3.3 Quantitative approach for changes of T

From Eq. (3.8) we find the van't Hoff equation

$$\frac{d\ln K}{dT} = -\frac{1}{R}\frac{d(\Delta_r G^0/T)}{dT} = \frac{\Delta_r H^0}{RT^2} \quad . \tag{3.11}$$

Here we used the Gibbs-Helmholtz equation

$$\frac{\partial G}{\partial T} = -S = \frac{G-H}{T} \quad \text{resp.} \quad \frac{\partial (G/T)}{\partial T} = \frac{1}{T}\frac{\partial G}{\partial T} + G\frac{d(1/T)}{dT} = \frac{1}{T}\left(-S - \frac{G}{T}\right) = -\frac{H}{T^2} \tag{3.12}$$

A second representation of the van't Hoff equation directly extracted from Eq. (3.11) is

$$\frac{d\ln K}{d(1/T)} = -\frac{\Delta_r H^0}{R} \quad . \tag{3.13}$$

As illustrated in Fig. 3.1 b) the Arrhenius-like plot allows to extract reaction enthalpies from the slope of the curve $\ln K$ vs. $1/T$.

- Assuming $\Delta_r H^0$ to be independent of T the integration of Eq. (3.13) leads to

$$-\int_{K(T_1)}^{K(T_2)} d\ln K = \frac{\Delta_r H^0}{R}\int_{1/T_1}^{1/T_2} d(1/T) \quad \text{thus} \quad \frac{\ln K(T_2)}{\ln K(T_1)} = \frac{\Delta_r H^0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad . \tag{3.14}$$

- Assuming Kirchhoff's law

$$\Delta_r H^0(T) = \Delta_r H^0(T=0) + \int_0^T \Delta C_p^0 dT \tag{3.15}$$

and taking the Taylor expansion

$$\Delta C_p^0 = \sum_i \nu_i C_{p,i} = A + BT + CT^2 + ... \tag{3.16}$$

Eq. (3.11) translates into

$$\begin{aligned} \frac{d\ln K}{dT} = \frac{\Delta_r H^0}{RT^2} &= \frac{\Delta_r H^0(T=0)}{RT^2} + \frac{1}{RT^2}\int_0^T \left(A + BT + CT^2 + ...\right) dT \\ &= \frac{\Delta_r H^0(T=0)}{RT^2} + \frac{1}{RT^2}\left(AT + \frac{BT^2}{2} + \frac{CT^3}{3} + ...\right) \end{aligned} \tag{3.17}$$

and finally the integration gives

$$\ln K = -\frac{\Delta_r H^0(T=0)}{RT} + \frac{A}{R}\ln T + \frac{B}{2R}T + \frac{C}{6R}T^2 + ... + I \tag{3.18}$$

where I is an additional integration constant determined by a measurement of K at one temperature.