# Thermodynamics and Equilibrium

Consider the reaction $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$, for which $\Delta H^o$ is –87.9 $kJ/mol_{rxn}$ and for which $\Delta S^o$ is –170.266 $J/K \bullet mol_{rxn}$. Describe how temperature affects this reaction.

*Answer*: With a negative change in enthalpy and a negative change in entropy, we know that the reaction is favorable at lower temperatures with a critical temperature of

$$t_{crit} = \frac{\Delta H^o}{\Delta S^o} = \frac{-87.9 \text{ kJ/mol}_{\text{rxn}}}{-0.170266 \text{ J/K} \bullet \text{mol}_{\text{rxn}}} = 516 \text{ K}$$

Assuming each species is present in its standard state, what is the standard state free energy for each of the following temperatures: 250 K, 350 K, 450 K, 550 K, 650 K, and 750 K. Are your results consistent with your answer to the first question? Explain.

*Answer*: Here we need to calculate $\Delta G^o$ using $\Delta G^o = \Delta H^o - T\Delta S^o$; thus

- at 250 K we have $\Delta G^o = -87.9 \text{ kJ/mol}_{\text{rxn}} - (250 \text{ K})(-0.170266 \text{ kJ/K} \bullet \text{mol}_{\text{rxn}}) = -45.3 \text{ kJ/K} \bullet \text{mol}_{\text{rxn}}$
- at 350 K we have $\Delta G^o = -87.9 \text{ kJ/mol}_{\text{rxn}} - (350 \text{ K})(-0.170266 \text{ kJ/K} \bullet \text{mol}_{\text{rxn}}) = -28.3 \text{ kJ/K} \bullet \text{mol}_{\text{rxn}}$
- at 450 K we have $\Delta G^o = -87.9 \text{ kJ/mol}_{\text{rxn}} - (450 \text{ K})(-0.170266 \text{ kJ/K} \bullet \text{mol}_{\text{rxn}}) = -11.3 \text{ kJ/K} \bullet \text{mol}_{\text{rxn}}$
- at 550 K we have $\Delta G^o = -87.9 \text{ kJ/mol}_{\text{rxn}} - (550 \text{ K})(-0.170266 \text{ kJ/K} \bullet \text{mol}_{\text{rxn}}) = +5.75 \text{ kJ/K} \bullet \text{mol}_{\text{rxn}}$
- at 650 K we have $\Delta G^o = -87.9 \text{ kJ/mol}_{\text{rxn}} - (650 \text{ K})(-0.170266 \text{ kJ/K} \bullet \text{mol}_{\text{rxn}}) = +22.8 \text{ kJ/K} \bullet \text{mol}_{\text{rxn}}$
- at 750 K we have $\Delta G^o = -87.9 \text{ kJ/mol}_{\text{rxn}} - (750 \text{ K})(-0.170266 \text{ kJ/K} \bullet \text{mol}_{\text{rxn}}) = +39.8 \text{ kJ/K} \bullet \text{mol}_{\text{rxn}}$

These results are consistent with the previous question as we find that $\Delta G^o$ is negative when the temperature is less than 516 K and that it is positive when the temperature is greater than 516 K.

Conclusions based on standard state conditions usually are not of much interest since a reaction seldom is in its standard state. Assuming each species is present with a partial pressure of 0.5 atm, what is the free energy for each of the following temperatures: 250 K, 350 K, 450 K, 550 K, 650 K, and 750 K?

*Answer*: To find $\Delta G$ under non-standard state conditions, we first find a value for $Q$ where

$$Q = \frac{P_{\text{PCl5}}}{P_{\text{PCl3}} P_{\text{Cl2}}} = \frac{0.5}{0.5 \times 0.5} = 2$$

With the value for $Q$ in hand, we then calculate $\Delta G^o$ using $\Delta G^o + RT\ln Q$; thus

- at 250 K we have $\Delta G = -45.3 \text{ kJ/mol}_{\text{rxn}} + (8.314 \times 10^{-3} \text{ kJ/mol}_{\text{rxn}})(250 \text{ K})\ln(2) = -43.9 \text{ kJ/K} \bullet \text{mol}_{\text{rxn}}$
- at 350 K we have $\Delta G = -28.3 \text{ kJ/mol}_{\text{rxn}} + (8.314 \times 10^{-3} \text{ kJ/mol}_{\text{rxn}})(350 \text{ K})\ln(2) = -26.3 \text{ kJ/K} \bullet \text{mol}_{\text{rxn}}$
- at 450 K we have $\Delta G = -11.3 \text{ kJ/mol}_{\text{rxn}} + (8.314 \times 10^{-3} \text{ kJ/mol}_{\text{rxn}})(450 \text{ K})\ln(2) = -8.71 \text{ kJ/K} \bullet \text{mol}_{\text{rxn}}$
- at 550 K we have $\Delta G = +5.75 \text{ kJ/mol}_{\text{rxn}} + (8.314 \times 10^{-3} \text{ kJ/mol}_{\text{rxn}})(550 \text{ K})\ln(2) = +8.92 \text{ kJ/K} \bullet \text{mol}_{\text{rxn}}$
- at 650 K we have $\Delta G = +22.8 \text{ kJ/mol}_{\text{rxn}} + (8.314 \times 10^{-3} \text{ kJ/mol}_{\text{rxn}})(650 \text{ K})\ln(2) = +26.3 \text{ kJ/K} \bullet \text{mol}_{\text{rxn}}$
- at 750 K we have $\Delta G = +39.8 \text{ kJ/mol}_{\text{rxn}} + (8.314 \times 10^{-3} \text{ kJ/mol}_{\text{rxn}})(750 \text{ K})\ln(2) = +44.1 \text{ kJ/K} \bullet \text{mol}_{\text{rxn}}$

What is the equilibrium constant for the reaction at each of the following temperatures: 250 K, 350 K, 450 K, 550 K, 650 K, and 750 K? Do your results make sense given your answers to the first three questions? Explain.

*Answer*: The relationship between free energy and the equilibrium constant is $\Delta G^o = -RT\ln K_{eq}$; thus

- at 250 K we have $\Delta G^o = -45.3\text{ kJ/mol}_{\text{rxn}} = -(8.314 \times 10^{-3}\text{ kJ/mol}_{\text{rxn}})(250\text{ K})\ln K_{eq}$ which we solve to find that $K_{eq} = 2.92 \times 10^9$
- at 350 K we have $\Delta G^o = -28.3\text{ kJ/mol}_{\text{rxn}} = -(8.314 \times 10^{-3}\text{ kJ/mol}_{\text{rxn}})(350\text{ K})\ln K_{eq}$ which we solve to find that $K_{eq} = 16,700$
- at 450 K we have $\Delta G^o = -11.3\text{ kJ/mol}_{\text{rxn}} = -(8.314 \times 10^{-3}\text{ kJ/mol}_{\text{rxn}})(450\text{ K})\ln K_{eq}$ which we solve to find that $K_{eq} = 20.5$
- at 550 K we have $\Delta G^o = +5.75\text{ kJ/mol}_{\text{rxn}} = -(8.314 \times 10^{-3}\text{ kJ/mol}_{\text{rxn}})(550\text{ K})\ln K_{eq}$ which we solve to find that $K_{eq} = 0.2844
- at 650 K we have $\Delta G^o = +22.8\text{ kJ/mol}_{\text{rxn}} = -(8.314 \times 10^{-3}\text{ kJ/mol}_{\text{rxn}})(650\text{ K})\ln K_{eq}$ which we solve to find that $K_{eq} = 0.0147$
- at 750 K we have $\Delta G^o = +39.8\text{ kJ/mol}_{\text{rxn}} = -(8.314 \times 10^{-3}\text{ kJ/mol}_{\text{rxn}})(750\text{ K})\ln K_{eq}$ which we solve to find that $K_{eq} = 0.0017$

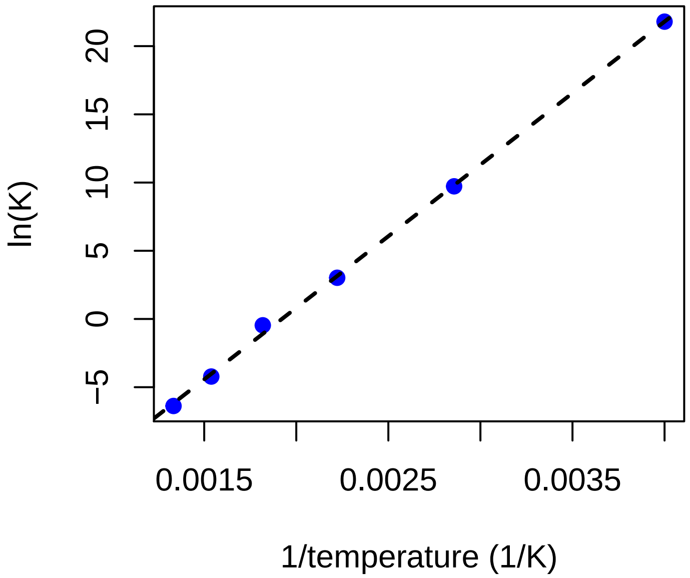
These results make sense because we know from an earlier example that for an exothermic reaction the equilibrium constant becomes smaller as the temperature increases. Additionally, when the temperature is below $T_{crit}$, where the reaction is favorable in the forward direction, the equilibrium constant shows that there are more products than reactants. Above the critical temperature, where the reaction no longer is favorable in the forward direction, the equilibrium constant shows that there are more reactants than there are products.

Comparing $Q$ and $K$ provides an alternative way to evaluate the direction a reaction must move to reach its equilibrium position. For the temperatures 250 K, 350 K, 450 K, 550 K, 650 K, and 750 K, use this method to determine the direction the system must move to reach equilibrium. Be sure to justify your decisions. Are your answers consistent with the conclusions you would reach using $\Delta G$? Explain.

*Answer*: Recall that $Q$ is 2. For a temperature of 250 K, 350 K, and 450 K the value of $Q$ is less than $K_{eq}$ and the reaction proceeds to the right to reach equilibrium. For a temperature of 550 K, 650 K, and 750 K, however, the value of $Q$ is greater than $K_{eq}$ and the reaction proceeds to the left to reach equilibrium.

Construct a graph of $\ln K_{eq}$ vs. $1/T$ and verify that the slope is equivalent to $-\Delta H^o/R$ and that the $y$-intercept is equivalent to $\Delta S^o/R$.

*Answer*: A plot of $\ln K_{eq}$ vs. $1/T$ is shown below along with the line of best fit determined by linear regression. The equation of the best fit line through the data has a slope of $1.05 \times 10^4\text{ K}^{-1}$ and a $y$-intercept of –20.2. The slope is equivalent to $-\Delta H^o/R$, which, when we solve for $\Delta H^o$ gives its value as –87.2 $\text{kJ/mol}_{\text{rxn}}$. The $y$-intercept is equivalent to $\Delta S^o/R$, which, when we solve for $\Delta S^o$ gives its value as –167.9 $\text{J/K} \bullet \text{mol}_{\text{rxn}}$. Both values are close to the known values of –87.9 $\text{kJ/mol}_{\text{rxn}}$ for $\Delta H^o$ of –170.266 $\text{J/K} \bullet \text{mol}_{\text{rxn}}$ for $\Delta S^o$.


ln(K)
−5
0
5
10
15
20
0.0015
0.0025
0.0035
1/temperature (1/K)