

Free Energy Calculations Demonstrating Consistency with Chemical Reversibility

At 25°C, the reaction $H_2O(g) + Cl_2O(g) \leftrightarrow 2 HOCl(g)$ is initiated with 0.10 moles of water and dichlorine monoxide in a 1.0 L vessel.

(a) What are the equilibrium concentrations of each component of the reaction?

We must first calculate a value for the thermodynamic equilibrium constant, K_T .

$$\begin{aligned}\Delta G_f^\circ (H_2O, g) &= -228.6 \text{ kJ/mol} & \Delta G_f^\circ (Cl_2O, g) &= +97.9 \text{ kJ/mol} \\ \Delta G_f^\circ (HOCl, g) &= -69.9 \text{ kJ/mol}\end{aligned}$$

$$\Delta G_{RXN}^\circ = 2 \times \Delta G_f^\circ (HOCl, g) - [\Delta G_f^\circ (H_2O, g) + \Delta G_f^\circ (Cl_2O, g)] = -9.1 \text{ kJ/mol}$$

$$K_T = e^{-\Delta G_{RXN}^\circ / RT} = e^{+3.673} = 39.4$$

| | | | | | |
|---|------------------|---|-------------------|---|--------|
| | H ₂ O | + | Cl ₂ O | ↔ | 2 HOCl |
| I | 0.10 | | 0.10 | | 0 |
| C | -x | | -x | | +2x |
| E | 0.10-x | | 0.10-x | | 0 +2x |

$$\sqrt{39.4} = \sqrt{\frac{[HOCl]^2}{[H_2O][Cl_2O]}} = \sqrt{\frac{(2x)^2}{(0.10-x)^2}}$$

$$6.277 = \frac{2x}{0.10-x}$$

$$x = 0.0758$$

$$[H_2O] = [Cl_2O] = 0.0242M$$

$$[HOCl] = 0.1516M$$

(b) Calculate the equilibrium concentrations using the reverse reaction but the same initial starting conditions. The reaction is now: $2 \text{HOCl}(g) \leftrightarrow \text{H}_2\text{O}(g) + \text{Cl}_2\text{O}(g)$

$$\Delta G_{RXN}^{\circ} = [\Delta G_f^{\circ}(\text{H}_2\text{O}, g) + \Delta G_f^{\circ}(\text{Cl}_2\text{O}, g)] - 2 \times \Delta G_f^{\circ}(\text{HOCl}, g) = +9.1 \text{ kJ/mol}$$

$$K_T = e^{-\Delta G_{RXN}^{\circ}/RT} = e^{-3.673} = 0.0254$$

| | | | | | |
|---|--------|-------------------|------------------|---|-------------------|
| | 2 HOCl | \leftrightarrow | H ₂ O | + | Cl ₂ O |
| I | 0 | | 0.10 | | 0.10 |
| C | +2x | | -x | | -x |
| E | 2x | | 0.10-x | | 0.10-x |

$$\sqrt{0.0254} = \sqrt{\frac{[\text{H}_2\text{O}][\text{Cl}_2\text{O}]}{[\text{HOCl}]^2}} = \sqrt{\frac{(0.10-x)^2}{(2x)^2}}$$

$$0.1594 = \frac{0.10-x}{2x}$$

$$x = 0.0758$$

$$[\text{H}_2\text{O}] = [\text{Cl}_2\text{O}] = 0.0242M$$

$$[\text{HOCl}] = 0.1516M$$

The answers for parts (a) and (b) are identical although they were arrived at from different points of view in terms of the chemical equations. This is consistent with the physical world, which did not change. We mixed two reagents together and allowed a reaction to occur. What will happen occurs regardless of our calculation and point of view. After this you can see that the order in which we write a chemical reaction is arbitrary. Because of this, I generally discuss the right-hand-side and left-hand-side materials rather than reagents or products since this seems to give a permanent assignment to the materials.

This example also shows that $k_{\text{forward}} = \frac{1}{k_{\text{reverse}}}$ from the stoichiometric perspective.