Lecture 22: Maxwell Relations: Harder Applications

Maxwell Relations Part 3, Gibbs-Helmholtz

Example: Non-Ideal Gas Expansion

A non-ideal gas obeys equation of state: $P = \frac{T}{V} + \frac{f(T)}{V^2}$ and undergoes a reversible, isothermal expansion from V_0 to $2V_0$. Find the associated work and heat.

$$w = -\int_{V_0}^{2V_0} P\,dV$$

$$= -\int_{V_0}^{2V_0} \left(\frac{T}{V} + \frac{f(T)}{V^2}\right) dV$$

$$= -\left[T\ln V - \frac{f(T)}{V}\right]_{V_0}^{2V_0}$$

$$= -\left(T\ln(2V_0) - \frac{f(T)}{2V_0} - T\ln V_0 + \frac{f(T)}{V_0}\right)$$

$$\boxed{w = -\left(T\ln 2 + \frac{f(T)}{2V_0}\right)}$$

$$dq = T\,dS \implies q = T\int dS$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$q = T\int \left(\frac{\partial S}{\partial V}\right) dV$$

$$= T\int_{V_0}^{2V_0} \left(\frac{1}{V} + \frac{f'(T)}{V^2}\right) dV$$

$$= T\left[\ln V - \frac{f'(T)}{V}\right]_{V_0}^{2V_0}$$

$$\boxed{q = T\ln 2 - \frac{T f'(T)}{2V_0}}$$

Gibbs vs Gibbs–Helmholtz

Gibbs Free Energy

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G^\circ_{\text{rxn}} = \sum n\Delta G^\circ_f(\text{products}) - \sum n\Delta G^\circ_f(\text{reactants})$$

Gibbs–Helmholtz

Accounts for temperature dependence of Gibbs

$$\left(\frac{\partial G/T}{\partial T}\right)_P = -\frac{H}{T^2}$$

$$\frac{\Delta G(T_2)}{T_2} - \frac{\Delta G(T_1)}{T_1} = \Delta H\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Gibbs–Helmholtz Derivation

Starting from:

$$G = H - TS$$

Show that:

$$\left(\frac{\partial G/T}{\partial T}\right)_P = -\frac{H}{T^2}$$

Rearrange:

$$\frac{G}{T} = \frac{H}{T} - S$$

Differentiate:

$$\left(\frac{\partial G/T}{\partial T}\right)_P = -\frac{H}{T^2} + \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_P$$

Recall from last lecture:

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \implies \boxed{\left(\frac{\partial G/T}{\partial T}\right)_P = -\frac{H}{T^2}}$$

Gibbs–Helmholtz Derivation

State functions so we can take differences:

$$\left(\frac{\partial(\Delta G/T)}{\partial T}\right)_P = -\frac{\Delta H}{T^2}$$

Integrate from T_1 to T_2:

$$\int_{T_1}^{T_2} \left(\frac{\partial(\Delta G/T)}{\partial T}\right)_P dT = -\int_{T_1}^{T_2} \frac{\Delta H}{T^2} dT$$

Assume ΔH is constant:

$$\boxed{\frac{\Delta G(T_2)}{T_2} - \frac{\Delta G(T_1)}{T_1} = \Delta H\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

Example: Gibbs–Helmholtz

$$\text{Given:} \quad \Delta G^\circ = -40\,\tfrac{\text{kJ}}{\text{mol}} \qquad \Delta H^\circ = -80\,\tfrac{\text{kJ}}{\text{mol}}$$

$$\text{Find:} \quad \Delta G_{350}$$

$$\frac{\Delta G(T_2)}{T_2} = \frac{\Delta G(T_1)}{T_1} + \Delta H\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Plug in values:

$$\frac{\Delta G_2}{350\,\text{K}} = \frac{-40\,\frac{\text{kJ}}{\text{mol}}}{298\,\text{K}} + \left(-80\,\frac{\text{kJ}}{\text{mol}}\right)\left(\frac{1}{350\,\text{K}} - \frac{1}{298\,\text{K}}\right)$$

$$\frac{\Delta G_2}{350\,\text{K}} = -0.134\,\frac{\text{kJ}}{\text{mol}\cdot\text{K}} + 0.0399\,\frac{\text{kJ}}{\text{mol}\cdot\text{K}} = -0.0941\,\frac{\text{kJ}}{\text{mol}\cdot\text{K}}$$

$$\Delta G_2 = -0.0941\,\frac{\text{kJ}}{\text{mol}\cdot\text{K}} \times 350\,\text{K} = \boxed{-32.9\,\frac{\text{kJ}}{\text{mol}}}$$