

I. ENTROPY OF MIXING

This is an interesting result which is relevant to many fields of Physics as a given system is comprised of several subsystems, or distinct species, all mixed. The properties of the aggregate system are (approximately) the sum of the properties of the constituents, but **not** so the entropy. The calculation in the general case of an interacting system is not possible, but the idea can be illustrated for the so called “ideal mixture” (in effect, a mixture of ideal gases). In practice, entropies of mixing in real systems are almost always approximated by the ideal entropy of mixing.

Consider $i = 1, r$ individual species that form a mixture. Let v_i^0 and u_i^0 be the equilibrium volume and internal energy per particle of the pure species at the **same** conditions of the mixture (e.g., temperature and pressure). Then the volume V and internal energy U of an ideal mixture are defined as,

$$V = \sum_{i=1}^r N_i v_i^0$$

$$U = \sum_{i=1}^r N_i u_i^0$$

Consider mixing the r species by imagining a volume V filled with r partitions that contain each of the separate species in equilibrium. In this case, the entropy of each species i occupying a volume V_i is (assuming an ideal gas),

$$S_i = S_{0i} + N_i C_{V,i} \ln \frac{T}{T_0} + N_i R \ln \frac{V_i}{V_{0i}}$$

where S_{0i} is some, unimportant constant of integration that refers to some reference state for each species (sub 0 in the equation).

Now the partition is removed, so that all molecules of each species have the total volume V available. The final entropy,

$$S_{final} = \sum_{i=1}^r \left(S_{0i} + N_i C_{V,i} \ln \frac{T}{T_0} \right) + R \sum_{i=1}^r N_i \ln \frac{V}{V_{0i}}$$

which rewriting $\frac{V}{V_{0i}} = \frac{V}{V_i} \frac{V_i}{V_{0i}}$ can be expressed as

$$S_{final} = \underbrace{\sum_{i=1}^r \left(S_{0i} + N_i C_{V,i} \ln \frac{T}{T_0} \right) + R \sum_{i=1}^r N_i \ln \frac{V_i}{V_{0i}}}_{\text{Initial entropy}} + R \sum_{i=1}^r N_i \ln \frac{V}{V_i}$$

Therefore, even though the state of each individual species has not changed (e.g., same temperature and pressure) the entropy of the system has increased by,

$$\Delta S = R \sum_{i=1}^r N_i \ln \frac{V}{V_i}. \quad (1)$$

This is called the (ideal) entropy of mixing. The entropy change is positive and reflects the **irreversible** nature of the mixing process. In effect, ideal gases spontaneously mix, but do not spontaneously demix ! It is well known, that demixing (or separating) the constituents of mixture costs a great deal of energy.

By using the equation of state of the ideal gas, and the fraction $x_i = N_i/N$, where $N = \sum_{i=1}^r N_i$, one can write a more familiar expression,

$$\Delta S = -NR \sum_{i=1}^r x_i \ln x_i. \quad (2)$$

A. Gibbs free energy of mixing

The internal energy of the mixture is simply the sum of the internal energies of the constituents, but this is not the case with the entropy: the entropy of the mixture is the sum of the entropies of the constituents plus the entropy of mixing. As a consequence, other thermodynamic potentials also incorporate a mixing term that derives from the entropy of mixing. For example, the Gibbs free energy, $G = U + pV - TS$ can be written for a mixture at some (T, p) as

$$G = \sum N_i u_i^0 + p \sum N_i v_i^0 - T \sum N_i (s_i^0 - R \ln x_i)$$

where we have added to the last term the contribution from the entropy of mixing, and s_i^0 is the entropy per particle of the pure species i at the conditions of the mixture. Now, the chemical potential of species i in the mixture is,

$$\mu_i = \left(\frac{\partial G}{\partial N_i} \right)_{T, p, N_j} = \underbrace{N_i^0 + p v_i^0 - T s_i^0}_{\mu_i^0} + RT \ln x_i$$

Hence, for given temperature and pressure, $\mu_i^0(T, p)$ is the chemical potential of species i pure, while its chemical potential in the mixture is,

$$\mu_i(T, p) = \mu_i^0(T, p) + RT \ln x_i \quad (3)$$

Since, in equilibrium, the chemical potential of each species in the mixture is uniform, the entropy of mixing appears frequently in multi phase systems that involve mixtures.