

Van't Hoff Equation

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This equation gives the quantitative temperature dependence of equilibrium constant (K). The relation between standard free energy change (ΔG°) and equilibrium constant is

$$\Delta G^\circ = -RT \ln K \quad (1)$$

We know that

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2)$$

Substituting (1) in equation (2)

$$-RT \ln K = \Delta H^\circ - T\Delta S^\circ$$

Rearranging

$$\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (3)$$

Differentiating equation (3) with respect to temperature,

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (4)$$

Equation 4 is known as differential form of van't Hoff equation.

On integrating the equation 4, between T_1 and T_2 with their respective equilibrium constants K_1 and K_2 .

Problem

For an equilibrium reaction $K_p = 0.0260$ at 25°C $\Delta H = 32.4 \text{ kJmol}^{-1}$, calculate K_p at 37°C

Solution:

$$T_1 = 25 + 273 = 298 \text{ K}$$

$$T_2 = 37 + 273 = 310 \text{ K}$$

$$\Delta H = 32.4 \text{ KJmol}^{-1} = 32400 \text{ Jmol}^{-1}$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$K_{p1} = 0.0260$$

$$K_{p2} = ?$$

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303 R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$$

$$\log \frac{K_2}{K_1} = \frac{32400}{2.303 \times 8.314} \left(\frac{310 - 298}{310 \times 298} \right)$$

$$= \frac{32400 \times 12}{2.303 \times 8.314 \times 310 \times 298}$$

$$= 0.2198$$

$$\frac{K_2}{K_1} = \text{antilog } 0.2198 = 1.6588$$

$$K_2 = 1.6588 \times 0.026 = 0.0431$$