a diagram to show the apparatus used to carry out electrophoresis. You should label each of the relevant parts of the apparatus. [4]

(b) How far an amino acid will travel during electrophoresis depends on the pH of the solution. For a given potential difference, state **two other** factors that will affect how far a given amino acid travels in a fixed time during electrophoresis. [2]

[N13/P4/Q7 (a,b)]

Suggested Solution:

(a)



(b) 1. Mr of the amino acid species.
2. Charge on the amino acid species.

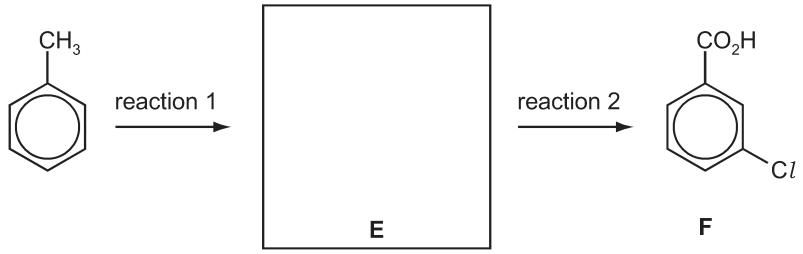
Question 7

(d) When methylbenzene is nitrated, 4-nitromethylbenzene is formed, but when benzoic acid is nitrated, 3-nitrobenzoic acid is produced.

Consider the following synthesis of 3-chlorobenzoic acid, **F**, from methylbenzene.

Use the information given above to suggest

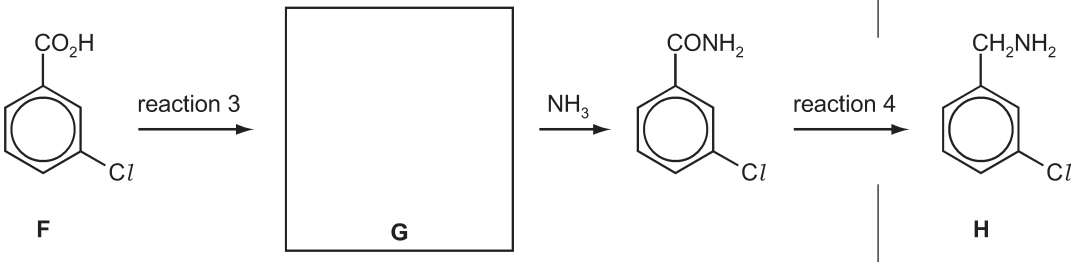
- the structure of the intermediate **E**,
- the reagents and conditions needed for reactions 1 and 2.



[3]

(e) Consider the following synthesis of 3-chlorophenylmethylamine, **H**, from **F**. Suggest

- the structure of the intermediate **G**,
- the reagents for reactions 3 and 4.



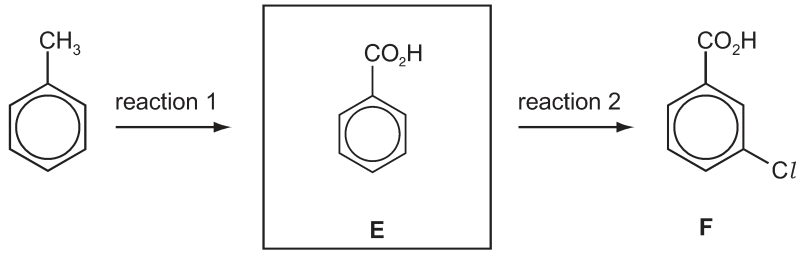
F **G** **H**

[3]

[J14/P4/Q4 (d,e)]

Suggested Solution:

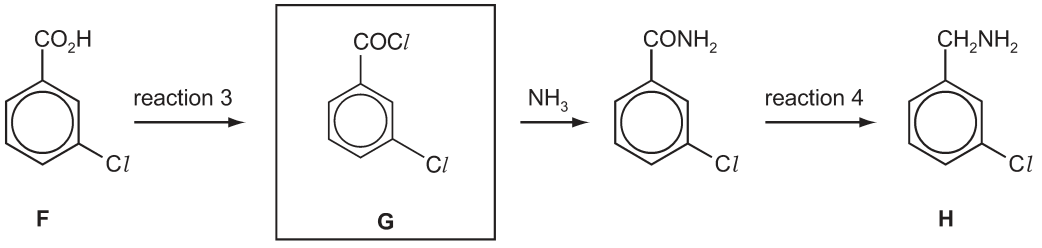
(d)



reagents and conditions for reaction 1: Heat with Acidified $KMnO_4$

reagents and conditions for reaction 2: Heat with Cl_2 + $AlCl_3$

(e)



F **G** **H**

reagents for reaction 3: $SOCl_2$

reagents for reaction 4: $LiAlH_4$

Question 8

(a) Organohalogen compounds can undergo hydrolysis.

$$R{-}Cl + H_2O \rightarrow R{-}OH + HCl$$

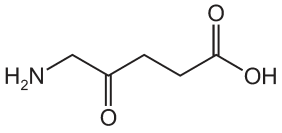
State the relative rates of hydrolysis of the following compounds.

$CH_3CH_2CH_2Cl$ CH_3CH_2COCl C_6H_5Cl

Explain your answer. [3]

Learning CORNER

(b) Aminolaevulinic acid is involved in the synthesis of haemoglobin and chlorophyll.

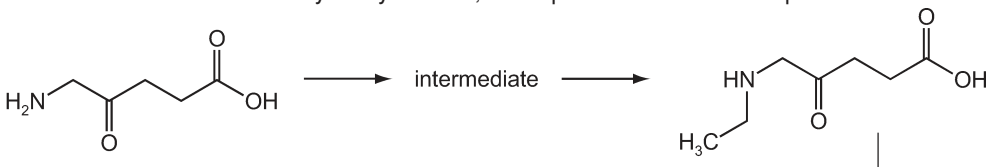


aminolaevulinic acid

Name the **three** functional groups in aminolaevulinic acid. [2]

(c) Aminolaevulinic acid reacts readily with bromoethane.

(i) Show the mechanism of the **first step** of this reaction on the diagram. Include all necessary curly arrows, lone pairs and relevant dipoles.

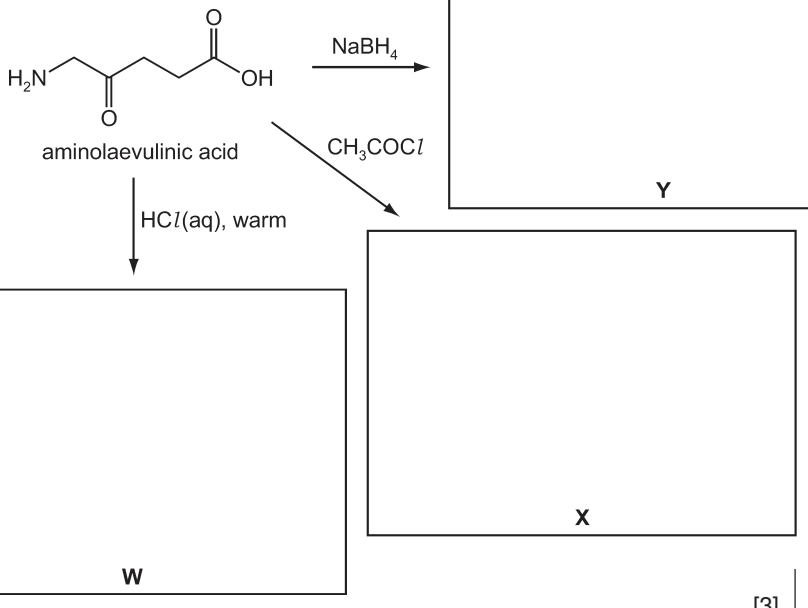


$H_3C—CH_2—Br$

(ii) Name the mechanism in **(c)(i)**.

(iii) Identify the non-organic product formed in this reaction. [5]

(d) Three reactions of aminolaevulinic acid are shown. Draw the structures of the products **W**, **X** and **Y** in the boxes below.



[3]

(e) Aminolaevulinic acid can undergo polymerisation.
Draw the structure of the polymer showing **two** repeat units. The linkages between the monomer units should be shown fully displayed. [2]

[N14/P4/Q5]

Learning CORNER

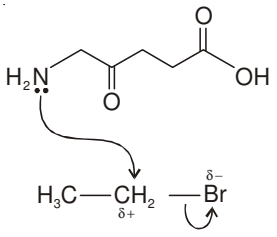
Suggested Solution:

(a) Relative rates of Hydrolysis: $CH_3CH_2COCl > CH_3CH_2CH_2Cl > C_6H_5Cl$.
The C—C*l* bond strength in CH_3CH_2COCl is weakest as the presence of two highly electronegative O and C*l* atoms make the carbon atom in —COC*l* highly electron deficient.

C_6H_5Cl is very difficult to hydrolyse since the C—C*l* bond is part of a delocalized system.

(b) Ketone, Amine, Carboxylic acid.

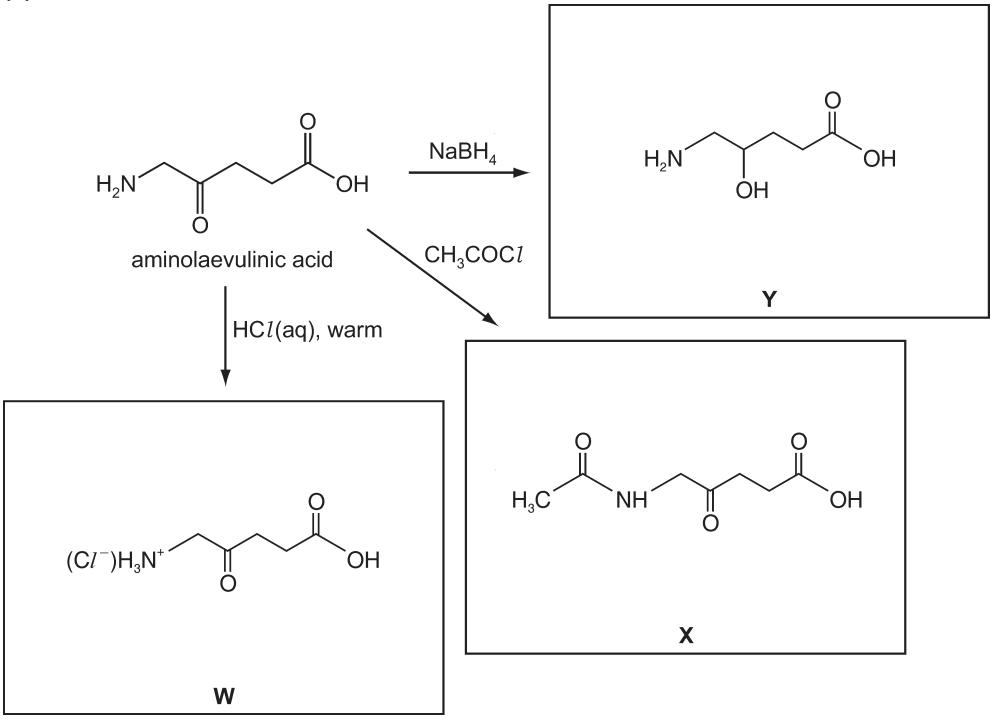
(c) (i)



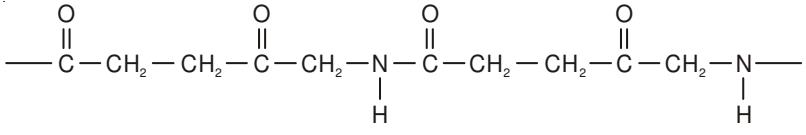
(ii) Nucleophilic substitution.

(iii) Hydrogen Bromide.

(d)



(e)



Learning CORNER

Question 28

(a) State the reactants and conditions for two different types of reactions that both produce diethylamine, $CH_3CH_2NHCH_2CH_3$. [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

[3]

(c) Phenylamine reacts with $HNO_2(aq)$ at 4 °C to form compound **P**. Compound **P** reacts with phenol under alkaline conditions at 4 °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**. [2]

(d) $CH_3CH_2NHCH_2CH_3$ reacts with ethanoyl chloride, CH_3COCl, to give the amide N,N-diethylethanamide, $CH_3CON(C_2H_5)_2$.

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

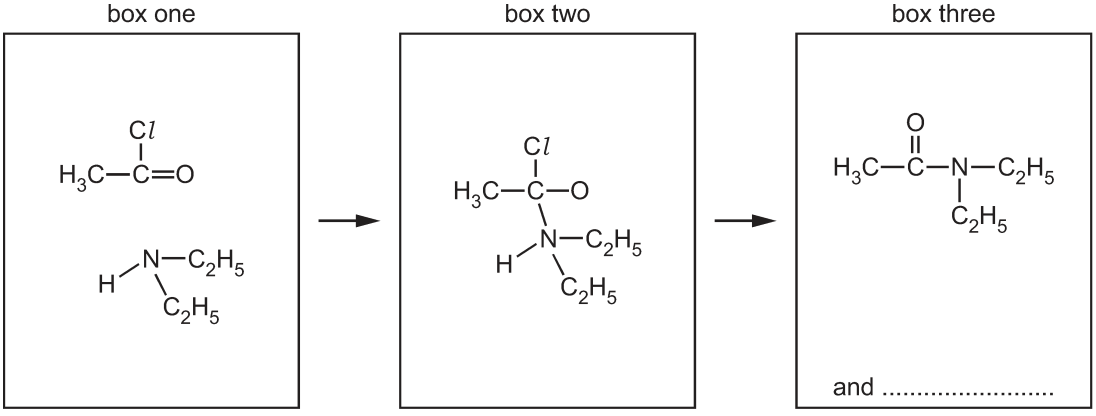


Fig. 9.1

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

- all relevant dipoles (δ+ and δ–) 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]

[N23/P4/Q9]

Suggested Solution:

Learning CORNER

(a) Reaction one: React chloroethane with ethylamine in the presence of heat, pressure and ethanol.

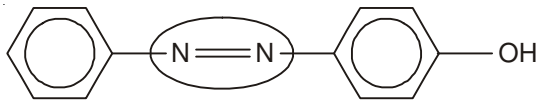
Reaction two: N-ethyl ethanamide with $LiAlH_4$.

(b)

Phenyl amine	Ammonia	diethylamine
least basic		most basic

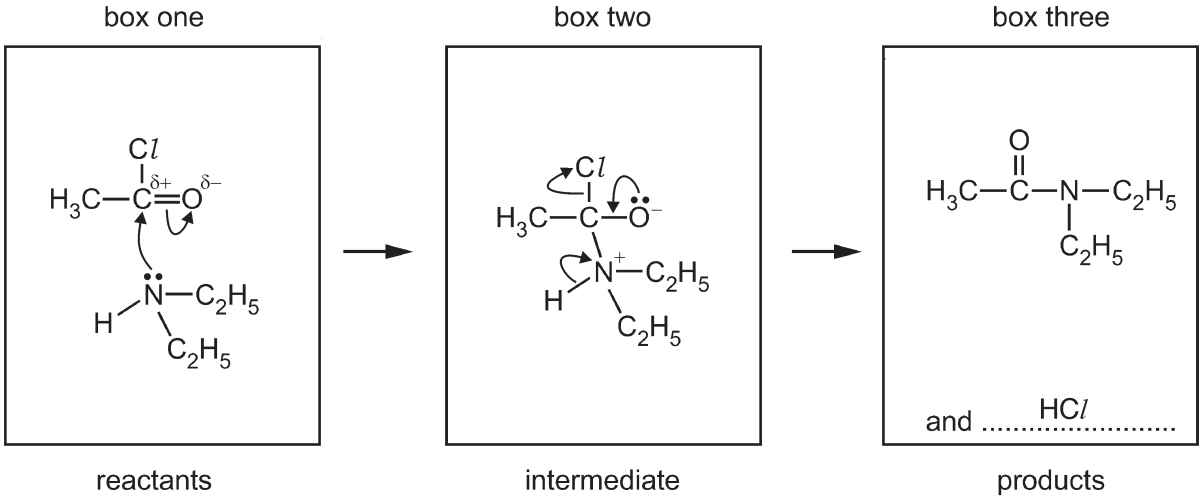
Explanation: The relative basicities of these compounds is decided based on the availability of the lone pair on Nitrogen to receive H^+. In Phenylamine, the lone pair is delocalised into the ring which is why it is the least basic. In diethylamine, the ethly groups are electron donating which makes the lone pair more available, making it most basic of the three.

(c) compound **Q**:



An azo compound can be used: as a dye / coloring.

(d) (i)



(ii) Addition-elimination.

learning CORNER

Question 29

(a) State the relative basicities of phenylamine, $C_6H_5NH_2$, benzylamine, $C_6H_5CH_2NH_2$, and ammonia, NH_3, in aqueous solution. Explain your answer.

..... > ..... > .....
most basic least basic

[3]

(b) An excess of $Br_2(aq)$ is added to separate samples of $C_6H_5NH_2$ and benzene, C_6H_6.

(i) $C_6H_5NH_2$ reacts readily with $Br_2(aq)$ to form organic product **M**. State the expected observations for this reaction. Draw the structure of **M**. [2]

(ii) C_6H_6 does **not** react with $Br_2(aq)$.
Suggest why $Br_2(aq)$ reacts with $C_6H_5NH_2$ but **not** with C_6H_6. [2]

(c) Explain why benzamide, $C_6H_5CONH_2$, is a much weaker base than ammonia, NH_3. [1]

(d) $C_6H_5CONH_2$ is formed by reacting benzoyl chloride, C_6H_5COCl, with NH_3.

Complete the mechanism in Fig. 8.1 for the reaction of C_6H_5COCl with NH_3.

Include all relevant lone pairs of electrons, curly arrows, charges and dipoles. Draw the structure of the organic intermediate.

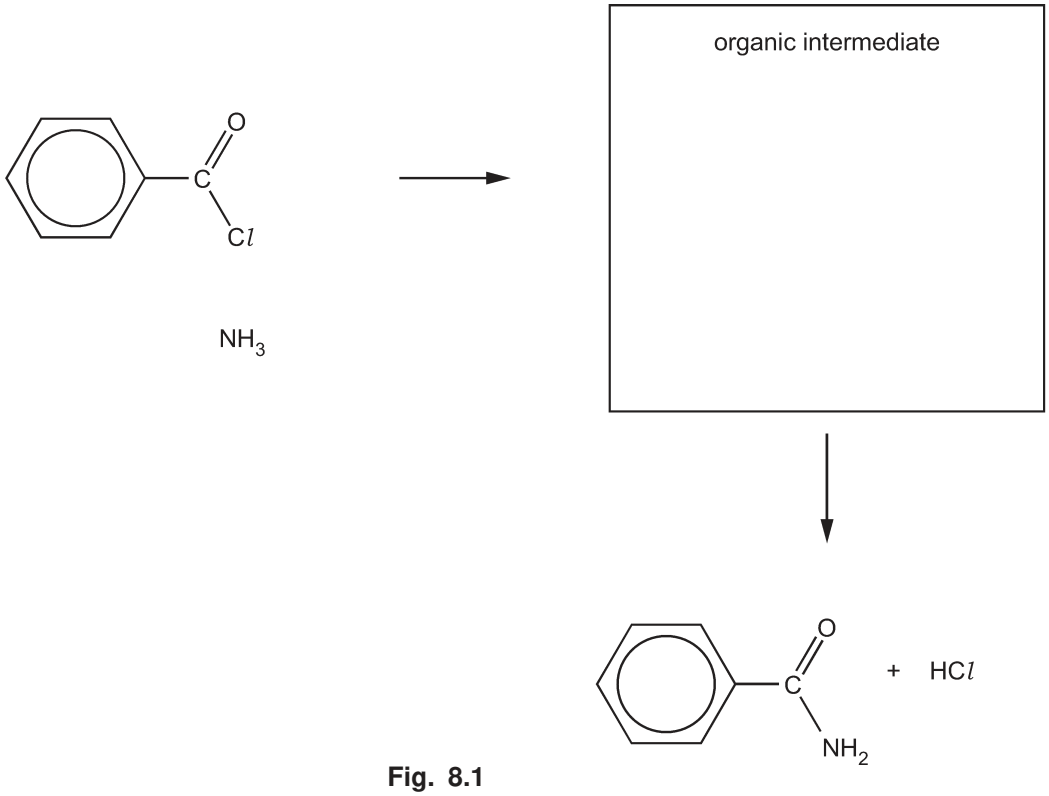


Fig. 8.1

[4]

Learning CORNER

(e) Phenylalanine, $C_6H_5CH_2CH(NH_2)COOH$, is an amino acid with an isoelectric point of 5.5.

(i) State what is meant by isoelectric point. [1]

(ii) Draw the structure of $C_6H_5CH_2CH(NH_2)COOH$ at pH 10. [1]

(f) $C_6H_5CH_2CH(NH_2)COOH$ and alanine, $CH_3CH(NH_2)COOH$, react to form a dipeptide containing both amino acid residues.

Draw the structure of this dipeptide.

The peptide functional group formed should be displayed. [2]

[J24/P4/Q8]

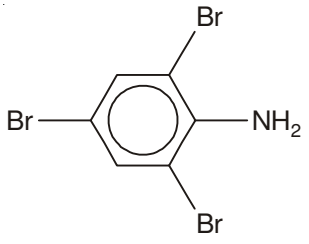
Suggested Solution:

(a) Benzylamine (most basic) > Ammonia > Phenylamine (least basic)

The basicity of these compounds is linked with the availability of the lone pair on the nitrogen atom. The $–CH_2–$ (benzyl) group does not withdraw electrons from the $–NH_2$ group. The lone pair on nitrogen remains readily available for protonation, making benzylamine more basic than ammonia. Ammonia has a lone pair on nitrogen that can accept protons. Since there are no electron-withdrawing or donating effects, its basicity is moderate. The lone pair on nitrogen interacts with the benzene ring via delocalization. This reduces the availability of the nitrogen lone pair for protonation, making phenylamine less basic than ammonia.

(b) (i) observations: White precipitates are observed.

structure of **M**:

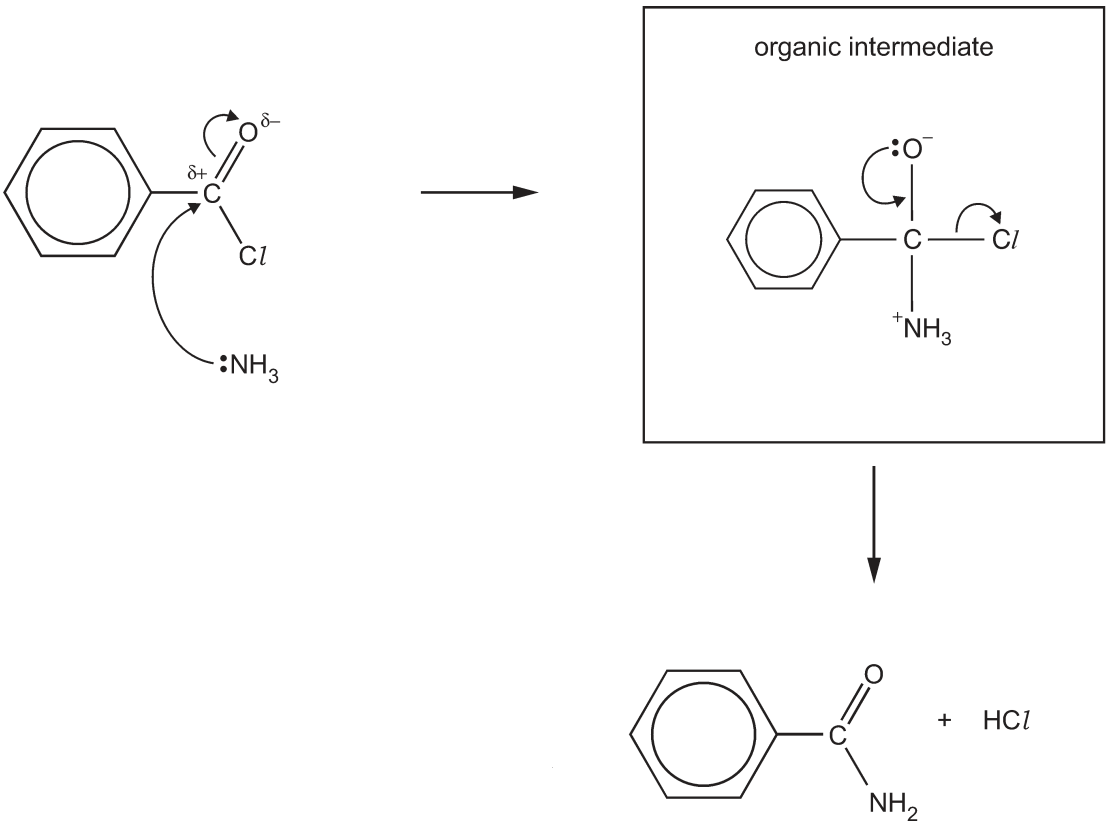


(ii) The $–NH_2$ group in $C_6H_5NH_2$ is an electron-donating group. It increases the electron density in the benzene ring. This activates the ring, making it more reactive towards electrophilic substitution. As a result, $Br_2(aq)$ reacts readily with $C_6H_5NH_2$ even without a catalyst.

(c) The lone pair on the nitrogen in the $–CONH_2$ group is delocalized due to resonance with the adjacent C=O bond. This means the nitrogen lone pair is not readily available to accept protons (H^+), reducing its basicity.

(d)

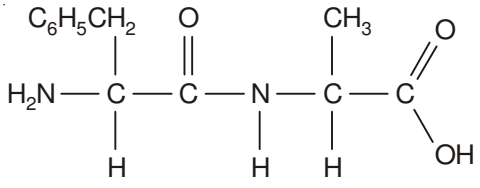
learning CORNER



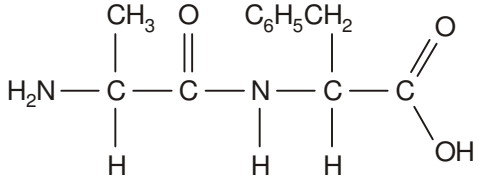
(e) **(i)** The isoelectric point is the pH at which an amino acid has no overall net charge because the number of positive and negative charges are equal. At this pH, the amino acid exists primarily as a zwitterion (having both a positively charged $–NH_3$ group and a negatively charged $–COO^-$ group).

(ii) $C_6H_5CH_2CH(NH_2)COO^-$

(f)



OR



learning CORNER

Question 30

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.

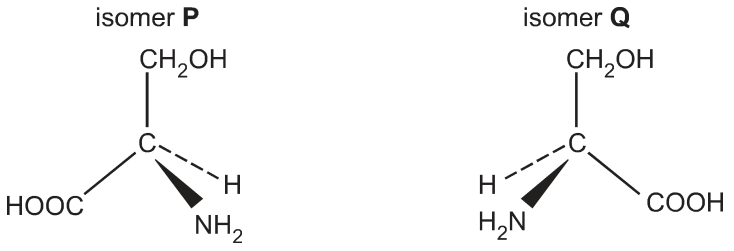


Fig. 8.1

(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

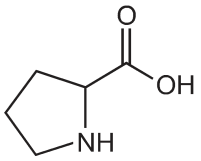
group responsible for peak	name of splitting pattern shown by peak	explanation for splitting pattern

[3]

Learning CORNER

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

proline

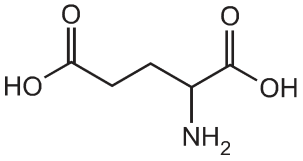


State the number of peaks in the carbon-13 (^{13}C) NMR spectrum of proline. [1]

(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 pH1	at pH3
at pH9	at pH14

[3]

[N24/P4/Q8]

Learning CORNER

Suggested Solution:

(a) The isomers differ in their biological activity.

(b) Isomer **Q** rotates the plane polarised light by 5.0° in anticlockwise direction.

(c) Enantiomers.

(d) Racemic mixture.

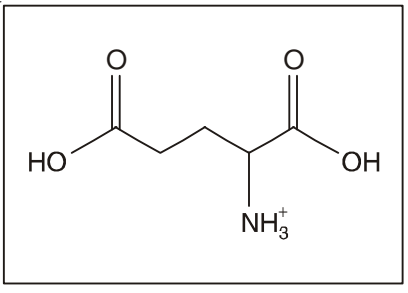
(e) By using a chiral catalyst, the formation of a specific enantiomer can be directed.

(f)

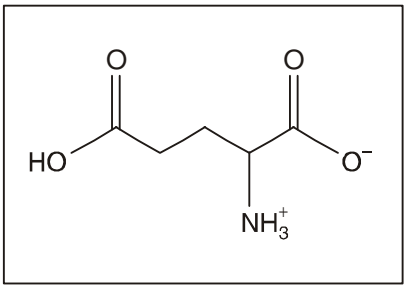
group responsible for peak	name of splitting pattern shown by peak	explanation for splitting pattern
C–H	Triplet	The adjacent carbon atom has 2 hydrogen atoms attached to it so the peak will be split in 3.
CH_2	Doublet	The adjacent carbon atom has only 1 hydrogen atom attached to it, so a doublet will be observed.

(g) 5

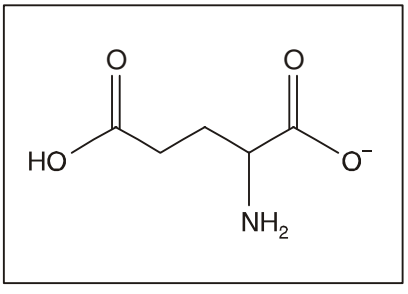
(h)



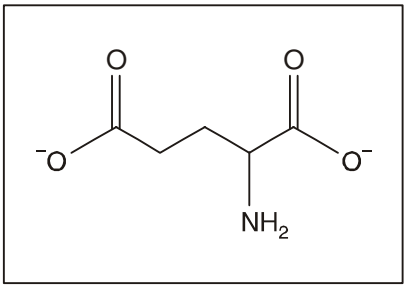
at pH1



at pH3



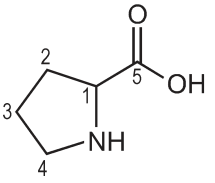
at pH9



at pH14

(f) Since serine is dissolved in D_2O, the NH_2 and OH protons do not appear in the spectrum.

(g) proline



(h) At pH 1, due to the highly acidic conditions, both the carboxy groups remain protonated and amine ($–NH_2$) group is protonated as $–NH_3^+$.

At pH 3, only one carboxyl group deprotonates.

At pH 9, the amine group deprotonates. Finally, at pH 14, the other carboxyl group also deprotonates due to highly alkaline condtions.