

10.11: The Gibbs-Helmholtz Equation

When temperature and pressure are the independent variables, the Gibbs free energy is the change criterion that takes the most simple form:

$$dG = -SdT + VdP.$$

In chemical applications, temperature and pressure are often the most convenient choice of independent variables, making the Gibbs free energy a particularly useful function. Constant Gibbs free energy is the criterion for equilibrium at constant pressure and temperature. The Gibbs free energy of the system does not change when the system goes from one equilibrium state to another at the same temperature and pressure, $(dG)_{PT} = 0$. An equilibrium system of ice and water is one example; we can melt a portion of the ice, changing the composition of the system, while maintaining equilibrium at constant pressure and temperature. Similarly, we may be able to change the equilibrium composition of an equilibrium system that consists of reacting gases by changing the volume of the system while maintaining constant pressure and temperature.

Consider a system that undergoes some arbitrary change from a state A, in which its Gibbs free energy is G_A , to a second state B, in which its Gibbs free energy is G_B . In general, $G_A \neq G_B$; in the most general case, the pressures and temperatures of states A and B are different. (For example, state A might be a mole of ice at -10°C and 0.5 bar, while state B is a mole of water at $+10^\circ\text{C}$ and 2.0 bar. Either of these states can be converted to the other; however, they are not at equilibrium with one another, and their Gibbs free energies are not equal.) Representing the pressures and temperatures as P_1, T_1, P_2, T_2 , we can express the Gibbs free energies of these two states as $G_A = G_A(P_1, T_1)$ and $G_B = G_B(P_2, T_2)$, respectively. The difference is the change in the Gibbs free energy when the system passes from state A to state B:

$$\Delta_{AB}G = G_B(P_2, T_2) - G_A(P_1, T_1)$$

Often, we are interested in Gibbs free energy differences between states that are at the same pressure and temperature, say P_1 and T_1 . Then the Gibbs free energy difference is

$$\Delta_{AB}G(P_1, T_2) = G_B(P_1, T_2) - G_A(P_1, T_1)$$

(For example, state A might be a mole of ice at -10°C and 0.5 bar, while state B is a mole of water, also at -10°C and 0.5 bar. This would be a super-cooled state of liquid water. These states are not at equilibrium with one another, and their Gibbs free energies are not equal. The difference between the Gibbs free energies of these states is the change in the Gibbs free energy when ice goes to super-cooled water at -10°C and 0.5 bar.)

Similar considerations apply to expressing differences between the enthalpies and the entropies of two states that are available to a system. The Gibbs free energy is defined by

$$G = H - TS.$$

When we are interested in a process that converts some state A to a second state B at constant pressure and temperature, we usually write

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

which relies on the context for the information about the pressure and temperature and the initial and final states. To explicitly denote that the change is one that occurs at a constant temperature, T_0 , we can write

$$\Delta G(T_0) = \Delta H(T_0) - T_0\Delta S(T_0).$$

Frequently we are interested in the way that ΔG , ΔH , and ΔS vary with temperature at constant pressure. If we know how G , H , and S vary with temperature for each of the two states of interest, we can find the temperature dependence of ΔG , ΔH , and ΔS . The Gibbs-Helmholtz equation is a frequently useful expression of the temperature dependence of G or ΔG . Since it is a mathematical consequence of our thermodynamic relationships, we derive it here.

At constant pressure, the temperature derivative of the Gibbs free energy is $+S$; that is,

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

Using this result and the definition, $G = H - TS$, we obtain the temperature dependence of G as

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

However, the Gibbs-Helmholtz equation can be expressed most compactly as the temperature derivative of G/T . As a matter of calculus, we have

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

Using the relationships above, this becomes

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

Since $\Delta_{AB}G = G_B + G_A$, we have

$$(\partial \Delta_{AB}G / \partial T)_P = -(S_B + S_A) = -\Delta_{AB}S$$

and

$$\begin{aligned} \left(\frac{\partial (\Delta_{AB}G/T)}{\partial T} \right)_P &= \left(\frac{\partial (G_B/T)}{\partial T} \right)_P + \left(\frac{\partial (G_A/T)}{\partial T} \right)_P \\ &= -\left(\frac{H_B}{T^2} + \frac{H_A}{T^2} \right) \quad (\text{The Gibbs-Helmholtz equation}) \\ &= -\frac{\Delta_{AB}H}{T^2} \end{aligned}$$

If we know the temperature dependence of ΔS or ΔH , we can find the temperature dependence of ΔG by integrating the relationships above. That is, given ΔG at T_1 , we can find ΔG at T_2 . Thus, from $(\partial G / \partial T)_P = -S$, we have

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

and from $(\partial (\Delta G/T) / \partial T)_P = -\Delta H/T^2$, we have

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

For small temperature differences, ΔH is often approximately constant. Then, we can evaluate the change in ΔG from

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

Another common application arises when we know ΔG at several temperatures. A plot of $\Delta G/T$ versus $1/T$ is then approximately linear with a slope that approximates the average value of ΔH in the temperature interval.

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