

Answers to Exercise 7.4

Standard Free Energies and Equilibrium Constants

1. In Question 1 of Exercise 7.3, the standard free energy change for this reaction was calculated to be $\Delta_r G^\circ = -184.94 \frac{\text{kJ}}{\text{mol}}$ (with one significant decimal place).

Step 1: Convert temperature to Kelvin

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

Step 2: Calculate the equilibrium constant from the standard free energy change

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

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

$$\ln K = -\frac{\left(-184.9 \frac{\text{kJ}}{\text{mol}}\right)}{\left(8.314 \text{ 462} \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(298.15 \text{ K})} \times \frac{1000 \text{ J}}{1 \text{ kJ}}$$

$$\ln K = 74.60$$

$$K = e^{74.60}$$

$$K = 2.5 \times 10^{32}$$

Step 3: Check your work

Does your answer seem reasonable?

A large equilibrium constant is consistent with a significantly negative standard free energy of formation for the forward reaction.

2.

(a) **Step 1: Convert temperature to Kelvin**

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

Step 2: Calculate the standard free energy change from the equilibrium constant

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

$$\Delta_r G^\circ = -\left(8.314 \text{ 462} \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(298.15 \text{ K}) \ln(1.8 \times 10^{-5})$$

$$\Delta_r G^\circ = \left(2.71 \times 10^4 \frac{\text{J}}{\text{mol}}\right) \left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)$$

$$\Delta_r G^\circ = +27.1 \frac{\text{kJ}}{\text{mol}}$$

Step 3: Check your work

Does your answer seem reasonable?

A positive standard free energy of formation is consistent with an equilibrium constant smaller than 1.

(b) **Step 1: Calculate the standard free energy of formation for CH_3CO_2^- (aq)**

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

$$\Delta_r G^\circ = [\Delta_f G^\circ(\text{H}_{(\text{aq})}^+) + \Delta_f G^\circ(\text{CH}_3\text{CO}_2^-_{(\text{aq})})] - \Delta_f G^\circ(\text{CH}_3\text{CO}_2\text{H}_{(\text{aq})})$$

$$\Delta_f G^\circ(\text{CH}_3\text{CO}_2^-_{(\text{aq})}) = \Delta_r G^\circ - \Delta_f G^\circ(\text{H}_{(\text{aq})}^+) + \Delta_f G^\circ(\text{CH}_3\text{CO}_2\text{H}_{(\text{aq})})$$

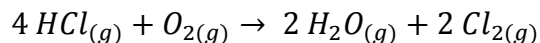
$$\Delta_f G^\circ(\text{CH}_3\text{CO}_2^-_{(\text{aq})}) = \left(+27.1 \frac{\text{kJ}}{\text{mol}}\right) - \left(0 \frac{\text{kJ}}{\text{mol}}\right) + \left(-396.46 \frac{\text{kJ}}{\text{mol}}\right)$$

$$\Delta_f G^\circ(\text{CH}_3\text{CO}_2^-_{(\text{aq})}) = -369.4 \frac{\text{kJ}}{\text{mol}}$$

Step 2: Check your work

Does your answer seem reasonable?

3. **Step 1: Write a balanced chemical equation for the reaction**



Step 2: Convert temperature to Kelvin (if necessary)

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

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

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

$$\Delta_r G^\circ = [2 \Delta_f G^\circ(\text{H}_2\text{O}_{(\text{g})}) + 2 \Delta_f G^\circ(\text{Cl}_{2(\text{g})})] - [4 \Delta_f G^\circ(\text{HCl}_{(\text{g})}) + \Delta_f G^\circ(\text{O}_{2(\text{g})})]$$

$$\Delta_r G^\circ = \left[2 \left(-228.6 \frac{\text{kJ}}{\text{mol}}\right) + 2 \left(0 \frac{\text{kJ}}{\text{mol}}\right)\right] - \left[4 \left(-95.3 \frac{\text{kJ}}{\text{mol}}\right) + \left(0 \frac{\text{kJ}}{\text{mol}}\right)\right]$$

$$\Delta_r G^\circ = -76.0 \frac{\text{kJ}}{\text{mol}}$$

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

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

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

$$\ln K = -\frac{\left(-76.0 \frac{\text{kJ}}{\text{mol}}\right)}{\left(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(298.15 \text{ K})} \times \frac{1000 \text{ J}}{1 \text{ kJ}}$$

$$\ln K = 30.7$$

$$K = e^{30.7}$$

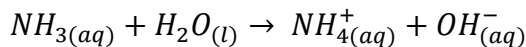
$$K = 2 \times 10^{13}$$

Step 5: Check your work

Does your answer seem reasonable?

An equilibrium constant greater than 1 is consistent with a negative standard free energy of formation for the forward reaction.

4. **Step 1: Write a balanced chemical equation for the reaction**



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

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

$$\Delta_r G^\circ = [\Delta_f G^\circ(\text{NH}_4^+(\text{aq})) + \Delta_f G^\circ(\text{OH}^-(\text{aq}))] - [\Delta_f G^\circ(\text{NH}_3(\text{aq})) + \Delta_f G^\circ(\text{H}_2\text{O}(\text{l}))]$$

$$\Delta_r G^\circ = \left[\left(-79.31 \frac{\text{kJ}}{\text{mol}} \right) + \left(-157.2 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left[\left(-26.50 \frac{\text{kJ}}{\text{mol}} \right) + \left(-237.1 \frac{\text{kJ}}{\text{mol}} \right) \right]$$

$$\Delta_r G^\circ = 27.09 \frac{\text{kJ}}{\text{mol}}$$

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

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

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

$$\ln K = -\frac{\left(27.09 \frac{\text{kJ}}{\text{mol}} \right)}{\left(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) (298.15\text{ K})} \times \frac{1000\text{ J}}{1\text{ kJ}}$$

$$\ln K = -10.93$$

$$K = e^{-10.93}$$

$$K = 1.8 \times 10^{-5}$$

Step 5: Check your work

Does your answer seem reasonable?

An equilibrium constant smaller than 1 is consistent with a positive standard free energy of formation for the forward reaction.

If you were to look up the K_b value for NH_3 , it would be the same as the equilibrium constant you just calculated.