• For the reaction \(2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})\) at 25 \(^\circ\text{C}\)

\[\Delta H^\circ = -198.4 \text{ kJ mol}^{-1}\] and \[\Delta S^\circ = -187.9 \text{ J K}^{-1} \text{ mol}^{-1}\]

Show that this reaction is spontaneous at 25 \(^\circ\text{C}\).

A reaction is spontaneous if \(\Delta G^\circ < 0\). Using \(\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ\):

\[\Delta G^\circ = (-198.4 \times 10^3) - (25 + 273) \times (-187.9) = -142000 \text{ J mol}^{-1} = -142 \text{ kJ mol}^{-1}\]

Hence, \(\Delta G^\circ < 0\) and the reaction is spontaneous.

If the volume of the reaction system is increased at 25 \(^\circ\text{C}\), in which direction will the reaction move?

In the reaction, three moles of gas are converted into two moles of gas. Increasing the volume lowers the pressure. The system responds by acting to increase the pressure – it shifts to the left (more reactants).

Calculate the value of the equilibrium constant, \(K\), at 25 \(^\circ\text{C}\).

Using \(\Delta G^\circ = -RT\ln K\), the equilibrium constant is given by:

\[K = e^{-\Delta G^\circ / RT} = e^{(142000) / (8.314(25+273))} = 7.8 \times 10^{24}\]

\[K = 7.8 \times 10^{24} \ast\]

Assuming \(\Delta H^\circ\) and \(\Delta S^\circ\) are independent of temperature, in which temperature range is the reaction non-spontaneous?

The reaction is non-spontaneous if \(\Delta G^\circ > 0\). As \(\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ\), this occurs when

\[(-198.4 \times 10^3) - T \times (-187.9) > 0\]

Hence,

\[T > \frac{198.4 \times 10^3}{187.9} \text{ or } T > 1055 \text{ K}\]

Answer: \(T > 1055 \text{ K}\)

\ast\ The variation in the value of \(K\) due to the accuracy used for \(\Delta G^\circ\) is large as the uncertainty is magnified by the use of the exponential function.

\(K\) is very big \((-10^{25})\) and corresponds to essentially all reactants going to products.
A mixture of 0.500 mol of \( \text{NO}_2(g) \) and 0.500 mol of \( \text{N}_2\text{O}_4(g) \) is allowed to reach equilibrium in a 10.0 L vessel maintained at 298 K. The equilibrium is described by the equation below. \( \Delta H^\circ = -15 \text{ kJ mol}^{-1} \) for the forward reaction.

\[
\text{2NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g) \quad K_c = 1.2 \times 10^2 \text{ M}^{-1}
\]

Show that the system is at equilibrium when the concentration of \( \text{NO}_2(g) \) is 0.023 M.

The concentrations of \( \text{NO}_2(g) \) and \( \text{N}_2\text{O}_4(g) \) at the start are:

\[
[\text{NO}_2(g)] = [\text{N}_2\text{O}_4(g)] = \frac{\text{number of moles}}{\text{volume}} = \frac{0.500}{10.0} = 0.0500 \text{ M}
\]

[\( \text{NO}_2(g) \)] decreases during the reaction and so [\( \text{N}_2\text{O}_4(g) \)] increases. From the chemical equation, one mole of \( \text{N}_2\text{O}_4(g) \) is produced for every two moles of \( \text{NO}(g) \) that are lost.

The change in [\( \text{NO}_2(g) \)] = 0.0500 – 0.023 = 0.027 M. Hence,

\[
[\text{N}_2\text{O}_4(g)]_{\text{equilibrium}} = 0.0500 + \frac{1}{2} \times 0.027 = 0.064 \text{ M}
\]

With these concentrations, the reaction quotient, \( Q \), is given by:

\[
Q = \frac{[\text{N}_2\text{O}_4(g)]]}{[\text{NO}_2(g)]^2} = \frac{(0.064)}{(0.023)^2} = 120 = 1.2 \times 10^2
\]

As \( Q = K \), the reaction is at equilibrium.

Discuss the effect an increase in temperature, at constant volume, would have on the concentration of \( \text{NO}_2(g) \).

As \( \Delta H^\circ = -15 \text{ kJ mol}^{-1} \) for the forward reaction, the reaction is exothermic. If the temperature is increased, the system will respond by removing heat. It will do this by shifting towards the reactant (\( \text{NO}_2(g) \)) as the backward reaction is endothermic. Hence, [\( \text{NO}_2(g) \)] will increase.

State with a brief reason whether the concentration of \( \text{NO}_2(g) \) is increased, decreased, or unchanged when argon gas (0.2 mol) is injected while the temperature and volume remain constant.

Adding argon will increase the pressure inside the vessel will increase. However, the inert gas does not change the volume so all reactant and product concentrations remain the same.
• A key step in the metabolism of glucose for energy is the isomerism of glucose-6-phosphate (G6P) to fructose-6-phosphate (F6P);

\[ \text{G6P} \rightleftharpoons \text{F6P} \]

At 298 K, the equilibrium constant for the isomerisation is 0.510. Calculate \( \Delta G^\circ \) at 298 K.

Using \( \Delta G^\circ = -RT\ln K \):

\[ \Delta G^\circ = -(8.314) \times (298) \times \ln(0.510) = +1670 \text{ J mol}^{-1} = +1.6 \text{ kJ mol}^{-1} \]

**Answer:** +1.6 kJ mol\(^{-1}\)

Calculate \( \Delta G \) at 298 K when the \([\text{F6P}] / [\text{G6P}]\) ratio = 10.

Using \( \Delta G = \Delta G^\circ + RT\ln Q \), when the reaction quotient \( Q = \frac{[\text{F6P}]}{[\text{G6P}]} = 10 \):

\[ \Delta G = (+1670) + (8.314) \times (298) \times \ln(10) = +7400 \text{ J mol}^{-1} = +7.4 \text{ kJ mol}^{-1} \]

**Answer:** +7.4 kJ mol\(^{-1}\)

In which direction will the reaction shift in order to establish equilibrium? Why?

As \( Q > K \), the reaction will shift to decrease \( Q \). It will do this by reducing the amount of product and increasing the amount of reactant: it will shift to the left.

Equivalently, as \( \Delta G = +7.4 \text{ kJ mol}^{-1} \), the forward process is non-spontaneous and the backward reaction is spontaneous.
The specific heat capacity of water is 4.18 J g⁻¹ K⁻¹ and the specific heat capacity of copper is 0.39 J g⁻¹ K⁻¹. If the same amount of energy were applied to a 1.0 mol sample of each substance, both initially at 25 °C, which substance would get hotter? Show all working.

As \( q = C \times m \times \Delta T \), the temperature increase is given by \( \Delta T = \frac{q}{C \times m} \).

As \( \text{H}_2\text{O} \) has a molar mass of \( 2 \times 1.008 \, (\text{H}) + 16.00 \, (\text{O}) = 18.016 \), 1.0 mol has a mass of 18 g. The temperature increase is therefore:

\[
\Delta T = \frac{q}{C_{\text{H}_2\text{O}} \times m_{\text{H}_2\text{O}}} = \frac{q}{(4.18) \times (18)} = \frac{q}{75}
\]

As \( \text{Cu} \) has an atomic mass of 63.55, 1.0 mol has a mass of 64 g. The temperature increase is therefore:

\[
\Delta T = \frac{q}{C_{\text{Cu}} \times m_{\text{Cu}}} = \frac{q}{(0.39) \times (64)} = \frac{q}{25}
\]

As the same amount of energy is supplied to both, \( q \) is the same for both. The temperature increase of the copper is therefore higher.

Answer: copper