Example Calculate K at $145\,^{\circ}C$ for the following reaction:

$$\overset{(1)}{C_2H_4\,(g)} + \overset{(2)}{H_2O\,(g)} \longrightarrow \overset{(3)}{C_2H_5OH\,(g)}$$

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

Solution

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

$$\frac{\Delta G^{\circ}}{RT} = \frac{\Delta G_0^{\circ} - \Delta H_0^{\circ}}{R T_0} + \frac{\Delta H_0^{\circ}}{RT} + \frac{1}{T}\int_{T_0}^{T} \frac{\Delta C_p^{\circ}}{R}\, dT - \int_{T_0}^{T} \frac{\Delta C_p^{\circ}}{RT}\, dT$$

From Appindix C4: $(T_0 = 298\,K)$

$$\Delta H_0^{\circ} = -235100 - 52510 - (-241818) = -45792 \ \frac{J}{mol}$$

$$\Delta G_0^{\circ} = -168490 - 68460 - (-228572) = -8378 \ \frac{J}{mol}$$

From Appindix C.1

$$\frac{C_{p_i}^{ig}}{R} = A_i + B_i T + C_i T^2 + \frac{D_i}{T^2}$$

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

$$= -1.376 + 4.157 \times 10^{-3}\, T - 1.61 \times 10^{-6}\, T^2 - 1.21 \times 10^{6}\, \frac{1}{T^2}$$

$$\int_{T_0}^{T} \frac{\Delta G_f^\circ}{R} = -1.376\,(T - T_0) + 4.157 * 10^{-3}\left(\frac{T^2 - T_0^2}{2}\right)$$

$$- 1.61 * 10^{-6}\left(\frac{T^3 - T_0^3}{3}\right) + 1.21 * 10^{6}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

$T = 145 + 273.15 = 418.15\ K$ $\qquad$ $T_0 = 298\ K$

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

$$\int_{T_0}^{T} \frac{\Delta G_f^\circ}{RT}\, dT = -1.376 \ln\left(\frac{T}{T_0}\right) + 4.157 * 10^{-3}\,(T - T_0)$$

$$-1.61 * 10^{-6}\left(\frac{T^2 - T_0^2}{2}\right) + \frac{1.21 * 10^{6}}{2}\left(\frac{1}{T^2} - \frac{1}{T_0^2}\right)$$

$$= -0.06924$$

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

$$+ \frac{1}{418.15}(-23.121) - (-0.06924)$$

$$= 1.936$$

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

Other method

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

$$\ln\left(\frac{K}{K_o}\right) = -\frac{\Delta H_o^o}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)$$

$$K_o = \exp\left(\frac{-\Delta G_o^o}{R T_o}\right) = \exp\left(\frac{-(-8378)}{(8.314)(298.15)}\right)$$

$$= 29.366$$

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

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

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

$$= -1.46\ \%$$ not bad!

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