Marks 5

- Consider the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

  $\Delta H° = -198.4$ kJ mol^{-1} and $\Delta S° = -187.9$ J K^{-1} mol^{-1} at 25 °C.

  Show that this reaction is spontaneous at 25 °C.

Using $\Delta G° = \Delta H° - T\Delta S°$,

$$\Delta G° = (-198.4\times10^3 \text{ J mol}^{-1}) - ((25+273) \text{ K}) \times(-187.9 \text{ J mol}^{-1})$$
$$= -142400 \text{ J mol}^{-1} = -142.4 \text{ kJ mol}^{-1}$$

As $\Delta G° < 0$, the reaction is spontaneous.

If the volume of the reaction system is increased at 25 °C, in which direction will the reaction move?

An increase in volume corresponds to a decrease in pressure. According to Le Chatelier's principle, the reaction will shift to increase the pressure. It does this by favouring the side with a *greater* number of gaseous molecules:

The reaction will shift to the left (3 moles of gas on the left, 2 moles of gas on the right).

Calculate the value of the equilibrium constant, K, at 25 °C.

Using $\Delta G° = -RT\ln K$,

$$-142.2 \times 10^3 \text{ J mol}^{-1} = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times ((25 + 273) \text{ K}) \times \ln K$$

$$K = 9.170 \times 10^{24} \quad \text{(essentially complete conversion to products)}$$

$K = 9.170 \times 10^{24}$ **(no units)**

Assuming $\Delta H°$ and $\Delta S°$ are independent of temperature, in which temperature range is the reaction non-spontaneous?

The reaction is non-spontaneous when $\Delta G° > 0$, or when $\Delta H° - T\Delta S° > 0$:

$$(-198.4 \times 10^3 \text{ J mol}^{-1}) - T \times (-187.9 \text{ J mol}^{1}) > 0$$

$$T > \frac{-198.4\times10^3 \text{ J mol}^{-1}}{-187.9 \text{ J mol}^{-1}} \quad \text{so } T > 1055 \text{ K}$$

Note that, as demonstrated above, the reaction is spontaneous at 298 K and, as the reaction is exothermic, it becomes less favourable as the temperature increases (Le Chatelier's principle).

Answer: $T > 1055$ K