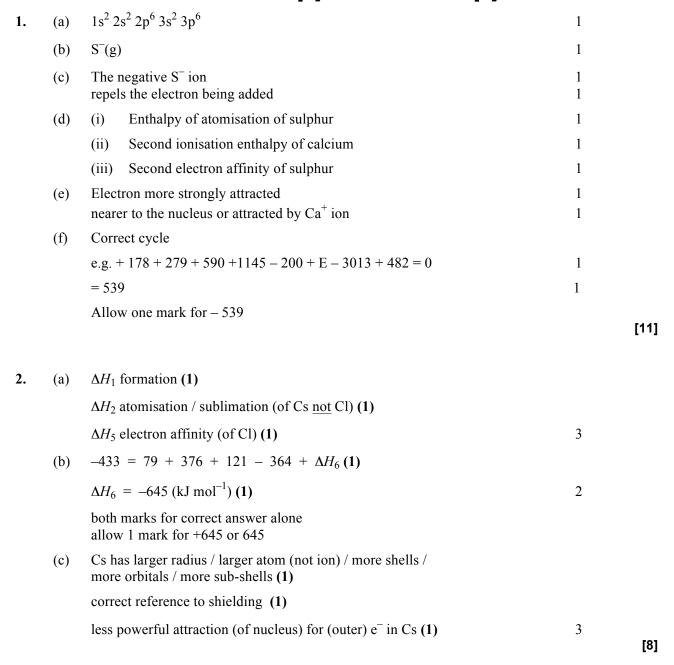
F325 - Equilibria, Energetics & Elements

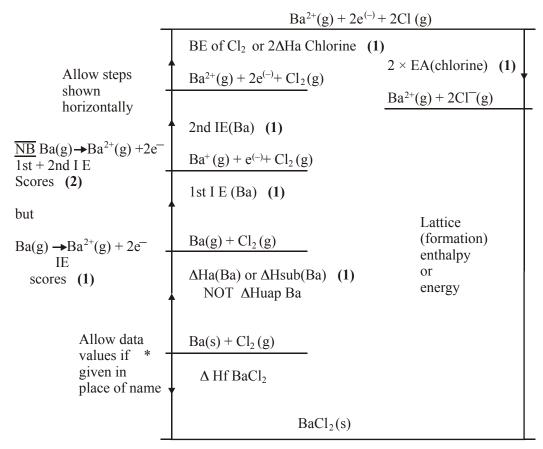
Enthalpy and Entropy



3.	(a)	(i)	diagram shows in top box $Rb^+(g) + e^- + I(g) / e^-$ must be there (1)		
			diagram shows in lower box $Rb(\underline{s}) + \frac{1}{2} I_2(\underline{s})$ (1)	2	
		(ii)	ΔH_1 = electron affinity (of iodine)/allow correct symbols		
			including I_2 , Γ , (1)		
			$\Delta H_2 = \text{lattice enthalpy / energy (of RbI)}$ (1)	2	
		(iii)	$\Delta H_1 = -(+402) - (+107) - (+85.8) + (-328) - (-609)$ (1)		
			$=-314 \text{ (kJ mol}^{-1}) \text{ (1)}$	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)	Parti	cles are in maximum state of order (or perfect order or completely ordered or perfect crystal or minimum disorder or no disorder)	1	
			(entropy is zero at 0 k by definition)		
	(b)	(Ice)	melts (or freezes or changes from solid to liquid or from liquid to solid)	1	
	(c)	Incre	ease in disorder	1	
			er (at T_2)	1	
		Seco	nd 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 \text{ (kJ mol}^{-1}\text{)}
                                                                                                                1
                        (allow 41 to 41.1, two sig. figs.)
                        (penalise -41 (negative value), also penalise wrong units but
                        allow kJ only)
                \Delta G = \Delta H - T\Delta S
        (ii)
                                                                                                                1
                \Delta H = T\Delta S or \Delta S = \Delta H/T
        (iii)
                                                                                                                1
                        (penalise if contradiction)
                \Delta S = 41.1/373 = 0.110 \text{ kJ K}^{-1} \text{ (mol}^{-1}\text{) (or } 110 \text{ (J K}^{-1} \text{ (mol}^{-1}\text{))}
                                                                                                                1
                        (allow 2 sig. figs.)
                        (if use value given of 45, answer is 0.12 (or 120 to 121)
                        (if \Delta H is negative in (d) (i), allow negative answer)
                        (if \Delta H is negative in (d) (i), allow positive answer)
                        (if \Delta H is positive in (d) (i), penalise negative answer)
                Correct units as above (mol<sup>-1</sup> 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 × 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
$$= (63 + 223) - 124 = 162 \text{ (1)}$$

$$\Delta G = \Delta H - T\Delta S \quad \text{or} \quad \Delta H = T\Delta S \quad \text{or} \quad T = \Delta H/\Delta S \text{ (1)}$$

$$or \ used \ correctly$$

$$\Delta H = 859 \times 10^3 \text{ (1)} = T \times 162$$

$$T = (5 \ 300 \ \text{to} \ 5304) \text{ K (1)}$$

$$Penalise \ if \ units \ ^{\circ}C$$

$$-1 \ for \ each \ error + mark \ conseq.$$

[13]

7. (a) Standard enthalpy change: $\Delta H_R = \sum_{\Delta} H_f$ products $-\sum_{\Delta} H_f$ 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) Δ 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)
$$T = \frac{\Delta H}{\Delta S}$$
 or $T = \frac{\Delta H \text{ value from above}}{\Delta S \text{ value from above}}$ (1)

Penalise wrong sign

$$T = \frac{-258 \times 1000}{-35.6} = 7245 \text{ to } 7250 \text{ (1)}$$

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) Standard enthalpy change: $\Delta H_R = \Delta \Sigma H_f(\text{products}) - \Delta \Sigma H_f(\text{reactants})$ (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: $\Delta S = \Sigma S(products) - \Sigma S(reactants)$ (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⁻¹mol⁻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)

(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

penanse missing 1000 by one mark

(c) ΔG (b) = ΔG (a) $(492.7 \times 10^3 - T \times 542.6) = (-24.8 \times 10^3 - T \times 15.2)$ (1) $517.5 \times 10^3 = 527.4 \text{ T (1)}$ T = 981.2 K(1)

Allow 980 - 982

Penalise missing 1000 by one mark

[15]

3

3

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

$$= \Delta H_f \text{CO}_2 - (\Delta H_f \text{CH}_4 + 2 \Delta H_f \text{H}_2 \text{O}) \text{ (1)}$$

$$= -393.5 + (74.8 + [2 \times 241.8]) \text{ (1)}$$

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

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

More moles gas gives more disorder (1)

(ii)
$$\Delta S = \sum S \text{ prducts} - \sum S \text{ reactants (1)}$$

= $(213.6 + [4 \times 130.6]) - (186.2 + [2 \times 188.7])$ (1)
= $+172.4 \text{ JK}^{-1} \text{ mol}^{-1}$ (1)

(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)

[13]

5

4

3

10. (a)
$$\Delta H^{\bullet}$$
 $\Delta H^{\bullet} = \Sigma \Delta H_{\mathbf{f}}^{\bullet}$ (products) $-\Sigma \Delta H_{\mathbf{f}}^{\bullet}$ (reactants) (1)
$$= -201 + 110$$
$$= -91 \text{ kJmol}^{-1}$$
 (1)

$$\Delta S^{\bullet}$$
 $\Delta S^{\bullet} = \Sigma S^{\bullet}$ (products) $-\Sigma S^{\bullet}$ (reactants) (1)
= $+240 - 2 \times 131 - 198$
= $-220 \text{ JK}^{-1} \text{ mol}^{-1}$ (1)

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

Temperature $\Delta G = \Delta H - T\Delta S \quad \textbf{(1)}$ For $\Delta G = O$, $T = \Delta H/\Delta S = -91 \times 1000/(-220)$ = 414 K $\quad \textbf{(1)}$

[7]

11. (a)
$$\Delta H^{\mbox{\ensuremath{\ensurema$$

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

$$\Delta G^{\bullet} = \Delta H^{\bullet} - T\Delta S^{\bullet} \text{ (1)}$$

$$= -198 - 298 (-186/1000) \text{ (1)}$$

$$= -143 \text{ kJ mol}^{-1} \text{ (1)}$$

7

3

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

$$T = \frac{\Delta H}{\Delta S} \text{ when } \Delta G = O \text{ (1)}$$

$$= \frac{-198 \times 1000}{-186} = 1100 \text{K (1)}$$

[10]

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

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

2

(ii) $25 \, ^{\circ}\text{C} = 298 \, \text{K}$ (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

$$\Delta G$$
 -ve: reaction feasible (1)

4

[6]

13. (a) (i) Steps

Sublimation/atomisation enthalpy or

$$\Delta H_{\text{fus}} + \Delta H_{\text{vap}} \text{ Ca(s)} \rightarrow \text{Ca(g)(1)}$$

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 $\times \Delta H_a$ chlorine

$$Cl_2(g) \rightarrow 2Cl(g)$$
 (1)

 $2 \times \text{First electron affinity of chlorine } 2\text{Cl}(g) + 2e^- \rightarrow 2\text{Cl}^-(g)$ (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)

(ii) 2nd IE needed when CaCl₂ formed or only 1st IE for CaCl (1) BE of Cl₂ needed when CaCl₂ formed but BE/2 for CaCl (or equivalent) (1)

 $2 \times$ electron affinity when CaCl2 formed but $1 \times$ EA for CaCl (1)

LE of CaCl₂ greater (or different) than LE CaCl (1)

 $Ca^{2+}(g) + 2Cl^{-}(g)$ $CaCl_{2}(s)$ $Ca^{2+}(aq) + 2Cl^{-}(g)$ $Ca^{2+}(aq) + 2Cl^{-}(aq)$

+LE + $(\Delta H_{\text{hyd}} \text{Ca}^{2^+})$ + $2(\Delta H_{\text{hyd}} \text{Cl}^-)$ - $\Delta H_{\text{soln}} \text{CaCl}_2$ = CaCl₂ = 0 or correct cycle (1)

 $\Delta H_{\text{soln}} \text{ CaCl2} = 2255 - 1650 - 768$ (1)

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

(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)

[17]

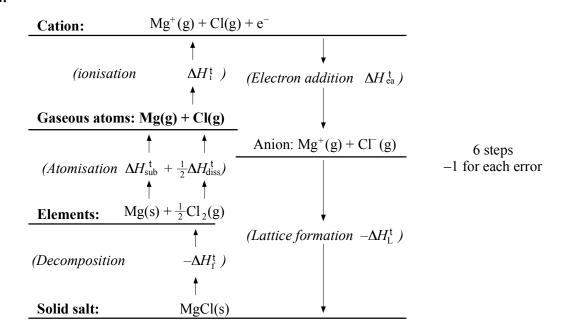
7

4

3

3

14.



$$0 = -\Delta H_{\mathbf{f}}^{\mathbf{G}} + \Delta H_{\mathbf{Sub}}^{\mathbf{G}} + \Delta H_{\mathbf{f}}^{\mathbf{G}} + \Delta H_{\mathbf{f}}^{\mathbf{G}} + \Delta H_{\mathbf{f}}^{\mathbf{G}}$$

$$\Delta H_{\mathbf{f}}^{\mathbf{G}} = \Delta H_{\mathbf{Sub}}^{\mathbf{G}} + \Delta H_{\mathbf{diss}}^{\mathbf{G}} + \Delta H_{\mathbf{f}}^{\mathbf{G}} + \Delta H_{\mathbf{G}}^{\mathbf{G}}$$

$$\Delta H_{\mathbf{f}}^{\mathbf{G}} = \Delta H_{\mathbf{Sub}}^{\mathbf{G}} + \Delta H_{\mathbf{diss}}^{\mathbf{G}} + \Delta H_{\mathbf{G}}^{\mathbf{G}} + \Delta H_{\mathbf{G}}^{\mathbf{G}}$$

$$\Delta H_{\mathbf{f}}^{\mathbf{G}} = 146 + 121 + 736 - 364 - 753$$

$$\Delta H_{\mathbf{f}}^{\mathbf{G}} = -114 \text{ kJ mol}^{-1} \quad (\mathbf{3}) \quad [-1 \text{ for each error}] \quad 2$$

$$\Delta H_{\mathbf{f}}^{\mathbf{G}} = \Delta H_{\mathbf{f}}^{\mathbf{G}} \quad (\text{MgCl}_2) - \Delta H_{\mathbf{f}}^{\mathbf{G}} \quad (\text{MgCl}) = -653 - 2 \quad (-114) = -425 \text{ kJ mol}^{-1} \quad 1$$

$$\Delta S_{\mathbf{G}}^{\mathbf{G}} \approx 0 \text{ since } 2 \text{ mol solid} \quad 2 \text{ mol solid} \quad 1$$

$$\text{If } \Delta S_{\mathbf{G}}^{\mathbf{G}} = 0, \text{ then } \Delta G_{\mathbf{G}}^{\mathbf{G}} = \Delta H_{\mathbf{G}}^{\mathbf{G}} \quad 1$$

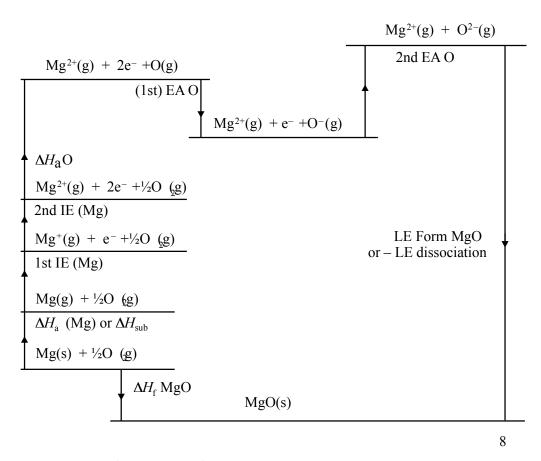
$$\text{So } \Delta G_{\mathbf{G}}^{\mathbf{G}} \text{ for the reaction is } < 0 \text{ (at all } T) - \text{ hence } \text{MgCl}_2 \text{ is always favoured over MgCl} \quad 1$$

[10]

15 (a) Heat (energy)/ internal energy change (not energy change) (1)

Measured at constant pressure (1)

(b)



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:

$$\Delta H_{\rm a} {\rm Mg} + 1^{\rm st} {\rm IE} {\rm Mg} + 2^{\rm nd} {\rm IE} {\rm Mg} + \Delta H_{\rm a} {\rm O} + 1^{\rm st} {\rm EA} {\rm O} + 2^{\rm nd} {\rm EA} {\rm O} + {\rm LE} {\rm Form} - {\rm MgO} \Delta H_{\rm f} {\rm MgO} = 0$$
 (1)
Hence; $148 + 738 + 1451 + 249 - 141 + 798 + {\rm LE} + 602 = 0$ (1)
(NB This scores 2)
LE formation MgO = -3845 (kJ mol⁻¹) (1)
(Allow $+3845 {\rm Max} 2$)

2

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

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

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

$$\Delta S \text{ is negative/ entropy decreases (as order increases) (1)}$$

$$\Delta G = \Delta H - T\Delta S \text{ (1)}$$

$$\Delta G \text{ must (always) be positive (since } \Delta H_r \text{ and } - T\Delta S \text{ are both positive) (1)}$$
Reaction never/not feasible (or equivalent) (1)
$$\Delta S = \Sigma S \text{ products } - \Sigma S \text{ reactants}$$

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

$$\Delta S = 84 \text{ (JK}^{-1} \text{ mol}^{-1}\text{) (Ignore units)}$$

$$Allow - 84 \text{ to score (I) mark}$$

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

$$= -21.6 - 298 \times 84/1000$$

$$= -46.6 \text{ kJ mol}^{-1} \text{ or } -46.6 \text{ out thout units}$$

$$(Mark \Delta G \text{ consequentially to incorrect } \Delta S)$$

$$(e.g. \Delta S = -84 \text{ gives } \Delta G = +3.4 \text{ kJ mol}^{-1}\text{)}$$

17. (a) Reaction 1

$$\Delta H = \Sigma \Delta H_{\rm f} \text{ products} - \Sigma \Delta H_{\rm f} \text{ reactants }$$
 (1)
= $(\Delta H_{\rm f} \text{CO}) - (\Delta H_{\rm f} \text{CH}_4 + \Delta H_{\rm f} \text{H}_2 \text{O})$
= $(-110.5) - (-74.8 - 241.8) = +206.1 \text{ (kJ mol}^{-1})$ (1)
 $\Delta S = \Sigma S \text{ products} - \Sigma S \text{ reactants }$ (1)
= $(197.6 + [3 \times 130.6]) - (186.2 + 188.7) = 214.5 \text{ (J K}^{-1} \text{mol}^{-1})$ (1)
 $\Delta G = \Delta H - T\Delta S$ (1)
 $0 = +206.1 - T \times 214.5/1000$ (1)
 $T = 206.1 \times 1000/214.5 = 960.8 \text{ (K)}$ (1)

(allow 961)

Penalise incorrect units in calculation of temperature by 2 marks

Mark T consequentially

Reaction 2

$$\Delta H = 2\Delta H_{\rm f} N H_3 = -92.2 \text{ (kJ mol}^{-1})$$
 (1)
 $\Delta S = (2 \times 192.3) - (191.6 + [3 \times 130.6]) = -198.8 \text{ (J K}^{-1} \text{mol}^{-1})$ (1)
 $\Delta G = 0 = -92.2 + \text{T} \times 198.8/1000$
 $T = 92.2 \times 1000/198.8 = 463.8 \text{ (k)}$ (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)
$$Calculation of \Delta H; \ \Delta H_{reaction} = \Sigma \Delta H_{Prolucts} - \Sigma \Delta H_{Reactants}$$
 (1)
$$= (2 \times -110.5) - (-3935) = + 172.5 \text{ Allow } 172 - 173 \text{ kJ mol}^{-1}$$
 (1)
$$Calculation of \Delta S; \ \Delta S_{reaction} = \Sigma \Delta S_{Products} - \Sigma S_{Reactants}$$
 (1)
$$= (2 \times 197.6) - (5.7 + 213.6) = 175.9 \text{ J mol}^{-1} \text{ K}^{-1}$$
 (1)
$$Calculation of T \quad \Delta G = 172.5 - T \times 175.9/1000 = 0$$
 (1)
$$T \times 175.9/1000 = 172.5$$

$$T = 172.5 \times 1000/175.9 = 980.7 \text{ K}$$
 (1)
$$S = \frac{3675 \text{ J vaporise } 1.50 \text{ g water}}{3675 \times 18/1.50 \text{ vaporise } 1.00 \text{ mole water}}$$

$$= 44.1 \text{ kJ mol}^{-1}$$
 (1)

 $\Delta G = 0 = 44.1 - 373 \times \Delta S / 1000 \text{ or } \Delta S = \Delta H / T$ (1)

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

18.

(a)

Calculation of ΔS ;

3

[11]

19. (a)
$$\Delta H^{\bullet} = \Sigma \Delta H^{\bullet} \text{ (products)} - \Delta H^{\bullet} \text{ (reactants)} \text{ (1)}$$

$$= (-110.5) - (-271.9) = +161.4 \text{ [Allow } 161 - 161.5] \text{ kJ mol}^{-1} \text{ (1)}$$

$$\Delta S^{\bullet} = \Sigma S^{\bullet} \text{ (products)} - \Sigma S^{\bullet} \text{ (reactants)} \text{ (1)}$$

$$= (27.3 + 197.6) - (58.5 + 5.7) = +160.7$$

$$[Allow } 160.6 - 161] \text{ J mol}^{-1} \text{ K}^{-1} \text{ (1)}$$

$$\Delta G = \Delta H - T\Delta S \text{ [Stated or correctly used]} \text{ (1)}$$

$$\Delta G = +161.4 - 450 \times 160.7/1000 \text{ (1)}$$

$$= +89.1 \text{ [Allow } 88.5 - 89.1] \text{ kJ mol}^{-1} \text{ (1)}$$

$$\Delta H^{\bullet} = (-393.5) - (-271.9 - 110.5) = -11.1 \text{ kJ mol}^{-1} \text{ (1)}$$

$$\Delta G^{\bullet} = (213.6 + 27.3) - (58.5 + 197.6) = -15.2 \text{ J mol}^{-1} \text{ K}^{-1} \text{ (1)}$$

$$\Delta G = -11.1 + 450 \times 15.2/1000 = -4.26 \text{ [Allow-4.3] kJ mol}^{-1} \text{ (1)}$$

$$\text{(b)} \text{ Feasible when } \Delta G \leq 0 \text{ or } \Delta G \text{ is negative (1)}$$

$$\text{Process 1 is more feasible as temperature is increased (1)}$$

$$\text{Because } \Delta S \text{ is positive or } -T\Delta S \text{ is negative or } T\Delta S \text{ is negative (1)}$$

$$\text{Process 2 is less feasible as temperature is increased (1)}$$