Question - 01

This question is about enthalpy changes.

(a) Theoretical values for enthalpies of lattice dissociation can be calculated using a perfect ionic model.

State the meaning of the term perfect ionic model.

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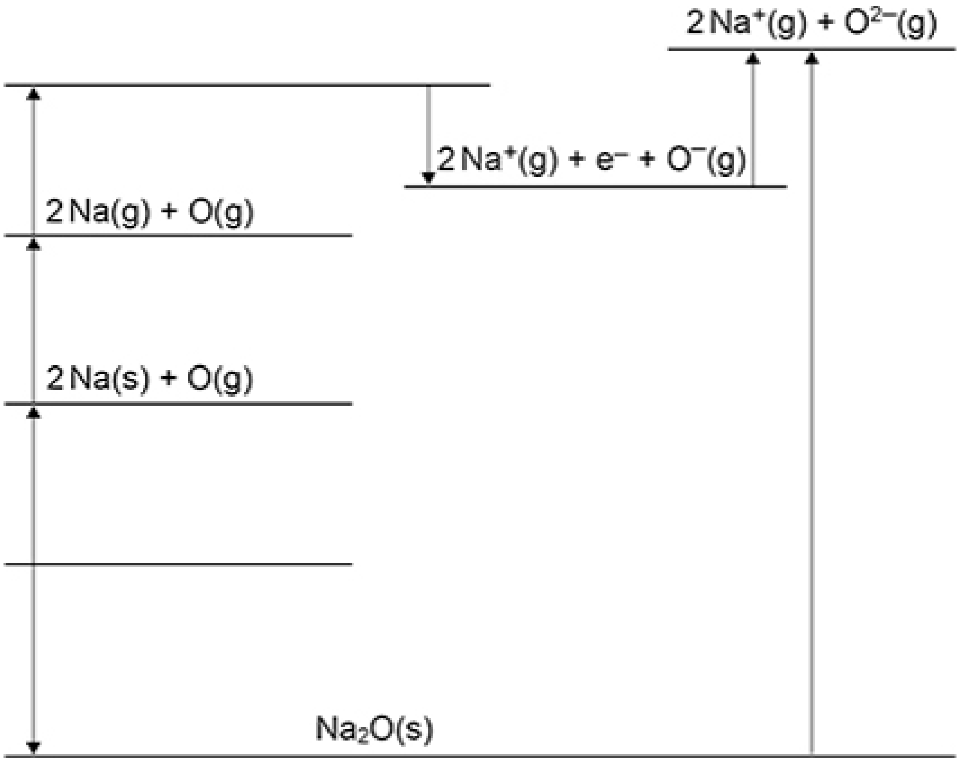
(1)

(b) Enthalpies of lattice dissociation can also be obtained from Born–Haber cycles.

The figure below shows an incomplete Born–Haber cycle for the formation of sodium oxide.



Complete above figure by writing formulas, including state symbols, of the appropriate species on each of the two blank lines.

(2)

(c) **Table 1** shows some enthalpy changes.

Table 1

Enthalpy change	**ΔH / kJ mol^{-1}**
Enthalpy of atomisation of oxygen	+248
Enthalpy of atomisation of sodium	+109
Enthalpy of formation of sodium oxide	–416
First ionisation energy of sodium	+494
First electron affinity of oxygen	–142
Second electron affinity of oxygen	+844

Use the data in **Table 1** to calculate the enthalpy of lattice dissociation of sodium oxide.

Enthalpy of lattice dissociation ____________________ kJ mol^{-1}

(2)

(d) Explain why the second electron affinity of oxygen has a positive value.

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____

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(1)

(e) Explain why the enthalpy of lattice dissociation for sodium oxide is greater than the enthalpy of lattice dissociation for sodium chloride.

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____

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(2)

(f) Sodium chloride dissolves in water.

Table 2 shows some more enthalpy changes.

Table 2

Enthalpy change	**ΔH / kJ mol^{-1}**
Enthalpy of hydration for Cl^- ions	–364
Enthalpy of hydration for Na^+ ions	–406
Enthalpy of lattice dissociation for NaCl	+771

Use the data in **Table 2** to calculate the enthalpy of solution for sodium chloride.

Enthalpy of solution ____________________ kJ mol^{-1}

(2)

(g) Give a reason why data books do **not** contain a value for the enthalpy of solution of sodium oxide.

____

____

(1)

(h) Calculate the temperature, in °C, at which this reaction becomes feasible.

$NaCl(s) \rightarrow Na(s) + \frac{1}{2}Cl_2(g)$ $\Delta H = +411\ \text{kJ mol}^{-1}$

$\Delta S = +90.1\ \text{J K}^{-1}\ \text{mol}^{-1}$

Temperature ______________________ °C

(3)

(a) (Ions are) point charges
OR
(Ions are) perfect spheres
OR
No covalent character

Do not accept atoms or molecules in answer

Allow no polarisation of ions

1

(b) $2\ Na^+(g) + 2\ e^- + O(g)$

$2\ Na(s) + \frac{1}{2}O_2(g)$

2

(c) $-416 + x = 248 + (2 \times 109) + (2 \times 494) - 142 + 844$

enthalpy of lattice dissociation = (+) 2572 (kJ mol^{-1})

−2572 (kJ mol^{-1}) scores 1 mark

2

(d) O^- repels the electron (being added)

Allow negative ion repels electron

1

(e) Oxide ions

M1 have higher (negative) charge
OR
smaller size
OR
higher charge density/higher charge:size ratio (than chloride ions).

M2 stronger attraction between (O^{2-} and Na^+/oppositely charged) ions

Ignore electronegativity

2

(f) Enthalpy of solution = 771 - 406 - 364

= (+)1 (kJ mol^{-1})

Allow 1 mark for -1 (kJmol^{-1})

2

(g) It reacts with water
OR
It reacts to form (a solution of) NaOH

Do not accept - It dissolves in water

1

(h) **M1** T = $\Delta H/\Delta S$

M2 T = $\frac{411}{90.1\times10^{-3}}$ = 4562 (K)

M3 T = 4562 - 273 = 4289 (°C)

M3 = M2 - 273
M3: Allow 4290 (°C)

3

Question - 02

This question is about ethanedioic acid (HOOCCOOH) and the ethanedioate ion ($^{-}OOCCOO^{-}$).

(a) Ethanedioic acid reacts with propane-1,3-diol ($HOCH_2CH_2CH_2OH$) to form a polyester.

Draw the repeating unit of this polyester.

(2)

(b) Explain why polyesters are biodegradable but polyalkenes are not biodegradable.

(2)

(c) Sodium ethanedioate is used to find the concentration of solutions of potassium manganate(VII) by titration. The equation for this reaction is

$$2\ MnO_4^{-} + 16\ H^{+} + 5\ C_2O_4^{2-} \rightarrow 2\ Mn^{2+} + 8\ H_2O + 10\ CO_2$$

A standard solution is made by dissolving 162 mg of $Na_2C_2O_4$ (M_r = 134.0) in water and making up to 250 cm^3 in a volumetric flask.

25.0 cm^3 of this solution and an excess of sulfuric acid are added to a conical flask.
The mixture is warmed and titrated with potassium manganate(VII) solution.
The titration is repeated until concordant results are obtained.
The mean titre is 23.85 cm^3

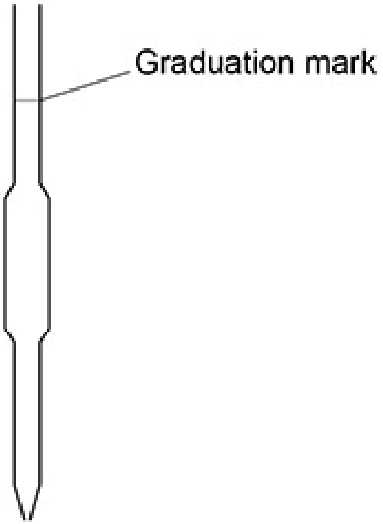
Calculate the concentration, in mol dm^{-3}, of the potassium manganate(VII) solution.

Concentration _______________ mol dm^{-3}

(4)

(d) **Figure 1** shows the 25.0 cm^3 pipette used to measure the sodium ethanedioate solution.

Figure 1



On **Figure 1**, draw the meniscus of the solution when the pipette is ready to transfer 25.0 cm^3 of the sodium ethanedioate solution.

(1)

(e) Potassium manganate(VII) is oxidising and harmful.
Sodium ethanedioate is toxic.

Suggest safety precautions, other than eye protection, that should be taken when:

- filling the burette with potassium manganate(VII) solution
- dissolving the solid sodium ethanedioate in water.

Filling the burette ____

____

Dissolving the solid ____

____

(2)

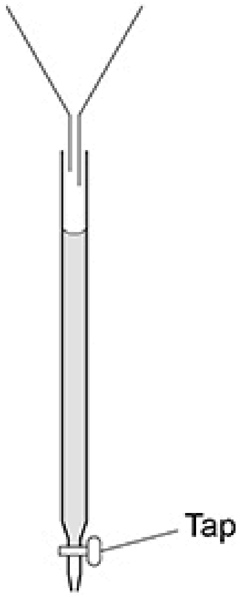
(f) State the colour change seen at the end point of each titration.

____

(1)

(g) **Figure 2** shows the burette containing potassium manganate(VII) solution.

Figure 2



Give **two** practical steps needed before recording the initial burette reading.

1 ____

2 ____

(2)

(h) When $Na_2C_2O_4(aq)$ is added to a solution containing $[Fe(H_2O)_6]^{3+}$ ions, a reaction occurs in which all six water ligands are replaced by ethanedioate ions.

Explain why the replacement of the water ligands by ethanedioate ions is favourable. In your answer refer to:

- the enthalpy and entropy changes for the reaction
- how the enthalpy and entropy changes influence the free-energy change for the reaction.

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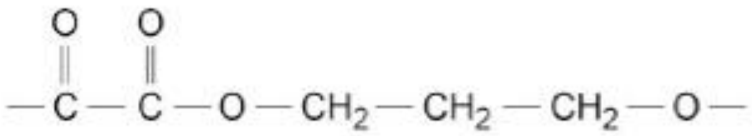
(a)



$$-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_2-CH_2-O-$$

M1 ester link including C−O−C

__ignore__ brackets and 'n'

__allow__ $(CH_2)_3$

−O− at either end but __not__ both

1

M2 rest of structure including trailing bonds

__not__ M2 if more than one repeating unit

__allow__ for one mark −OOCCOOCH$_2$CH$_2$CH$_2$− as long as trailing bonds included

1

(b) polyesters: C=O/C−O **OR** polar bonds / chain **AND**
polyalkenes: (only) C−C **OR** non-polar bonds / chain

__not__ just 'polyesters are polar'

__not__ M1 if C=C mentioned

1

(polyesters) susceptible to nucleophilic attack / can be hydrolysed

1

(c) **M1** amount of $Na_2C_2O_4 = \frac{0.162}{134.0} = 0.00121$ mol

M1 x $\frac{2}{5}$

1

M2 stoichiometry $(\frac{2}{5})$ (4.84×10^{-4})

1

M3 scaling (÷10)

$= 0.00121 \times \frac{2}{5} \div 10 = 4.84 \times 10^{-5}$ mol

M2 ÷ 10 (conc/40)

M3 x $\frac{1000}{23.85}$

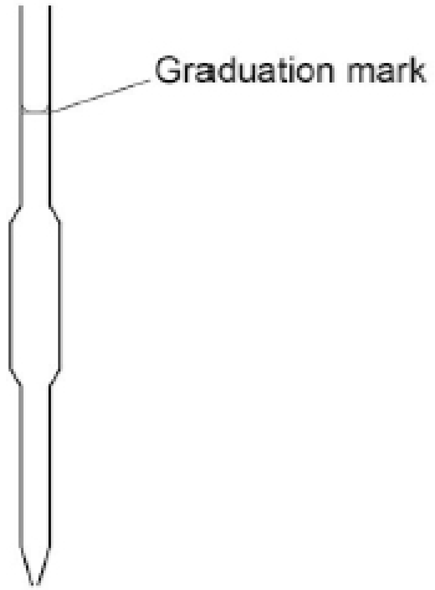
1

M4 concentration of $MnO_4^- = \frac{4.84 \times 10^{-5}}{\frac{23.85}{1000}} = 0.00203$ mol dm^{-3}

Min 2 sig figs

1

(d)



Meniscus curved with the bottom of the curve on the horizontal line

1

(e) (burette) fill below/at eye level

***ignore** make sure tap closed / funnel / gloves*

1

(solution) wear gloves

***allow** wash/rinse hands after any spillage **not** fume cupboard*

***ignore** lab coat / stir carefully*

1

(f) colourless to pink/pale purple

***not** just purple*

***not** 'clear' for 'colourless'*

1

(g) remove funnel

1

ensure jet is filled / no (air) bubbles

allow *open tap to fill space below tap*

1

(h)

This question is marked using Levels of Response. Refer to the Mark Scheme Instructions for Examiners for guidance.	
Level 3 **5-6 marks**	All stages are covered and each stage is generally correct and virtually complete. Answer is communicated coherently and shows a logical progression from Stage 1 to Stages 2 and 3 Covers at least 2 point for stage 1, 1 for stage 2 and 2 for stage 3. If given equation must show correct stoichiometry for six marks
Level 2 **3-4 marks**	All stages are covered but stage(s) may be incomplete or may contain inaccuracies**OR** two stages are covered and are generally correct and virtually complete. Answer is communicated mainly coherently and shows a logical progression from Stage 1 to Stages 2 and 3.
Level 1 **1-2 marks**	Two stages are covered but stage(s) may be incomplete or may contain inaccuracies**OR** only one stage is covered but is generally correct and virtually complete. Answer includes isolated statements but these are not presented in a logical order.
Level 0	Insufficient correct chemistry to gain a mark.

Stage 1 - ΔH

1a ΔH negligible

1b make & break same number of bonds 1c make & break same type of bonds / bonds have similar enthalpies

Stage 2 - ΔS

2a increase in entropy

2b increase in particles in solution / from 4 to 7 particles (ecf from incorrect equation showing increase in no. of moles)

Stage 3 - ΔG

3a $\Delta G = \Delta H - T\Delta S$

3b ΔG negative (for forward reaction)

3c correct discussion of why ΔG is negative based on ΔH and TΔS

6

Question - 03

This question is about thermodynamics.
Consider the reaction shown.

$$2\,Al_2O_3(s) + 3\,C(s) \rightarrow 4\,Al(s) + 3\,CO_2(g)$$

The table below shows some thermodynamic data.

Substance	**Al_2O_3(s)**	**Al(s)**	**C(s)**	**CO_2(g)**
$\Delta_f H^\ominus$/ kJ mol^{-1}	–1669	0	0	–394
$S^\ominus$/ J K^{-1} mol^{-1}	51	28	6	214

(a) Explain why the standard entropy value for carbon dioxide is greater than that for carbon.

____

____

(1)

(b) State the temperature at which the standard entropy of aluminium is 0 J K^{-1} mol^{-1}

____

(1)

(c) Use the equation and the data in the table above to calculate the minimum temperature, in K, at which this reaction becomes feasible.

Minimum temperature ____________ K

(7)

(a) CO_2 / gas is more disordered (than solid)

Allow answers based on carbon

Ignore CO_2 is a gas and C is a solid

1

(b) 0 K

Units essential

Allow absolute zero ***OR*** *–273 °C*

1

(c) M1 $\Delta H = (\mathbf{3} \times -394) - (-1669 \times \mathbf{2})$

M1 correct expression

1

M2 = 2156 (kJ mol^{-1})

M2 if –2156 seen allow 1 mark out M1 and M2

1

M3 $\Delta S = (28 \times \mathbf{4} + 214 \times \mathbf{3}) - (51 \times \mathbf{2} + 6 \times \mathbf{3})$

M3 correct expression

1

M4 = 634 (J K^{-1} mol^{-1})

M4 if – 634 allow 1 mark from M4 and M4

1

M5 $\Delta G = \Delta H - T\Delta S$ or $\Delta H = T\Delta S$ or $T = \Delta H \div \Delta S$

M5 expression or rearranged expression or with numbers

1

M6 $\Delta S = 0.634$ kJ $K^{-1}mol^{-1}$

M6 ΔS = M4 ÷ 1000

1

M7 $T = \dfrac{2156}{0.634}$ = 3400 to 3401 (K)

M7 = M2 ÷ M6 but must be a positive answer

1

End of Question

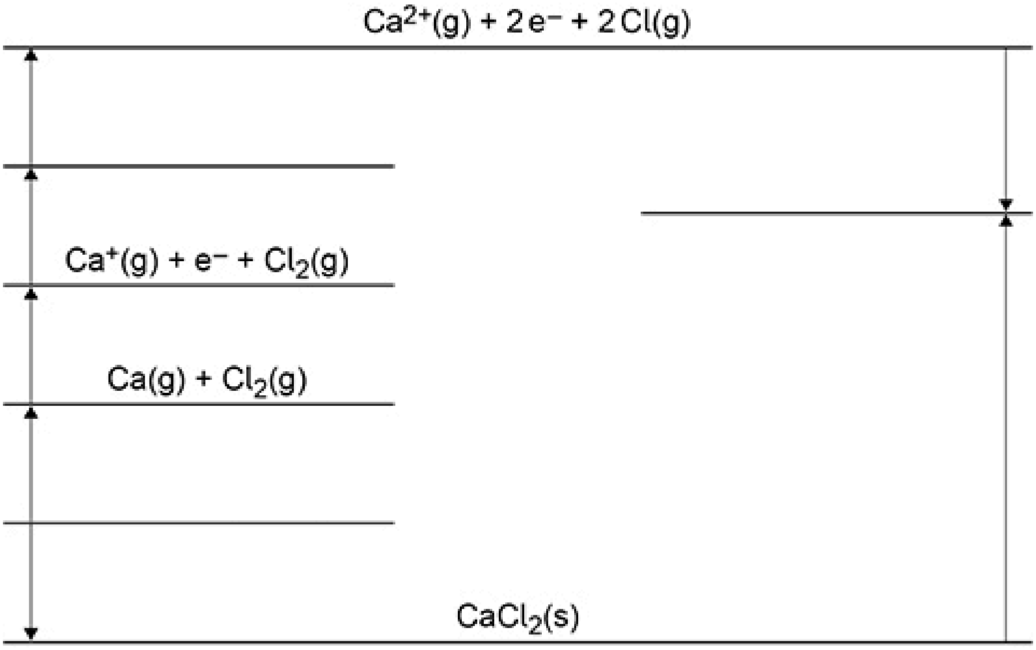
Question - 04

This question is about enthalpy changes for calcium chloride and magnesium chloride.

(a) State the meaning of the term enthalpy change.

(1)

The figure below shows an incomplete Born–Haber cycle for the formation of calcium chloride.



(b) Complete the figure above by writing the formulas, including state symbols, of the appropriate species on each of the three blank lines.

(3)

(c) **Table 1** shows some enthalpy data.

Table 1

	Enthalpy change / kJ mol^{-1}
Enthalpy of formation of calcium chloride	–795
Enthalpy of atomisation of calcium	+193
First ionisation energy of calcium	+590
Second ionisation energy of calcium	+1150
Enthalpy of atomisation of chlorine	+121
Electron affinity of chlorine	–364

Use the figure in part (a) and the data in **Table 1** to calculate a value for the enthalpy of lattice dissociation of calcium chloride.

Enthalpy of lattice dissociation ______________ kJ mol^{-1}

(2)

(d) Magnesium chloride dissolves in water.

Give an equation, including state symbols, to represent the process that occurs when the enthalpy of solution of magnesium chloride is measured.

____

(1)

(e) **Table 2** shows some enthalpy data.

Table 2

	Enthalpy change / kJ mol^{-1}
Enthalpy of lattice dissociation of $MgCl_2$	+2493
Enthalpy of hydration of $Mg^{2+}(g)$	–1920
Enthalpy of hydration of $Cl^{-}(g)$	–364

Use your answer to part (d) and the data in **Table 2** to calculate a value for the enthalpy of solution of magnesium chloride.

Enthalpy of solution ______________ kJ mol^{-1}

(2)

(f) The enthalpy of hydration of $Ca^{2+}(g)$ is –1650 kJ mol^{-1}

Suggest why this value is less exothermic than that of $Mg^{2+}(g)$

____

____

(a) Heat (energy) change at constant pressure

Ignore conditions even if wrong

Ignore energy change

1

(b) M2 $Ca^{2+}(g) + 2\,e^- + Cl_2(g)$

Alternative M2 $Ca^+(g) + e^- + 2\,Cl(g)$

1

M3 $Ca^{2+}(g) + 2\,Cl^-(g)$

1

M1 $Ca(s) + Cl_2(g)$

1

(c) M1 –795 + LE = 193 + 590 +1150 + (**2** x 121) + (**2** x –364)

Numbers and factors used correctly from cycle

1

M2 LE = (+) 2242 (kJ mol^{-1})

Rearrangement to calculate LE

If one or both factors of 2 missing award 1 mark for (+) 2485, (+)2121 or (+)2606 (kJ mol^{-1}*)*

Allow 1 mark for – 2242 (kJ mol^{-1}*)*

1

(d) $MgCl_2(s) \rightarrow Mg^{2+}(aq) + 2\,Cl^-(aq)$

Allow $MgCl_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,Cl^-(aq)$

Allow $MgCl_2(s) + aq \rightleftharpoons Mg^{2+}(aq) + 2\,Cl^-(aq)$

1

(e) M1 ΔH soln $MgCl_2$ = ΔH latt diss+ ΔH hyd Mg^{2+} + **2**ΔH hyd Cl^-

OR 2493 –1920 + (**2** x –364)

M1 for expression with or without numbers

1

M2 = – 155 (kJ mol^{-1})

M2 for answer

If factor of 2 missing for ΔH *hyd* Cl^- *allow 1 mark for 209*

1

(f) M1 Ca^{2+} (ion) bigger/lower charge to size ratio (than Mg^{2+})

Allow converse answers

M1 Do not accept Ca^{2+} *is a bigger atom/molecule*

M1 Allow Ca^{2+} *has more shells/ more distance of outer e to nucleus*

Ignore more shielding

1

M2 weaker attraction/bond to ($O^{\delta-}$ in) water

1

Question - 05

A value for enthalpy of solution can be determined in two ways:

- from a cycle, using lattice enthalpy and enthalpies of hydration
- from the results of a calorimetry experiment.

(a) Define the term enthalpy of lattice dissociation.

____

____

____

____

(2)

(b) The enthalpy of solution for ammonium nitrate is the enthalpy change for the reaction shown.

$$NH_4NO_3(s) + aq \rightarrow NH_4^+(aq) + NO_3^-(aq) \qquad \Delta H = +26 \text{ kJ mol}^{-1}$$

Table 1

	$NH_4^+(g)$	$NO_3^-(g)$
Enthalpy of hydration $\Delta_{hyd}H$ / kJ mol^{-1}	−307	−314

Draw a suitably labelled cycle and use it, with data from **Table 1**, to calculate the enthalpy of lattice dissociation for ammonium nitrate.

Enthalpy of lattice dissociation ________________ kJ mol^{-1}

(3)

(c) A student does an experiment to determine a value for the enthalpy of solution for ammonium nitrate.

The student uses this method.

- Measure 25.0 cm^3 of distilled water in a measuring cylinder.
- Pour the water into a beaker.
- Record the temperature of the water in the beaker.
- Add 4.00 g of solid NH_4NO_3 to the water in the beaker.
- Stir the solution and record the lowest temperature reached.

Table 2 shows the student's results.

Table 2

Initial temperature / °C	20.2
Lowest temperature / °C	12.2

Calculate the enthalpy of solution, in kJ mol^{-1}, for ammonium nitrate in this experiment.

Assume that the specific heat capacity of the solution, c = 4.18 J K^{-1} g^{-1}

Assume that the density of the solution = 1.00 g cm^{-3}

Enthalpy of solution _______________ kJ mol^{-1}

(3)

(d) The uncertainty in each of the temperature readings from the thermometer used in this experiment is ±0.1°C

Calculate the percentage uncertainty in the temperature change in this experiment.

Percentage uncertainty

(1)

(e) Suggest a change to the student's method, using the same apparatus, that would reduce the percentage uncertainty in the temperature change.

Give a reason for your answer.

Change ____

____

Reason ____

____

(2)

(f) Another student obtained a value of +15 kJ mol^{-1} using the same method.

Suggest the main reason for the difference between this experimental value for the enthalpy of solution and the correct value of +26 kJ mol^{-1}

____

____

(1)

(g) **Table 3** shows some entropy data at 298 K

Table 3

	Entropy *S* / J K^{-1} mol^{-1}
$NH_4NO_3(s)$	151
$NH_4^+(aq)$	113
$NO_3^-(aq)$	146

Calculate a value for the Gibbs free-energy change (ΔG), at 298 K, for the reaction when ammonium nitrate dissolves in water.

$$NH_4NO_3(s) + aq \rightarrow NH_4^+(aq) + NO_3^-(aq) \qquad \Delta H = +26 \text{ kJ mol}^{-1}$$

Use data from **Table 3** and the value of ΔH from the equation.
Assume for the solvent, water, that the entropy change, $\Delta S = 0$

Explain what the calculated value of ΔG indicates about the feasibility of this reaction at 298 K

ΔG ______________ kJ mol^{-1}

Explanation ____

____

____

(4)

(h) Ammonium nitrate decomposes as shown.

$$NH_4NO_3(s) \rightarrow N_2(g) + \tfrac{1}{2}\,O_2(g) + 2\,H_2O(g) \qquad \Delta H = +123\ \text{kJ mol}^{-1}$$

The entropy change (ΔS) for this reaction is +144 J K^{-1} mol^{-1}

Calculate the temperature at which this reaction becomes feasible.

Temperature ______________ K

(2)

(a) The enthalpy change / ΔH when one mole of a (solid) ionic compound

__Ignore__ standard states / conditions

__Allow__ heat change at constant pressure when...

__Ignore__ heat change (alone) / energy change

1

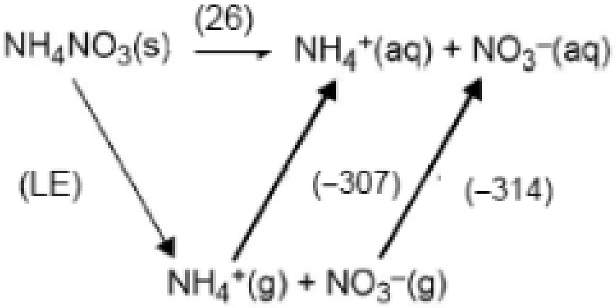
dissociates (fully) into gaseous ions

__M2 Allow__ suitable equation with state symbols for ions

__Not__ one mole of gaseous ions

1

(b)



__Allow__ + water or +aq

M1 = cycle (3 'corners' with formulae and state symbols and suitable arrows)

__Allow__ equivalent Born-Haber style energy cycle

__Not__ ecf to M2 and M3 from incorrect cycle

1

LE = 26 + 307 + 314

M2 = working e.g. 26 = LE − 307 − 314

= (+)647

1

M3 = answer (+)647 gets 3/3 if M1 given or 2/3 if not
−647 = 2/3 if M1 given or 1/3 if not
+595 / −595 = 2/3 if M1 given or 1/3 if not
−621/+621 = 1/3 if M1 given
__Not__ ecf for M3 from incorrect expression in M2

1

(c) ($q = mc\Delta T$ =) 25.0 × 4.18 × (20.2 − 12.2) **OR** 25.0 × 4.18 × 8
(= 836 (J) or 0.836 (kJ))

Not *if m = 29*

Ignore *sign of q*

1

4.00 g NH_4NO_3 = 4.00/80 **OR** 0.0500 mol

1

$\Delta H^{\ominus}_{soln}$ = 836/0.05 = 16720 = (+)16.7(2) kJ mol^{-1}

Allow *ecf from M1 and/or from M2*

–16.7(2) = 2/3

+19.4 = 2/3 (using m = 29 in M1)

−19.4 = 1/3

+2.68 = 2/3

−2.68 = 1/3

+587 or +588 = 2/3

−587 or −588 = 1/3

Allow *2 sig figs or more*

1

(d) (2 × 0.1/8) × 100 = 2.5%

Allow *ecf from ΔT in (c)*

1

(e) use a larger mass/amount of NH_4NO_3 / solid

Marking points are independent

***Allow** smaller volume of water / less water*

***Allow** use more NH_4NO_3*

***Not** larger volume of water*

***Ignore** higher concentration (of NH_4NO_3)*

***Ignore** any references to changing apparatus e.g. insulation*

1

so temperature change/decrease is greater
OR final temperature is lower

***Allow** temperature increase is greater*

***Not** final temperature is higherr*

1

(f) heat gain (from the surroundings) / incomplete dissolvingg

***Allow** incomplete reaction*

***Allow** thermal energy gain*

***Not** heat loss*

***Ignore** energy gain*

***Ignore** references to mistakes in method*

1

(g) $\Delta S = (113 + 146) - 151 = +108$ ($\text{J K}^{-1}\ \text{mol}^{-1}$)

1

$\Delta G = \Delta H - T\Delta S$ OR $26 - (298 \times 108 \times 10^{-3})$

Allow ecf $26 - (298 \times M1 \times 10^{-3})$

Allow ecf $26 - (298 \times M1)$

*Allow **M2** for $26000 - (298 \times 108)$*

*Allow **M2** for $26 - (298 \times 108)$*

1

$\Delta G = -6.184$ / -6.18 / -6.2

*-32158 = **M1** and **M2***

*-32.2 = **M1** and **M2***

*-6184 = **M1** and **M2***

*$(+)58.2$ = **M2** and **M3** (ecf if -108 for M1)*

1

negative value for ΔG indicates reaction is feasible/spontaneous

Allow positive value for ΔG indicates reaction is NOT feasible/spontaneous

Allow < 0 or > 0 as appropriate

M4 is standalone

1

(h) Converting ΔH into J OR ΔS into kJ

1

($T = \Delta H / \Delta S = 123/144 \times 10^{-3}$ OR $123000/144$) = 854(.1666666) (K)

0.854 (K) = 1/2

0.00117 (K) = 1/2 (calculation upside down)

2SF minimum

1