Thermodynamics I: Basic Problems

Consider the reaction

$$2\ NO(g)\ +\ O_2(g)\ \rightleftarrows\ 2\ NO_2(g)$$
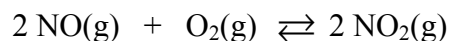
1. Calculate $\Delta G°$ from $\Delta H°$ and $\Delta S°$ at 25°C

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

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

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

3. Calculate the thermodynamic equilibrium constant, K_p.

$$\Delta G° = -RT \ln K_p$$
$$-70.48 \times 10^3\ \tfrac{J}{mol\ O_2} = -(8.314\tfrac{J}{mol\cdot K})(298.2\ K) \ln K_p$$
$$\ln K_p = 28.43$$
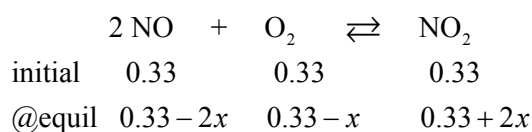$$K_p = 2.2 \times 10^{12}$$

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

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

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

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

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

$$2 \text{ NO} \quad + \quad O_2 \quad \rightleftarrows \quad NO_2$$

initial	0.33	0.33	0.33
@equil	$0.33 - 2x$	$0.33 - x$	$0.33 + 2x$

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

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

$$P_{O_2} = 0.33 - 0.165 = 0.165 \text{ atm}$$

$$P_{NO_2} = 0.33 + 2(0.165) = 0.66 \text{ atm}$$

$$P_T = 0.165 \text{ atm} + 0.66 \text{ atm} = 0.83 \text{ atm}$$

6. Estimate the K_p at 100.0°C assuming ΔH°_f and ΔS°_f remain constant at this temperature.

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

$$\Delta G^\circ = -RT \ln K_p$$

$$-59.45 \times 10^3 \tfrac{J}{mol \, O_2} = -(8.314 \tfrac{J}{mol \cdot K})(373.2 \text{ K}) \ln K_p$$

$$\ln K_p = 19.16$$

$$K_p = 2.1 \times 10^8$$