Thermodynamics I: Basic Problems

Consider the reaction

$$2\ NO(g) \ + \ O_2(g) \rightleftarrows 2\ NO_2(g)$$

1. Calculate $\Delta G°$ from $\Delta H°$ and $\Delta S°$ at 25°C

$$\Delta H° = 2(33.18\ \text{kJ}) - 2(90.25\ \text{kJ}) = -114.14\ \text{kJ}$$
$$\Delta S° = 2(240.06\,\tfrac{\text{J}}{\text{K}}) - \left[2(210.76\,\tfrac{\text{J}}{\text{K}}) + 205.14\,\tfrac{\text{J}}{\text{K}}\right] = -146.54\,\tfrac{\text{J}}{\text{K}}$$
$$\Delta G° = \Delta H° - T\Delta S° = -114.14 \times 10^3\ \text{J} - (298.2\ \text{K})(-146.54\,\tfrac{\text{J}}{\text{K}}) = -70,442\ \text{J} = -70.44\ \text{kJ}$$

2. Calculate $\Delta G°$ from standard free energies of formation.

$$\Delta G° = 2(51.31\ \text{kJ}) - 2(86.55\ \text{kJ}) = -70.48\ \text{kJ}$$

3. Calculate the thermodynamic equilibrium constant, K_p.

$$\Delta G° = -RT \ln K_\text{p}$$
$$-70.48 \times 10^3\ \tfrac{\text{J}}{\text{mol O}_2} = -(8.314\,\tfrac{\text{J}}{\text{mol}\cdot\text{K}})(298.2\ \text{K}) \ln K_\text{p}$$
$$\ln K_\text{p} = 28.43$$
$$K_\text{p} = 2.2 \times 10^{12}$$

4. Determine the direction the reaction would proceed and the free energy when starting pressure of each gas is 0.33 atm.

$$\Delta G = \Delta G° + RT \ln Q = -70.48 \times 10^3 \tfrac{\text{J}}{\text{mol}} + (8.314 \tfrac{\text{J}}{\text{mol·K}})(298.2 \text{ K}) \ln\left(\frac{0.33^2}{(0.33)^2(0.33)}\right)$$

$$\Delta G = -67,731 \tfrac{\text{J}}{\text{mol}}$$

$\Delta G < 0$; reaction proceeds to right

5. What will be the total pressure in the container at equilibrium?

	2 NO	+	O_2	$\rightleftarrows$	NO_2
initial	0.33		0.33		0.33
@equil	$0.33 - 2x$		$0.33 - x$		$0.33 + 2x$

$$2.2 \times 10^{12} = \frac{(0.33 + 2x)^2}{(0.33 - 2x)^2 (0.33 - x)} \qquad x = 0.165 \text{ atm}$$

$$P_{\text{NO}} = 0.33 - 2(0.165) = 0$$

$$P_{\text{O}_2} = 0.33 - 0.165 = 0.165 \text{ atm}$$

$$P_{\text{NO}_2} = 0.33 + 2(0.165) = 0.66 \text{ atm}$$

$$P_{\text{T}} = 0.165 \text{ atm} + 0.66 \text{ atm} = 0.83 \text{ atm}$$

6. Estimate the K_p at 100.0°C assuming $\Delta H°_f$ and $\Delta S°_f$ remain constant at this temperature.

$$\Delta G = \Delta H - T\Delta S = -114.14 \times 10^3 \text{ J} - (373.2 \text{ K})(-146.54 \tfrac{\text{J}}{\text{K}}) = -59,451 \text{ J}$$

$$\Delta G° = -RT \ln K_{\text{p}}$$

$$-59.45 \times 10^3 \tfrac{\text{J}}{\text{mol O}_2} = -(8.314 \tfrac{\text{J}}{\text{mol·K}})(373.2 \text{ K}) \ln K_{\text{p}}$$

$$\ln K_{\text{p}} = 19.16$$

$$K_{\text{p}} = 2.1 \times 10^8$$