van 't Hoff equation
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The van 't Hoff equation relates the change in the equilibrium constant, K_{eq}, of a chemical reaction to the change in temperature, T, given the standard enthalpy change, $\Delta H^\ominus$, for the process. It was proposed by Dutch chemist Jacobus Henricus van 't Hoff in 1884 in his book "Études de Dynamique chimique" (Studies in dynamic chemistry).

The van 't Hoff equation has been widely utilized to explore the changes in state functions in a thermodynamic system. The van 't Hoff plot, which is derived from this equation, is especially effective in estimating the change in enthalpy, or total energy, and entropy, or amount of disorder, of a chemical reaction

The chemical potential is

$$\mu(P) = k_B T \ln(\frac{1}{k_B T n_Q}) + k_B T \ln P$$

At the standard pressure $P = P_0 = 1$ bar,

$$\mu(P_0) = k_B T \ln(\frac{1}{k_B T n_Q}) + k_B T \ln P_0$$

From these relations, we have

$$\mu(P) = \mu(P_0) + k_B T \ln \frac{P}{P_0}$$

For convenience, we multiply the Avogadro's number N_A. For 1 mole of the system, we have

$$N_A \mu(P) = N_A \mu(P_0) + RT \ln \frac{P}{P_0} \qquad \text{(for 1 mole)}$$

The chemical reaction is given by

$$\sum_i \nu_i \mu_i = 0$$

or

$$\sum_i v_i [N_A \mu_i(P_0) + RT \ln(\frac{P_i}{P_0})] = 0$$

or

$$\sum_i v_i \mu_i(P_0) = -RT \sum_i v_i \ln(\frac{P_i}{P_0})$$

$$= -RT \sum_i \ln(\frac{P_i}{P_0})^{v_i}$$

$$= -RT \ln[(\frac{P_1}{P_0})^{v_1} (\frac{P_2}{P_0})^{v_2} ....]$$

The equilibrium constant is defined as

$$K = (\frac{P_1}{P_0})^{v_1} (\frac{P_2}{P_0})^{v_2} ....$$

and the Gibbs free energy $\Delta_r G_0$ is defined as

$$\Delta_r G_0 = N_A \sum_i v_i \mu_i(P_0).$$

Thus we have

$$\Delta_r G_0 + RT \ln K = 0$$

or

$$\ln K = -\frac{1}{R} \frac{\Delta_r G_0}{T}$$

Noting that the enthalpy H is expressed in terms of G as

$$H = G + TS = G - T\left(\frac{\partial G}{\partial T}\right)_P = -T^2 \left(\frac{\partial}{\partial T} \frac{G}{T}\right)_P. \qquad \text{(Gibbs-Helmholtz)}$$
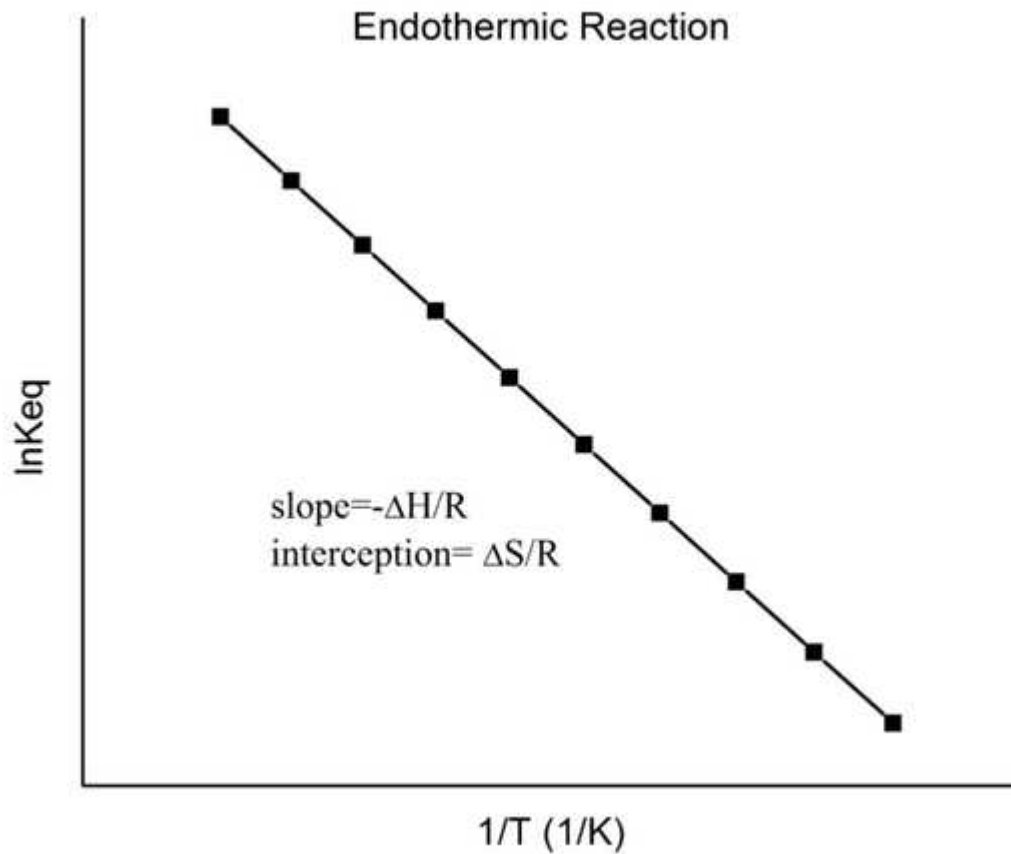
we have

$$\frac{d}{dT}\ln K = -\frac{1}{R}\frac{d}{dT}\frac{\Delta_r G_0}{T}$$

$$= \frac{1}{RT^2}\Delta_r H_0$$

where $\Delta_r G_0$ is the Gibbs free energy of the reaction at 1 bar. This can be rewritten as

$$\frac{d}{d(1/T)}\ln K = -\frac{1}{R}\Delta_r H_0 \qquad \text{(van 't Hoff equation)}$$

(a)   Endothermic reaction

Endothermic Reaction

slope=-ΔH/R
interception= ΔS/R

InKeq

1/T (1/K)

(b)   Exothermic reaction

Exothermic Reaction

slope=-ΔH/R
interception= ΔS/R

lnKeq

1/T (1/K)