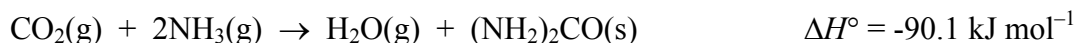
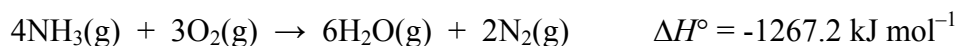


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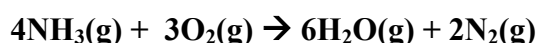
- The final step in the industrial production of urea, $(\text{NH}_2)_2\text{CO}$, is:



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



Using $\Delta_{\text{rxn}}H^\circ = \sum m\Delta_f H^\circ(\text{products}) - \sum n\Delta_f H^\circ(\text{reactants})$ for the reaction,



$$\Delta_{\text{rxn}}H^\circ = [6\Delta_f H^\circ(\text{H}_2\text{O}(\text{g}))] - [4\Delta_f H^\circ(\text{NH}_3(\text{g}))]$$

as $\Delta_f H^\circ(\text{N}_2(\text{g}))$ and $\Delta_f H^\circ(\text{O}_2(\text{g}))$ are both zero for elements in the standard states. Using $\Delta_{\text{rxn}}H^\circ = -1267.2 \text{ kJ mol}^{-1}$ and $\Delta_f H^\circ(\text{H}_2\text{O}(\text{g})) = 0.5 \times -483.6 \text{ kJ mol}^{-1}$,

$$\Delta_{\text{rxn}}H^\circ = [6 \times 0.5 \times -483.6] - [4\Delta_f H^\circ(\text{NH}_3(\text{g}))] = -1267.2 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(\text{NH}_3(\text{g})) = -45.9 \text{ kJ mol}^{-1}$$

Using $\Delta_{\text{rxn}}H^\circ = \sum m\Delta_f H^\circ(\text{products}) - \sum n\Delta_f H^\circ(\text{reactants})$ for the reaction,



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

As $\Delta_{\text{rxn}}H^\circ = -90.1 \text{ kJ mol}^{-1}$ and $\Delta_f H^\circ(\text{H}_2\text{O}(\text{g}))$, $\Delta_f H^\circ(\text{CO}_2(\text{g}))$ and $\Delta_f H^\circ(\text{NH}_3(\text{g}))$ are 0.5×-483.6 , -393.5 and $-45.9 \text{ kJ mol}^{-1}$ respectively,

$$\Delta_{\text{rxn}}H^\circ = [(0.5 \times -483.6) + \Delta_f H^\circ((\text{NH}_2)_2\text{CO}(\text{g}))]$$

$$-[-393.5 + (2 \times -45.9)] = -90.1 \text{ kJ mol}^{-1}$$

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

Answer: $-333.6 \text{ kJ mol}^{-1}$

ANSWER CONTINUES ON THE NEXT PAGE

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

The reaction is spontaneous when $\Delta G^\circ < 0$. As $\Delta G^\circ = \Delta H^\circ - T\Delta S$ and assuming that ΔH° and ΔS° are independent of temperature, this occurs at temperatures below $T = 821 \text{ }^\circ\text{C}$

$$\Delta H^\circ - T\Delta S < 0$$

Using $\Delta H^\circ = -90.1 \text{ kJ mol}^{-1}$ for the industrial, at $T = (821 + 273) = 1094 \text{ K}$,

$$(-90.1 \times 10^3) - (1094)\Delta S^\circ = 0 \quad \text{so } \Delta S^\circ = -82.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

Answer: **$-82.4 \text{ J K}^{-1} \text{ mol}^{-1}$**

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

The reaction,



involves the conversion of 3 moles of gas \rightarrow 1 mole of gas. This corresponds to an increase in ordering which is consistent with a reduction in entropy (so $\Delta S^\circ < 0$).