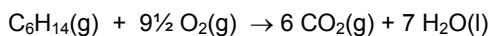
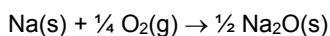
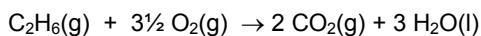
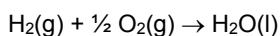
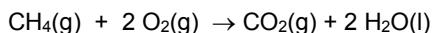
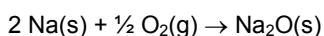
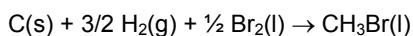
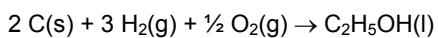
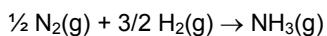
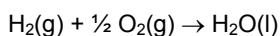
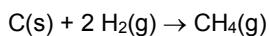


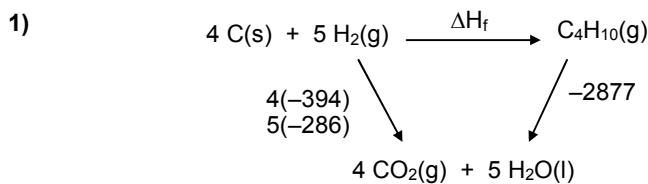


THERMODYANMICS



TASK 1 – A MIXTURE OF SIMPLE AS THERMODYNAMICS QUESTIONS

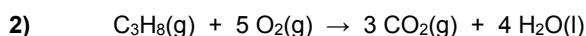
1	-129 kJ mol ⁻¹	2	-2222 kJ mol ⁻¹	3	-1194 kJ mol ⁻¹
4	-2008 kJ mol ⁻¹	5	-184 kJ mol ⁻¹	6	-125 kJ mol ⁻¹
7	-1669 kJ mol ⁻¹	8	-57.3 kJ mol ⁻¹	9	-5116 kJ mol ⁻¹
10	+288, -277 kJ mol ⁻¹	12	+507 kJ mol ⁻¹		
13	a -1823 kJ mol ⁻¹	b	-1311 kJ mol ⁻¹	c	-1690 kJ mol ⁻¹



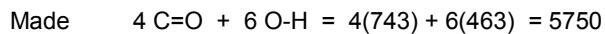
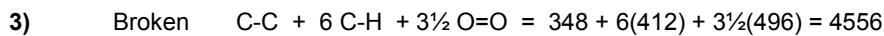
$$\Delta H_f - 2877 = 4(-394) + 5(-286) \quad \Delta H_f = 4(-394) + 5(-286) + 2877 \\ = -129 \text{ kJ mol}^{-1}$$

OR $\Delta H = [\text{Sum of } \Delta H_c \text{ reactants}] - [\text{Sum } \Delta H_c \text{ products}]$

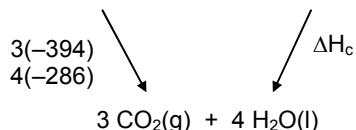
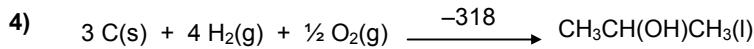
$$= [4(-394) + 5(-286)] - [-2877]$$
$$= -129 \text{ kJ mol}^{-1}$$



$$\begin{aligned}\Delta H &= [\text{Sum of } \Delta H_f \text{ products}] - [\text{Sum } \Delta H_f \text{ reactants}] \\ &= [3(-394) + 4(-286)] - [-104] \\ &= \mathbf{-2222 \text{ kJ mol}^{-1}}\end{aligned}$$



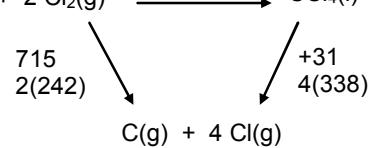
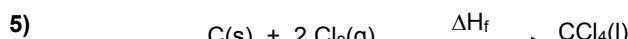
$$\Delta H = [\text{Bond broken}] - [\text{Bonds made}] = 4556 - 5750 = \mathbf{-1194 \text{ kJ mol}^{-1}}$$



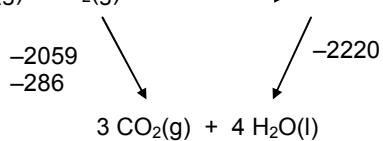
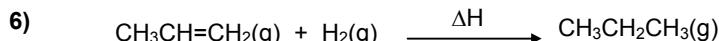
$$\begin{aligned}-318 + \Delta H_c &= 3(-394) + 4(-286) & \Delta H_c &= 3(-394) + 4(-286) + 318 \\ & & &= \mathbf{-2008 \text{ kJ mol}^{-1}}\end{aligned}$$

OR $\Delta H = [\text{Sum of } \Delta H_c \text{ reactants}] - [\text{Sum } \Delta H_c \text{ products}]$

$$\begin{aligned}-318 &= [3(-394) + 4(-286)] - [\Delta H_c] \\ \Delta H_c &= 3(-394) + 4(-286) + 318 = \mathbf{-2008 \text{ kJ mol}^{-1}}\end{aligned}$$



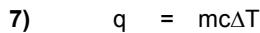
$$\begin{aligned}\Delta H_f + 31 + 4(338) &= 715 + 2(242) & \Delta H_f &= 715 + 2(242) - 31 - 4(338) \\ & & &= \mathbf{-184 \text{ kJ mol}^{-1}}\end{aligned}$$



$$\begin{aligned}\Delta H - 2220 &= -2059 + -286 & \Delta H &= -2059 - 286 + 2220 \\ & & &= \mathbf{-125 \text{ kJ mol}^{-1}}\end{aligned}$$

OR $\Delta H = [\text{Sum of } \Delta H_c \text{ reactants}] - [\text{Sum } \Delta H_c \text{ products}]$

$$\begin{aligned}&= [-2059 - 286] - [-2220] \\ &= \mathbf{-125 \text{ kJ mol}^{-1}}\end{aligned}$$



$$= 80 \times 4.18 \times 47.3 = 15820 \text{ J} = 15.82 \text{ kJ}$$

$$\text{moles CH}_3\text{COCH}_3 = \text{mass} / M_r = 0.55 / 58.0 = 0.00948$$

$$\Delta H = q / \text{moles} = -15.82 / 0.00948$$

$$= \mathbf{-1669 \text{ kJ mol}^{-1}}$$

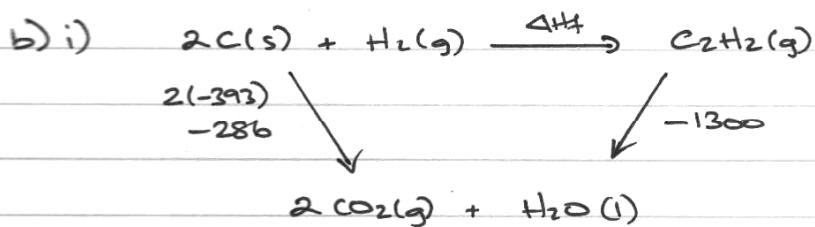
8) $q = mc\Delta T$
 $= 50 \times 4.18 \times (33.9 - 20.2) = 2863 \text{ J} = 2.863 \text{ kJ}$

moles KOH = conc x vol (dm³) = 2.0 x 25/1000 = 0.0500
 moles HNO₃ = conc x vol (dm³) = 2.0 x 25/1000 = 0.0500

$\Delta H = q / \text{moles} = -2.863 / 0.0500$
 $= -57.3 \text{ kJ mol}^{-1}$

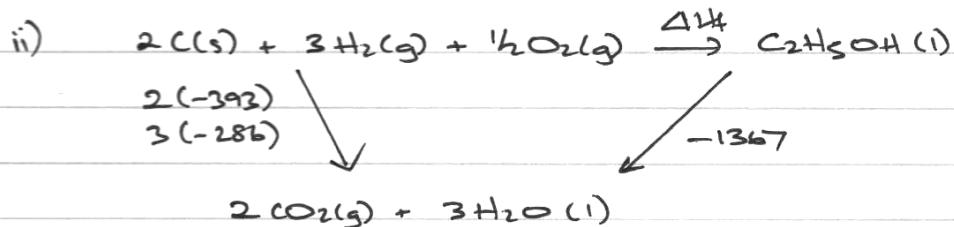
9) $\Delta H = (\text{Sum } \Delta H_f \text{ products}) - (\text{Sum } \Delta H_f \text{ reactants})$
 $= [4(-393) + 12(-286) + 0] - [4(53) + 5(-20)]$
 $= -5116 \text{ kJ/mol}$

10 a) enthalpy change for a reaction is independent of the route taken



$$\Delta H_f - 1300 = 2(-393) - 286$$

$$\Delta H_f = +228 \text{ kJ/mol}$$

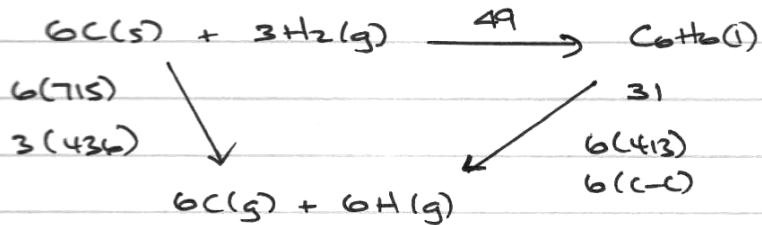


$$\Delta H_f - 1367 = 2(-393) + 3(-286)$$

$$\Delta H_f = -277 \text{ kJ/mol}$$

- 11 a) burning -ve
 b) forming H-bonds -ve
 c) breaking H-bonds +ve

12

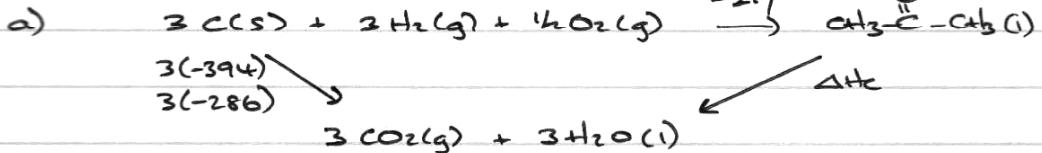


$$49 + 31 + 6(413) + 6(C-C) = 6(715) + 3(436)$$

$$6(C-C) = 3040$$

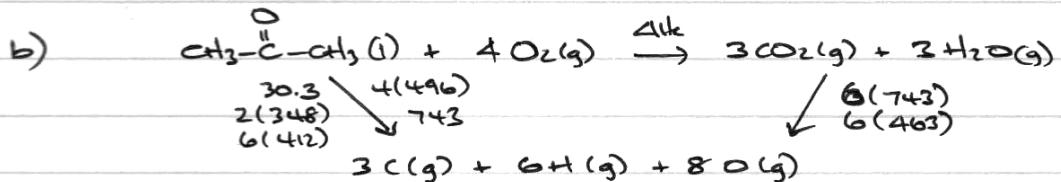
$$C-C = \underline{507 \text{ kJ/mol}}$$

13



$$-217 + \Delta H_c = 3(-394) + 3(-286)$$

$$\Delta H_c = \underline{-1823 \text{ kJ/mol}}$$



$$\Delta H_c + 6(743) + 6(463) = 30.3 + 2(348) + 6(412) + 4(496) + 6(743)$$

$$\Delta H_c = \underline{-1311 \text{ kJ/mol}}$$

c) $q_f = mc\Delta T = 3.34 \times 25.3 = 84.50 \text{ kJ}$

$$\text{mol } CH_3COCH_3 = \frac{2.90}{58.0} = 0.05$$

$$\Delta H_c = -\frac{84.50}{0.05} = \underline{-1690 \text{ kJ/mol}}$$

d) ✓ (a) is correct value

✗ (b) uses mean bond enthalpies + missing $H_2O(l) \rightarrow (g)$

✗ (c) heat loss so not as exothermic as should be

TASK 2 – EXTRA BOND ENTHALPY CALCULATIONS

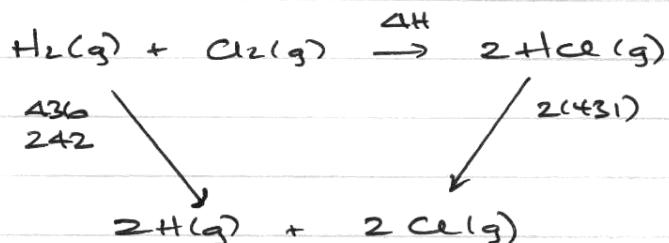
- 1 a -184 kJ mol⁻¹
 2 391 kJ mol⁻¹
 5 508 kJ mol⁻¹

- b -95 kJ mol⁻¹
 3 464 kJ mol⁻¹

- c -103 kJ mol⁻¹
 4 452 kJ mol⁻¹

1

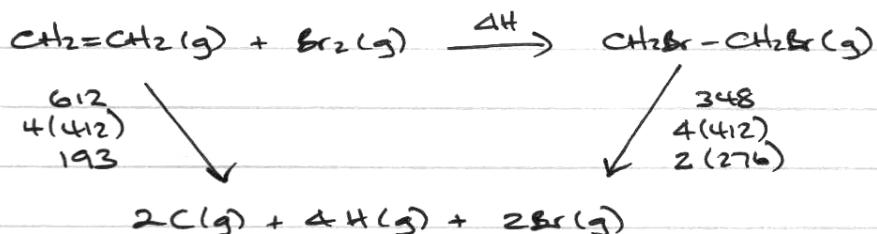
a)



$$\Delta H + 2(+31) = 436 + 242$$

$$\Delta H = \underline{-184 \text{ kJ/mol}}$$

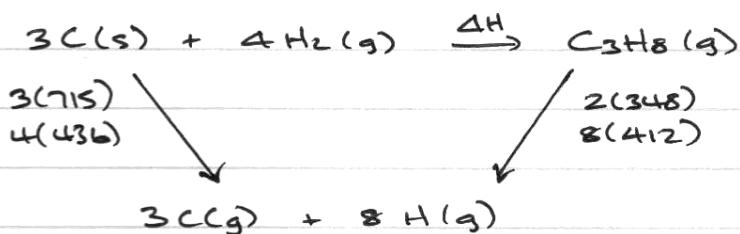
b)



$$\Delta H + 348 + 4(412) + 2(276) = 612 + 4(412) + 193$$

$$\Delta H = \underline{-95 \text{ kJ/mol}}$$

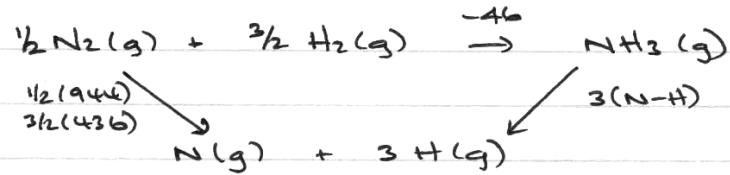
c)



$$\Delta H + 2(348) + 8(412) = 3(715) + 4(436)$$

$$\Delta H = \underline{-103 \text{ kJ/mol}}$$

2

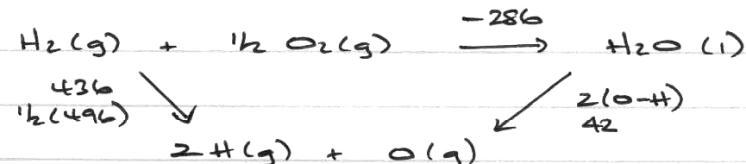


$$-46 + 3(\text{N-H}) = 1/2(946) + 3/2(436)$$

$$3(\text{N-H}) = 1172$$

$$\text{N-H} = \underline{391 \text{ kJ/mol}}$$

3

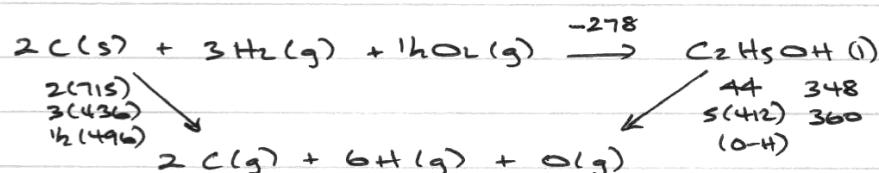


$$-286 + 42 + 2(\text{O-H}) = 436 + 1/2(496)$$

$$2(\text{O-H}) = 928$$

$$(\text{O-H}) = \underline{464 \text{ kJ/mol}}$$

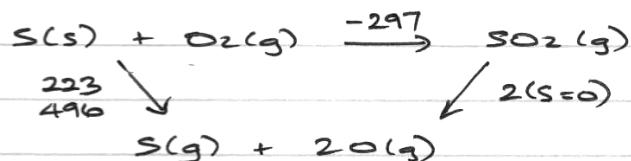
4



$$-278 + 44 + 348 + 5(412) + 360 + (\text{O-H}) = 2(715) + 3(436) + 1/2(496)$$

$$(\text{O-H}) = \underline{452 \text{ kJ/mol}}$$

5



$$-297 + 2(\text{S=O}) = 223 + 496$$

$$2(\text{S=O}) = 1016$$

$$\text{S=O} = \underline{508 \text{ kJ/mol}}$$

TASK 3 – DEFINITIONS

- 1) ΔH_f° of C₆H₆(l) $6C(s) + 3H_2(g) \rightarrow C_{6}H_6(l)$
- 2) ΔH_f° of CH₃COOH(l) $2C(s) + 2H_2(g) + O_2(g) \rightarrow CH_3COOH(l)$
- 3) ΔH_c° of H₂(g) $H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$
- 4) ΔH_c° of CH₃COOH(l) $CH_3COOH(l) + 2O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$
- 5) 1st ionisation energy of aluminium $Al(g) \rightarrow Al^+(g) + e^-$
- 6) 2nd ionisation energy of aluminium $Al^+(g) \rightarrow Al^{2+}(g) + e^-$
- 7) 3rd ionisation energy of aluminium $Al^{2+}(g) \rightarrow Al^{3+}(g) + e^-$
- 8) 1st electron affinity of chlorine $Cl(g) + e^- \rightarrow Cl^-(g)$
- 9) lattice enthalpy of formation of sodium oxide $2Na^+(g) + O^{2-}(g) \rightarrow Na_2O(s)$
- 10) lattice enthalpy of dissociation of aluminium oxide $Al_2O_3(s) \rightarrow 2Al^{3+}(g) + 3O^{2-}(g)$
- 11) ΔH_{hyd}° of sodium ions $Na^+(g) \rightarrow Na^+(aq)$
- 12) ΔH_{hyd}° of oxide ions $O^{2-}(g) \rightarrow O^{2-}(aq)$
- 13) ΔH_{sol}° of sodium oxide $Na_2O(s) \rightarrow 2Na^+(aq) + O^{2-}(aq)$
- 14) ΔH_{sol}° of magnesium carbonate $MgCO_3(s) \rightarrow Mg^{2+}(aq) + CO_3^{2-}(aq)$
- 15) Bond dissociation enthalpy of water $1/2H_2O(g) \rightarrow H(g) + 1/2O(g)$
- 16) Bond dissociation enthalpy of hydrogen $H_2(g) \rightarrow 2H(g)$
- 17) ΔH_a° of bromine $1/2Br_2(l) \rightarrow Br(g)$
- 18) Bond dissociation enthalpy of bromine $Br_2(g) \rightarrow 2Br(g)$
- 19) Enthalpy of vaporisation of bromine $Br_2(l) \rightarrow Br_2(g)$
- 20) 1st electron affinity of bromine $Br(g) + e^- \rightarrow Br^-(g)$

TASK 4 – MAKING SURE OF DEFINITIONS

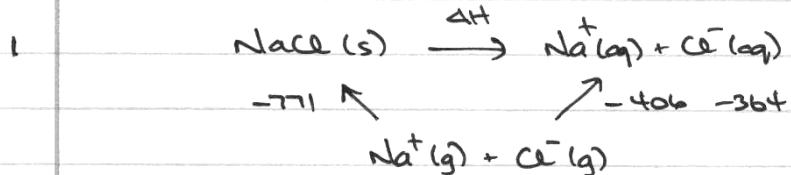
- 1) $\text{Ca(g)} \rightarrow \text{Ca}^+(g) + e^-$... 1st ionisation of Ca
- 2) $\text{S(g)} + 2e^- \rightarrow \text{S}^{2-}(g)$... 1st + 2nd electron affinity S
- 3) $\text{Al}_2\text{O}_3(\text{s}) \rightarrow 2\text{Al}^{3+}(\text{g}) + 3\text{O}^{2-}(\text{g})$... lattice dissociation Al₂O₃
- 4) $\text{NaBr(s)} \rightarrow \text{Na}^+(\text{aq}) + \text{Br}^-(\text{aq})$... solution NaBr
- 5) $\text{I}_2(\text{s}) \rightarrow 2\text{I(g)}$... 2 x atomisation of I
- 6) $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O(l)}$... combustion C₃H₈
- 7) $4\text{Al(s)} + 3\text{O}_2(\text{g}) \rightarrow 2\text{Al}_2\text{O}_3(\text{s})$... 2 x formation Al₂O₃
- 8) $\text{Ca}^{2+}(\text{g}) + \text{O}^{2-}(\text{g}) \rightarrow \text{CaO(s)}$... lattice formation CaO
- 9) $\text{Na(s)} \rightarrow \text{Na(g)}$... atomisation Na
- 10) $\text{P}_4(\text{s}) \rightarrow 4\text{P(g)}$... 4 x atomisation P
- 11) $\text{HCl(g)} \rightarrow \text{H(g)} + \text{Cl(g)}$... bond enthalpy H-Cl
- 12) $\text{H}_2\text{O(l)} \rightarrow 2\text{H(g)} + \text{O(g)}$... vapourisation H₂O + 2 x bond enthalpy O-H
- 13) $\text{Al(g)} \rightarrow \text{Al}^{3+}(\text{g}) + 3e^-$... 1st + 2nd + 3rd ionisation Al
- 14) $\text{Ca}^{2+}(\text{g}) \rightarrow \text{Ca}^{2+}(\text{aq})$... hydration Ca²⁺
- 15) $\text{Mg(s)} \rightarrow \text{Mg}^{2+}(\text{g}) + 2e^-$... atomisation Mg + 1st + 2nd ionisation Mg
- 16) $\text{Mg(s)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{MgO(s)}$... formation MgO

TASK 5 – SOLUTION CALCULATIONS

1 $+1 \text{ kJ mol}^{-1}$
4 -25 kJ mol^{-1}

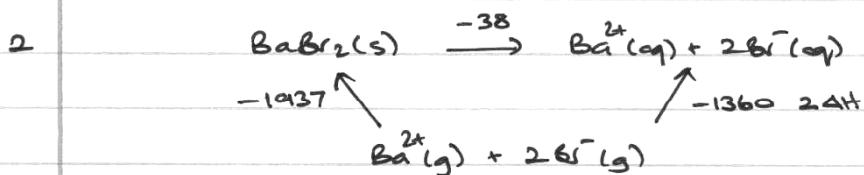
2 $-307.5 \text{ kJ mol}^{-1}$

3 $-2316 \text{ kJ mol}^{-1}$



$\Delta H - 771 = -406 - 364$

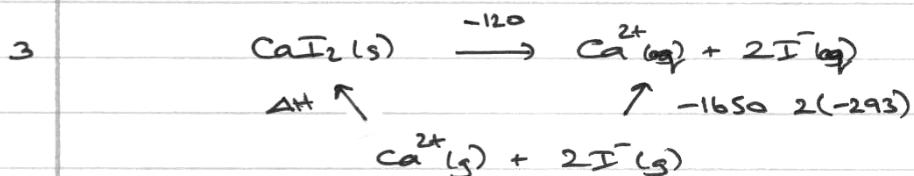
$\Delta H = +1 \text{ kJ/mol}$



$-1360 + 2\Delta H = -1937 - 38$

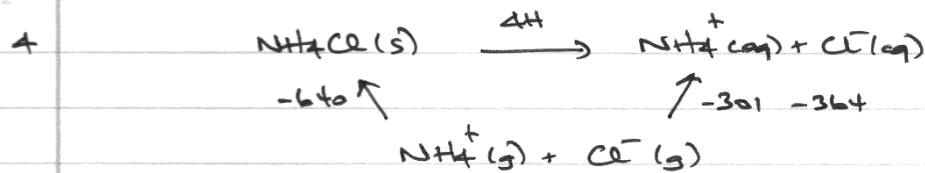
$2\Delta H = -615$

$\Delta H = -307.5 \text{ kJ/mol}$



$\Delta H - 120 = -1650 + 2(-293)$

$\Delta H = -2316 \text{ kJ/mol}$



$\Delta H - 640 = -301 - 364$

$\Delta H = -25 \text{ kJ/mol}$

TASK 6 – BORN HABER CYCLES

$$1 \quad -445 \text{ kJ mol}^{-1}$$

$$4 \quad -3518 \text{ kJ mol}^{-1}$$

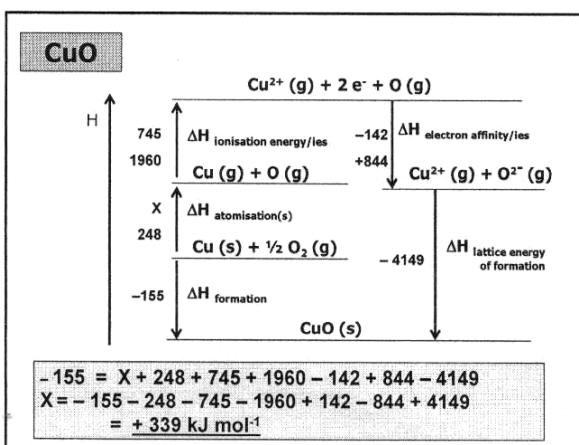
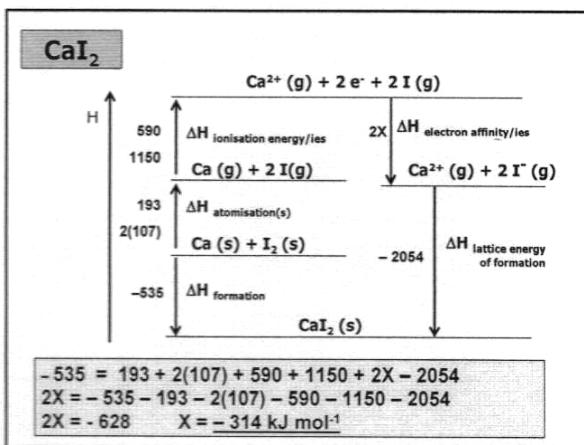
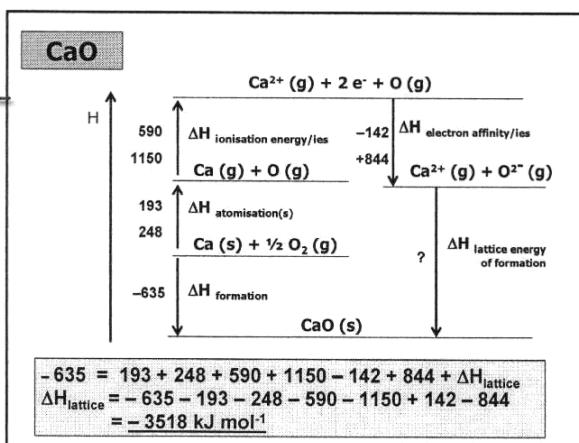
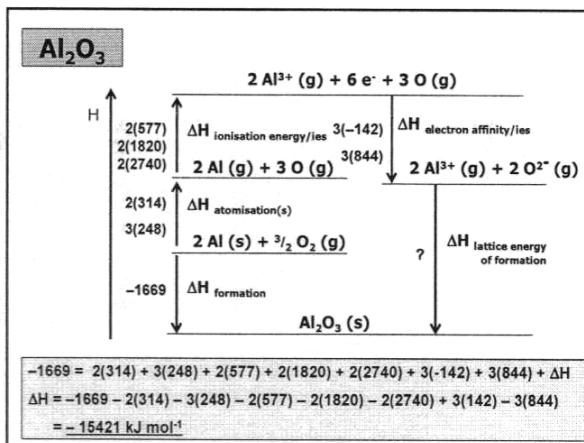
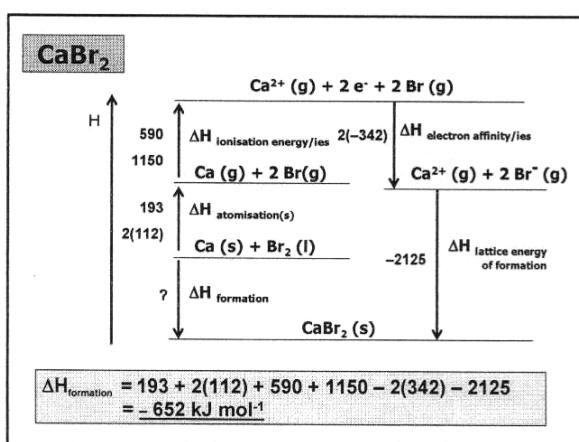
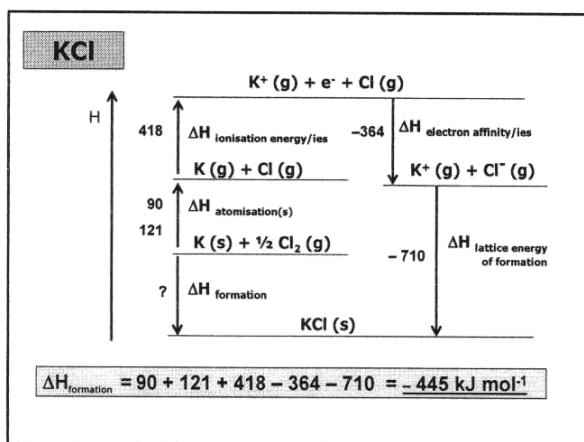
$$7 \quad \text{CoCl} = +241 \text{ kJ mol}^{-1}, \text{ CoCl}_2 = -286 \text{ kJ mol}^{-1}, \text{ CoCl}_3 = -25 \text{ kJ mol}^{-1}$$

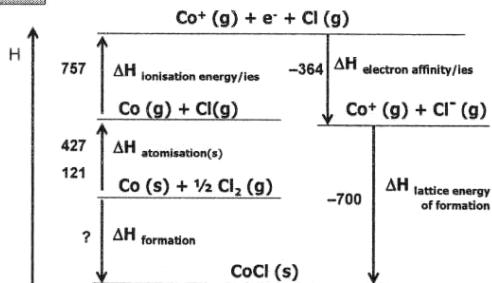
$$2 \quad -652 \text{ kJ mol}^{-1}$$

$$5 \quad -314 \text{ kJ mol}^{-1}$$

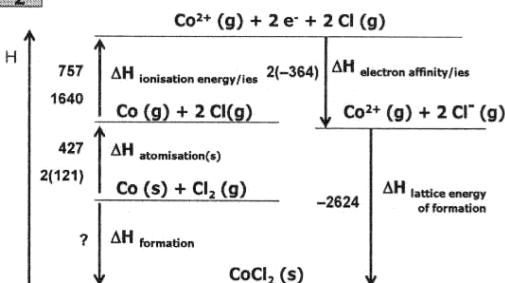
$$3 \quad -15421 \text{ kJ mol}^{-1}$$

$$6 \quad +339 \text{ kJ mol}^{-1}$$

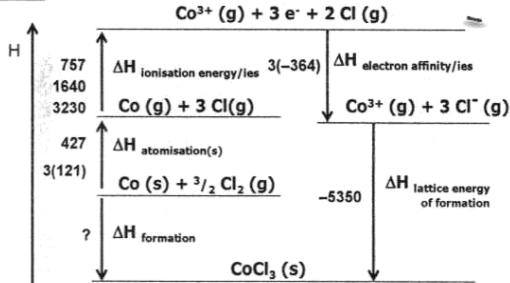


CoCl

$$\Delta H_{\text{formation}} = 427 + 121 + 757 - 364 - 700 \\ = +241 \text{ kJ mol}^{-1}$$

CoCl₂

$$\Delta H_{\text{formation}} = 427 + 2(121) + 757 + 1640 - 2(364) - 2624 \\ = -286 \text{ kJ mol}^{-1}$$

CoCl₃

$$\Delta H_{\text{formation}} = 427 + 3(121) + 757 + 1640 + 3230 - 3(364) - 5350 \\ = -25 \text{ kJ mol}^{-1}$$

TASK 7 – A VARIETY OF ΔH QUESTIONS

2b -92 kJ mol⁻¹

3 +463 kJ mol⁻¹

4 +330 kJ mol⁻¹

5a -2222 kJ mol⁻¹. b -1690 kJ mol⁻¹

8 -463 kJ mol⁻¹

9 -307.5 kJ mol⁻¹

10a -62 kJ mol⁻¹, b +110 kJ mol⁻¹

$$12 \text{ CaCl} = -179, \text{CaCl}_2 = -771, \text{CaCl}_3 = +1494 \text{ kJ mol}^{-1}$$

13a -15421 kJ mol⁻¹, b -288 kJ mol⁻¹, c -342 kJ mol⁻¹, d = +1810 kJ mol⁻¹

16 +523 kJ mol⁻¹

- 1 a) The symbol ΔH° is often used. Explain what the ΔH and $^\circ$ each mean. (2)

b) Define standard enthalpy of formation. (3)

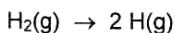
c) Write an equation representing the standard enthalpy of formation of:
i) water ii) propan-1-ol (2)

d) Define standard enthalpy of combustion. (2)

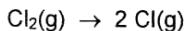
e) Write an equation representing the standard enthalpy of combustion of:
i) hydrogen ii) propan-1-ol (2)

2 a) State Hess's law. (1)

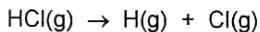
b) Calculate the enthalpy of formation of HCl using the data below.



$$\Delta H^\circ = +436 \text{ kJ mol}^{-1}$$



$$\Delta H^\circ = +242 \text{ kJ mol}^{-1}$$



$$\Delta H^\circ = +431 \text{ kJ mol}^{-1}$$

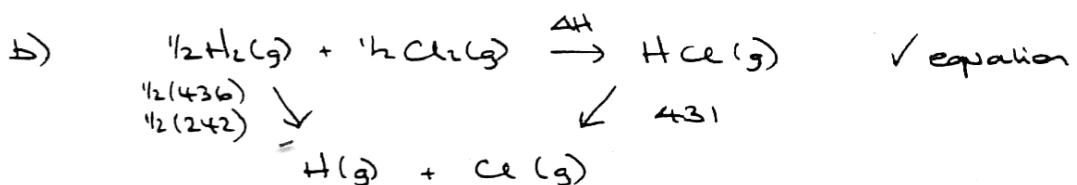
(3)

c) What will be the first step in the mechanism for the reaction for the formation of HCl? (1)

d) Explain your answer to (c). (1)

(Total 5)

a) ✓ enthalpy change for reaction is the same regardless of the route taken



$$\checkmark \Delta H + 431 = \frac{1}{2}(436) + \frac{1}{2}(242)$$

$$\checkmark \Delta H = -92 \text{ kJ mol}^{-1}$$

c) ✓ Cl-Cl bond breaks

d) ✓ weakest bond

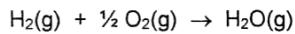
3 Calculate a value for the mean bond enthalpy of the O-H bond in water using the data below.



$$\Delta H^\circ = +436 \text{ kJ mol}^{-1}$$

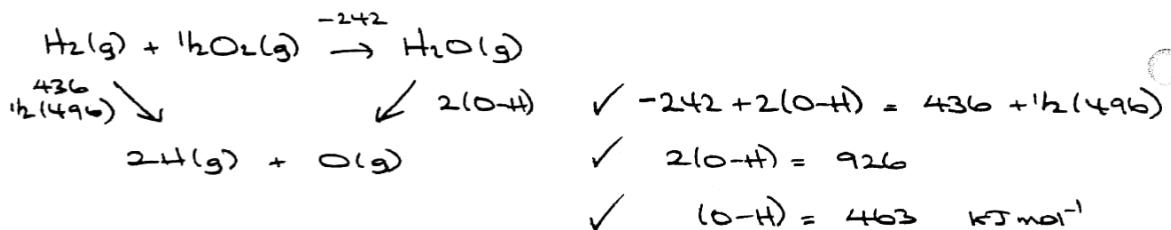


$$\Delta H^\circ = +496 \text{ kJ mol}^{-1}$$



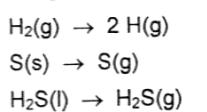
$$\Delta H^\circ = -242 \text{ kJ mol}^{-1}$$

(Total 3)



4

Hydrogen sulphide, H_2S , is a liquid at room temperature. Calculate the average H-S bond enthalpy in hydrogen sulphide given that the enthalpy of formation of hydrogen sulphide is -20 kJ mol^{-1} and the following data.

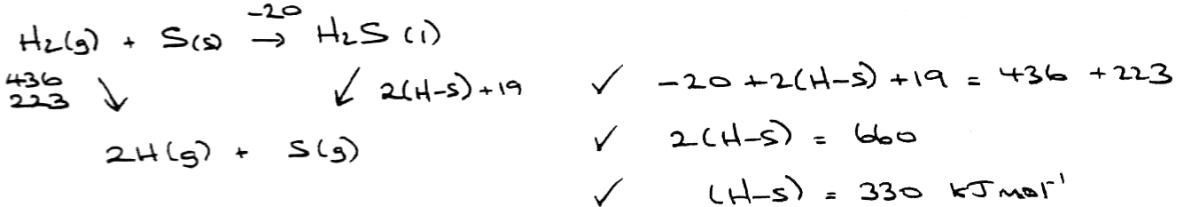


$$\Delta H^\circ = +436 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ = +223 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ = +19 \text{ kJ mol}^{-1}$$

(Total 3)



5

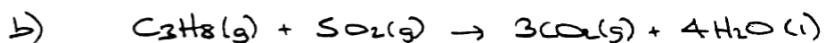
- a) The standard enthalpy of formation of propane is -104 kJ mol^{-1} . Given that the standard enthalpies of formation of carbon dioxide and water are -394 and -286 kJ mol^{-1} respectively, calculate the standard enthalpy change of combustion of propane. (3)

b) Using bond enthalpies only, calculate the standard enthalpy of combustion of propane.
 $\text{C-C } 348, \text{ C-H } 412, \text{ O=O } 496, \text{ C-O } 360, \text{ C=O } 743, \text{ H-O } 463 \text{ kJ mol}^{-1}$ (3)

c) Compare your answers to (a) and (b) and comment on any difference. (2)

(Total 8)

a) $3C(s) + 4H_2(g) \xrightarrow{-104} C_3H_8(g)$ ✓ $-104 + \Delta H = 3(-394) + 4(-286)$
 $\frac{3(-394)}{4(-286)} \downarrow \quad \downarrow \Delta H \quad \checkmark \quad \Delta H = -2222 \text{ kJ mol}^{-1}$



BREAK: $2(c-c) + 8(c+4) + 5(0=0)$

$$= 2(348) + 8(412) + 5(496) = 6472 \quad \checkmark$$

MAKE: $b(c=0) + s(0-H)$

$$= 6(743) + 8(463) = 8142 \quad \checkmark$$

$$\Delta H = 6472 - 8162 = -1690 \text{ kJ mol}^{-1}$$

c) ✓ (a) is the accurate answer
✓ (b) is inaccurate due to using mean bond enthalpies
✓ and not taking into account $\Delta H \text{ H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(g)}$

6

What is the sign (+ or -) of the following standard enthalpy changes (justify your answer)?

- a) condensing steam b) combustion of octane c) boiling ethanol

(Total 3)

- a) ✓ exothermic (H-bonds form releasing energy)
 b) ✓ exothermic (lots of heat released)
 c) ✓ endothermic (overcoming intermolecular forces)

7

Write equations representing each of the following:

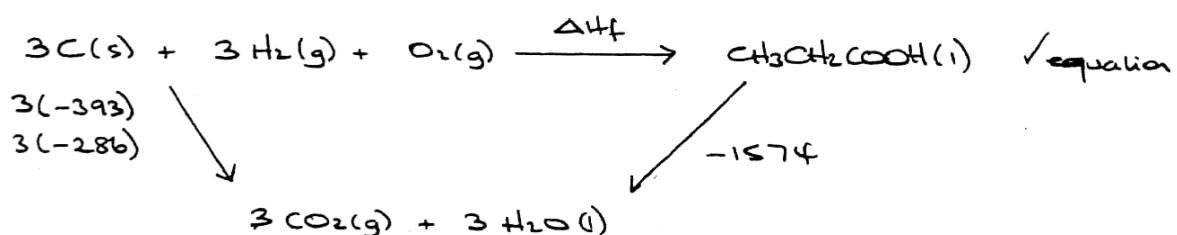
- | | |
|--|---|
| a) 1st electron affinity of iodine | e) bond dissociation energy of iodine |
| b) lattice enthalpy of formation of magnesium iodide | f) enthalpy of solution of magnesium iodide |
| c) enthalpy of atomisation of iodine | g) 2nd ionisation energy of magnesium |
| d) enthalpy of solution of sodium carbonate | h) enthalpy of hydration of calcium ions |
- (Total 8)

- a) ✓ $I(g) + e^- \rightarrow I^-(g)$
 b) ✓ $Mg^{2+}(s) + 2I^-(g) \rightarrow MgI_2(s)$
 c) ✓ $\frac{1}{2} I_2(s) \rightarrow I(g)$
 d) ✓ $Na_2CO_3(s) \xrightarrow{aq} Na_2CO_3(aq)$
 e) ✓ $I_2(g) \rightarrow 2I(g)$
 f) ✓ $MgI_2(s) \xrightarrow{aq} MgI_2(aq)$
 g) ✓ $Mg^+(g) \rightarrow Mg^{2+}(g) + e^-$
 h) ✓ $Ca^{2+}(g) \xrightarrow{aq} Ca^{2+}(aq)$

8

The standard enthalpy change of combustion of propanoic acid is $-1574 \text{ kJ mol}^{-1}$. Given that the standard enthalpies of formation of carbon dioxide and water are -393 and -286 kJ mol^{-1} respectively, calculate the standard enthalpy change of formation of propanoic acid.

(Total 3)



$$\Delta H_f - 1574 = 3(-393) + 3(-286)$$

$$\Delta H_f = \underline{-463 \text{ kJ mol}^{-1}}$$

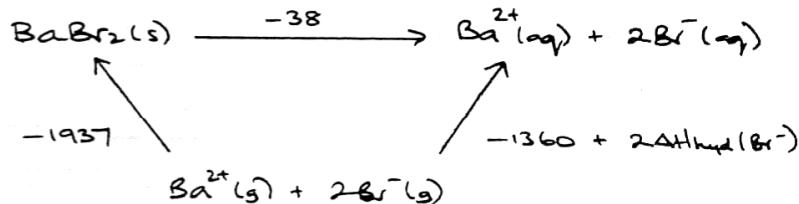
✓

✓

9

Calculate the enthalpy of hydration of bromide ions given that the hydration enthalpy of barium ions is -1360 kJ mol⁻¹, the lattice enthalpy for BaBr₂ is -1937 kJ mol⁻¹ and the enthalpy of solution of BaBr₂ = -38 kJ mol⁻¹.

(Total 3)



$$-1937 - 38 = -1360 + 2\Delta H_{\text{hydr}}(\text{Br}^-) \quad \checkmark$$

$$2\Delta H_{\text{hydr}}(\text{Br}^-) = -615 \quad \checkmark$$

$$\Delta H_{\text{hydr}}(\text{Br}^-) = \underline{-307.5 \text{ kJ mol}^{-1}} \quad \checkmark$$

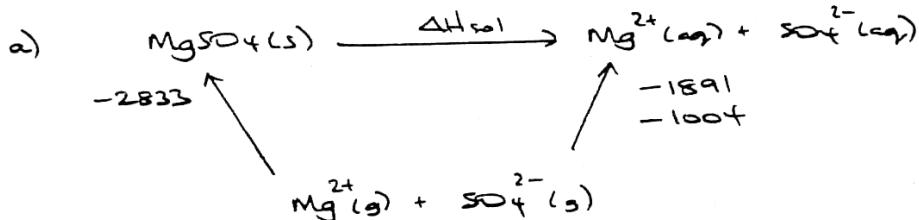
10

Use the data below to calculate the enthalpy of solution of

- a) magnesium sulphate b) barium sulphate

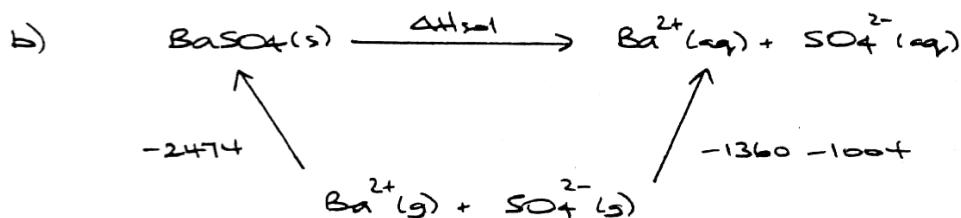
Lattice enthalpy of formation (kJ mol⁻¹): MgSO₄ = -2833; BaSO₄ = -2474Hydration enthalpy (kJ mol⁻¹): Mg²⁺ = -1891; Ba²⁺ = -1360; SO₄²⁻ = -1004

(Total 5)



$$-2833 + \Delta H_{\text{sol}} = -1891 - 1004 \quad \checkmark$$

$$\Delta H_{\text{sol}} = \underline{-62 \text{ kJ mol}^{-1}} \quad \checkmark$$



$$-2474 + \Delta H_{\text{sol}} = -1360 - 1004 \quad \checkmark$$

$$\Delta H_{\text{sol}} = \underline{+110 \text{ kJ mol}^{-1}} \quad \checkmark$$

- 11 a) Define lattice enthalpy of formation. (1)
- b) For each pair of compounds, predict which will have the lattice enthalpy of greatest magnitude, and explain why.
- i) LiF or NaF ii) CaO or MgO iii) NaCl or MgCl₂ (6)
- (Total 7)

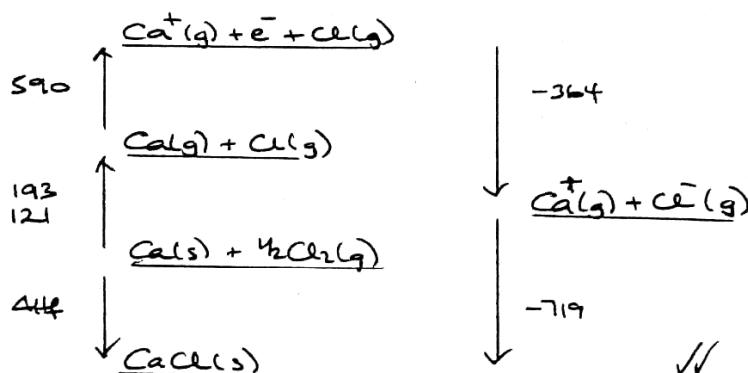
a) ✓ Enthalpy change when one mole of an ionic compound is formed from its constituent ions in the gas phase

- b)
- i) LiF ✓ Li⁺ smaller than Na⁺ ✓
 - ii) MgO ✓ Mg²⁺ smaller than Ca²⁺ ✓
 - iii) MgCl₂ ✓ Mg²⁺ smaller + higher charge than Na⁺ /

Show why calcium and chlorine react together to form CaCl_2 rather than CaCl or CaCl_3 (you will need three Born-Haber cycles to do this). The lattice enthalpies of formation of the chlorides are: $\text{CaCl} = -719$; $\text{CaCl}_2 = -2218$; $\text{CaCl}_3 = -4650 \text{ kJ mol}^{-1}$. You will also need to use data in the table in question 5.

(Total 10)

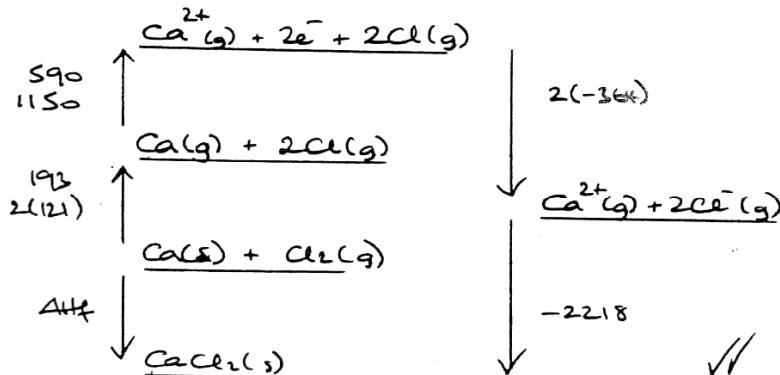
CaCl:



$$\Delta H_f = 121 + 193 + 590 - 364 - 719$$

$$\checkmark = -179 \text{ kJ mol}^{-1}$$

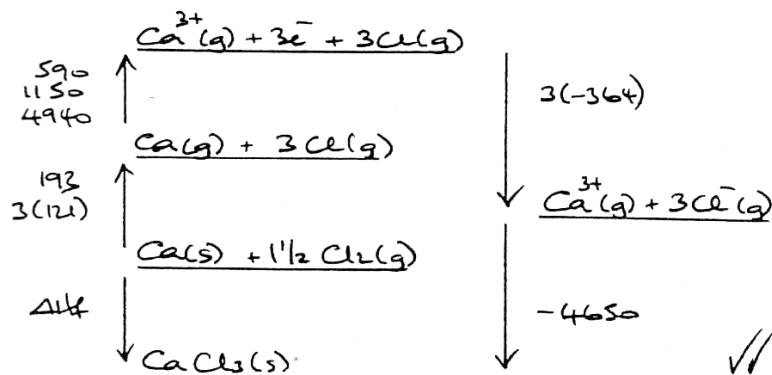
CaCl₂:



$$\Delta H_f = 193 + 2(121) + 590 + 1150 + 2(-364) - 2218$$

$$\checkmark = -771 \text{ kJ mol}^{-1}$$

CaCl₃:



$$\Delta H_f = 193 + 3(121) + 590 + 1150 + 4940 + 3(-364) - 4650 \checkmark = +1494 \text{ kJ mol}^{-1}$$

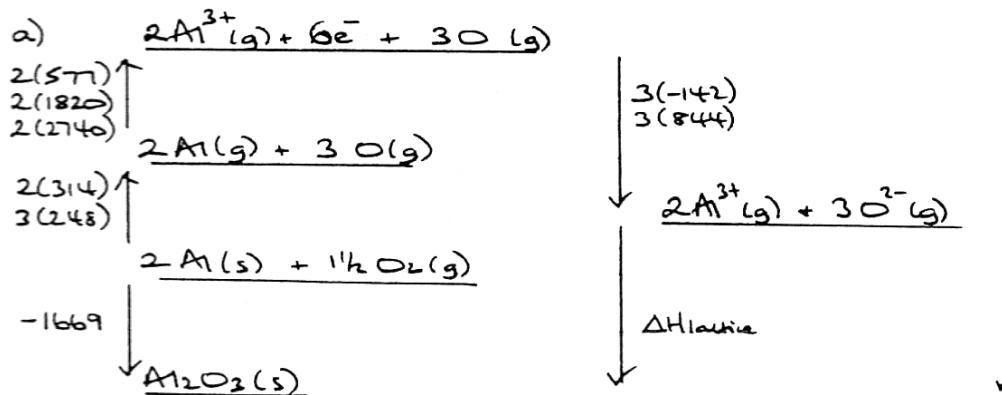
\checkmark CaCl_2 is most stable with respect to the elements.

In each of the following questions you should draw a clear Born-Haber cycle and use data from the table below.

kJ mol^{-1}	Na	Al	Hg	Ca	Cl	Br	I	O
enthalpy of atomisation	109	314	61	193	121	112	107	248
1st ionisation energy	494	577	1010	590				
2nd ionisation energy	4560	1820		1150				
3rd ionisation energy	6940	2740	3300	4940				
1st electron affinity					-364		-314	-142
2nd electron affinity								+844

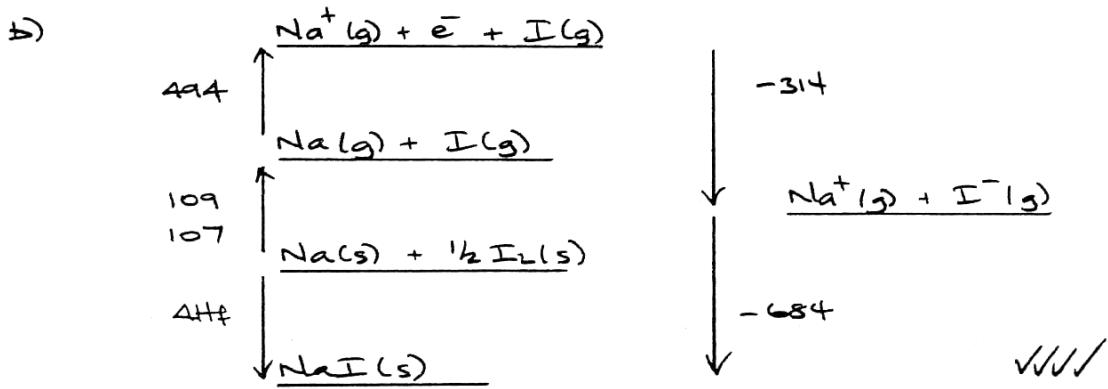
- a) Calculate the lattice enthalpy of formation of aluminium oxide given that its enthalpy of formation is -1669 kJ mol^{-1} . (6)
- b) Calculate the enthalpy of formation of sodium iodide given that its lattice enthalpy of formation is -684 kJ mol^{-1} . (6)
- c) Calculate the first electron affinity of bromine given that the lattice enthalpy of formation of calcium bromide is -2148 kJ mol^{-1} and the enthalpy of formation is calcium bromide is -675 kJ mol^{-1} . (6)
- d) Calculate the second ionisation energy of mercury given that the lattice enthalpy of dissociation of mercury (II) chloride is +2625 kJ mol^{-1} and the enthalpy of formation is mercury (II) chloride is -230 kJ mol^{-1} . (6)

(Total 24)



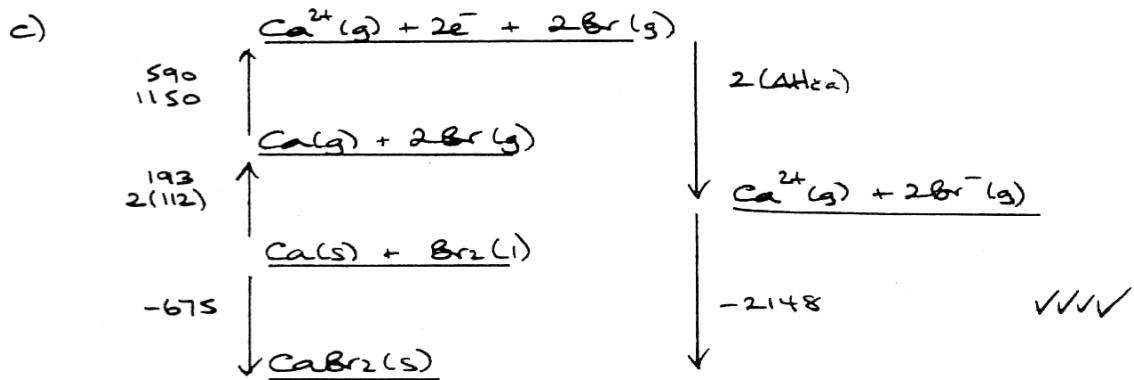
$\checkmark -1669 = 3(248) + 2(314) + 2(577 + 1820 + 2740) + 3(-142 + 844) + \Delta H_{\text{lattice}}$

$\checkmark \Delta H_{\text{lattice}} = -15421 \text{ kJ mol}^{-1}$



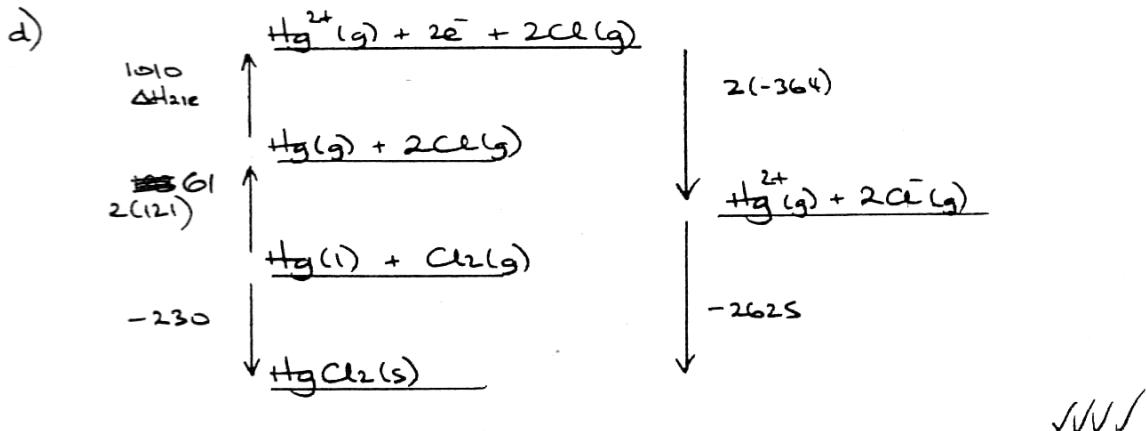
$$\checkmark \quad \Delta H_f^\circ = 109 + 107 + 494 - 314 - 684$$

$$\checkmark \quad = -288 \text{ kJ mol}^{-1}$$



$$\checkmark \quad -675 = 2(112) + 193 + 590 + 1150 + 2\Delta H_{\text{ea}} - 2148$$

$$2\Delta H_{\text{ea}} = -684 \quad \Delta H_{\text{ea}} = -342 \text{ kJ mol}^{-1}$$



$$\checkmark \quad -230 = \cancel{61} + 2(121) + 1010 + \Delta H_{\text{clc}} + 2(-364) - 2625$$

$$\checkmark \quad \Delta H_{\text{clc}} = \cancel{1810} \text{ kJ mol}^{-1}$$

Calculate the enthalpy of formation of magnesium sulphide given the following data.

Lattice enthalpy of formation of magnesium sulphide $\Delta H^\circ = -3255 \text{ kJ mol}^{-1}$

$\text{Mg(s)} \rightarrow \text{Mg(g)}$ $\Delta H^\circ = +150 \text{ kJ mol}^{-1}$

$\text{Mg(g)} \rightarrow \text{Mg}^+(g) + e^-$ $\Delta H^\circ = +736 \text{ kJ mol}^{-1}$

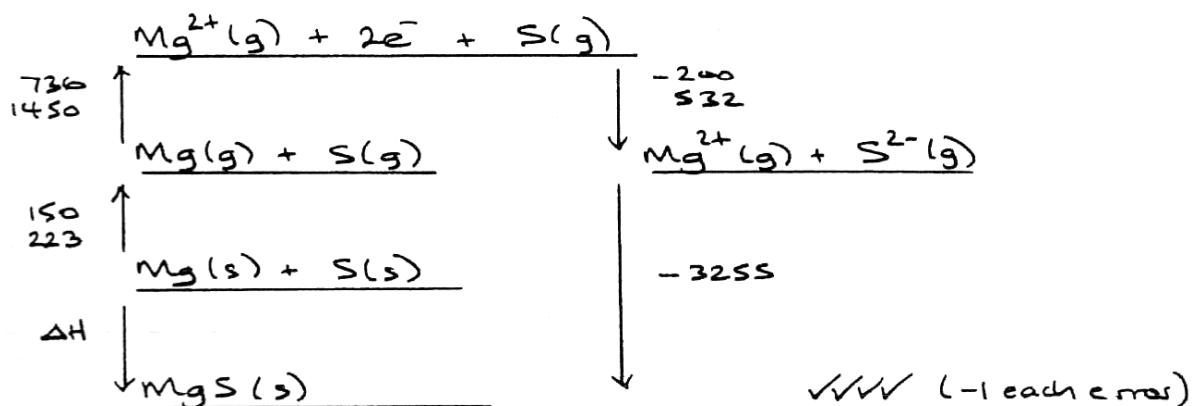
$\text{Mg}^+(\text{g}) \rightarrow \text{Mg}^{2+}(\text{g}) + e^-$ $\Delta H^\circ = +1450 \text{ kJ mol}^{-1}$

$\text{S(s)} \rightarrow \text{S(g)}$ $\Delta H^\circ = +223 \text{ kJ mol}^{-1}$

$\text{S(g)} + e^- \rightarrow \text{S}^-(\text{g})$ $\Delta H^\circ = -200 \text{ kJ mol}^{-1}$

$\text{S}^-(\text{g}) + e^- \rightarrow \text{S}^{2-}(\text{g})$ $\Delta H^\circ = +532 \text{ kJ mol}^{-1}$

(Total 6)



$$\checkmark \Delta H = 150 + 223 + 736 + 1450 - 200 + 532 - 3255$$

$$\checkmark \Delta H = -364 \text{ kJ mol}^{-1}$$

15

Lattice enthalpy gives us useful information about the structure of an ionic compound.

a) Explain why the magnitude of the lattice enthalpy of:

- i) KCl (-701) is less than CaCl₂ (-2237)
- ii) NaF (-902) is greater than KF (-801)

(3)

b) Using the sizes and charges of ions and the laws of electrostatics, theoretical values can be calculated for lattice enthalpies. The table below shows a comparison between values measured using experimental data with Born-Haber cycles, and theoretical values.

	NaCl	NaBr	NaI	AgCl	AgBr	AgI
Experimental value (kJ mol ⁻¹)	-776	-742	-699	-890	-877	-867
Theoretical value (kJ mol ⁻¹)	-766	-731	-686	-768	-759	-736

For many substances, the measured and theoretical values are very similar, such as the sodium halides, but for some substances there is a significant difference, such as the silver halides. Account for this difference.

(2)

(Total 7)

- a) i) ✓ Ca²⁺ smaller than K⁺
 ✓ Ca²⁺ higher charge than K⁺
 ✓ stronger attraction between + and - ions
- ii) ✓ Na⁺ smaller than K⁺
 ✓ strong attraction between + and - ions
- b) ✓ difference is due to covalent character
 ✓ silver halides have more covalent character than sodium halides

16

Use the following data to calculate the average C-S bond energy in $\text{CS}_2(\text{l})$.

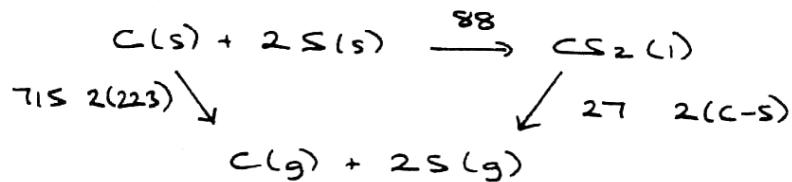
Enthalpy of atomisation of sulphur = + 223 kJ mol^{-1}

Enthalpy of atomisation of carbon = + 715 kJ mol^{-1}

Enthalpy of formation of $\text{CS}_2(\text{l})$ = + 88 kJ mol^{-1}

Enthalpy of vaporisation of $\text{CS}_2(\text{l})$ = +27 kJ mol^{-1} i.e. $\text{CS}_2(\text{l}) \rightarrow \text{CS}_2(\text{g})$

(Total 4)



$$\checkmark 88 + 27 + 2(\text{C-S}) = -715 + 2(223)$$

$$\checkmark 2(\text{C-S}) = 1046 \quad (\text{C-S}) = \underline{\underline{523 \text{ kJ mol}^{-1}}}$$

17

The enthalpy of hydration of magnesium and sodium ions are -1920 and -406 kJ mol^{-1} respectively. Explain why the enthalpy of hydration of Mg^{2+} has a greater magnitude than that of Na^+ . (Total 2)

- ✓ Mg^{2+} has higher charge than Na^+
- ✓ Mg^{2+} smaller than Na^+

TASK 8 – ENTROPY CALCULATIONS

1b i $-119 \text{ J mol}^{-1} \text{ K}^{-1}$

ii $+20 \text{ J mol}^{-1} \text{ K}^{-1}$

iii $-373 \text{ J mol}^{-1} \text{ K}^{-1}$

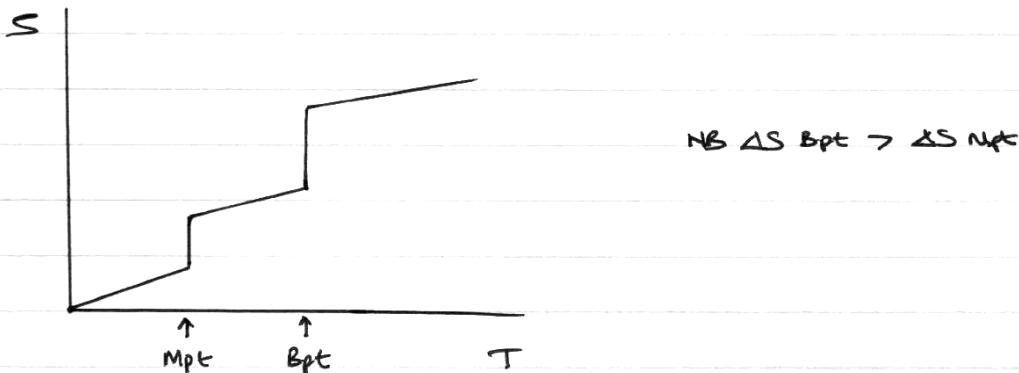
1

- a) i) $1 \text{ mol g} \rightarrow 1 \text{ mol l}$ $\Delta S -\text{ve}$
ii) $2 \text{ mol g} \rightarrow 2 \text{ mol g}$ ~ 0
iii) $8 \text{ mol g} \rightarrow 3 \text{ mol g} + 4 \text{ mol l}$ $\Delta S -\text{ve}$

b) $\Delta S = (\text{Sum } S_{\text{products}}) - (\text{Sum } S_{\text{reactants}})$

i) $\Delta S = 70 - 189 = -119 \text{ J mol}^{-1} \text{ K}^{-1}$
ii) $\Delta S = 2(187) - (131 + 223) = +20 \text{ J mol}^{-1} \text{ K}^{-1}$
iii) $\Delta S = [3(214) + 4(70)] - [270 + 5(205)] = -373 \text{ J mol}^{-1} \text{ K}^{-1}$

2



TASK 9 – GIBBS FREE ENERGY CALCULATIONS

1a -191 kJ mol^{-1}

2a $\Delta H = +129 \text{ kJ mol}^{-1}$, $\Delta S = +335 \text{ J mol}^{-1} \text{ K}^{-1}$, b $+29.2 \text{ kJ mol}^{-1}$, c $T \geq 385 \text{ K}$

3 $\Delta H = -394 \text{ kJ mol}^{-1}$, $\Delta S = +3.3 \text{ J mol}^{-1} \text{ K}^{-1}$, $\Delta G = -395 \text{ kJ mol}^{-1}$

4 $\Delta H = -822 \text{ kJ mol}^{-1}$, $\Delta S = -272 \text{ J mol}^{-1} \text{ K}^{-1}$, $\Delta G = -741 \text{ kJ mol}^{-1}$, $T \leq 3028 \text{ K}$

5 $\Delta S = -107 \text{ J mol}^{-1} \text{ K}^{-1}$

6 $\Delta H = +96 \text{ kJ mol}^{-1}$, $\Delta S = +138 \text{ J mol}^{-1} \text{ K}^{-1}$, $\Delta G = +54.9 \text{ kJ mol}^{-1}$, $T \geq 696 \text{ K}$

7a $\Delta S = +10.3 \text{ J mol}^{-1} \text{ K}^{-1}$, b 112 K

8a $\Delta H = +15 \text{ kJ mol}^{-1}$, d $\Delta S = +50.3 \text{ J mol}^{-1} \text{ K}^{-1}$

9a $\Delta H = +178 \text{ kJ mol}^{-1}$, $\Delta S = +164 \text{ J mol}^{-1} \text{ K}^{-1}$, $\Delta G = +129 \text{ kJ mol}^{-1}$, $T \geq 1085 \text{ K}$

9b $\Delta H = +117 \text{ kJ mol}^{-1}$, $\Delta S = +175 \text{ J mol}^{-1} \text{ K}^{-1}$, $\Delta G = +64.9 \text{ kJ mol}^{-1}$, $T \geq 669 \text{ K}$

1 a)
$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= -185 - 298 \left(\frac{335}{1000} \right) \\ &= -191 \text{ kJ mol}^{-1}\end{aligned}$$

b) Yes – feasible

c) High E_a

2 a)
$$\begin{aligned}\Delta H &= [\text{Sum } \Delta H_f \text{ products}] - [\text{Sum } \Delta H_f \text{ reactants}] \\ &= [-1131 - 394 - 242] - [2(-948)] \\ &= +129 \text{ kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta S &= [\text{Sum } S \text{ products}] - [\text{Sum } S \text{ reactants}] \\ &= [136 + 214 + 189] - [2(102)] \\ &= +335 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

b)
$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= 129 - 298 \left(\frac{335}{1000} \right) \\ &= +29.2 \text{ kJ mol}^{-1}\end{aligned}$$

c) when $\Delta G = 0$ $T = \frac{\Delta H}{\Delta S} = \frac{129}{335/1000} = 385 \text{ K}$

\therefore feasible when $T \geq 385 \text{ K}$

3 $\Delta H = -394 \text{ kJ mol}^{-1}$

$$\Delta S = (214) - (5.7 + 205) = 3.3 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\begin{aligned}\Delta G &= -394 - 298 \left(\frac{3.3}{1000} \right) \\ &= -395 \text{ kJ mol}^{-1}\end{aligned}$$

4 $\Delta H = (-822) - (0+0) = -822 \text{ kJ mol}^{-1}$

$$\Delta S = (90) - (2(27) + 3/2(205)) = -271.5 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta G = -822 - 298 \left(\frac{-271.5}{1000} \right) = -741 \text{ kJ mol}^{-1}$$

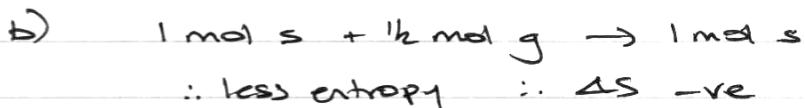
$$\Delta G = 0 \quad T = \frac{\Delta H}{\Delta S} = \frac{-822}{-271.5} = 3028 \text{ K}$$

Feasible if $T \leq 3028 \text{ K}$

5 a) $\Delta G = \Delta H - T\Delta S$

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

$$\begin{aligned}\Delta S &= \frac{\Delta H - \Delta G}{T} = \frac{-602 - (-570)}{298} \\ &= -0.107 \text{ kJ mol}^{-1} \text{ K}^{-1} \\ &= -107 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$



6 a) $\Delta H = [0 + 3(-242)] - [-822 + 0] = +96 \text{ kJ mol}^{-1}$
 $\Delta S = [2(27) + 3(189)] - [90 + 3(131)] = +138 \text{ J mol}^{-1} \text{ K}^{-1}$
 $\Delta G = 96 - 298 \left(\frac{138}{1000}\right) = +54.9 \text{ kJ mol}^{-1}$

b) not feasible

c) $\Delta G = 0 \quad T = \frac{\Delta H}{\Delta S} = \frac{96}{\frac{138}{100}} = 696 \text{ K}$

Feasible if $T \geq 696 \text{ K}$

7 a) At 91 K, $\Delta G = 0 \quad \therefore \Delta H - T\Delta S = 0$

$$\Delta H = T\Delta S$$

$$\Delta S = \frac{\Delta H}{T} = \frac{0.94}{91} = 0.0103 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

$$= 10.3 \text{ J mol}^{-1} \text{ K}^{-1}$$

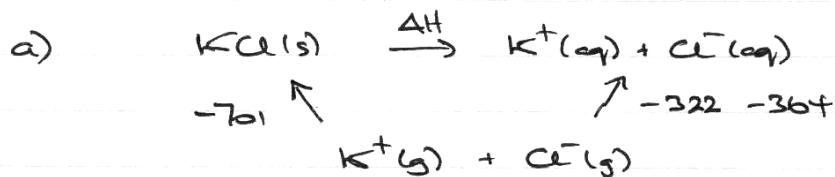
b) At bpt $\Delta G = 0 \quad T = \frac{\Delta H}{\Delta S} = \frac{8.2}{\frac{73.2}{1000}} = 112 \text{ K}$

c) $\Delta S_{\text{boiling}} > \Delta S_{\text{melting}}$

increase in disorder of particles much greater on
 liquid \rightarrow gas than solid \rightarrow liquid

d) driving force is increase in entropy

8



$$\Delta H - 701 = -322 - 364$$

$$\Delta H = +15 \text{ kJ mol}^{-1}$$

b)
+ c)

$\Delta S +ve$

Increase in disorder as ions become dissolved

ΔS must be +ve for $\Delta G < 0$ as $\Delta H +ve$

d)

If $\Delta G = 0 \quad \Delta H = T\Delta S$

$$\Delta S = \frac{\Delta H}{T} = \frac{15}{298} = 0.0503 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

$$= 50.3 \text{ J mol}^{-1} \text{ K}^{-1}$$

9

a) i) $\Delta H = [\text{sum } \Delta H_f \text{ products}] - [\text{sum } \Delta H_f \text{ reactants}]$
 $= [-635 - 394] - [-1207]$
 $= +178 \text{ kJ mol}^{-1}$ ✓

ii) $\Delta S = [\text{sum } S \text{ products}] - [\text{sum } S \text{ reactants}]$
 $= [40 + 214] - [90]$
 $= +164 \text{ J mol}^{-1} \text{ K}^{-1}$ ✓

iii) $\Delta G = \Delta H - T\Delta S$
 $= 178 - 298 \left(\frac{164}{1000} \right)$
 $= +129.1 \text{ kJ mol}^{-1}$ ✓

iv) ✓ reaction is not spontaneous / feasible at 298 K

v) $\Delta G = 178 - T \left(\frac{164}{1000} \right)$
✓ as T increases, ΔG more -ve

vi) ✓ $\Delta G = 0$, $T = \frac{\Delta H}{\Delta S}$
✓ $T = \frac{178}{\left(\frac{164}{1000} \right)}$
✓ = 1085 K

vii) ✓ spontaneous if $T \geq 1085 \text{ K}$

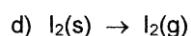
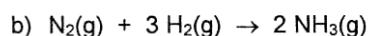
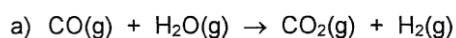
viii) ✓ due to increase in entropy

b) i) $\Delta H = [-602 - 394] - [-1113] = +117 \text{ kJ mol}^{-1}$ ✓
ii) $\Delta S = [27 + 214] - [66] = +175 \text{ J mol}^{-1} \text{ K}^{-1}$ ✓
iii) $\Delta G = 117 - 298 \left(\frac{175}{1000} \right) = +64.9 \text{ kJ mol}^{-1}$ ✓
iv) $T = \frac{117}{\left(\frac{175}{1000} \right)} = 668.6 \text{ K}$ ✓

c) ✓ CaCO_3 more stable
✓ Ca^{2+} less polarising than Mg^{2+}

10

State the sign of the entropy change in the following reactions (or whether it stays roughly constant), justifying your answer in each case.



(Total 4)

- a) ✓ not sure ($2\text{gas} \rightarrow 2\text{gas}$)
- b) ✓ - ($4\text{gas} \rightarrow 2\text{gas}$)
- c) ✓ + ($\text{solid} \rightarrow \text{dissolved}$)
- d) ✓ + ($\text{solid} \rightarrow \text{gas}$)