

## 9.2: Temperature Dependence of $\Delta G$

$$\left(\frac{\partial G}{\partial T}\right)_{P,\{n_i\}} = -S$$

Let's analyze the first coefficient that gives the dependence of the Gibbs energy on temperature. Since this coefficient is equal to  $-S$  and the entropy is always positive,  $G$  must decrease when  $T$  increases at constant  $P$  and  $\{n_i\}$ , and vice versa.

If we replace this coefficient for  $-S$  in the Gibbs equation, [Equation 9.1.3](#), we obtain:

$$\Delta G = \Delta H + T \left(\frac{\partial \Delta G}{\partial T}\right)_{P,\{n_i\}}, \quad (9.2.1)$$

and since [Equation 9.2.1](#) includes both  $\Delta G$  and its partial derivative with respect to temperature  $\left(\frac{\partial \Delta G}{\partial T}\right)_{P,\{n_i\}}$  we need to rearrange it to include the temperature derivative only. To do so, we can start by evaluating the partial derivative of  $\left(\frac{\Delta G}{T}\right)$  using the chain rule:

$$\left[\frac{\partial \left(\frac{\Delta G}{T}\right)}{\partial T}\right]_{P,\{n_i\}} = \frac{1}{T} \left(\frac{\partial \Delta G}{\partial T}\right)_{P,\{n_i\}} - \frac{1}{T^2} \Delta G, \quad (9.2.2)$$

which, replacing  $\Delta G$  from [Equation 9.2.1](#) into [Equation 9.2.2](#), becomes:

$$\begin{aligned} \left[\frac{\partial \left(\frac{\Delta G}{T}\right)}{\partial T}\right]_{P,\{n_i\}} &= \frac{1}{T} \left(\frac{\partial \Delta G}{\partial T}\right)_{P,\{n_i\}} - \frac{1}{T^2} \left[\Delta H + T \left(\frac{\partial \Delta G}{\partial T}\right)_{P,\{n_i\}}\right] \\ &= \frac{1}{T} \left(\frac{\partial \Delta G}{\partial T}\right)_{P,\{n_i\}} - \frac{\Delta H}{T^2} - \frac{1}{T} \left(\frac{\partial \Delta G}{\partial T}\right)_{P,\{n_i\}}, \end{aligned} \quad (9.2.3)$$

which simplifies to:

$$\left[\frac{\partial \left(\frac{\Delta G}{T}\right)}{\partial T}\right]_{P,\{n_i\}} = -\frac{\Delta H}{T^2}. \quad (9.2.4)$$

[Equation 9.2.4](#) is known as the **Gibbs–Helmholtz equation**, and is useful in its integrated form to calculate the Gibbs free energy for a chemical reaction at any temperature  $T$  by knowing just the standard Gibbs free energy of formation and the standard enthalpy of formation for the individual species, which are usually reported at  $T = 298 \text{ K}$ . The integration is performed as follows:

$$\begin{aligned} \int_{T_i=298 \text{ K}}^{T_f=T} \frac{\partial \left(\frac{\Delta_{\text{rxn}} G}{T}\right)}{\partial T} &= - \int_{T_i=298 \text{ K}}^{T_f=T} \frac{\Delta_{\text{rxn}} H}{T^2} \\ \frac{\Delta_{\text{rxn}} G^\ominus(T)}{T} &= \frac{\Delta_{\text{rxn}} G^\ominus}{298 \text{ K}} + \Delta_{\text{rxn}} H^\ominus \left(\frac{1}{T^2} - \frac{1}{(298 \text{ K})^2}\right), \end{aligned} \quad (9.2.5)$$

giving the integrated Gibbs–Helmholtz equation:

$$\frac{\Delta_{\text{rxn}} G^\ominus(T)}{T} = \frac{\sum_i \nu_i \Delta_f G_i^\ominus}{298 \text{ K}} + \sum_i \nu_i \Delta_f H_i^\ominus \left(\frac{1}{T^2} - \frac{1}{(298 \text{ K})^2}\right) \quad (9.2.6)$$

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