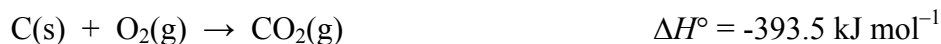
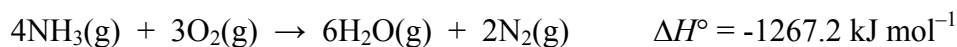


Marks
6

- The final step in the industrial production of urea, $\text{CO}(\text{NH}_2)_2$, is:



Using the following data, calculate the standard enthalpy of formation ΔH°_f of solid urea.



Using $\Delta_{\text{rxn}} H^\circ = \sum m \Delta_f H^\circ (\text{products}) - \sum n \Delta_f H^\circ (\text{reactants})$, $\Delta_{\text{rxn}} H^\circ$ for the industrial production of urea is given by

$$\Delta_{\text{rxn}} H^\circ = [\Delta_f H^\circ (\text{H}_2\text{O}(\text{l})) + \Delta_f H^\circ (\text{CO}(\text{NH}_2)_2(\text{s}))] - [\Delta_f H^\circ (\text{CO}_2(\text{g})) + 2\Delta_f H^\circ (\text{NH}_3(\text{g}))]$$

$\Delta_f H^\circ (\text{NH}_3(\text{g}))$ is not known. $\text{NH}_3(\text{g})$ is produced in the reverse of reaction (1). Reaction (1) requires formation of $\text{H}_2\text{O}(\text{l})$ which is given by reaction (3). Combining these two reactions therefore allows $\Delta_f H^\circ (\text{NH}_3(\text{g}))$ to be calculated.



Therefore, $\Delta_f H^\circ (\text{NH}_3) = \frac{1}{4} (1267.2 - 3 \times 483.8) \text{ kJ mol}^{-1} = -46.05 \text{ kJ mol}^{-1}$.

Hence for the industrial production of urea,

$$\begin{aligned} \Delta_{\text{rxn}} H^\circ &= [(0.5 \times -483.6) + \Delta_f H^\circ (\text{CO}(\text{NH}_2)_2(\text{s}))] - [(-393.5) + (2 \times -46.05)] \text{ kJ mol}^{-1} \\ &= -90.1 \text{ kJ mol}^{-1} \end{aligned}$$

Hence, $\Delta_f H^\circ (\text{CO}(\text{NH}_2)_2(\text{s})) = 333.6 \text{ kJ mol}^{-1}$

$$\Delta H^\circ_f = -333.6 \text{ kJ mol}^{-1}$$

ANSWER CONTIUNES ON THE NEXT PAGE

The formation of urea in this process is only spontaneous above 821 °C. What is the value of the entropy change ΔS° (in $\text{J K}^{-1} \text{mol}^{-1}$) for the reaction?

For a reaction to be spontaneous requires $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ < 0$.

At 821 °C, $\Delta H^\circ - T\Delta S^\circ = 0$ so

$$\Delta S^\circ = \frac{\Delta H^\circ}{T} = \frac{(-90.1 \times 10^3 \text{ J mol}^{-1})}{(821+273)\text{K}} = -82.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

Actually, the question is incorrect. Above this temperature, ΔG° is positive and the reaction is non-spontaneous. This can be verified by substituting a higher temperature into $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$.

$$\Delta S^\circ = -82.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

Rationalise the sign of ΔS° in terms of the physical states of the reactants and products.

ΔS° is negative as 3 moles of gas react to give 1 mole of gas and 1 mole of solid. There is a decrease in randomness.