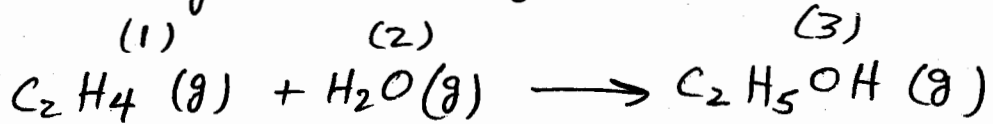


Example Calculate K at 145°C for the following reaction:



$$\Delta \equiv (3) - (1) - (2)$$

Solution

$$K = \exp \left[- \frac{\Delta G^\circ}{RT} \right]$$

$$\frac{\Delta G^\circ}{RT} = \frac{\Delta G^\circ_0 - \Delta H^\circ_0}{RT_0} + \frac{\Delta H^\circ_0}{RT} + \frac{1}{T} \int_{T_0}^T \frac{\Delta C_p^\circ}{R} dT - \int_{T_0}^T \frac{\Delta C_p^\circ}{RT} dT$$

From Appendix C4: ($T_0 = 298\text{K}$)

$$\Delta H^\circ_0 = -235100 - 52510 - (-241818) = -45792 \frac{\text{J}}{\text{mol}}$$

$$\Delta G^\circ_0 = -168490 - 68460 - (-228572) = -8378 \frac{\text{J}}{\text{mol}}$$

From Appendix C.1

$$\frac{C_{p,i}^\circ}{R} = A_i + B_i T + C_i T^2 + \frac{D_i}{T^2}$$

$$\frac{\Delta C_p^\circ}{R} = \Delta A + \Delta B T + \Delta C T^2 + \frac{\Delta D}{T^2}$$

$$= -1.376 + 4.157 \times 10^{-3} T - 1.61 \times 10^{-6} T^2$$

$$- 1.21 \times 10^6 \frac{1}{T^2}$$

$$\int_{T_0}^T \frac{\Delta G^\circ}{R} = -1.376 (T - T_0) + 4.157 \times 10^{-3} \left(\frac{T^2 - T_0^2}{2} \right) \\ - 1.61 \times 10^{-6} \left(\frac{T^3 - T_0^3}{3} \right) + 1.21 \times 10^6 \left(\frac{1}{T} - \frac{1}{T_0} \right)$$

$$T = 145 + 273.15 = 418.15 \text{ K}$$

$$T_0 = 298 \text{ K}$$

$$\Rightarrow \int_{T_0}^T \frac{\Delta G^\circ}{R} = -23.121$$

$$\int_{T_0}^T \frac{\Delta G^\circ}{RT} dT = -1.376 \ln\left(\frac{T}{T_0}\right) + 4.157 \times 10^{-3} (T - T_0) \\ - 1.61 \times 10^{-6} \left(\frac{T^2 - T_0^2}{2} \right) + \frac{1.21 \times 10^6}{2} \left(\frac{1}{T^2} - \frac{1}{T_0^2} \right) \\ = -0.06924$$

$$\Rightarrow \frac{\Delta G^\circ}{RT} = \frac{-8378 - (-45792)}{(8.314)(298.15)} + \frac{-45792}{(8.314)(418.15)} \\ + \frac{1}{418.15} (-23.121) - (-0.06924) \\ = 1.936$$

$$K = \exp[-1.936] = 14.43 \times 10^{-2}$$

Other method

(5)

Assume $\Delta H^\circ \neq f(T)$ (not true)

$$\ln\left(\frac{K}{K_0}\right) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)$$

$$K_0 = \exp\left(\frac{-\Delta G_0^\circ}{RT_0}\right) = \exp\left(\frac{-(-8378)}{(8.314)(298.15)}\right)$$

$$= 29.366$$

$$\Rightarrow \ln\left(\frac{K}{29.366}\right) = \frac{-(-45792)}{8.314} \left(\frac{1}{418.15} - \frac{1}{298.15}\right)$$

$$\Rightarrow K = 14.64 \times 10^{-2}$$

$$\text{Error} = \frac{14.43 \times 10^{-2} - 14.64 \times 10^{-2}}{14.43 \times 10^{-2}} \times 100$$

$$= -1.46\% \quad \text{not bad!}$$

As T increases higher and higher than 298 K error increases.