THERMODYNAMICS

Answers

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Most answers in this topic are to the nearest unit unless stated otherwise (as data is to nearest unit and it is addition or subtraction

PAGE 3 EXAMPLES

$C(s) + 2 H_2(g) \rightarrow CH_4(g)$

$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$

$\frac{1}{2} N_2(g) + 3/2 H_2(g) \rightarrow NH_3(g)$

$2 C(s) + 3 H_2(g) + \frac{1}{2} O_2(g) \rightarrow C_2H_5OH(l)$

$C(s) + 3/2 H_2(g) + \frac{1}{2} Br_2(l) \rightarrow CH_3Br(l)$

$2 Na(s) + \frac{1}{2} O_2(g) \rightarrow Na_2O(s)$

$CH_4(g) + 2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(l)$

$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$

$C_2H_6(g) + 3\frac{1}{2} O_2(g) \rightarrow 2 CO_2(g) + 3 H_2O(l)$

$C_2H_5OH(g) + 3 O_2(g) \rightarrow 2 CO_2(g) + 3 H_2O(l)$

$Na(s) + \frac{1}{4} O_2(g) \rightarrow \frac{1}{2} Na_2O(s)$

$C_6H_{14}(g) + 9\frac{1}{2} O_2(g) \rightarrow 6 CO_2(g) + 7 H_2O(l)$

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

$\frac{1}{2}H_2SO_4(aq) + NaOH(aq) \rightarrow \frac{1}{2} Na_2SO_4(aq) + H_2O(l)$

$HNO_3(aq) + KOH(aq) \rightarrow KNO_3(aq) + H_2O(l)$

$HNO_3(aq) + \frac{1}{2}Ba(OH)_2(aq) \rightarrow \frac{1}{2} Ba(NO_3)_2(aq) + H_2O(l)$

$\frac{1}{2}H_2SO_4(aq) + \frac{1}{2}Ba(OH)_2(aq) \rightarrow \frac{1}{2}BaSO_4(aq) + H_2O(l)$
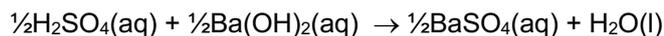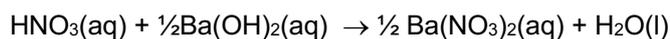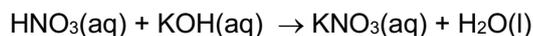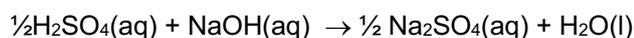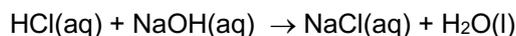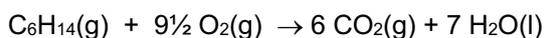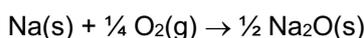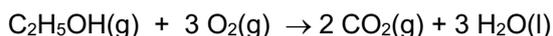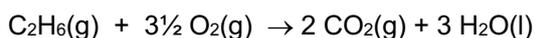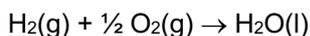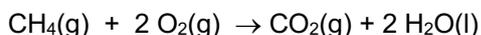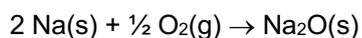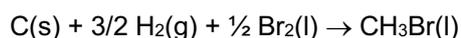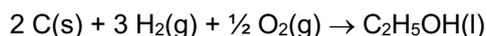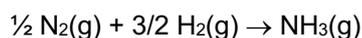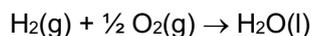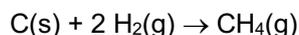
PAGE 4 EXAMPLES

Ex1 ΔH = [Sum of ΔH_f products] – [Sum ΔH_f reactants]

= [-394 + 2(-286)] – [–75 + 0]

= –891 kJ mol⁻¹

Ex2 ΔH = [Sum of ΔH_f products] – [Sum ΔH_f reactants]

-2877 = [4(-394) + 5(-286)] – [$\Delta_f H$ + 0]

$\Delta_f H$ = 2877 + 4(-394) + 5(-286)

= –129 kJ mol⁻¹

PAGE 5 EXAMPLES

Ex 1

C(s) + 2 H₂(g)   —ΔH→   CH₄(g)

–394
2(–286)   –890

CO₂(g) + 2 H₂O(l)

ΔH – 890 = –394 + 2(–286)

ΔH = –394 + 2(–286) + 890

= –76 kJ mol⁻¹

Ex 2

$$2\ C(s)\ +\ 3\ H_2(g)\ +\ \tfrac{1}{2}\ O_2(g)\ \xrightarrow{\ -75\ }\ CH_3CH_2OH(l)$$

2(−394)
3(−286) $\searrow$ Δ_cH $\swarrow$

$$2\ CO_2(g)\ +\ 3\ H_2O(l)$$
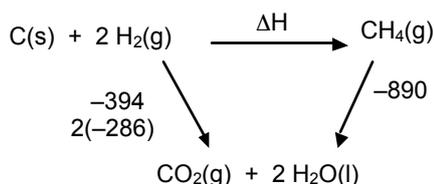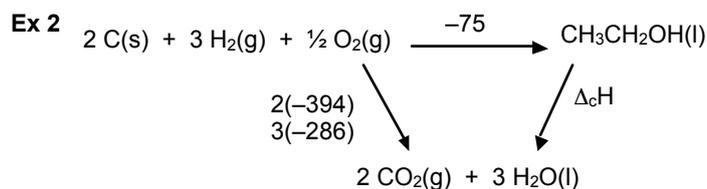
$\Delta_cH - 75\ =\ 2(-394) + 3(-286)$

$\Delta_cH\ =\ 2(-394) + 3(-286) + 75$

= −1571 kJ mol^{-1}

PAGE 6/7 EXAMPLES

Ex 1

$$N_2H_4(g) + O_2(g)\ \xrightarrow{\ -583\ }\ N_2(g) + 2\ H_2O(g)$$

N-N
4(N-H) $\searrow$ N≡N
O=O   4(O-H) $\swarrow$

$$2N(g) + 4H(g) + 2O(g)$$
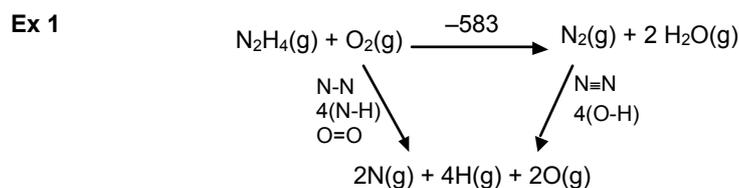
$-583 + (N≡N) + 4(O\text{-}H)\ =\ (N\text{-}N) + 4(N\text{-}H) + (O=O)$

$(N\text{-}N)\ =\ -583 + (N≡N) + 4(O\text{-}H) - 4(N\text{-}H) - (O=O)$

$(N\text{-}N)\ =\ -583 + 944 + 4(463) - 4(388) - (498)$

= +163 kJ mol^{-1}

Ex 2

$$C_2H_5OH(l) + 3\ O_2(g)\ \xrightarrow{\ -1015\ }\ 2\ CO_2(g) + 3\ H_2O(g)$$

44   C-O $\searrow$ 4(C=O)
C-C   O-H   6(O-H) $\swarrow$
5(C-H) 3(O=O) $\searrow$

$$2C(g) + 6H(g) + 7O(g)$$
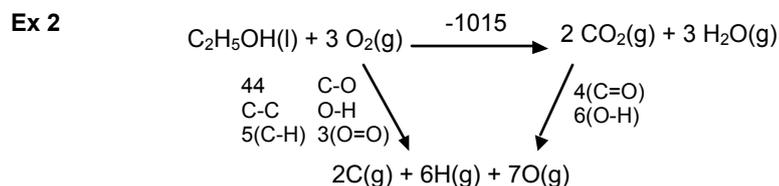
$-1015 + 4(C=O) + 6(O\text{-}H)\ =\ 44 + (C\text{-}C) + 5(C\text{-}H) + (C\text{-}O) + (O\text{-}H) + 3(O=O)$

$(C\text{-}C)\ =\ -1015 + 4(C=O) + 6(O\text{-}H)\ -\ 44 - 5(C\text{-}H) - (C\text{-}O) - (O\text{-}H) - 3(O=O)$

$(C\text{-}C)\ =\ -1015 + 4(743) + 6(463)\ -\ 44 - 5(412) - (360) - (463) - 3(498)$

= +314 kJ mol^{-1}

PAGE 8 EXAMPLES

Ex 1 $q\ =\ mc\Delta T$

$=\ 100\ \times\ 4.18\ \times\ 36\ =\ 15048\ J\ =\ 15.048\ kJ$

moles $CH_3CH_2CH_2OH$ = mass / M_r = 0.500 / 60.0 = 0.00833

$\Delta H\ =\ q\ /\ moles\ =\ -15.048\ /\ 0.00833$

= − 1810 kJ mol^{-1} (3sf)

Ex 2 $q = mc\Delta T$

$= 50 \times 4.18 \times 6.7 = 1400 \text{ J} = 1.400 \text{ kJ}$

moles NaOH = conc x vol (dm^3) = $1.0 \times 25/1000 = 0.0250$

moles HCl = conc x vol (dm^3) = $1.0 \times 25/1000 = 0.0250$

$\Delta H = q / \text{moles} = -1.400 / 0.0250$

$= -56 \text{ kJ mol}^{-1}$ (2sf)

Ex 3 $q = mc\Delta T$

$= 50 \times 4.18 \times 24 = 5016 \text{ J} = 5.016 \text{ kJ}$

moles $CuSO_4$ = conc x vol (dm^3) = $0.5 \times 50.0/1000 = 0.0250$

moles Zn = mass / M_r = $2.0 / 65.4 = 0.0306$

∴ zinc is in excess and 0.0250 moles of $CuSO_4$ reacts with 0.025 moles of Zn

$\Delta H = q / \text{moles} = -5.016 / 0.0250$

$= -201 \text{ kJ mol}^{-1}$ (3sf)

TASK 1 – AS Energetics Revision

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 -1700 kJ mol^{-1} (2sf)	8 -57.3 kJ mol^{-1} (3sf)	9 -5116 kJ mol^{-1}
10 +507 kJ mol^{-1}		

1)

$$4 \text{ C(s)} + 5 \text{ H}_2\text{(g)} \xrightarrow{\Delta H_f} \text{C}_4\text{H}_{10}\text{(g)}$$

4(–394)
5(–286)   –2877

$$4 \text{ CO}_2\text{(g)} + 5 \text{ H}_2\text{O(l)}$$
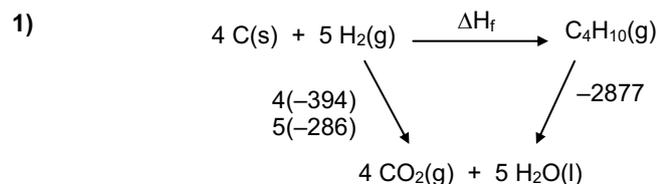
$\Delta H_f - 2877 = 4(-394) + 5(-286)$ $\Delta H_f = 4(-394) + 5(-286) + 2877$

$= -129 \text{ kJ mol}^{-1}$

OR ΔH = [Sum of ΔH_c reactants] – [Sum ΔH_c products]

$= [4(-394) + 5(-286)] - [-2877]$

$= -129 \text{ kJ mol}^{-1}$

2) $C_3H_8\text{(g)} + 5 \text{ O}_2\text{(g)} \rightarrow 3 \text{ CO}_2\text{(g)} + 4 \text{ H}_2\text{O(l)}$
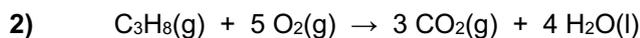
ΔH = [Sum of ΔH_f products] – [Sum ΔH_f reactants]

$= [3(-394) + 4(-286)] - [-104]$

$= -2222 \text{ kJ mol}^{-1}$

3) Broken   C-C + 6 C-H + 3½ O=O = 348 + 6(412) + 3½(496) = 4556

       Made   4 C=O + 6 O-H = 4(743) + 6(463) = 5750

ΔH = [Bond broken] – [Bonds made] = 4556 – 5750 = **-1194 kJ mol^{-1}**

4)

$$3\ C(s)\ +\ 4\ H_2(g)\ +\ \tfrac{1}{2}\ O_2(g)\ \xrightarrow{\ -318\ }\ CH_3CH(OH)CH_3(l)$$

3(–394)
4(–286) ΔH_c

$$3\ CO_2(g)\ +\ 4\ H_2O(l)$$
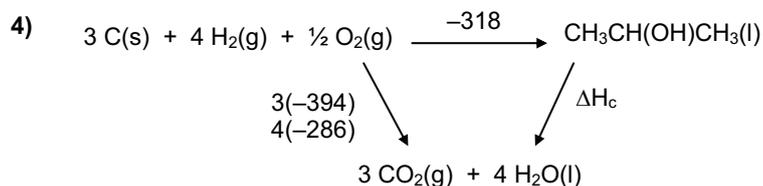
$-318 + \Delta H_c = 3(-394) + 4(-286)$ $\Delta H_c = 3(-394) + 4(-286) + 318$

                                                = –2008 kJ mol^{-1}

_**OR**_ ΔH = [Sum of ΔH_c reactants] – [Sum ΔH_c products]

    -318 = [3(-394) + 4(-286)] – [ΔH_c]

    ΔH_c = 3(-394) + 4(-286) + 318   **= –2008 kJ mol^{-1}**

5)

$$C(s)\ +\ 2\ Cl_2(g)\ \xrightarrow{\ \Delta H_f\ }\ CCl_4(l)$$

715
2(242)   +31
                     4(338)

$$C(g)\ +\ 4\ Cl(g)$$
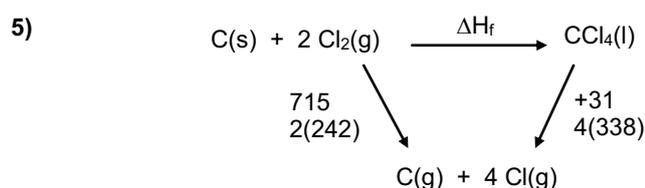
$\Delta H_f + 31 + 4(338) = 715 + 2(242)$ $\Delta H_f = 715 + 2(242) - 31 - 4(338)$

                                                = –184 kJ mol^{-1}

6)

$$CH_3CH{=}CH_2(g)\ +\ H_2(g)\ \xrightarrow{\ \Delta H\ }\ CH_3CH_2CH_3(g)$$

–2059
–286   –2220

$$3\ CO_2(g)\ +\ 4\ H_2O(l)$$
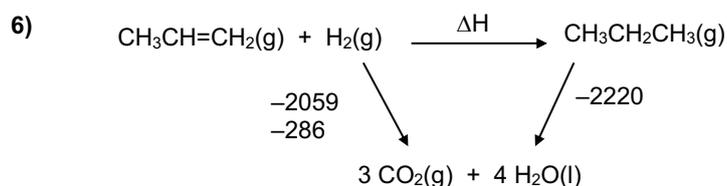
$\Delta H - 2220 = -2059 + -286$ $\Delta H = -2059 - 286 + 2220$

                                               = –125 kJ mol^{-1}

_**OR**_ ΔH = [Sum of ΔH_c reactants] – [Sum ΔH_c products]

        = [-2059 - 286] – [–2220]

        = –125 kJ mol^{-1}

7) q = $mc\Delta T$

          = 80 x 4.18 x 47.3 = 15820 J = 15.82 kJ

    moles CH_3COCH_3 = mass / M_r = 0.55 / 58.0 = 0.00948

    ΔH = q / moles = -15.82 / 0.00948

          = – 1700 kJ mol^{-1} (2sf)

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 (dm^3) $= 2.0 \times 25/1000 = 0.0500$

moles HNO$_3$ $=$ conc x vol (dm^3) $= 2.0 \times 25/1000 = 0.0500$

$\Delta H = q / \text{moles} = -2.863 / 0.0500$

$= -57.3 \text{ kJ mol}^{-1}$ (3sf)

9

$\Delta H = (\text{Sum } \Delta Hf \text{ products}) - (\text{Sum } \Delta Hf \text{ reactants})$

$= [4(-393) + 12(-286) + 0] - [4(53) + 5(-20)]$

$= \underline{-5116} \text{ kJ/mol}$

10

$6C(s) + 3H_2(g) \xrightarrow{49} C_6H_6(l)$

$6(715)$ 31

$3(436)$ $6(413)$

                         $6(C-C)$

$6C(g) + 6H(g)$

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

$6(C-C) = 3040$

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

TASK 2 – Enthalpy Change Definitions

1 $\Delta_f H$ of $C_6H_6(l)$ .... $6C(s) + 3H_2(g) \rightarrow C_6H_6(l)$

2 $\Delta_f H$ of $CH_3COOH(l)$ .... $2C(s) + 2H_2(g) + O_2(g) \rightarrow CH_3COOH(l)$

3 $\Delta_c H$ of $H_2(g)$ .... $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$

4 $\Delta_c H$ of $CH_3COOH(l)$ .... $CH_3COOH(l) + 2O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$

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 $\Delta_{hyd}H$ of sodium ions .... $Na^+(g) \xrightarrow{aq} Na^+(aq)$

12   Enthalpy of vaporisation of bromine .... $Br_2(l) \rightarrow Br_2(g)$

13 $\Delta_{sol}H$ of sodium hydroxide .... $NaOH(s) \xrightarrow{aq} Na^+(aq) + OH^-(aq)$

14   Enthalpy of fusion of sodium chloride .... $NaCl(s) \rightarrow NaCl(l)$

15   Bond dissociation enthalpy of water .... $\frac{1}{2}H_2O(g) \rightarrow H(g) + \frac{1}{2}O(g)$

16   Bond dissociation enthalpy of hydrogen .... $H_2(g) \rightarrow 2H(g)$

17 $\Delta_{atm}H$ of bromine .... $\frac{1}{2}Br_2(l) \rightarrow Br(g)$

18   Bond dissociation enthalpy of bromine .... $Br_2(g) \rightarrow 2Br(g)$

19   1st electron affinity of bromine .... $Br(g) + e^- \rightarrow Br^-(g)$

20   2nd electron affinity of sulfur .... $S^-(g) + e^- \rightarrow S^{2-}(g)$

TASK 3 – More Enthalpy Change Definitions

1) $Ca(g) \rightarrow Ca^+(g) + e^-$ .... 1st ionisation of Ca ....

2) $S(g) + 2e^- \rightarrow S^{2-}(g)$ .... 1st + 2nd electron affinity S ....

3) $Al_2O_3(s) \rightarrow 2 Al^{3+}(g) + 3 O^{2-}(g)$ .... lattice dissociation Al_2O_3 ....

4) $NaBr(s) \rightarrow Na^+(aq) + Br^-(aq)$ .... solution NaBr ....

5) $I_2(s) \rightarrow 2 I(g)$ .... 2 x atomisation of I ....

6) $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ .... combustion C_3H_8 ....

7) $4 Al(s) + 3 O_2(g) \rightarrow 2 Al_2O_3(s)$ .... 2 x formation Al_2O_3 ....

8) $Ca^{2+}(g) + O^{2-}(g) \rightarrow CaO(s)$ .... lattice formation CaO ....

9) $Na(s) \rightarrow Na(g)$ .... atomisation Na ....

10) $P_4(s) \rightarrow 4 P(g)$ .... 4 x atomisation P ....

11) $HCl(g) \rightarrow H(g) + Cl(g)$ .... bond enthalpy HCl ....

12) $H_2O(l) \rightarrow 2 H(g) + O(g)$ .... vaporisation H_2O + 2x bond enthalpy OH ....

13) $Al(g) \rightarrow Al^{3+}(g) + 3 e^-$ .... 1st + 2nd + 3rd ionisation Al ....

14) $Ca^{2+}(g) \rightarrow Ca^{2+}(aq)$ .... hydration Ca^{2+} ....

15) $Mg(s) \rightarrow Mg^{2+}(g) + 2 e^-$ .... atomisation Mg + 1st + 2nd ionisation Mg ....

16) $Mg(s) + \frac{1}{2} O_2(g) \rightarrow MgO(s)$ .... formation MgO ....

TASK 4 – Enthalpy of solution calculations

1   +1 kJ mol^{-1} 2   -307.5 kJ mol^{-1}

3   -2116 kJ mol^{-1} 4   -25 kJ mol^{-1}

1

$$NaCl\,(s) \xrightarrow{\Delta H} Na^+\,(aq) + Cl^-\,(aq)$$

$-771 \nearrow \qquad \nearrow -406 \;\; -364$

$$Na^+\,(g) + Cl^-\,(g)$$

$\Delta H - 771 = -406 - 364$ $\Delta H = \underline{+1\ kJ/mol}$

2

$$BaBr_2\,(s) \xrightarrow{-38} Ba^{2+}\,(aq) + 2Br^-\,(aq)$$

$-1937 \nearrow \qquad \nearrow -1360 \;\; 2\Delta H$

$$Ba^{2+}\,(g) + 2Br^-\,(g)$$
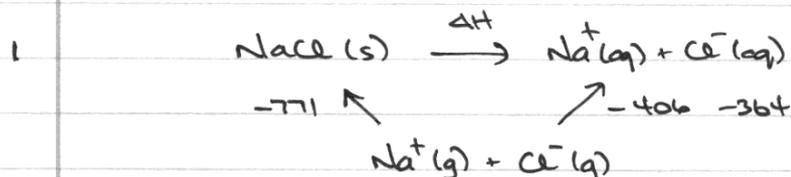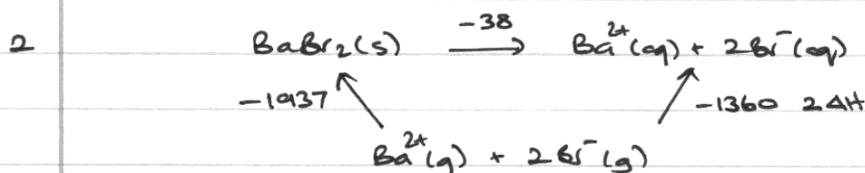
$-1360 + 2\Delta H = -1937 - 38$

$\qquad 2\Delta H = -615$ $\Delta H = \underline{-307.5\ kJ/mol}$

3

$$CaI_2\,(s) \xrightarrow{-120} Ca^{2+}\,(aq) + 2I^-\,(aq)$$

$\Delta H \nearrow \qquad \nearrow -1650 \;\; 2(-293)$

$$Ca^{2+}\,(g) + 2I^-\,(g)$$
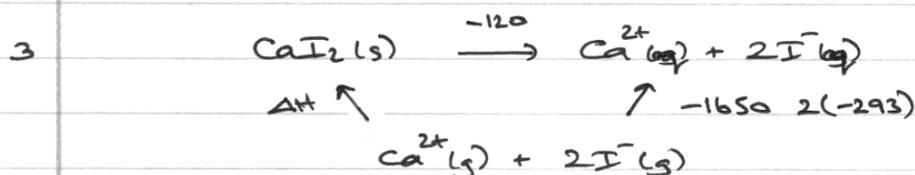
$\Delta H - 120 = -1650 + 2(-293)$ $\Delta H =$ -2116 kJ/mol

4

$$NH_4Cl\,(s) \xrightarrow{\Delta H} NH_4^+\,(aq) + Cl^-\,(aq)$$

$-640 \nearrow \qquad \nearrow -301 \;\; -364$

$$NH_4^+\,(g) + Cl^-\,(g)$$
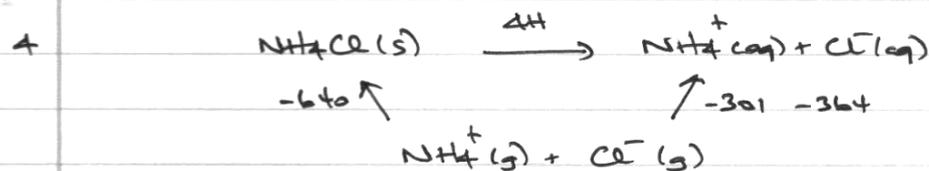
$\Delta H - 640 = -301 - 364$ $\Delta H = \underline{-25\ kJ/mol}$

PAGE 14 EXAMPLE

Al_2O_3 > MgO > CaO

Al^{3+} has highest charge and smallest of the three positive ions and so the strongest attraction between the positive ions and the oxide ions

Of the other two positive ions, Mg^{2+} is smaller than Ca^{2+} and therefore there will be a stronger attraction between the Mg^{2+} and oxide ions than between the Ca^{2+} and oxide ions

TASK 5 – Born-Haber cycle problems

| 1 | -445 kJ mol⁻¹ | 2 | -2304 kJ mol⁻¹ | 3 | -652 kJ mol⁻¹ |

1   -445 kJ mol^{-1} 2   -2304 kJ mol^{-1} 3   -652 kJ mol^{-1}

4   -15421 kJ mol^{-1} 5   -314 kJ mol^{-1} 6   +339 kJ mol^{-1}

6   CoCl = +241 kJ mol^{-1},   CoCl$_2$ = -286 kJ mol^{-1},   CoCl$_3$ = -25 kJ mol^{-1}

KCl

$K^+ (g) + e^- + Cl (g)$

418 — 1st ionisation of K   −364 — 1st electron affinity of Cl

$K (g) + Cl (g)$ $K^+ (g) + Cl^- (g)$

121 — Atomisation of Cl

$K (s) + ½ Cl_2 (g)$ −710 — Lattice enthalpy of formation of KCl

90 — Atomisation of K

$K (s) + ½ Cl_2 (g)$

? — Formation of KCl

$KCl (s)$

$\Delta H_{formation}$ = 90 + 121 + 418 − 364 − 710 = **− 445 kJ mol^{-1}**

Na₂S

$2Na^+(g) + S^{2-}(g)$
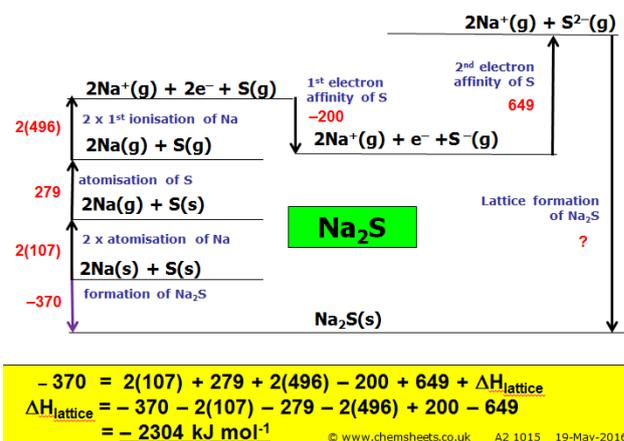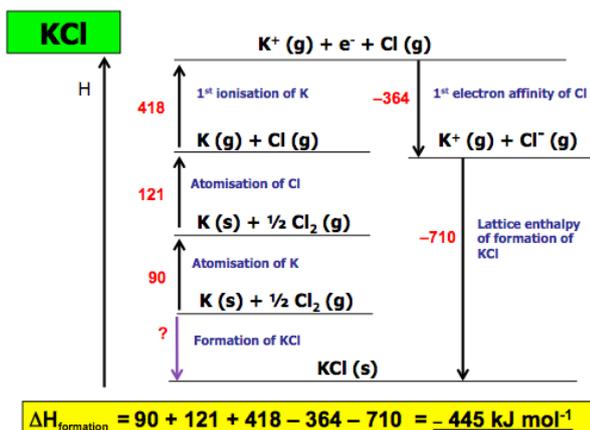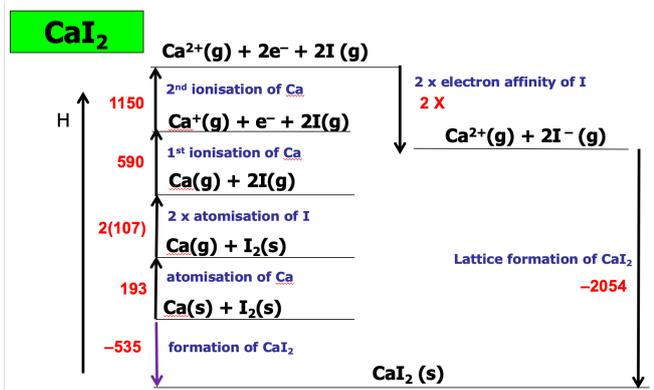
$2Na^+(g) + 2e^- + S(g)$ — 1st electron affinity of S −200   2nd electron affinity of S 649

2(496) — 2 x 1st ionisation of Na

$2Na(g) + S(g)$ $2Na^+(g) + e^- + S^-(g)$

279 — atomisation of S

$2Na(g) + S(s)$ Lattice formation of Na₂S ?

2(107) — 2 x atomisation of Na

$2Na(s) + S(s)$

−370 — formation of Na₂S

$Na_2S(s)$

− 370 = 2(107) + 279 + 2(496) − 200 + 649 + $\Delta H_{lattice}$
$\Delta H_{lattice}$ = − 370 − 2(107) − 279 − 2(496) + 200 − 649
= **− 2304 kJ mol^{-1}**   © www.chemsheets.co.uk   A2 1015   19-May-2016

CaBr₂

$Ca^{2+}(g) + 2e^- + 2Br (g)$

1150 — 2nd ionisation of Ca   2 x electron affinity of Br 2(−342)

$Ca^+(g) + e^- + 2Br(g)$ $Ca^{2+}(g) + 2Br^-(g)$

590 — 1st ionisation of Ca

$Ca(g) + 2Br(g)$

2(112) — 2 x atomisation of Br

$Ca(g) + Br_2(l)$ Lattice formation of CaBr₂ −2125

193 — atomisation of Ca

$Ca(s) + Br_2(l)$

? — formation of CaBr₂

$CaBr_2 (s)$

$\Delta H_{formation}$ = 193 + 2(112) + 590 + 1150 − 2(342) − 2125
= **− 652 kJ mol^{-1}**

Al₂O₃

$2Al^{3+}(g) + 6e^- + 6O(g)$ $2Al^{3+}(g) + 3O^{2-}(g)$

2(2740) — 2 x 3rd ionisation of Al

$2Al^{2+}(g) + 4e^- + 3O(g)$ 3 x 1st electron affinity of O 3(−142)   3 x 2nd electron affinity of O 3(844)

2(1820) — 2 x 2nd ionisation of Al

$2Al^+(g) + 2e^- + 3O(g)$ $2Al^{3+}(g) + 3e^- + 3O^-(g)$

2(577) — 2 x 1st ionisation of Al

$2Al(g) + 3O(g)$

3(248) — 3 x atomisation of O   Lattice formation of Al₂O₃ ?

$2Al(g) + ^3/_2O_2(g)$

2(314) — 2 atomisation of Al

$2Al(s) + ^3/_2O_2(g)$

−1669 — formation of Al₂O₃

$Al_2O_3(s)$

−1669 = 2(314) + 3(248) + 2(577) + 2(1820) + 2(2740) + 3(-142) + 3(844) + ΔH
ΔH = −1669 − 2(314) − 3(248) − 2(577) − 2(1820) − 2(2740) + 3(142) − 3(844)
= **− 15421 kJ mol^{-1}**   © www.chemsheets.co.uk   A2 1015   19-May-2016

CaI₂

CaI₂

$Ca^{2+}(g) + 2e^- + 2I(g)$

1150 — 2nd ionisation of Ca

2 x electron affinity of I
2 X

H

$Ca^+(g) + e^- + 2I(g)$

$Ca^{2+}(g) + 2I^-(g)$

590 — 1st ionisation of Ca

$Ca(g) + 2I(g)$

2(107) — 2 x atomisation of I

$Ca(g) + I_2(s)$

193 — atomisation of Ca

Lattice formation of CaI₂
−2054

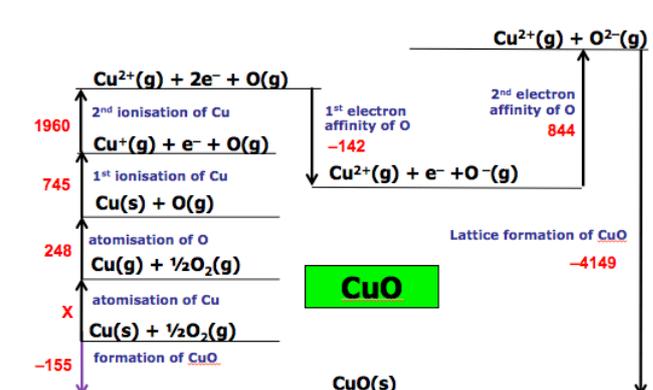$Ca(s) + I_2(s)$

−535 — formation of CaI₂

$CaI_2 (s)$

$- 535 = 193 + 2(107) + 590 + 1150 + 2X - 2054$
$2X = - 535 - 193 - 2(107) - 590 - 1150 + 2054$
$2X = -628 \qquad X = \underline{-314 \text{ kJ mol}^{-1}}$
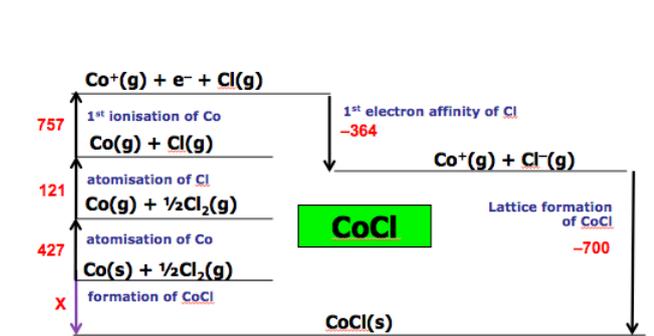
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CuO

$Cu^{2+}(g) + O^{2-}(g)$

$Cu^{2+}(g) + 2e^- + O(g)$

1960 — 2nd ionisation of Cu

1st electron affinity of O
−142

2nd electron affinity of O
844

$Cu^+(g) + e^- + O(g)$

745 — 1st ionisation of Cu

$Cu^{2+}(g) + e^- + O^-(g)$

$Cu(s) + O(g)$

248 — atomisation of O

Lattice formation of CuO
−4149

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

X — atomisation of Cu

CuO

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

−155 — formation of CuO

$CuO(s)$

$- 155 = X + 248 + 745 + 1960 - 142 + 844 - 4149$
$X = - 155 - 248 - 745 - 1960 + 142 - 844 + 4149$
$\quad = + 339 \text{ kJ mol}^{-1}$

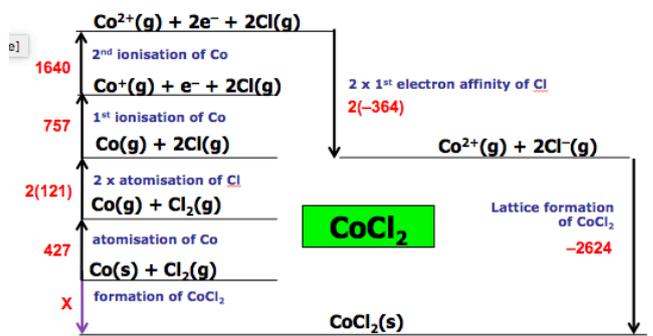© www.chemsheets.co.uk   A2 1015   19-May-2016

$Co^+(g) + e^- + Cl(g)$

757 — 1st ionisation of Co

1st electron affinity of Cl
−364

$Co(g) + Cl(g)$

$Co^+(g) + Cl^-(g)$

121 — atomisation of Cl

$Co(g) + \frac{1}{2}Cl_2(g)$

CoCl

Lattice formation of CoCl
−700

427 — atomisation of Co

$Co(s) + \frac{1}{2}Cl_2(g)$

X — formation of CoCl

$CoCl(s)$

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

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$Co^{2+}(g) + 2e^- + 2Cl(g)$

1640 — 2nd ionisation of Co

2 x 1st electron affinity of Cl
2(−364)

$Co^+(g) + e^- + 2Cl(g)$

757 — 1st ionisation of Co

$Co(g) + 2Cl(g)$

$Co^{2+}(g) + 2Cl^-(g)$

2(121) — 2 x atomisation of Cl

$Co(g) + Cl_2(g)$

CoCl₂

Lattice formation of CoCl₂
−2624

427 — atomisation of Co

$Co(s) + Cl_2(g)$

X — formation of CoCl₂

$CoCl_2(s)$

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

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$Co^{3+}(g) + 3e^- + 3O(g)$

3230 — 3rd ionisation of Co

$Co^{2+}(g) + 2e^- + 3Cl(g)$

3 x 1st electron affinity of Cl
3(−364)

1640 — 2nd ionisation of Co

$Co^+(g) + e^- + 3Cl(g)$

$Co^{3+}(g) + 3Cl^-(g)$

757 — 1st ionisation of Co

$Co(g) + 3Cl(g)$

3(121) — 3 x atomisation of Cl

Lattice formation of CoCl₃
−5350

$Co(g) + \frac{3}{2}Cl_2(g)$

CoCl₃

427 — atomisation of Co

$Co(s) + \frac{3}{2}Cl_2(g)$

X — formation of CoCl₃
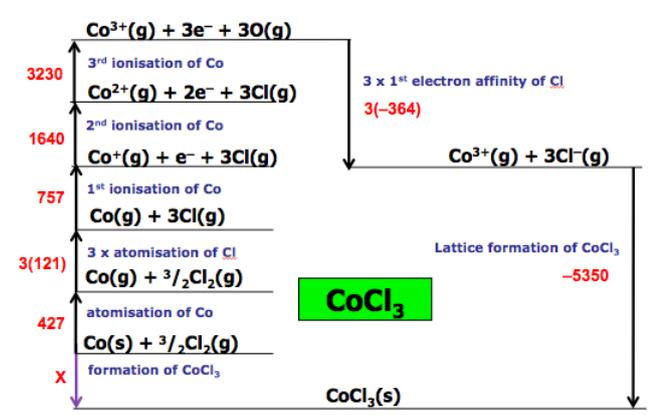
$CoCl_3(s)$

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

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$CoCl(s)$

+241

cobalt(s) + chlorine (g)
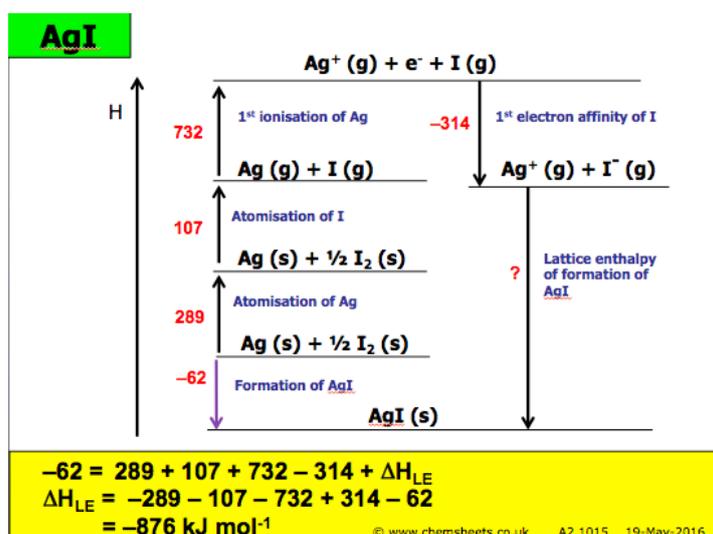
−25

$CoCl_3(s)$

−286
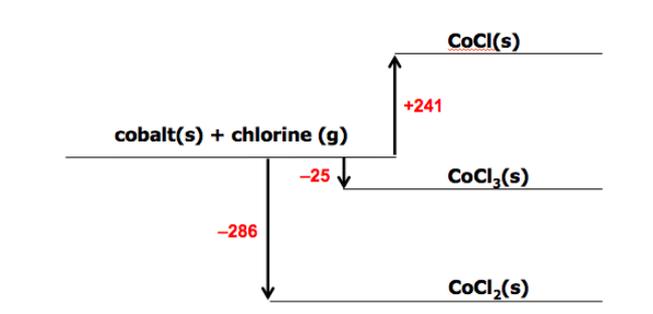
$CoCl_2(s)$

- CoCl is unstable relative to the elements
- CoCl₃(s) and CoCl₂(s) are stable relative to elements
- CoCl₂(s) is most stable form of cobalt chloride (and so most likely to form when the elements react

1 a) formation – as energy is released when electrostatic attractions between ions form

b) silver bromide – greatest magnitude of lattice enthalpy (using real values, i.e. the experimental values)

c) silver bromide – greatest difference between experimental and theoretical lattice enthalpy values

d) silver bromide has significant covalent character

2 a) $100 \times 36/3513 = 1.02\%$

b) high lattice enthalpy   (NB – not due to covalent character as it is only small)

3 a)

AgI

Ag⁺ (g) + e⁻ + I (g)

732 1st ionisation of Ag   −314 1st electron affinity of I

Ag (g) + I (g)   Ag⁺ (g) + I⁻ (g)

107 Atomisation of I

Ag (s) + ½ I₂ (s)   ?   Lattice enthalpy of formation of AgI

289 Atomisation of Ag

Ag (s) + ½ I₂ (s)

−62 Formation of AgI

AgI (s)

$$-62 = 289 + 107 + 732 - 314 + \Delta H_{LE}$$
$$\Delta H_{LE} = -289 - 107 - 732 + 314 - 62$$
$$= -876 \text{ kJ mol}^{-1}$$

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b) using the charge and size of ions assuming that the structure is perfectly ionic

c) -876 kJ mol^{-1}

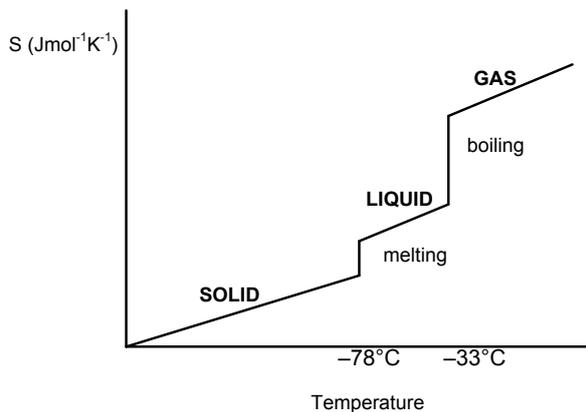d) significant covalent character

PAGE 21 EXAMPLES

ΔS = [Sum of S products] – [Sum S reactants]

= [2(214) + 3(70)] – [161 + 3(205)]

= -138 kJ mol^{-1}

$NH_4NO_3(s) \rightarrow N_2O(g) + 2 H_2O(g)$ increase as go from 1 mole of solid to 2 moles of gas

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ close to zero as go from 3 moles of gas to 3 moles of gas

TASK 7 – Entropy change calculations

1

2 a) increase as go from one mole of solid to two moles of aqueous ions (one mole of Na^+(aq) and one mole of Cl^-(aq))

   b) decrease as go from one mole of liquid to one mole of solid

   c) increase as go from two moles of gas to three moles of gas

   d) decrease as go from four moles of gas to two moles of gas

   e) close to zero as go from two moles of gas to two moles of gas

   f) increase as go from one mole of solid to one mole of solid and one mole of gas

   g) decrease as go from six moles of aqueous ions (Ba^{2+}, $2NO_3^-$, $2K^+$, SO_4^{2-}) to four moles of aqueous ions ($2K^+$, $2NO_3^-$) and one mole of solid

3 a) ΔS = [Sum of S products] – [Sum S reactants]

   = [70] – [189]

   = –119 J mol^{-1} K^{-1}

   b) ΔS = [Sum of S products] – [Sum S reactants]

   = [40 + 214] – [93]

   = +161 J mol^{-1} K^{-1}

   c) ΔS = [Sum of S products] – [Sum S reactants]

   = [3(214) + 4(70)] – [270 + 5(205)]

   = –373 J mol^{-1} K^{-1}

   d) ΔS = [Sum of S products] – [Sum S reactants]

   = [2(35) + 3(214)] – [90 + 3(198)]

   = +28 J mol^{-1} K^{-1}

PAGE 24 EXAMPLE

a) ΔH = [Sum of ΔH_f products] – [Sum ΔH_f reactants]

= [–348 – 394] – [–812]

= +70 kJ mol⁻¹

ΔS = [Sum of S products] – [Sum S reactants]

= [44 + 214] – [83]

= +175 J mol⁻¹ K⁻¹

ΔG = ΔH – TΔS

= 70 – 298(175/1000)

= +17.9 kJ mol⁻¹

b) Reaction is not feasible at 298 K (as ΔG is positive)

c) When ΔG = 0:

0 = ΔH – TΔS

ΔH = TΔS

$T = \dfrac{\Delta H}{\Delta S} = \dfrac{70}{175/1000}$ = 400 K **(2sf)**

Reaction is feasible at temperatures greater and above 400 K

PAGE 25 EXAMPLES

Ex1 When ΔG = 0:

0 = ΔH – TΔS

ΔH = TΔS

$T = \dfrac{\Delta H}{\Delta S} = \dfrac{25.5}{24.5/1000}$ = 1040 K **(3 sf)**

Ex2 When ΔG = 0:

0 = ΔH – TΔS

ΔH = TΔS

$\Delta S = \dfrac{\Delta H}{T} = \dfrac{43.5}{351}$ = 0.124 kJ mol⁻¹ K⁻¹ = 124 J mol⁻¹ K⁻¹ **(allow 2 or 3 sf)**

1 a)   -191 kJ mol⁻¹ (3sf), b) yes, feasible, c) high activation energy

2 a) ΔH = +129 kJ mol⁻¹, ΔS = +335 J mol⁻¹ K⁻¹, b) +29.2 kJ mol⁻¹ (3sf),   c) T ≥ 385 K (3sf)

3 a) ΔH = -822 kJ mol⁻¹, ΔS = -272 J mol⁻¹ K⁻¹, b) ΔG = -741 kJ mol⁻¹ (3sf), c) T ≤ 3030 K (3sf)

4 a) ΔS = -107 J mol⁻¹ K⁻¹

5 a) ΔH = +96 kJ mol⁻¹, ΔS = +138 J mol⁻¹ K⁻¹, ΔG = +54.9 kJ mol⁻¹ (3sf),   b) no, c) T ≥ 696 K (3sf)

6 a) ΔS = +10 J mol⁻¹ K⁻¹ (2sf), b) 110 K (2sf)

7 a) ΔH = +15 kJ mol⁻¹,   d) ΔS = +50.3 J mol⁻¹ K⁻¹

8 a) ΔH = +178 kJ mol⁻¹, ΔS = +164 J mol⁻¹ K⁻¹, ΔG = +129 kJ mol⁻¹ (3sf), T ≥ 1090 K (3sf)

   b) ΔH = +117 kJ mol⁻¹, ΔS = +175 J mol⁻¹ K⁻¹, ΔG = +64.9 kJ mol⁻¹ (3sf), T ≥ 669 K (3sf)

1

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

   $= -185 - 298\left(\frac{20}{1000}\right)$

   $= -191 \text{ kJ mol}^{-1}$

b)   Yes – feasible

c)   High Ea

2

a) $\Delta H = [\text{Sum } \Delta H f \text{ products}] - [\text{Sum } \Delta H f \text{ reactants}]$

   $= [-1131 - 394 - 242] - [2(-948)]$

   $= +129 \text{ kJ mol}^{-1}$

   $\Delta S = [\text{Sum S products}] - [\text{Sum S reactants}]$

   $= [136 + 214 + 189] - [2(102)]$

   $= +335 \text{ J mol}^{-1} \text{ K}^{-1}$

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

   $= 129 - 298\left(\frac{335}{1000}\right)$

   $= +29.2 \text{ kJ mol}^{-1}$ _3sf_

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

   ∴ feasible when T ≥ 385 K   _3sf_

3

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

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

$$\Delta G = -822 - 298\left(\frac{-271.5}{1000}\right) = -741 \text{ kJ mol}^{-1} \quad \underline{\textbf{3sf}}$$

$$\Delta G = 0 \quad T = \frac{\Delta H}{\Delta S} = \frac{-822}{\frac{-271.5}{1000}} = 3030 \text{ K} \quad \underline{\textbf{3sf}}$$

Feasible if $T \le 3028$ K

4

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

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

$$\Delta S = \frac{\Delta H - \Delta G}{T} = \frac{-602 - (-570)}{298}$$

$$= -0.107 \text{ kJ mol}^{-1}\text{K}^{-1}$$

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

b) 1 mol s + ½ mol g → 1 mol s
∴ less entropy ∴ ΔS −ve

5

a) $\Delta H = [0 + 3(-242)] - [-822 + 0] = +96 \text{ kJ mol}^{-1}$

$\Delta S = [2(27) + 3(189)] - [90 + 3(131)] = +138 \text{ J mol}^{-1}\text{K}^{-1}$

$\Delta G = 96 - 298\left(\frac{138}{1000}\right) = +54.9 \text{ kJ mol}^{-1} \quad \underline{\textbf{3sf}}$

b) Not feasible

c) $\Delta G = 0 \quad T = \frac{\Delta H}{\Delta S} = \frac{96}{\frac{138}{1000}} = 696 \text{ K} \quad \underline{\textbf{3sf}}$
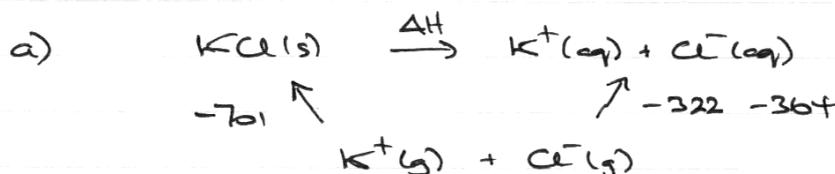
Feasible if $T \ge 696$ K

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

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

$$\Delta S = \frac{\Delta H}{T} = \frac{0.94}{91} = 0.0103 \text{ kJmol}^{-1}\text{k}^{-1}$$

$$= \boxed{10} \quad \text{Jmol}^{-1}\text{k}^{-1} \qquad \underline{\textit{2sf}}$$

b)   At bpt $\Delta G = 0$ $T = \dfrac{\Delta H}{\Delta S} = \dfrac{8.2}{\frac{73.2}{1000}} = \boxed{110}$ K $\underline{\textit{2sf}}$

c) $\underset{(73.2)}{\Delta S \text{ boiling}} > \underset{(10.3)}{\Delta S \text{ melting}}$

increase in disorder of particles much greater on

liquid $\rightarrow$ gas   than   solid $\rightarrow$ liquid

d)   driving force is increase in entropy

---

7   **a)**

$$KCl(s) \xrightarrow{\Delta H} K^+(aq) + Cl^-(aq)$$

$-701 \nwarrow \qquad\qquad\qquad \nearrow -322 \; -364$

$$K^+(g) + Cl^-(g)$$

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

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

b) ΔS +ve
+ c)

increase in disorder as ions become dissolved

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

d)   If $\Delta G = 0$ $\Delta H = T\Delta S$

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

$$= 50.3 \text{ Jmol}^{-1}\text{k}^{-1}$$

8

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) $\Delta S = [\text{Sum S products}] - [\text{Sum S reactants}]$

$= [40 + 214] - [90]$

$= +164 \text{ J mol}^{-1} \text{K}^{-1}$ ✓

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

$= 178 - 298 \left(\frac{164}{1000}\right)$

$= \pm 129 \text{ kJ mol}^{-1}$ ✓ **3sf**

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) ✓ $\Delta G = 0$, $T = \frac{\Delta H}{\Delta S}$

✓ $T = \dfrac{178}{\left(\frac{164}{1000}\right)}$

✓ $= 1090 \text{ K}$ **3sf** **allow 1080 K**

vii) ✓ spontaneous if $T \geqslant 1090$ 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) $\Delta G = 117 - 298 \left(\frac{175}{1000}\right) = +64.9 \text{ kJ mol}^{-1}$ **3sf**

iv) $T = \dfrac{117}{\left(\frac{175}{1000}\right)} = 669 \text{ K}$ **3sf** ✓

c) ✓ $CaCO_3$ more stable

✓ Ca^{2+} less polarising than Mg^{2+}