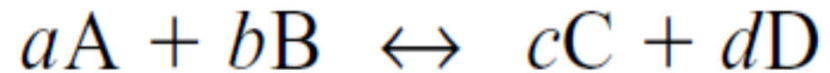# Kimyasal Reaksiyonlarda Enerji Dengesi: Gibbs Serbest Enerjisi

Gibbs Serbest Enerjisi

Reaksiyon denge sabiti (K) ve Gibbs Serbest Enerjisi (ΔGr) ile ilişkisi

$$a\text{A} + b\text{B} \leftrightarrow c\text{C} + d\text{D}$$

$$\Delta G_r^0 = -RT \ln \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

$\Delta G_r > 0$ the reaction proceeds to the left;
$\Delta G_r = 0$ the reaction is at equilibrium;
$\Delta G_r < 0$ the reaction proceeds to the right.

$$\Delta G_r^0 = -RT \ln K$$

$$\Delta G_r^0 = \sum \Delta G_{f\ products}^0 - \sum \Delta G_{f\ reactants}^0$$

Evrensel Gaz Sabiti R= 8.3141×10^3 kJ/mol/deg   Kelvin, 0 °K= -273.15 °C

Örnek hesaplama (Gibbs serbest enerjisi)

EXAMPLE 4.4. *Calculation of solubility products from Gibbs free energy data*
Calculate the solubility product of calcite from the Gibbs free energies of formation at 25°C (Wagman et al., 1982):

$$\Delta G^0_{f\,CaCO_3} = -1128.8 \text{ kJ/mol}$$

$$\Delta G^0_{f\,Ca^{2+}} = -553.6 \text{ kJ/mol}$$

$$\Delta G^0_{f\,CO_3^{2-}} = -527.8 \text{ kJ/mol}$$

ANSWER:
For the reaction $CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$
we obtain

$$\Delta G^0_r = \Delta G^0_{f\,Ca^{2+}} + \Delta G^0_{f\,CO_3^{2-}} - \Delta G^0_{f\,CaCO_3}$$

$$\Delta G^0_r = -553.6 - 527.8 + 1128.8 = 47.4 \text{ kJ/mol}$$

$$\Delta G^0_r = -RT \ln K$$

$$47.4 = -8.314 \times 10^{-3} \times 298.15 \times 2.303 \log K = -5.708 \log K$$

$$\log K = 47.4/-5.708 = -8.30$$

*Calculation of mass action constants at
different temperature*

Örnek hesaplama Van't Hoff eşitliği

$$\log K_{T_1} - \log K_{T_2} = \frac{-\Delta H_r^0}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

EXAMPLE 4.5. *Temperature dependency of the solubility product*

Calculate the solubility product of calcite at 10°C from the following enthalphies of formation (Wagman et al., 1982):

$$\Delta H_{f\,CaCO_3}^0 = -1206.9 \text{ kJ/mol}$$
$$\Delta H_{f\,Ca^{2+}}^0 = -542.8 \text{ kJ/mol}$$
$$\Delta H_{f\,CO_3^{2-}}^0 = -677.1 \text{ kJ/mol}$$

ANSWER:
For the reaction $CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$
we may write,

$$\Delta H_r^0 = -542.8 + (-677.1) - (-1206.9) = -13.0 \text{ kJ/mol}$$

which means that the reaction is exothermal: the system heats up when calcite dissolves. The difference in $\log K$ between 25°C and 10°C, according to Equation (4.29) is:

$$\log K_{25} - \log K_{10} = \frac{-\Delta H_r^0}{2.303\,R}\left(\frac{1}{298.15} - \frac{1}{283.15}\right)$$

$$= \frac{-13.0}{2.303 \times 8.314 \times 10^{-3}}\left(\frac{1}{298.15} - \frac{1}{283.15}\right)$$

$$= -0.12$$

In EXAMPLE 4.4 it was calculated that $\log K_{calcite}$ at 25°C is -8.30, so that at 10°C $K_{calcite} = -8.30 + 0.12 = -8.18$. Thus for an exothermal reaction the solubility increases with decreasing temperature and vice versa for an endothermal reaction.