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.

$PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$

Step 2: Calculate activities for all reactants and products

$a_{PCl_{3(g)}} = \frac{p_{PCl_{3(g)}}}{1\ bar} = \frac{2.5\times10^{-3}\ bar}{1\ bar} = 2.5 \times 10^{-3}$

$a_{PCl_{5(g)}} = \frac{p_{PCl_{5(g)}}}{1\ bar} = \frac{0.75\ bar}{1\ bar} = 0.75$

$a_{Cl_{2(g)}} = \frac{p_{Cl_{2(g)}}}{1\ bar} = \frac{9.1\times10^{-5}\ bar}{1\ bar} = 9.1 \times 10^{-5}$

Step 3: Calculate equilibrium constant

$K = \frac{a_{PCl_{5(g)}}}{\left(a_{PCl_{3(g)}}\right)\left(a_{Cl_{2(g)}}\right)} = \frac{0.75}{(2.5\times10^{-3})(9.1\times10^{-5})} = 3.3 \times 10^6$

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* $ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H°}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$. *Keeping organized is key to success.*

Step 1: Match equilibrium constants to the corresponding temperature

$T_1 = 25\ ℃ = 298.15\ K$

$K_1 = 3.3 \times 10^6$

$T_2 = 250\ ℃ = 523.15\ K$

$K_2 = ???$

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

$\Delta_r H° = -87.9 \frac{kJ}{mol} = -8.79 \times 10^4 \frac{J}{mol}$ *provided in question*

Step 3: Crunch the numbers

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

$ln\left(\frac{K_2}{3.3\times10^6}\right) = \left(\frac{-8.79\times10^4 \frac{J}{mol}}{8.314\ 462 \frac{J}{mol\cdot K}}\right)\left(\frac{1}{298.15\ K} - \frac{1}{523.15\ K}\right)$

$ln\left(\frac{K_2}{3.3\times10^6}\right) = -15.2$

$\frac{K_2}{3.3\times10^6} = e^{-15.2}$

$\frac{K_2}{3.3\times10^6} = 2 \times 10^{-7}$

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

$K_2 = 0.8$

Step 4: Check your work

Does your answer seem reasonable?

This reaction is exothermic $(\Delta_r H° < 0)$, *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.

$2\ ClO_{(g)}\ +\ O_{2(g)}\ \rightleftharpoons\ 2\ ClO_{2(g)}$

Step 2: Convert temperature to Kelvin (if necessary)

$T = 25\ ℃ = 298.15\ K$

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

$\Delta_r G° = \sum \Delta_f G°(products) - \sum \Delta_f G°(reactants)$

$\Delta_r G° = \left(2\ \Delta_f G°\left(ClO_{2(g)}\right)\right) - \left[2\ \Delta_f G°\left(ClO_{(g)}\right) + \Delta_f G°\left(O_{2(g)}\right)\right]$

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

$\Delta_r G° = 44.8\frac{kJ}{mol}$

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

$\Delta_r G° = -RT lnK$

$lnK = -\frac{\Delta_r G°}{RT}$

$lnK = -\frac{\left(44.8\frac{kJ}{mol}\right)}{\left(8.314\ 462\frac{J}{mol\cdot K}\right)(298.15\ K)} \times \frac{1000\ J}{1\ kJ}$

$lnK = -18.1$

$K = e^{-18.1}$

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

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* $ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H°}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$. *Keeping organized is key to success.*

Step 1: Match equilibrium constants to the corresponding temperature

$T_1 = 298.15\ K$ $\qquad T_2 = 750\ ℃ = 1023.15\ K$

$K_1 =\ 1.4 \times 10^{-8}$ $\qquad K_2 = ???$

Step 2: Calculate the standard enthalpy change for the reaction

$\Delta_r H° = \sum \Delta_f H°(products) - \sum \Delta_f H°(reactants)$

$\Delta_r H° = \left(2\ \Delta_f H°\left(ClO_{2(g)}\right)\right) - \left[2\ \Delta_f H°\left(ClO_{(g)}\right) + \Delta_f H°\left(O_{2(g)}\right)\right]$

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

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

Step 3: Crunch the numbers

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

$ln\left(\frac{K_2}{1.4\times10^{-8}}\right) = \left(\frac{1.4\times10^3\frac{J}{mol}}{8.314\ 462\frac{J}{mol\cdot K}}\right)\left(\frac{1}{298.15\ K} - \frac{1}{1023.15\ K}\right)$

$$ln\left(\frac{K_2}{1.4\times10^{-8}}\right) = 0.40$$
$$\frac{K_2}{1.4\times10^{-8}} = e^{0.40}$$
$$\frac{K_2}{1.4\times10^{-8}} = 1.5$$
$$K_2 = (1.4\times10^{-8})(1.5)$$
$$K_2 = 2.1\times10^{-8}$$

Step 4: Check your work

Does your answer seem reasonable?

This reaction is slightly endothermic ($\Delta_r H° > 0$)*, 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* $ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H°}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$*. 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

$$H_2O_{(l)} \rightleftharpoons H_2O_{(s)}$$

Step 2: Calculate the activities of reactant and product for <u>pure water</u>

$a_{H_2O_{(l)}} = 1$ $\qquad$ $a_{H_2O_{(s)}} = 1$

Step 3: Calculate the equilibrium constant for the freezing of <u>pure water</u>.

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

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

Step 4: Calculate the activities of reactant and product for <u>salt water</u>

$$n_{H_2O} = 500\ g \times \frac{1\ mol}{18.0152\ g} = 27.8\ mol$$
$$n_{Na^+} = n_{Cl^-} = n_{NaCl} = 125\ g \times \frac{1\ mol}{58.4425\ g} = 2.14\ mol$$

$$a_{H_2O_{(l)}} = X_{H_2O_{(l)}}$$
$$a_{H_2O_{(s)}} = 1$$
$$a_{H_2O_{(l)}} = \frac{n_{H_2O}}{n_{H_2O}+n_{Na^+}+n_{Cl^-}}$$
$$a_{H_2O_{(l)}} = \frac{27.8\ mol}{27.8\ mol+2.14\ mol+2.14\ mol}$$
$$a_{H_2O_{(l)}} = \frac{27.8\ mol}{32.0\ mol}$$
$$a_{H_2O_{(l)}} = 0.866$$

Step 5: Calculate the equilibrium constant for the freezing of <u>salt water</u>.

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

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

Step 6: Match equilibrium constants to the corresponding temperature

$T_1 = 0\ ℃ = 273.15\ K$ $\qquad$ $T_2 = ???$

$K_1 = 1$ $K_2 = 1.15$

Step 7: Calculate the standard enthalpy change for the reaction

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

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

Step 8: Crunch the numbers

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

$$ln\left(\frac{1.15}{1}\right) = \frac{-6007\frac{\mathrm{J}}{\mathrm{mol}}}{8.314\,462\,\frac{J}{mol\cdot K}}\left(\frac{1}{273.15\ K} - \frac{1}{T_2}\right)$$

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

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

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

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

$$T_2 = \frac{1}{3.86\times10^{-3}\frac{1}{K}}$$

$$T_2 = 259\ K = -14\ ℃$$

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 ℃ *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

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

$$M_{H_2O} = 2\left(1.0079\,\frac{g}{mol}\right) + \left(15.9994\,\frac{g}{mol}\right) = 18.0152\,\frac{g}{mol}$$

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

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

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

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

$$X_{H_2O} = \frac{n_{H_2O}}{n_{H_2O}+n_{Na^+}+n_{Cl^-}} = \frac{27.8\ mol}{27.8\ mol+2.14\ mol+2.14\ mol} = 0.866$$

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

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

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

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

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

$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$

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

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

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

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

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, $p_{H_2O_{(g)}} = 1\ atm$.

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

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

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

Step 6: Match equilibrium constants to the corresponding temperature

$T_1 = 25\ °C = 298.15\ K$ $\qquad$ $T_2 = ???$

$K_1 = 0.0317$ $\qquad$ $K_2 = 1.17$

Step 7: Calculate the standard enthalpy change for the reaction

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

That is the enthalpy change for this reaction.

Step 8: Crunch the numbers

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

$$ln\left(\frac{1.17}{0.0317}\right) = \frac{+4.066\times10^4 \frac{\text{J}}{\text{mol}}}{8.314\ 462\ \frac{J}{mol\cdot K}}\left(\frac{1}{298.15\ K} - \frac{1}{T_2}\right)$$

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

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

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

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

$$T_2 = \frac{1}{2.62\times10^{-3}\frac{1}{K}}$$

$$T_2 = 382\ K = 109\ ℃$$

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 ℃ *for the salt water is reasonable.*