

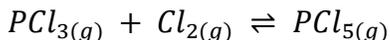
Answers to Exercise 8.4

More Variation of Equilibrium Constant with Temperature

1.

(a) **Step 1: Write a balanced chemical equation for the reaction**

This was provided in the question.



Step 2: Calculate activities for all reactants and products

$$a_{PCl_3(g)} = \frac{p_{PCl_3(g)}}{1 \text{ bar}} = \frac{2.5 \times 10^{-3} \text{ bar}}{1 \text{ bar}} = 2.5 \times 10^{-3} \quad a_{PCl_5(g)} = \frac{p_{PCl_5(g)}}{1 \text{ bar}} = \frac{0.75 \text{ bar}}{1 \text{ bar}} = 0.75$$

$$a_{Cl_2(g)} = \frac{p_{Cl_2(g)}}{1 \text{ bar}} = \frac{9.1 \times 10^{-5} \text{ bar}}{1 \text{ bar}} = 9.1 \times 10^{-5}$$

Step 3: Calculate equilibrium constant

$$K = \frac{a_{PCl_5(g)}}{(a_{PCl_3(g)})(a_{Cl_2(g)})} = \frac{0.75}{(2.5 \times 10^{-3})(9.1 \times 10^{-5})} = 3.3 \times 10^6$$

Step 4: Check your work

Does your answer seem reasonable? Are sig. fig. correct?

(b) *This is a "two temperatures; two equilibrium constants" question for which we can use $\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$. Keeping organized is key to success.*

Step 1: Match equilibrium constants to the corresponding temperature

$$T_1 = 25 \text{ }^\circ\text{C} = 298.15 \text{ K}$$

$$T_2 = 250 \text{ }^\circ\text{C} = 523.15 \text{ K}$$

$$K_1 = 3.3 \times 10^6$$

$$K_2 = ???$$

Step 2: Look up (or calculate) the standard enthalpy change for the reaction

$$\Delta_r H^\circ = -87.9 \frac{\text{kJ}}{\text{mol}} = -8.79 \times 10^4 \frac{\text{J}}{\text{mol}} \quad \textit{provided in question}$$

Step 3: Crunch the numbers

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{K_2}{3.3 \times 10^6}\right) = \left(\frac{-8.79 \times 10^4 \frac{\text{J}}{\text{mol}}}{8.314 \text{ J/mol}\cdot\text{K}}\right) \left(\frac{1}{298.15 \text{ K}} - \frac{1}{523.15 \text{ K}}\right)$$

$$\ln\left(\frac{K_2}{3.3 \times 10^6}\right) = -15.2$$

$$\frac{K_2}{3.3 \times 10^6} = e^{-15.2}$$

$$\frac{K_2}{3.3 \times 10^6} = 2 \times 10^{-7}$$

$$K_2 = (3.3 \times 10^6)(2 \times 10^{-7})$$

$$K_2 = 0.8$$

Step 4: Check your work

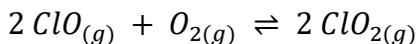
Does your answer seem reasonable?

This reaction is exothermic ($\Delta_r H^\circ < 0$), so it is expected to have a smaller equilibrium constant at the higher temperature.

2. *Equilibrium constants can be calculated from the standard free energy change for a reaction.*

Step 1: Write a balanced chemical equation for the reaction

This was provided in the question.



Step 2: Convert temperature to Kelvin (if necessary)

$$T = 25 \text{ }^\circ\text{C} = 298.15 \text{ K}$$

Step 3: Calculate the standard free energy change for the reaction

$$\Delta_r G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

$$\Delta_r G^\circ = \left(2 \Delta_f G^\circ(\text{ClO}_{2(g)}) \right) - \left[2 \Delta_f G^\circ(\text{ClO}_{(g)}) + \Delta_f G^\circ(\text{O}_{2(g)}) \right]$$

$$\Delta_r G^\circ = 2 \left(120.5 \frac{\text{kJ}}{\text{mol}} \right) - \left[2 \left(98.1 \frac{\text{kJ}}{\text{mol}} \right) + \left(0 \frac{\text{kJ}}{\text{mol}} \right) \right]$$

$$\Delta_r G^\circ = 44.8 \frac{\text{kJ}}{\text{mol}}$$

Step 4: Calculate the equilibrium constant from the standard free energy change

$$\Delta_r G^\circ = -RT \ln K$$

$$\ln K = -\frac{\Delta_r G^\circ}{RT}$$

$$\ln K = -\frac{\left(44.8 \frac{\text{kJ}}{\text{mol}} \right)}{\left(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) (298.15 \text{ K})} \times \frac{1000 \text{ J}}{1 \text{ kJ}}$$

$$\ln K = -18.1$$

$$K = e^{-18.1}$$

$$K = 1.4 \times 10^{-8}$$

Step 5: Check your work

Does your answer seem reasonable?

- (b) *This is a “two temperatures; two equilibrium constants” question for which we can use $\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$. Keeping organized is key to success.*

Step 1: Match equilibrium constants to the corresponding temperature

$$T_1 = 298.15 \text{ K}$$

$$T_2 = 750 \text{ }^\circ\text{C} = 1023.15 \text{ K}$$

$$K_1 = 1.4 \times 10^{-8}$$

$$K_2 = ???$$

Step 2: Calculate the standard enthalpy change for the reaction

$$\Delta_r H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

$$\Delta_r H^\circ = \left(2 \Delta_f H^\circ(\text{ClO}_{2(g)}) \right) - \left[2 \Delta_f H^\circ(\text{ClO}_{(g)}) + \Delta_f H^\circ(\text{O}_{2(g)}) \right]$$

$$\Delta_r H^\circ = 2 \left(102.5 \frac{\text{kJ}}{\text{mol}} \right) - \left[2 \left(101.8 \frac{\text{kJ}}{\text{mol}} \right) + \left(0 \frac{\text{kJ}}{\text{mol}} \right) \right]$$

$$\Delta_r H^\circ = +1.4 \frac{\text{kJ}}{\text{mol}} = 1.4 \times 10^3 \frac{\text{J}}{\text{mol}}$$

Step 3: Crunch the numbers

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{K_2}{1.4 \times 10^{-8}}\right) = \left(\frac{1.4 \times 10^3 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}}\right) \left(\frac{1}{298.15 \text{ K}} - \frac{1}{1023.15 \text{ K}}\right)$$

$$\ln\left(\frac{K_2}{1.4 \times 10^{-8}}\right) = 0.40$$

$$\frac{K_2}{1.4 \times 10^{-8}} = e^{0.40}$$

$$\frac{K_2}{1.4 \times 10^{-8}} = 1.5$$

$$K_2 = (1.4 \times 10^{-8})(1.5)$$

$$K_2 = 2.1 \times 10^{-8}$$

Step 4: Check your work

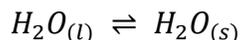
Does your answer seem reasonable?

This reaction is slightly endothermic ($\Delta_r H^\circ > 0$), so it is expected to have a slightly larger equilibrium constant at the higher temperature.

3. This is a “two temperatures; two equilibrium constants” question for which we can use $\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$. Keeping organized is key to success.

The equilibrium constants have to be calculated from activities, so you need to start with a balanced chemical equation. Then use the activities to calculate K for each freezing point (pure water vs. salt water).

Step 1: Write a balanced chemical equation for the reaction



Step 2: Calculate the activities of reactant and product for pure water

$$a_{H_2O_{(l)}} = 1$$

$$a_{H_2O_{(s)}} = 1$$

Step 3: Calculate the equilibrium constant for the freezing of pure water.

$$K_{\text{pure}} = \frac{a_{H_2O_{(s)}}}{a_{H_2O_{(l)}}} = \frac{1}{1} = 1$$

It is expected that you know that the freezing point of pure water is 0 °C.

Step 4: Calculate the activities of reactant and product for salt water

$$a_{H_2O_{(l)}} = X_{H_2O_{(l)}}$$

$$a_{H_2O_{(s)}} = 1$$

$$a_{H_2O_{(l)}} = \frac{n_{H_2O}}{n_{H_2O} + n_{Na^+} + n_{Cl^-}}$$

$$a_{H_2O_{(l)}} = \frac{27.8 \text{ mol}}{27.8 \text{ mol} + 2.14 \text{ mol} + 2.14 \text{ mol}}$$

$$a_{H_2O_{(l)}} = \frac{27.8 \text{ mol}}{32.0 \text{ mol}}$$

$$a_{H_2O_{(l)}} = 0.866$$

$$n_{H_2O} = 500 \text{ g} \times \frac{1 \text{ mol}}{18.0152 \text{ g}} = 27.8 \text{ mol}$$

$$n_{Na^+} = n_{Cl^-} = n_{NaCl} = 125 \text{ g} \times \frac{1 \text{ mol}}{58.4425 \text{ g}} = 2.14 \text{ mol}$$

Step 5: Calculate the equilibrium constant for the freezing of salt water.

$$K_{\text{salt}} = \frac{a_{H_2O_{(s)}}}{a_{H_2O_{(l)}}} = \frac{1}{0.866} = 1.15$$

The temperature corresponding to this K value is the freezing point of this salt water.

Step 6: Match equilibrium constants to the corresponding temperature

$$T_1 = 0 \text{ °C} = 273.15 \text{ K}$$

$$T_2 = ???$$

$$K_1 = 1$$

$$K_2 = 1.15$$

Step 7: Calculate the standard enthalpy change for the reaction

The enthalpy of fusion of water (enthalpy change for melting solid water) is $+6007 \frac{\text{J}}{\text{mol}}$.

Therefore, the enthalpy change for freezing water is $-6007 \frac{\text{J}}{\text{mol}}$.

Step 8: Crunch the numbers

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{1.15}{1}\right) = \frac{-6007 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}} \left(\frac{1}{273.15 \text{ K}} - \frac{1}{T_2}\right)$$

$$\ln(1.15) = -722.5 \text{ K} \left(\frac{1}{273.15 \text{ K}} - \frac{1}{T_2}\right)$$

$$\frac{\ln(1.15)}{-722.5 \text{ K}} = \frac{1}{273.15 \text{ K}} - \frac{1}{T_2}$$

$$\frac{1}{T_2} = \frac{1}{273.15 \text{ K}} + \frac{\ln(1.15)}{722.5 \text{ K}}$$

$$\frac{1}{T_2} = 3.86 \times 10^{-3} \frac{1}{\text{K}}$$

$$T_2 = \frac{1}{3.86 \times 10^{-3} \frac{1}{\text{K}}}$$

$$T_2 = 259 \text{ K} = -14 \text{ }^\circ\text{C}$$

Step 9: Check your work

Does your answer seem reasonable?

Adding salt to water should lower the freezing point, so a freezing point slightly below $0 \text{ }^\circ\text{C}$ for the salt water is reasonable.

4.

- (a) *Raoult's Law can be used to calculate the vapour pressure over a solution containing a nonvolatile solute as long as you know the vapour pressure of the solvent as a pure liquid.*

Step 1: Calculate the molar masses of salt and water

$$M_{\text{NaCl}} = 22.9898 \frac{\text{g}}{\text{mol}} + 35.4527 \frac{\text{g}}{\text{mol}} = 58.4425 \frac{\text{g}}{\text{mol}}$$

$$M_{\text{H}_2\text{O}} = 2 \left(1.0079 \frac{\text{g}}{\text{mol}}\right) + \left(15.9994 \frac{\text{g}}{\text{mol}}\right) = 18.0152 \frac{\text{g}}{\text{mol}}$$

Step 2: Calculate the moles of each species in solution. Don't forget that the salt dissociates into ions!

$$n_{\text{Na}^+} = n_{\text{Cl}^-} = n_{\text{NaCl}} = 125 \text{ g} \times \frac{1 \text{ mol}}{58.4425 \text{ g}} = 2.14 \text{ mol}$$

$$n_{\text{H}_2\text{O}} = 500 \text{ g} \times \frac{1 \text{ mol}}{18.0152 \text{ g}} = 27.8 \text{ mol}$$

Step 3: Calculate the mole fraction of water in the salt-water solution

$$X_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2\text{O}} + n_{\text{Na}^+} + n_{\text{Cl}^-}} = \frac{27.8 \text{ mol}}{27.8 \text{ mol} + 2.14 \text{ mol} + 2.14 \text{ mol}} = 0.866$$

Step 4: Use Raoult's law to calculate the vapour pressure of water above the salt-water solution

$$P_{\text{water over salt-water}} = X_{\text{water in salt-water}} P_{\text{pure water}}$$

$$P_{\text{water over salt-water}} = (0.866)(0.0317 \text{ bar})$$

$$P_{\text{water over salt-water}} = 0.0275 \text{ bar}$$

Step 5: Check your work

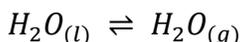
Does your answer seem reasonable? Are sig. fig. correct?

The vapour pressure above the salt-water solution should be slightly lower than that over pure water.

- (b) This is a "two temperatures; two equilibrium constants" question for which we can use $\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$. Keeping organized is key to success.

The equilibrium constants have to be calculated from activities, so you need to start with a balanced chemical equation.

Step 1: Write a balanced chemical equation for the reaction



Step 2: Calculate the activities of reactant and product at 25 °C (as in part (a))

$$a_{H_2O_{(l)}} = 0.866 \qquad a_{H_2O_{(g)}} = \frac{p_{H_2O_{(g)}}}{1 \text{ bar}} = \frac{0.0275 \text{ bar}}{1 \text{ bar}} = 0.0275$$

Step 3: Calculate the equilibrium constant for this reaction at 25 °C (as in part (a))

$$K_{25^\circ\text{C}} = \frac{a_{H_2O_{(g)}}}{a_{H_2O_{(l)}}} = \frac{0.0275}{0.866} = 0.0317$$

Step 4: Calculate the activities of reactant and product at the boiling point

By definition, the vapour pressure above a liquid equals atmospheric pressure when the liquid boils. So, at the normal boiling point, $p_{H_2O_{(g)}} = 1 \text{ atm}$.

$$a_{H_2O_{(l)}} = 0.866 \qquad a_{H_2O_{(g)}} = \frac{1 \text{ atm}}{1 \text{ bar}} \times \frac{1.01325 \text{ bar}}{1 \text{ atm}} = 1.01325$$

Step 5: Calculate the equilibrium constant for this reaction at the boiling point

$$K_{\text{boiling}} = \frac{a_{H_2O_{(g)}}}{a_{H_2O_{(l)}}} = \frac{1.01325}{0.866} = 1.17$$

Step 6: Match equilibrium constants to the corresponding temperature

$$T_1 = 25^\circ\text{C} = 298.15 \text{ K}$$

$$T_2 = ???$$

$$K_1 = 0.0317$$

$$K_2 = 1.17$$

Step 7: Calculate the standard enthalpy change for the reaction

The enthalpy of vaporization of water is $+40.66 \frac{\text{kJ}}{\text{mol}} = +4.066 \times 10^4 \frac{\text{J}}{\text{mol}}$.

That is the enthalpy change for this reaction.

Step 8: Crunch the numbers

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{1.17}{0.0317}\right) = \frac{+4.066 \times 10^4 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}} \left(\frac{1}{298.15 \text{ K}} - \frac{1}{T_2}\right)$$

$$\ln(36.9) = 4890 \text{ K} \left(\frac{1}{298.15 \text{ K}} - \frac{1}{T_2}\right)$$

$$\frac{\ln(36.9)}{4890 \text{ K}} = \frac{1}{298.15 \text{ K}} - \frac{1}{T_2}$$

$$\frac{1}{T_2} = \frac{1}{298.15 \text{ K}} - \frac{\ln(36.9)}{4890 \text{ K}}$$

$$\frac{1}{T_2} = 2.62 \times 10^{-3} \frac{1}{\text{K}}$$

$$T_2 = \frac{1}{2.62 \times 10^{-3} \frac{1}{\text{K}}}$$

$$T_2 = 382 \text{ K} = 109 \text{ }^\circ\text{C}$$

Step 9: Check your work

Does your answer seem reasonable?

Adding salt to water should raise the boiling point, so a boiling point slightly above 100 °C for the salt water is reasonable.