Thermodynamics and Equilibrium

Consider the following reaction:

$$PCl_3(g) + Cl_2(g) \leftrightarrows PCl_5(g)$$

Do you expect this reaction to be favorable at all temperatures, favorable only at higher temperatures, favorable only at lower temperatures, or is the reaction unfavorable at all temperature? Clearly explain your reasoning.

Answer: To decide how temperature will affect favorability, we need to know the signs of ΔH and ΔS. These values are

$$\Delta H^o = -87.9 \text{ kJ/mol}_{rxn} \quad \Delta S = -170.266 \text{ J/mol}_{rxn}\cdot\text{K}$$

With a negative (favorable) change in enthalpy and a negative (unfavorable) change in entropy, we know that the reaction will become less favorable at higher temperatures. To find the critical temperature, we set ΔG^o equal to zero and solve for T; thus

$$\Delta G^o = 0 = \Delta H^o - T\Delta S^o = (-87.9 \text{ kJ/mol}_{rxn}) - T_{crit}(-0.170266 \text{ kJ/mol}_{rxn}\cdot\text{K})$$

$$T_{crit} = 516 \text{ K}$$

Assuming that each species is present in its standard states, what is the standard state free energy for each of the following temperatures: 298 K, 400 K and 600 K. Are your results consistent with your answer to the first question. Explain.

Answer: Here we simply calculate $\Delta G^o = \Delta H^o - T\Delta S^o$; thus

$$\Delta G^o{}_{298} = (-87.9 \text{ kJ/mol}_{rxn}) - (298 \text{ K})(-0.170266 \text{ kJ/mol}_{rxn}\cdot\text{K}) = -37.2 \text{ kJ/mol}_{rxn}$$

$$\Delta G^o{}_{400} = (-87.9 \text{ kJ/mol}_{rxn}) - (400 \text{ K})(-0.170266 \text{ kJ/mol}_{rxn}\cdot\text{K}) = -19.8 \text{ kJ/mol}_{rxn}$$

$$\Delta G^o{}_{600} = (-87.9 \text{ kJ/mol}_{rxn}) - (600 \text{ K})(-0.170266 \text{ kJ/mol}_{rxn}\cdot\text{K}) = +14.3 \text{ kJ/mol}_{rxn}$$

These results are consistent with the previous question in that ΔG^o becomes less favorable at higher temperatures. Furthermore, ΔG^o is negative for the two cases where the temperature is lower than 516 K and positive for the one case where 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 that each species is present with a partial pressure of 0.5 atm, what is the free energy for each of the following temperatures: 298 K, 400 K and 600 K?

Answer: To find the ΔG under non-standard state conditions we first find a value for Q

$$Q = \frac{(\mathrm{PCl_5})}{(\mathrm{PCL_3})(\mathrm{Cl_2})} = \frac{0.5}{0.5 \times 0.5} = 2$$

Then we can calculate $\Delta G = \Delta G^o + RT\ln Q$

$$\Delta G_{298} = -37.2\ \mathrm{kJ/mol_{rxn}} + (8.314\times10^{-3}\ \mathrm{kJ/mol_{rxn}\cdot K})(298\ \mathrm{K})\ln(2) = -35.5\ \mathrm{kJ/mol_{rxn}}$$

$$\Delta G_{400} = -19.8\ \mathrm{kJ/mol_{rxn}} + (8.314\times10^{-3}\ \mathrm{kJ/mol_{rxn}\cdot K})(400\ \mathrm{K})\ln(2) = -17.5\ \mathrm{kJ/mol_{rxn}}$$

$$\Delta G_{600} = +14.3\ \mathrm{kJ/mol_{rxn}} + (8.314\times10^{-3}\ \mathrm{kJ/mol_{rxn}\cdot K})(600\ \mathrm{K})\ln(2) = +17.7\ \mathrm{kJ/mol_{rxn}}$$

What is the equilibrium constant for the reaction at each of the following temperatures: 298 K, 400 K and 600 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

$$-37.2\ \mathrm{kJ/mol_{rxn}} = -(8.314\times10^{-3}\ \mathrm{kJ/mol_{rxn}\cdot K})(298\ \mathrm{K})\ln K_{eq} \qquad (K_{eq})_{298} = 3.32\times10^{6}$$

$$-19.8\ \mathrm{kJ/mol_{rxn}} = -(8.314\times10^{-3}\ \mathrm{kJ/mol_{rxn}\cdot K})(400\ \mathrm{K})\ln K_{eq} \qquad (K_{eq})_{400} = 385$$

$$+14.3\ \mathrm{kJ/mol_{rxn}} = -(8.314\times10^{-3}\ \mathrm{kJ/mol_{rxn}\cdot K})(600\ \mathrm{K})\ln K_{eq} \qquad (K_{eq})_{600} = 0.0567$$

These results make sense. 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 present than reactants. Above the critical temperature, where the reaction is no longer favorable in the forward direction, the equilibrium constant shows that there are more reactants present 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 298 K, 400 K and 600 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 ΔG? Explain.

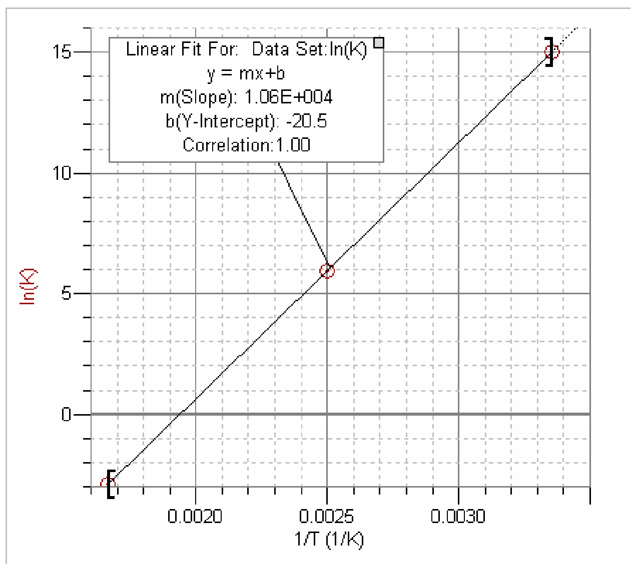
Answer: For a temperature of 298 K the value of Q, which is 2, is less than K_{eq}. As expected, therefore, the reaction proceeds to the right to reach equilibrium.

For a temperature of 400 K the value of Q, which is 2, is less than K_{eq}. As expected, therefore, the reaction proceeds to the right to reach equilibrium.

For a temperature of 600 K the value of Q, which is 2, is larger than K_{eq}. As expected, therefore, 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 copy of the graph is shown to the right.



The slope of 1.06×10^4 K^{-1} is equivalent to $-\Delta H^o/R$; thus

$$1.06\times10^4\ K^{-1} = -\Delta H^o/(8.314\times10^{-3}\ kJ/mol_{rxn}\cdot K)$$

$$\Delta H^o = -88.1\ kJ/mol_{rxn}$$

The intercept of -20.5 is equivalent to $\Delta S^o/R$; thus

$$-20.5 = \Delta S^o/(8.314\times10^{-3}\ kJ/mol_{rxn}\cdot K)$$

$$\Delta S^o = -0.1704\ kJ/mol_{rxn}\cdot K = -170.4\ J/mol_{rxn}\cdot K$$

These values are consistent with the known values for ΔH^o of -87.9 kJ/mol_{rxn} and for ΔS of -170.266 $J/mol_{rxn}\cdot K$.