

9.4: Composition Dependence of ΔG

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

The third and final coefficient gives the chemical potential as the dependence of G on the chemical composition at constant T and P . Similarly to the previous cases, we can take the definition of the coefficient and integrate it directly between the initial and final stages of a reaction. If we consider a reaction product, pure substance i , at the beginning of the reaction there will be no moles of it $n_i = 0$, and consequently $G = 0$.¹ We can then integrate the left-hand side between zero and the number of moles of product at the end of the reaction, n , and the right-hand side between zero and the Gibbs free energy of the product, G . The integral will become:

$$\int_0^G dG = \int_0^n \mu^* dn, \quad (9.4.1)$$

where μ^* indicates the chemical potential of a pure substance, which is independent on the number of moles by definition. As such, Equation 9.4.1 becomes:

$$\int_0^G dG = \mu^* \int_0^n dn \rightarrow G = \mu^* n \rightarrow \mu^* = \frac{G}{n}, \quad (9.4.2)$$

which gives a straightforward interpretation of the chemical potential of a pure substance as the molar Gibbs free energy.

We can start from Equation 9.3.3 and write for a pure substance that is brought from $P_i = P^\ominus$ to $P_f = P$ at constant T :

$$G - G^\ominus = nRT \ln \frac{P}{P^\ominus}, \quad (9.4.3)$$

dividing both sides by n , we obtain:

$$\frac{G}{n} - \frac{G^\ominus}{n} = RT \ln \frac{P}{P^\ominus}, \quad (9.4.4)$$

which, for a pure substance at $P^\ominus = 1$ bar, becomes:

$$\mu^* - \mu^\ominus = RT \ln P. \quad (9.4.5)$$

Notice that, while we use the pressure of the gas inside the logarithm in Equation 9.4.5, the quantity is formally divided by the standard pressure $P^\ominus = 1$ bar, and therefore it is a dimensionless quantity, as it should be. For simplicity of notation, however, we will omit the division by P^\ominus in the remaining of this textbook, especially wherever it does not create confusion. Let's now consider a mixture of ideal gases, and let's try to find out whether the chemical potential of a pure gas inside the mixture, μ_i^{mixture} , is the same as its chemical potential outside the mixture, μ^* . To do so, we can use Equation 9.4.5 and replace the pressure P with the partial pressure P_i :

$$\mu_i^{\text{mixture}} = \mu_i^\ominus + RT \ln P_i, \quad (9.4.6)$$

where the partial pressure P_i can be obtained from the simple relation that is known as **Dalton's Law**:

$$P_i = y_i P, \quad (9.4.7)$$

with y_i being the concentration of gas i measured as a mole fraction in the gas phase $y_i = \frac{n_i}{n_{\text{TOT}}} < 1$. Replacing Equation 9.4.7 into Equation 9.4.6, we obtain:

$$\begin{aligned} \mu_i^{\text{mixture}} &= \mu_i^\ominus + RT \ln(y_i P) \\ &= \underbrace{\mu_i^\ominus + RT \ln P}_{\mu_i^*} + RT \ln y_i, \end{aligned} \quad (9.4.8)$$

which then reduces to the following equation:

$$\mu_i^{\text{mixture}} = \mu_i^* + RT \ln y_i. \quad (9.4.9)$$

Analyzing Equation 9.4.9, we can immediately see that, since $y_i < 1$:

$$\mu_i^{\text{mixture}} < \mu_i^*, \quad (9.4.10)$$

or, in other words, the chemical potential of a substance in the mixture is always lower than the chemical potential of the pure substance. If we consider a process where we start from two separate pure ideal gases and finish with a mixture of the two, we can calculate the change in Gibbs free energy due to the mixing process with:

$$\Delta_{\text{mixing}} G = \sum n_i (\mu_i^{\text{mixture}} - \mu_i^*) < 0, \quad (9.4.11)$$

or, in other words, the process is spontaneous under all circumstances, and pure ideal gases will always mix.

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1. For reactants, the same situation usually applies but in reverse. More complicated cases where the reaction does not consume all reactants are possible, but insignificant for the following treatment.
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