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1 a) At 0 K water is solid and the atoms are highly ordered. [1] The crystals are not disrupted by molecular movement. [1]

b) The rises in entropy at T_1 and T_2 correspond to the changes of state:

melting and vaporising. [1]

There is a greater increase in disorder when molecules separate from a liquid and turn to gas than when molecules melt [1] because of the much greater freedom of movement of molecules in the gas phase. [1]

c) i) Water and steam are in equilibrium [1] at 373 K and 1 atmosphere pressure so there is no tendency for the change to go in either direction. [1]

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

Since $\Delta G = 0 \text{ kJ mol}^{-1}$, $\Delta S = \frac{\Delta H}{T}$ [1]

$$\Delta S = \frac{41.1 \text{ kJ mol}^{-1}}{373 \text{ K}} \quad [1]$$

$= 0.110 \text{ kJ mol}^{-1} \text{ K}^{-1}$

$= 110 \text{ J mol}^{-1} \text{ K}^{-1}$ [1]

2 a) $NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(g)$ [1]

Solid decomposing to two gases. Increased disorder. ΔS positive. [1]

b) $KCl(s) + aq \rightarrow KCl(aq)$ [1]

Ordered crystals breaking up to produce hydrated ions in solution. Increased disorder. ΔS positive. [1]

c) $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$ [1]

Three moles of gas combining to give two moles of gas. Less disorder. ΔS negative. [1]

d) $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$ [1]

Two moles of reactant producing three moles of product, one of which is a gas. Increased disorder. ΔS positive. [1]

e) $NH_3(g) + HI(g) \rightarrow NH_4I(s)$ [1]

Two moles of gas combining to give one mole of solid. Less disorder. ΔS negative. [1]

3 a) $Al_2O_3(s) + 3C(s) \rightarrow 2Al(s) + 3CO(g)$ [1]

b) Total enthalpy change of formation of products = $3 \times (-111 \text{ kJ mol}^{-1}) = -333 \text{ kJ mol}^{-1}$ [1]

Total enthalpy change of formation of reactants = $-1669 \text{ kJ mol}^{-1}$ [1]

Overall enthalpy change = $-333 \text{ kJ mol}^{-1} - (-1669 \text{ kJ mol}^{-1})$ [1]

$= +1336 \text{ kJ mol}^{-1}$

c) Total entropy of reactants = 50.9 J mol^{-1} K^{-1} + (3 × 5.7 J mol^{-1} K^{-1}) = 68 J mol^{-1} K^{-1} [1]

Total entropy of products = (2 × 28.3 J mol^{-1} K^{-1} + (3 × 198 J mol^{-1} K^{-1})

= 651 J mol^{-1} K^{-1} [1]

Overall entropy change = 651 J mol^{-1} K^{-1} – 68 J mol^{-1} K^{-1} [1]

= 583 J mol^{-1} K^{-1}

d) i) $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ [1]

$\Delta G^{\ominus}$ = +1336 kJ mol^{-1} – (298 K × 0.583 kJ mol^{-1} K^{-1}) [1]

= +1162 kJ mol^{-1}

ii) The reaction is not feasible at 298 K because the free energy change is positive. [1]

e) The reaction becomes feasible when $\Delta H - T\Delta S < 0$. [1] This is when $T\Delta S > \Delta H$.

This happens when T = 1336 kJ mol^{-1} ÷ 0.583 kJ mol^{-1} K^{-1}

= 2292 K [1]

f) Reactions between solids are slow. The reaction rate has to be very high for it to proceed at a measurable rate. [1]

4 a) (6 × 205 J mol^{-1} K^{-1}) + $S^{\ominus}$($C_6H_{12}O_6$) – (6 × 214 J mol^{-1} K^{-1} + 6 × 70 J mol^{-1} K^{-1}) = –256 J mol^{-1} K^{-1} [1]

$S^{\ominus}$($C_6H_{12}O_6$) = +218 J mol^{-1} K^{-1} [1]

b) ΔG = +2879 kJ mol^{-1} – (298 K × – 0.256 kJ mol^{-1} K^{-1}) [1] = +2955 kJ mol^{-1} [1]

c) i) ΔG is large and positive at 298 K so the reaction is not feasible under standard conditions. [1] The entropy change is negative and so $-T\Delta S$ is positive at all temperatures. [1] Changing the temperature cannot make the free energy change for the reaction negative. [1]

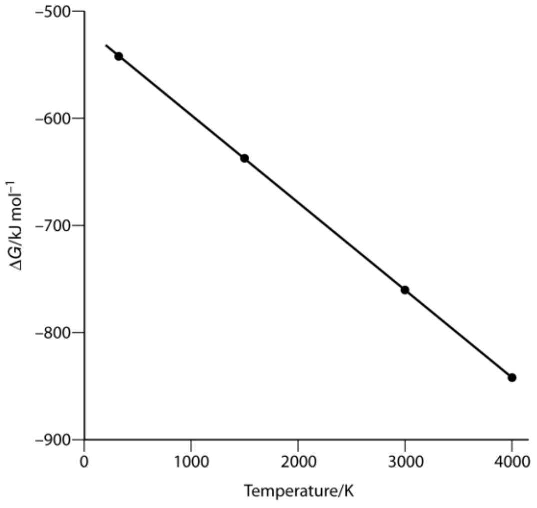
ii) A plant leaf is not a closed system. It is the input of energy from the Sun which makes photosynthesis possible. [1]

5 a) $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ [1]

$\Delta G^{\ominus}$ = –519 kJ mol^{-1} – (298 K × 0.082 kJ mol^{-1} K^{-1}) [1]

= –543 kJ mol^{-1}

b) i)



Labelled axes and appropriate scales [1]; accurate plot giving straight line. [1]

ii) The gradient of the graph is $-\Delta S$. [1] Since the graph is a straight line this shows that $-\Delta S$ does not vary with temperature. [1]

c) i) ΔG is negative across the whole temperature range [1], so the reaction is feasible at all these temperatures. [1]

ii) At 298 K the activation energy of the reaction is too high (the bonds in the molecules are too strong) [1] and the energy of collisions between molecules too low for the reaction to happen at a measurable rate. [1]

d) In the reaction forming CO and steam, 2.5 mol gases react to form 3 mol of gas. [1] This increases disorder so that the entropy change is substantially positive. [1] In the reaction forming soot, 2 mol gases react to form an ordered solid and 2 mol gas. [1] Overall there is little change in entropy. [1]

6 a) Bromine is a liquid under standard conditions while iodine is a solid. For comparable substances, liquids generally have higher standard entropy values than solids.[1] This is because there is greater randomness in the distribution of molecules and energy quanta in a liquid compared to a solid. [1]

b) At the boiling point the liquid and vapour are in equilibrium and so $\Delta S_{total} = 0$ [1]

$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$

$0 = \Delta S_{system} - \frac{\Delta H}{T}$, hence $\Delta S_{system} = \frac{\Delta H}{T}$ [1]

$= \frac{26\,000 \text{ J mol}^{-1}}{308 \text{ K}} = 84.4 \text{ J K}^{-1}$ [1] for 84.4, [1] for units

c) i) Highly endothermic change: ΔH +ve [1]

1 mol liquid produces 1.5 mol gas, so ΔS positive. [1]

Reaction is the reverse of hydrogen burning and so not expected to be feasible, so ΔG positive. [1]

ii) Highly exothermic change: ΔH negative [1]

1 mol liquid fuel reacts with oxygen to produce more moles of gas (CO_2 and H_2O), so ΔS positive. [1]

ΔG must be negative [1]

d) i) $\Delta G = \Delta H - T\Delta S$ [1]

$\Delta G = +132 \text{ kJ mol}^{-1} - (298 \text{ K} \times 0.233 \text{ kJ mol}^{-1} \text{ K}^{-1})$ [1]

$= +62.5 \text{ kJ mol}^{-1}$

ii) $\ln K = -\frac{\Delta G^{\ominus}}{RT} = -\frac{+62\,500 \text{ J mol}^{-1}}{8.31 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}$ [1] for numerator, [1] for denominator

$= -25.2$

$K = e^{-25.2} = 1.1 \times 10^{-11}$ [1]

iii) The positive value of $\Delta G^{\ominus}$ suggests that the reaction is not feasible at 298 K. [1] This is confirmed by the very small value of K, which shows that that the equilibrium is well over to the left-hand side. [1]

iv) The reaction becomes feasible when $T\Delta S > \Delta H$ [1]

This happens when

T = 132 kJ mol^{-1} ÷ 0.233 kJ mol^{-1} K^{-1}

= 566 K [1]