F325 – Equilibria, Energetics & Elements

Enthalpy and Entropy

1. (a) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ 1

(b) $S^-(g)$ 1

(c) The negative S^- ion 1
repels the electron being added 1

(d) (i) Enthalpy of atomisation of sulphur 1

(ii) Second ionisation enthalpy of calcium 1

(iii) Second electron affinity of sulphur 1

(e) Electron more strongly attracted 1
nearer to the nucleus or attracted by Ca^+ ion 1

(f) Correct cycle

e.g. + 178 + 279 + 590 +1145 – 200 + E – 3013 + 482 = 0 1

= 539 1

Allow one mark for – 539

[11]

2. (a) ΔH_1 formation **(1)**

ΔH_2 atomisation / sublimation (of Cs <u>not</u> Cl) **(1)**

ΔH_5 electron affinity (of Cl) **(1)** 3

(b) $-433 = 79 + 376 + 121 - 364 + \Delta H_6$ **(1)**

$\Delta H_6 = -645$ (kJ mol^{-1}) **(1)** 2

both marks for correct answer alone
allow 1 mark for +645 or 645

(c) Cs has larger radius / larger atom (not ion) / more shells / more orbitals / more sub-shells **(1)**

correct reference to shielding **(1)**

less powerful attraction (of nucleus) for (outer) e^- in Cs **(1)** 3

[8]

3. (a) (i) diagram shows in top box $Rb^+(g) + e^- + I(g)$ / e^- must be there **(1)**

diagram shows in lower box $Rb(\underline{s}) + ½ I_2(\underline{s})$ **(1)** 2

(ii) ΔH_1 = electron affinity (of iodine)/allow correct symbols including I_2, I^-, **(1)**

ΔH_2 = lattice enthalpy / energy (of RbI) **(1)** 2

(iii) $\Delta H_1 = -(+402) - (+107) - (+85.8) + (-328) - (-609)$ **(1)**

$= -314$ (kJ mol^{-1}) **(1)** 2

give 1 mark for +313.8 or +314
assume + if no sign given
significant figure penalty for 310

[6]

4. (i) **A** is (enthalpy change) of formation**(1)**

B is lattice enthalpy **(1)** 2

(ii) negative sign (only if a calculation) **(1)**

883 kJ mol^{-1} **(1)**

(only give both marks if working and answer correct)

hydration / solvation enthalpies (of Li^+ and Cl^-) **(1)** 3

[5]

5. (a) Particles are in maximum state of order 1

(or perfect order or completely ordered or perfect crystal or minimum disorder or no disorder)

(entropy is zero at 0 k by definition)

(b) (Ice) melts 1

(or freezes or changes from solid to liquid or from liquid to solid)

(c) Increase in disorder 1

Bigger (at T_2) 1

Second mark only given if first mark has been awarded

(d) (i) Moles of water = 1.53/18 (= 0.085) 1

Heat change per mole = 3.49/0.085 = 41.1 (kJ mol^{-1}) 1

(allow 41 to 41.1, two sig. figs.)

(penalise –41 (negative value), also penalise wrong units but allow kJ only)

(ii) $\Delta G = \Delta H - T\Delta S$ 1

(iii) $\Delta H = T\Delta S$ or $\Delta S = \Delta H/T$ 1

(penalise if contradiction)

ΔS = 41.1/373 = 0.110 kJ K^{-1} (mol^{-1}) (or 110 (J K^{-1} (mol^{-1})) 1

(allow 2 sig. figs.)

(if use value given of 45, answer is 0.12 (or 120 to 121)

(if ΔH is negative in (d) (i), allow negative answer)

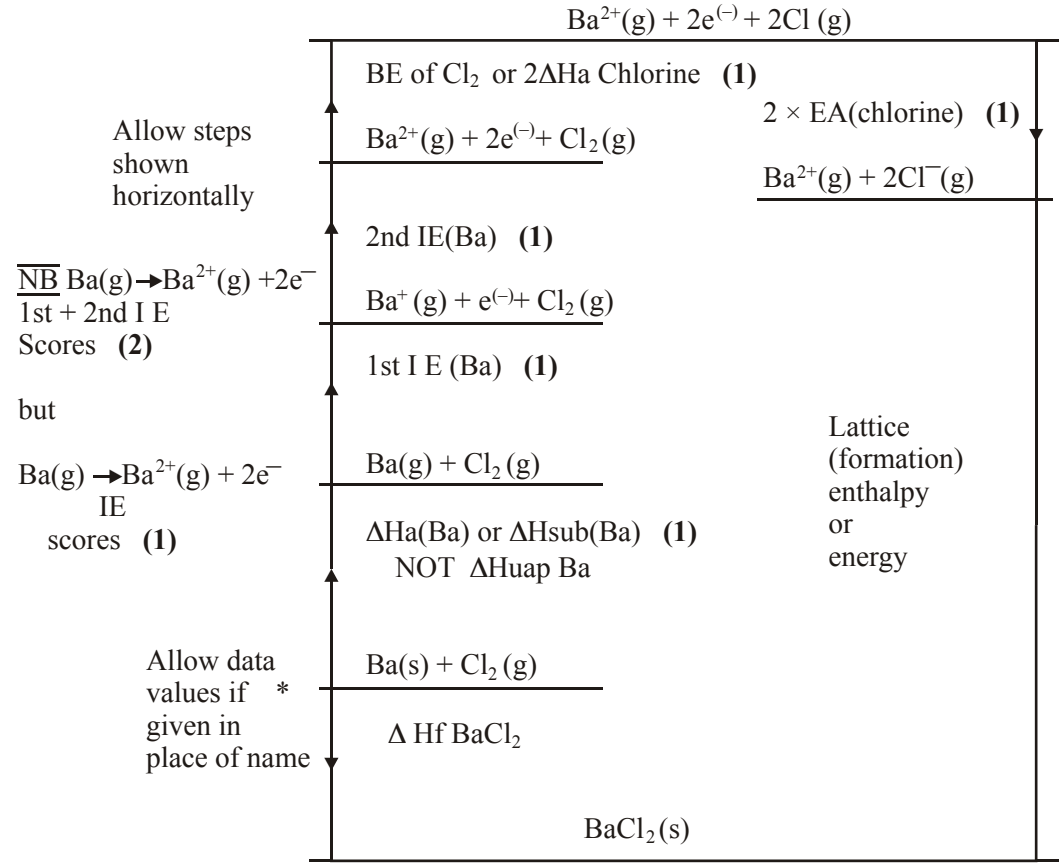
(if ΔH is negative in (d) (i), allow positive answer)

(if ΔH is positive in (d) (i), penalise negative answer)

Correct units as above (mol^{-1} not essential) 1

[10]

6. (a) (i)



ONLY consider species involved in the step marked

(ii) Cycling clockwise about (*)

CE if step missing

$\Delta H_a Ba + 1^{st}$ IEBa + 2^{nd} IE Ba + $2\Delta H_a Cl$ + 2EACl + LE – $\Delta H_f BaCl_2 = 0$ **(1)**

$+180 + 503 + 965 + 2 \times 122 + 2EA - 2056 + 859 = 0$ **(1)**

EA = –695/2 = – (347 to 348) **(1)** 9

Ignore units

Calculation –1 for each error

Mark conseq.

Notes: *–695 scores **(2)***
*+(347 to 348) scores **(2)***
*–(286 to 287) scores **(2)***
*+(286 to 287) scores **(1)***
*–573 scores **(1)***
*+573 scores **(0)***

(b) $\Delta S = \Sigma S$ products $- \Sigma$ S reactants
$= (63 + 223) - 124 = 162$ **(1)**

$\Delta G = \Delta H - T\Delta S$ or $\Delta H = T\Delta S$ or $T = \Delta H/\Delta S$ **(1)**
or used correctly

$\Delta H = 859 \times 10^3$ **(1)** $= T \times 162$
$T = (5\,300$ to $5304)$ K **(1)** 4
Penalise if units °C
–1 for each error + mark conseq.

[13]

7. (a) (i) *Standard enthalpy change*: $\Delta H_R = \Sigma\Delta H_f$ products $- \Sigma\Delta H_f$ reactants **(1)**
$\Delta H_R = (-804 - 394) - (-940)$ **(1) N.B: If answer wrong statement worth 2**
$= -258$ (kJ mol^{-1}; ignore units completely) **(1)**
Allow +258 (2) marks

Standard entropy change: $\Sigma\Delta$ S products $- \Sigma\Delta$ S reactants **(1)**
$\Delta S = (252 + 214) - (49.9 + 5.7 + [2 \times 223])$ **(1) N.B: If answer wrong statement worth 2**
$= -35.6$ (kJ mol^{-1}; ignore units completely) **(1)**
Allow +35.6 (2) marks
Mark –36 AE minus one
Allow max one for +187

(ii) $T = \dfrac{\Delta H}{\Delta S}$ **or** $T = \dfrac{\Delta H \text{ value from above}}{\Delta S \text{ value from above}}$ **(1)**
Penalise wrong sign

$T = \dfrac{-258 \times 1000}{-35.6} = 7245$ to 7250 **(1)**
Ignore letter after value
Ignore ≥ even if wrong way around
Mark answer conseq to ΔH and ΔS values from above
If negative temperature given max 2*
If °C used incorrectly max 2*
*** But only penalise one of these errors**

9

[9]

8. (a) (i) *Standard enthalpy change*: $\Delta H_R = \Delta\Sigma H_f$(products) - $\Delta\Sigma H_f$(reactants) **(1)**
or cycle

$\Delta H_R = ([2 \times 0] + [3 \times -393.5]) - (-824.2 + [3 \times -110.5])$ **(1)**
$= -24.8$ (kJ mol^{-1}) **(1)**
Allow + 24.8 max one

Standard entropy change: $\Delta S = \Sigma S$(products) - ΣS(reactants) **(1)**

$\Delta S = ([2 \times 27.3] + [3 \times 213.6]) - (87.4 + [3 \times 197.6])$ **(1)**
$= (54.6 + 640.8) - (87.4 + 592.8)$ **(1)**
$= 15.2$ ($JK^{-1}mol^{-1}$) **(1)**
Allow -15.2 max one

(ii) $\Delta G = \Delta H - T\Delta S$ **(1)**
ΔH negative and $-T\Delta S$ is negative **(or ΔS positive or or correct calc) (1)**
Hence ΔG is always negative **(or feasible when $\Delta G \leq 0$) (1)** 9

(b) $\Delta G = O = \Delta H - T\Delta S$ Hence $\Delta H = T\Delta S$ **(1)**
$T = \Delta H / \Delta S = 492.7 \times 1000 / 542.6$ **(1)**
$= 908$ K **(1)**
penalise missing 1000 by one mark

3

(c) ΔG (b) = ΔG (a)
$(492.7 \times 10^3 - T \times 542.6) = (-24.8 \times 10^3 - T \times 15.2)$ **(1)**
$517.5 \times 10^3 = 527.4\ T$ **(1)**
$T = 981.2$ K**(1)**
Allow 980 - 982
Penalise missing 1000 by one mark

3

[15]

9. (a) $\Delta Ha = \sum \Delta H_f$ products $- \sum \Delta H_f$ reactants or

$= \Delta H_f CO_2 - (\Delta H_f CH_4 + 2\ \Delta H_f H_2O)$ **(1)**

$= -393.5 + (74.8 + [2 \times 241.8])$ **(1)**

$= +164.9$ kJ mol^{-1} **(1)** 3

(b) (i) The number of moles of gas increases from 3 to 5 **(1)**

More moles gas gives more disorder **(1)**

(ii) $\Delta S = \sum S$ prducts $- \sum S$ reactants **(1)**

$= (213.6 + [4 \times 130.6]) - (186.2 + [2 \times 188.7])$ **(1)**

$= +172.4\ JK^{-1}\ mol^{-1}$ **(1)** 5

(c) (i) $\Delta G = \Delta H - T\Delta S$ or $\Delta H = T\Delta S$ **(1)**

$T = 164.9 \times 1000/172.4$ **(1)**

$= 956.5$ K **(1)**

Marked consequentially

(ii) Above this temperature **(1)**

this reaction is feasible or spontaneous **(1)** 5

[13]

10. (a) *ΔH*$^{\ominus}$ $\Delta H^{\ominus} = \Sigma\Delta H_f^{\ominus}$ (products) – $\Sigma\Delta H_f^{\ominus}$ (reactants) **(1)**

$= -201 + 110$

$= -91$ kJmol^{-1} **(1)**

ΔS$^{\ominus}$ $\Delta S^{\ominus} = \Sigma S^{\ominus}$ (products) – $\Sigma S^{\ominus}$ (reactants) **(1)**

$= +240 - 2 \times 131 - 198$

$= -220$ JK^{-1} mol^{-1} **(1)** 4

(b) *Feasible reaction* One for which $\Delta G \leq O$ **(1)**

Temperature $\Delta G = \Delta H - T\Delta S$ **(1)**

For $\Delta G = O$, $T = \Delta H/\Delta S = -91 \times 1000/(-220)$

$= 414$ K **(1)** 3

[7]

11. (a) $\Delta H^{\ominus} = \Sigma \Delta H_f^{\ominus}$ (products) - $\Sigma \Delta H_f^{\ominus}$ (reactants) **(1)**

$= 2 \times (-396) - 2 \times (-297)$

$= -198$ kJ mol^{-1} **(1)**

$\Delta S^{\ominus} = \Sigma S^{\ominus}$ (products) - $\Sigma S^{\ominus}$(reactants) **(1)**

$= 2 \times (257) - 204 - 2 \times (248)$

$= -186$ JK^{-1} mol^{-1} **(1)**

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ **(1)**

$= -198 - 298\ (-186/1000)$ **(1)**

$= -143$ kJ mol^{-1} **(1)** 7

(b) One for which $\Delta G \leq O$ **(1)**

$T = \dfrac{\Delta H}{\Delta S}$ when $\Delta G = O$ **(1)**

$= \dfrac{-198 \times 1000}{-186} = 1100$K **(1)** 3

[10]

12. (i) fewer moles of gas **(1)**

more 'order' in system **(1)**
dependent on idea of fewer moles for first mark 2

(ii) 25 °C = 298 K **(1)**

$\Delta S = \frac{-188}{1000}$ **or** $(\Delta H \times 1000)$ **(1)**

mark is for ensuring ΔH or ΔS are both expressed in terms of J or kJ

$\Delta G = -196 - 298(-188 \times 10^{-3})$
$= -140$ kJ mol^{-1} **or** -139976 J mol^{-1} **(1)**

ignore sig. figs
sign and unit must be correct in final answer

ΔG –ve ∴ reaction feasible **(1)** 4

[6]

13. (a) (i) Steps

Sublimation/atomisation enthalpy or
$\Delta H_{fus} + \Delta H_{vap}$ Ca(s) → Ca(g) **(1)**

First ionisation enthalpy of calcium $Ca(g) \rightarrow Ca^{+}(g) + e^{-}$ **(1)**

Second ionisation enthalpy of calcium $Ca^{+}(g) \rightarrow Ca^{2+}(g) + e^{-}$ **(1)**

Dissociation enthalpy/bond energy/2 × ΔH_a chlorine
$Cl_2(g) \rightarrow 2Cl(g)$ **(1)**

2 × First electron affinity of chlorine $2Cl(g) + 2e^{-} \rightarrow 2Cl^{-}(g)$ **(1)**

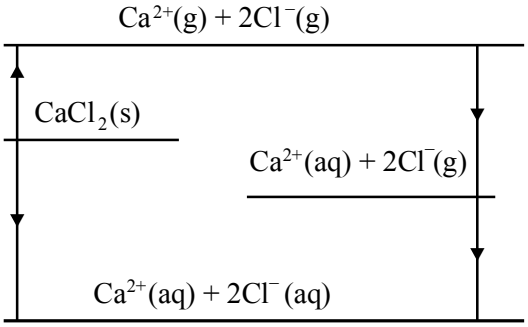
Lattice dissociation (or formation) enthalpy
$CaCl_2(s) \rightarrow Ca^{2+}(g) + 2Cl^{-}(g)$ **(1)**

Enthalpy of formation of calcium chloride
$Ca(s) + Cl_2(g) \rightarrow CaCl_2(g)$ **(1)**

7

(ii) 2nd IE needed when $CaCl_2$ formed or only 1st IE for CaCl **(1)**
BE of Cl_2 needed when $CaCl_2$ formed but BE/2 for CaCl
(or equivalent) **(1)**
2 × electron affinity when CaCl2 formed but 1 × EA for CaCl **(1)**
LE of $CaCl_2$ greater (or different) than LE CaCl **(1)** 4

(b) (i)



$+LE + (\Delta H_{hyd}Ca^{2+}) + 2(\Delta H_{hyd}Cl^{-}) - \Delta H_{soln}\ CaCl_2 = CaCl_2 = 0$ or correct cycle **(1)**

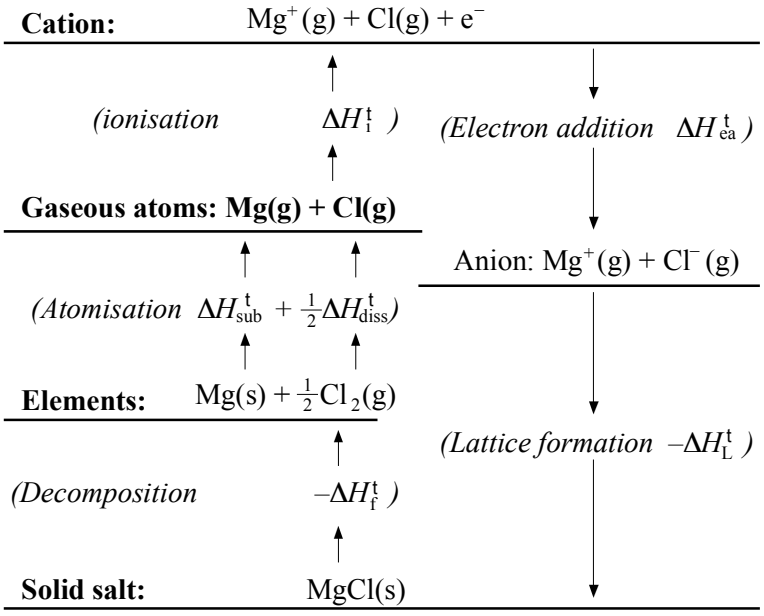
ΔH_{soln} CaCl2 = 2255 – 1650 – 768 **(1)**

$= -163\ kJ\ mol^{-1}$ **(1)** 3

(ii) Marked consequentially to answer in (c)(i)
Solubility decreases **(1)**
Enthalpy of solution negative or exothermic **(1)**
Equilibrium displaced as predicted by Le Chatelier **(1)** 3

[17]

14.



6 steps
–1 for each error

4

$0 = -\Delta H_f^{\ominus} + \Delta H_{sub}^{\ominus} + \Delta H_{diss}^{\ominus} + \Delta H_f^{\ominus} + \Delta H_{ea}^{\ominus} + \Delta H_f^{\ominus}$

$\Delta H_f^{\ominus} = \Delta H_{sub}^{\ominus} + \Delta H_{diss}^{\ominus} + \Delta H_f^{\ominus} + \Delta H_{ea}^{\ominus} + \Delta H$

$\Delta H_f^{\ominus} = + 146 + 121 + 736 - 364 - 753$

$\Delta H_f^{\ominus} = -114$ kJ mol $^{-1}$ **(3)** [–1 for each error] 2

$\Delta H^{\ominus} = \Delta H_f^{\ominus}$ $(MgCl_2) - \Delta H_f^{\ominus}$ $(MgCl) = -653 - 2(-114) = -425$ kJ mol^{-1} 1

$\Delta S^{\ominus} \approx 0$ since 2 mol solid → 2 mol solid 1

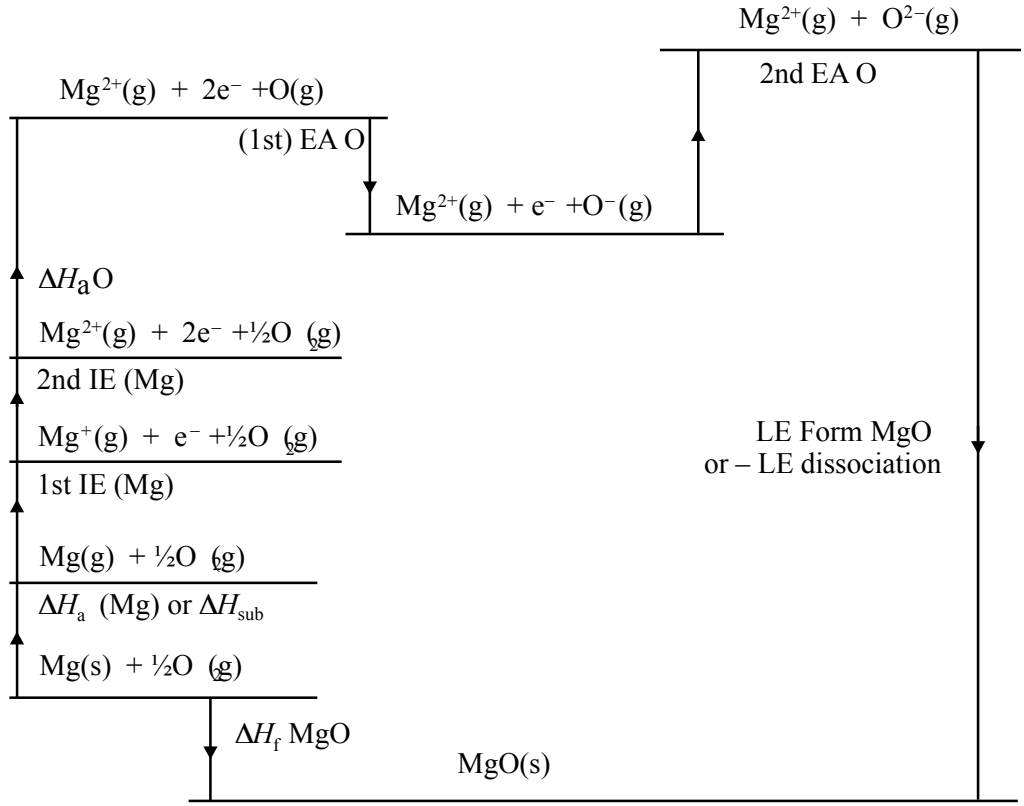
if $\Delta S^{\ominus} = 0$, then $\Delta G^{\ominus} = \Delta H^{\ominus}$ 1

So $\Delta G^{\ominus}$ for the reaction is < 0 (at all T)– hence $MgCl_2$ is always favoured over MgCl 1

[10]

15 (a) Heat (energy)/ internal energy change (not energy change) **(1)**
Measured at constant pressure **(1)** 2

(b)



8

Notes:– Ignore electrons in cycle

Penalise missing labels by max 2

Penalise missing state symbols in 'active step' by max 2

Penalise incorrect chemistry every time

Allow steps written horizontally

Calculation:

ΔH_aMg + 1st IE Mg + 2nd IE Mg + ΔH_a O + 1st EA O + 2nd EA O + LE Form –MgO ΔH_fMgO = 0 **(1)**

Hence; 148 + 738 + 1451 + 249 – 141 + 798 + LE + 602 = 0 **(1)**

(NB This scores 2)

LE formation MgO = –3845 (kJ mol^{-1}) **(1)**

(Allow +3845 Max 2)

(c) For the reaction $MgCl_2(s) + \frac{1}{2}Cl_2(g) \rightarrow MgCl_3(s)$

$\Delta H_r = \Delta H_f MgCl_3 - \Delta H_f MgCl_2$

$= +3904 - (-653) = 4557$ (kJ mol^{-1}) **(1)**

ΔS is negative/ entropy decreases (as order increases) **(1)**

$\Delta G = \Delta H - T\Delta S$ **(1)**

ΔG must (always) be positive (since ΔH_r and $-T\Delta S$ are both positive) **(1)**

Reaction never/not feasible (or equivalent) **(1)**

5

[15]

16. $\Delta S = \Sigma S$ products $- \Sigma S$ reactants 1

$\Delta S = (259 + 187) - (201 + 161)$ 1

$\Delta S = 84$ (JK^{-1} mol^{-1}) *(Ignore units)* 1
*Allow – 84 to score **(1)** mark*

$\Delta G = \Delta H - T\Delta S$ 1

$= -21.6 - 298 \times 84/1000$
$= -46.6$ kJ mol^{-1} or $-46\,600$ J mol^{-1} 1
*Allow **(2)** for – 46.6 without units*
(Mark ΔG consequentially to incorrect ΔS)
(e.g. ΔS = –84 gives ΔG = +3.4 kJ mol^{-1})

1

[6]

17. (a) Reaction 1

$\Delta H = \Sigma\Delta H_f$ products $- \Sigma\Delta H_f$ reactants **(1)**

$= (\Delta H_f CO) - (\Delta H_f CH_4 + \Delta H_f H_2O)$

$= (-110.5) - (-74.8 - 241.8) = +206.1$ (kJ mol^{-1}) **(1)**

$\Delta S = \Sigma S$ products $- \Sigma S$ reactants **(1)**

$= (197.6 + [3 \times 130.6]) - (186.2 + 188.7) = 214.5$ (J $K^{-1}mol^{-1}$) **(1)**

$\Delta G = \Delta H - T\Delta S$ **(1)**

$0 = + 206.1 - T \times 214.5/1000$ **(1)**

$T = 206.1 \times 1000/214.5 = 960.8$ (K) **(1)**

(allow 961)

Penalise incorrect units in calculation of temperature by 2 marks

Mark T consequentially

Reaction 2

$\Delta H = 2\Delta H_f NH_3 = -92.2$ (kJ mol^{-1}) **(1)**

$\Delta S = (2 \times 192.3) - (191.6 + [3 \times 130.6]) = -198.8$ (J $K^{-1}mol^{-1}$) **(1)**

$\Delta G = 0 = -92.2 + T \times 198.8/1000$

$T = 92.2 \times 1000/198.8 = 463.8$ (k) **(1)**

(allow 464)

Mark T consequentially

Note:– Allow first calculation max 7 and second calculation max 3 10

(b) Reaction 1 at higher temperatures

equilibrium yield increased/forward reaction favoured as reaction endothermic **(1)**

rate of reaction increased **(1)**

a compromise temperature used based on high cost of high temperature **(1)**

Reaction 2 at higher temperatures

equilibrium yield reduced/backward reaction favoured as reaction exothermic **(1)**

rate of reaction increased **(1)**

a compromise temperature used based on overall yield **(1)**

Mark consequentially to ΔH values in (a) max 5

[15]

18. (a) Spontaneous when $\Delta G < 0$ or $\Delta G = 0$ **(1)**

$\Delta G = \Delta H - T\Delta S$ **(1)**

Calculation of ΔH; $\Delta H_{reaction} = \Sigma\Delta H_{Prolucts} - \Sigma\Delta H_{Reactants}$ **(1)**

$= (2 \times -110.5) - (-3935) = +172.5$ Allow 172 – 173 kJ mol^{-1} **(1)**

Calculation of ΔS; $\Delta S_{reaction} = \Sigma\Delta S_{Products} - \Sigma S_{Reactants}$ **(1)**

$= (2 \times 197.6) - (5.7 + 213.6) = 175.9$ J mol^{-1} K^{-1} **(1)**

Calculation of T $\Delta G = 172.5 - T \times 175.9/1000 = 0$ **(1)**

$T \times 175.9/1000 = 172.5$

$T = 172.5 \times 1000/175.9 = 980.7$ K **(1)** 8

(b) Calculation of $\Delta H_{Vaporisation}$;

3675 J vaporise 1.50 g water

3675 × 18/1.50 vaporise 1.00 mole water

= 44.1 kJ mol^{-1} **(1)**

Calculation of ΔS; $\Delta G = 0 = 44.1 - 373 \times \Delta S/1000$ or $\Delta S = \Delta H/T$ **(1)**

$\Delta S = 44.1 \times 1000/373 = 118.2$ J mol^{-1} K^{-1} **(1)** 3

[11]

19. (a) $\Delta H_f^{\ominus} = \Sigma\Delta H_f^{\ominus}$ (products) – $\Delta H_f^{\ominus}$ (reactants) **(1)**

= (–110.5) – (–271.9) = +161.4 [Allow 161 – 161.5] kJ mol^{-1} **(1)**

$\Delta S^{\ominus} = \Sigma S^{\ominus}$(products) – $\Sigma S^{\ominus}$(reactants) **(1)**

= (27.3 + 197.6) – (58.5 + 5.7) = +160.7
[Allow 160.6 – 161] J mol^{-1} K^{-1}**(1)**

ΔG = ΔH – TΔS [Stated or correctly used] **(1)**

ΔG = +161.4 – 450 × 160.7/1000 **(1)**

= + 89.1[Allow 88.5 – 89.1] kJ mol^{-1}. **(1)**

$\Delta H_f^{\ominus}$ = (–393.5) – (–271.9 – 110.5)= –11.1 kJ mol^{-1}. **(1)**

$\Delta S^{\ominus}$ = (213.6 + 27.3) – (58.5 + 197.6) = –15.2 J mol^{-1} K^{-1}. **(1)**

ΔG = –11.1 + 450 × 15.2/1000 = –4.26 [Allow–4.3] kJ mol^{-1}. **(1)** 10

(b) Feasible when $\Delta G \leq 0$ or ΔG is negative **(1)**

Process 1 is more feasible as temperature is increased **(1)**

Because ΔS is positive or $-T\Delta S$ is negative or $T\Delta S$ is positive **(1)**

Process 2 is less feasible as temperature is increased **(1)**

Because ΔS is negative or $-T\Delta S$ is positive or $T\Delta S$ is negative **(1)** 5

[15]