# THERMODYNAMICS

## GIBBS FREE ENERGY (G) AND EQUILIBRIUM

CHEMISTRY 165 // SPRING 2020

DR. MIOY T. HUYNH | 2020

# PRACTICE PROBLEM 1

$$AgCl\,(s) \rightleftharpoons Ag^{+}\,(aq) + Cl^{-}\,(aq)$$

Given the following standard free energies of formations, calculate the solubility product ($K_{sp}$) for AgCl at 298.15 K.

| | AgCl (s) | $Ag^{+}$ (aq) | $Cl^{-}$ (aq) |
|---|---|---|---|
| $\Delta G_f^o \left(\frac{kJ}{mol}\right)$ | −109.8 | 77.1 | −131.2 |

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First, calculate the standard Gibbs free energy change.

$$\Delta G_{rxn}^o = \sum n_{prod}\,\Delta G_{f,prod}^o - \sum n_{react}\,\Delta G_{f,react}^o$$

$$= \left[(1\text{ mol Ag}^{+})\times\left(77.1\frac{kJ}{mol}\right) + (1\text{ mol Cl}^{-})\times\left(-131.2\frac{kJ}{mol}\right)\right] - (1\text{ mol AgCl})\times\left(-109.8\frac{kJ}{mol}\right)$$

$$\Delta G_{rxn}^o = 55.7\text{ kJ}$$

Then, calculate the equilibrium constant ($K_{sp}$).

$$K_{sp} = e^{\frac{-\Delta G_{rxn}^o}{RT}}$$

$$= e^{\frac{-(55.7\text{ kJ})}{\left(8.314\frac{J}{mol\cdot K}\right)(298.15\text{ K})}}$$

$$K_{sp} = 1.74\times 10^{-10}$$

# PRACTICE PROBLEM 2

Which of the following reactions has the largest value of $K_p$ at 25 °C?

| | | |
|---|---|---|
| (i) | $Cl_2$ (g) + $F_2$ (g) ⇌ 2 ClF (g) | $\Delta G° = 115.4$ kJ |
| (ii) | $Cl_2$ (g) + $Br_2$ (g) ⇌ 2 ClBr (g) | $\Delta G° = -2.0$ kJ |
| (iii) | $Cl_2$ (g) + $I_2$ (g) ⇌ 2 ClI (g) | $\Delta G° = -27.9$ kJ |

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| (iii) | $Cl_2\ (g) + I_2\ (g) \rightleftharpoons 2\ ClI\ (g)$ | $\Delta G° = -27.9\ \text{kJ}$ |

*— answer —*

Recall that the standard Gibbs free energy change can be related to the equilibrium constant via:

$$K = e^{\frac{-\Delta G°}{RT}} \quad or \quad \Delta G° = -RT\ln K \quad or \quad \ln K = \frac{\Delta G°}{RT}$$

Qualitatively, we know that a large $K_p$ value means that the equilibrium is products-favored.

This would correspond to a very negative (very spontaneous, products favored equilibrium) value of $\Delta G°$.

So, the answer is reaction (iii), which has:

$$K_p = e^{\frac{-\Delta G^o_{rxn}}{RT}}$$

$$= e^{\frac{-(-27.9\ \text{kJ})}{\left(8.314\frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(298.15\ \text{K})}}$$

$$K_p = 7.8 \times 10^4$$

# PRACTICE PROBLEM 3

$N_2\ (g) + 3\ H_2\ (g) \rightarrow 2\ NH_3\ (g)$ ; $\Delta G° = -33.0\ \text{kJ}$

What is the value of $\Delta G$ when $P_{N_2} = P_{H_2} = P_{NH_3} = 0.870$ atm and $T = 298$ K?

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*— answer —*

We can use the following relationship to find the nonstandard Gibbs free energy change:

$$\Delta G = \Delta G° + RT \ln Q$$

$$= \Delta G° + RT \ln \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}$$

$$= -33.0\text{ kJ} - \left(0.008314 \frac{\text{kJ}}{\text{mol} \cdot \text{K}}\right)(298\text{ K}) \ln \frac{(0.870)^2}{(0.870)(0.870)^3}$$

$$\Delta G = -32.3\text{ kJ}$$

# PRACTICE PROBLEM 4

$$N_2\,(g) + 3\,H_2\,(g) \rightarrow 2\,NH_3\,(g) \quad ; \quad \Delta H° = -92.2\ \text{kJ/mol}$$

(a) If the temperature is increased, how will the value of $K_p$ change?

(b) If $K_p$ = 41 at 400 K, what is the value of $K_p$ at 700 K?

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(a) Because the reaction is exothermic, we can treat heat as a product. Invoking Le Chatelier's Principle, increasing the temperature will decrease the value *K*.

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(a) Because the reaction is exothermic, we can treat heat as a product. Invoking Le Chatelier's Principle, increasing the temperature will decrease the value *K*.

(b) We can calculate the value of *K* at a different temperature using:

$$\ln \frac{K_{700}}{K_{400}} = -\frac{\Delta H°}{R}\left[\frac{1}{T_{700}} - \frac{1}{T_{400}}\right]$$

$$\ln K_{700} - \ln K_{400} = -\frac{\Delta H°}{R}\left[\frac{1}{T_{700}} - \frac{1}{T_{400}}\right]$$

$$\ln K_{700} - \ln(41) = -\frac{-92.2\,\frac{\text{kJ}}{\text{mol}}}{0.008314\,\frac{\text{J}}{\text{mol}\cdot\text{K}}}\left[\frac{1}{700\ \text{K}} - \frac{1}{400\ \text{K}}\right]$$

$$\ln K_{700} = -8.16_8$$

$$K_{700} = 2.8 \times 10^{-4}$$