

S2.B. Entropy of Mixing and the Gibbs Paradox

Consider an ideal gas composed of n_j moles of type j molecules, where $j = 1, \dots, m$. The gas is in a container of volume V at temperature T and pressure P . Let

$$n = \sum_{j=1}^m n_j$$

then the equation of state can be written as

$$P = \frac{n R T}{V} = \sum_{j=1}^m n_j \frac{R T}{V} \equiv \sum_{j=1}^m P_j \quad (2.210)$$

where

$$P_j = n_j \frac{R T}{V} \quad (2.211)$$

is called the **partial pressure** of the type j molecules.

The **mole fraction** is defined as

$$x_j \equiv \frac{n_j}{n} = \frac{n_j}{\sum_{k=1}^m n_k} \quad (2.212a)$$

$$= \frac{P_j}{P} \quad [(2.210-1) \text{ used. }] \quad (2.212)$$

Using

$$\mu_j' dN_j = \mu_j d n_j$$

the definition (2.108) becomes

$$dG = -S dT + V dP + \sum_{j=1}^m \mu_j d n_j \quad (2.213)$$

where μ_j is the (molar) **chemical potential** for type j molecules.

If there is only 1 species of molecules, i.e., $m = 1$, putting (2) of Ex.2.3 in §2.E into (2.107) of §2.F.4 gives

$$\begin{aligned} G &= \mu^{(0)} n \\ &= -n R T \ln \left[\frac{P_0}{P} \left(\frac{T}{T_0} \right)^{5/2} \right] + G_0 \\ &= -n R T \ln \left(\frac{T^{5/2}}{P} \right) + G^{(0)} \end{aligned} \quad (2.214)$$

where $\mu^{(0)}$ is the species-independent chemical potential of an ideal gas and

$$G_0 = G(T_0, P_0, n) \quad G^{(0)} = G_0 + n R T_0 \ln \frac{T^{5/2}}{P_0} \quad (2.214a)$$

Next, we consider the “unmixed” version of the gas. Thus, the container is divided into m compartments, each holding a single species of gas. The walls of the compartments are mobile and heat conducting so that, in equilibrium, every compartment have the same T and P . The Gibbs free energy is then simply

$$G_{\text{um}} = - \sum_{j=1}^m n_j \mu^{(0)}$$

$$= -\sum_{j=1}^m n_j R T \ln \left(\frac{T^{5/2}}{P} \right) + G_{\text{um}}^{(0)} \quad (2.215)$$

By removing the walls, we obtain the “mixed” version of the gas. Since there is no interaction between the molecules, each type of gas occupy the container as if the other type of gases do not exist. Hence,

$$G_{\text{mix}} = -\sum_{j=1}^m n_j \mu^{(0)}(T, P_j) \\ = -\sum_{j=1}^m n_j R T \ln \left(\frac{T^{5/2}}{P_j} \right) + G_{\text{mix}}^{(0)} \quad (2.215a)$$

$$= -\sum_{j=1}^m n_j R T \ln \left(\frac{T^{5/2}}{P x_j} \right) + G_{\text{mix}}^{(0)} \quad [(2.212) \text{ used. }]$$

$$= G_{\text{um}} - G_{\text{um}}^{(0)} + \sum_{j=1}^m n_j R T \ln x_j + G_{\text{mix}}^{(0)} \quad [(2.215) \text{ used. }] \quad (2.216)$$

Thus, the change in the Gibbs energy upon mixing is

$$\Delta G \equiv G_{\text{mix}} - G_{\text{um}} \\ = \sum_{j=1}^m n_j R T \ln x_j + G_{\text{mix}}^{(0)} - G_{\text{um}}^{(0)} \quad (2.217)$$

From (2.109) of §2.F.4, we obtain the corresponding change in entropy as

$$\Delta S = -\left(\frac{\partial \Delta G}{\partial T} \right)_{P, \{n_j\}} \\ = -\sum_{j=1}^m n_j R \ln x_j \quad (2.218)$$

$$\geq 0 \quad [0 < x_j \leq 1] \quad (2.218a)$$

where the equal sign holds only for $m = 1$ so that $x_1 = 1$.

Hence, entropy always increases after mixing.

Since (2.218) is independent of the species of molecules in the gas, it should hold when the gases in the m compartments are all of the same type, i.e., when a gas mixes with itself. In which case, the result $\Delta S > 0$ given by (2.218) is contrary to the self-evident value of $\Delta S = 0$. This is called the **Gibbs paradox** and can be resolved only by introducing the (quantum mechanical) concept of identical (or indistinguishable) particles.