Answers to Exercise 8.3
Variation of Equilibrium Constant with Temperature

1.

(a)   25 °C

The standard free energy values found in the standard thermodynamic data tables at the back of most introductory chemistry textbooks all refer to the substances at 25 °C.

To calculate the equilibrium constant for a reaction at 25 °C:

- Write a balanced equation.
- Use standard free energies of formation to calculate standard free energy change for the reaction.
- Use $\Delta G° = -RT\ln K$ (rearranged to $K = e^{-\frac{\Delta G°}{RT}}$) to calculate K from $\Delta G°$, making sure that temperature is in Kelvin and that all units cancel.

(b)   The equation relating equilibrium constants at different temperatures is

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

To use it, you would need to know an equilibrium constant at one temperature (often 25°C), what the second temperature is, and the standard enthalpy change for the reaction (often calculated from standard enthalpies of formation).

If you have access to standard enthalpies of formation and standard entropies, you could instead calculate $\Delta H°$ and $\Delta S°$ for the reaction then use $\Delta G° = \Delta H° - T\Delta S°$ to calculate $\Delta G°$ at the temperature of interest. Then use $\Delta G° = -RT\ln K$ (rearranged to $K = e^{-\frac{\Delta G°}{RT}}$) to calculate K from $\Delta G°$ at the temperature of interest.

Note that $\Delta G°$ can vary greatly with temperature. You CANNOT take $\Delta G°$ at 25 °C and plug it into $\Delta G° = -RT\ln K$ with any temperature other than 25 °C. The temperature in that equation and the temperature at which $\Delta G°$ was calculated MUST match!!!

2.   *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

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

$K_1 = \ 6.6 \times 10^{-58}$ 　　　　　　　　　　　　$K_2 = 2(6.6 \times 10^{-58})$

Step 2: Calculate the standard enthalpy change for the reaction

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

$\Delta_r H° = \left(2\Delta_f H°(O_{3(g)})\right) - \left(3\Delta_f H°(O_{2(g)})\right)$

$\Delta_r H° = 2\left(142.7\frac{kJ}{mol}\right) - 3\left(0\frac{kJ}{mol}\right)$

$\Delta_r H° = +285.4\frac{kJ}{mol} = 2.854 \times 10^5\frac{J}{mol}$

Step 3: Crunch the numbers

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

$$\ln\left(\frac{2(6.6\times10^{-58})}{6.6\times10^{-58}}\right) = \left(\frac{2.854\times10^5\frac{J}{mol}}{8.314\,462\,\frac{J}{mol\cdot K}}\right)\left(\frac{1}{298.15\,K} - \frac{1}{T_2}\right)$$

$$\ln(2) = (3.433\times10^4 K)\left(\frac{1}{298.15\,K} - \frac{1}{T_2}\right)$$

$$\frac{\ln(2)}{3.433\times10^4 K} = \frac{1}{298.15\,K} - \frac{1}{T_2}$$

$$\frac{1}{T_2} = \frac{1}{298.15\,K} - \frac{\ln(2)}{3.433\times10^4 K}$$

$$\frac{1}{T_2} = 3.334\times10^{-3}\,\frac{1}{K}$$

$$T_2 = \frac{1}{3.3338\times10^{-3}\frac{1}{K}}$$

$$T_2 = 299.96\,K = 26.81\,°C$$

Step 4: Check your work

*Does your answer seem reasonable?*

This reaction has a large positive enthalpy change, so it is quite endothermic. As such, the equilibrium constant of the reaction should increase with temperature. The fact that it doesn't take a very large increase in temperature to double the equilibrium constant is consistent with the reaction being so endothermic.

3.

(a)   *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.

$$PbSO_{4(s)} \rightleftharpoons Pb^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$
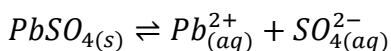
Step 2: Convert temperature to Kelvin (if necessary)

$$T = 25\,°C = 298.15\,K$$

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

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

$$\Delta_r G° = \left[\Delta_f G°\left(Pb^{2+}_{(aq)}\right) + \Delta_f G°\left(SO^{2-}_{4(aq)}\right)\right] - \left(\Delta_f G°\left(PbSO_{4(s)}\right)\right)$$

$$\Delta_r G° = \left[\left(-24.43\,\frac{kJ}{mol}\right) + \left(-744.5\,\frac{kJ}{mol}\right)\right] - \left(-813.14\,\frac{kJ}{mol}\right)$$

$$\Delta_r G° = 44.2\,\frac{kJ}{mol}$$

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

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

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

$\ln K = -\dfrac{\left(44.2 \frac{kJ}{mol}\right)}{\left(8.314\,462 \frac{J}{mol \cdot K}\right)(298.15\ K)} \times \dfrac{1000\ J}{1\ kJ}$

$\ln K = -17.8$

$K = e^{-17.8}$

$K = 1.8 \times 10^{-8}$

Step 5: Check your work

Does your answer seem reasonable?

The equilibrium constant value suggests that a very tiny amount of $PbSO_4$ can dissolve in water, but that most of it will remain undissolved. This is consistent with solubility rules.

(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

$T_1 = 298.15\ K$ $\qquad\qquad\qquad\qquad\qquad$ $T_2 = 65\ °C = 338.15\ K$

$K_1 = 1.8 \times 10^{-8}$ $\qquad\qquad\qquad\qquad\qquad$ $K_2 = ???$

Step 2: Calculate the standard enthalpy change for the reaction

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

$\Delta_r H^\circ = \left[\Delta_f H^\circ\left(Pb^{2+}_{(aq)}\right) + \Delta_f H^\circ\left(SO^{2-}_{4(aq)}\right)\right] - \left(\Delta_f H^\circ\left(PbSO_{4(s)}\right)\right)$

$\Delta_r H^\circ = \left[\left(-1.7\frac{kJ}{mol}\right) + \left(-909.3\frac{kJ}{mol}\right)\right] - \left(-919.94\frac{kJ}{mol}\right)$

$\Delta_r H^\circ = +8.9\frac{kJ}{mol} = 8.9 \times 10^3 \frac{J}{mol}$

Step 3: Crunch the numbers

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

$\ln\left(\frac{K_2}{1.8\times10^{-8}}\right) = \left(\frac{8.9\times10^3 \frac{J}{mol}}{8.314\,462\frac{J}{mol \cdot K}}\right)\left(\frac{1}{298.15\ K} - \frac{1}{338.15\ K}\right)$

$\ln\left(\frac{K_2}{1.8\times10^{-8}}\right) = 0.43$

$\frac{K_2}{1.8\times10^{-8}} = e^{0.43}$

$\frac{K_2}{1.8\times10^{-8}} = 1.5$

$K_2 = (1.8 \times 10^{-8})(1.5)$

$K_2 = 2.8 \times 10^{-8}$

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. This is also consistent with the generalization that the solubility of ionic solids increases with temperature.