CHEMICAL POTENTIAL OF A MIXTURE OF IDEAL GASES

Link to: physicspages home page.

To leave a comment or report an error, please use the auxiliary blog and include the title or URL of this post in your comment.

Post date: 15 July 2021.

The chemical potential is defined in terms of the entropy as

$$\mu \equiv -T\left(\frac{\partial S}{\partial N}\right)_{U,V} \tag{1}$$

This definition leads to a general thermodynamic identity

$$dU = TdS - PdV + \mu dN \tag{2}$$

For a mixture of ideal gases, each species i constitutes a molar fraction x_i of the total number N_{total} of molecules, so each species has its own chemical potential defined as

$$\mu_i = -T\left(\frac{\partial S}{\partial N_i}\right)_{U,V,N_{j\neq i}} \tag{3}$$

where all N_j with $j \neq i$ are held constant in the derivative.

Also, for an ideal gas, each species contributes its own portion of the overall entropy, independently of the other species. We can see this by noting that if we have a mixture of, say, 2 gases, then for each configuration of the gas A molecules there is a multiplicity of Ω_B of the gas B molecules and since for an ideal gas, the molecules don't interact, the total multiplicity of the mixture is $\Omega_{\text{total}} = \Omega_A \Omega_B$, so the entropy is the sum of the entropies for the separate species: $S_{\text{total}} = k \ln \Omega_{\text{total}} = S_A + S_B$.

Since ideal gas molecules don't interact, species i contributes a fraction x_i of the total pressure, or in other words, its partial pressure is

$$P_i = x_i P \tag{4}$$

We can therefore write the thermodynamic identity for a mixture of ideal gases as

$$dU = T\sum_i dS_i - \left(\sum_i P_i\right) dV + \sum_i \mu_i dN_i \tag{5}$$

Since $dS_{j\neq i}=0$ in 3 (because only the number N_i of species i is changing, and no properties of any of the other species are changing), we can write the chemical potential of species i as

$$\mu_i=-T\left(\frac{\partial S_i}{\partial N_i}\right)_{U,V,N_{j\neq i}} \tag{6}$$

But this is the definition of chemical potential in a system containing only species i at partial pressure P_i in volume V. Thus, for a mixture of ideal gases, the chemical potential of each species is independent of the other species. In a mixture of real gases, however, this is probably not the case, since interactions between the species means the total entropy isn't a simple sum of the entropies of the individual species.