

Třetí věta termodynamická

1
05

Nernst: $\lim_{T \rightarrow 0} \Delta S = 0$

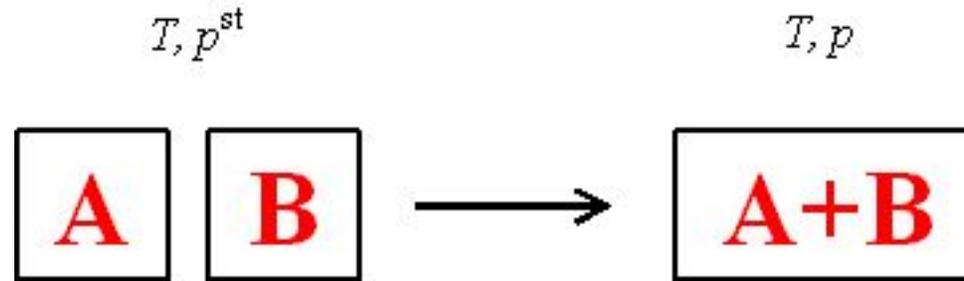
Planck: $\lim_{T \rightarrow 0} S = 0$

Lewis+Randall: $\lim_{T \rightarrow 0} S = 0$ pro čisté látky ve stavu dokonalého krystalu

Důsledek: nedosažitelnost absolutní nuly

Důsledek: **absolutní entropie** – integrace od 0 K

Uvažujme děj:



$$\Delta G = \Delta H - T\Delta S = -T\Delta S \quad [\Delta H = 0]$$

$$\begin{aligned} \Delta S &= n_1 \Delta S_{1,m}(p^{\text{st}} \rightarrow p) + n_2 \Delta S_{2,m}(p^{\text{st}} \rightarrow p) + \Delta_{\text{mix}} S \\ &= -n_1 R \ln \frac{p}{p^{\text{st}}} - n_2 R \ln \frac{p}{p^{\text{st}}} - (n_1 + n_2) R (x_1 \ln x_1 + x_2 \ln x_2) \\ &= -n_1 R \ln \frac{px_1}{p^{\text{st}}} - n_2 R \ln \frac{px_2}{p^{\text{st}}} \end{aligned}$$

$$\begin{aligned}\Delta G &= n_1 RT \ln \frac{px_1}{p^{\text{st}}} + n_2 RT \ln \frac{px_2}{p^{\text{st}}} \\ &= n_1 RT \ln a_1 + n_2 RT \ln a_2\end{aligned}$$

kde

$$a_1 = \frac{px_1 \gamma_1}{p^{\text{st}}}$$

Alternativní zápis:

$$\begin{aligned}G(T, p) &= G_{st}(T, p_{st}) + n_1 RT \ln a_1 + n_2 RT \ln a_2 \\ &= n_1 G_{1,m}^{\text{st}}(T, p_{st}) + n_2 G_{2,m}^{\text{st}}(T, p_{st}) + n_1 RT \ln a_1 + n_2 RT \ln a_2 \\ &= n_1 \mu_1 + n_2 \mu_2\end{aligned}$$

kde

$$\mu_1 = \mu_1^{\text{st}} + RT \ln a_1 = \mu_1^{\text{st}} + RT \ln \frac{px_1 \gamma_1}{p^{\text{st}}}$$

$$p^{\text{st}} = 101,325 \text{ kPa}$$

$$G_{\text{m}}(p, T) = \sum_{i=1}^k x_i \mu_i^{\circ} + RT \sum_{i=1}^k x_i \ln \frac{px_i}{p^{\text{st}}}$$

⇒

$$\mu_i = \mu_i^{\circ} + RT \ln \frac{px_i}{p^{\text{st}}} = \mu_i^{\circ} + RT \ln \frac{p_i}{p^{\text{st}}}$$

a

$$a_1 = \frac{px_1}{p^{\text{st}}}$$

$$p^{\text{st}} = p$$

$$G_m(p, T) = \sum_{i=1}^k x_i \mu_i^{\bullet} + RT \sum_{i=1}^k x_i \ln x_i \gamma_i$$

⇒

$$\mu_i = \mu_i^{\bullet} + RT \ln x_i \gamma_i$$

a

$$a_i = x_i \gamma_i$$

$$p^{\text{st}} = p \quad \text{a} \quad x_i = 1$$

$$G_m(p, T) = \sum_{i=1}^k x_i \mu_i^\bullet$$

⇒

$$\mu_1 = \mu_i^\bullet$$

a

$$a_1 = 1$$