

14.11: Back to the Fugacity- the Fugacity of A Component of A Gas Mixture

In Chapter 11, we introduce the fugacity as an alternative measure of the difference between the Gibbs free energy of one mole of a pure gas in its hypothetical ideal gas standard state and its Gibbs free energy in any other state at the same temperature. This definition makes the fugacity of a gas an intensive function of pressure and temperature. At a fixed temperature, the state of one mole of a pure gas is specified by its pressure, and the fugacity is a function of pressure only. Fugacity has the units of pressure. Giving effect to our decision to let the fugacity of the gas be unity when the gas is in its hypothetical ideal gas standard state (HIG^o) and using the Gibbs free energy of formation for the gas in this state as the standard Gibbs free energy for fugacity, we define the fugacity of a pure gas, A , by the equation

$$\bar{G}_A(P) = \Delta_f G^o(A, HIG^o) + RT \ln \left[\frac{f_A(P)}{f_A(HIG^o)} \right]$$

For substance A in any system, the chemical potential is the partial molar free energy; that is, $\mu_A(P, T) = \bar{G}_A(P, T)$. Since the Gibbs free energy of formation is defined for one mole of pure substance at a specified pressure and temperature, it is a partial molar quantity. When we elect to use the hypothetical ideal gas at a pressure of one bar as the standard state for the Gibbs free energy of formation of the gas, we also establish the Gibbs free energy of formation of the hypothetical ideal gas in its standard state as the standard-state chemical potential; that is, $\mu_A^o = \Delta_f G^o(A, HIG^o)$. Hence, we can also express the fugacity of a gas by the equation

$$\mu_A(P) = \Delta_f G^o(A, HIG^o) + RT \ln \left[\frac{f_A(P)}{f_A(HIG^o)} \right]$$

or

$$\mu_A(P) = \mu_A^o + RT \ln \left[\frac{f_A(P)}{f_A(HIG^o)} \right]$$

(pure real gas)

For a mixture of real gases, we can extend the definition of fugacity in a natural way. We want the fugacity of a component gas to measure the difference between its chemical potential in the mixture, μ , and its chemical potential in its standard state, μ^o , where its standard state is the pure hypothetical ideal gas at one bar pressure. If gas A is a component of a constant-temperature mixed-gas system, we have $d\mu_A = \bar{V}_A dP$, where \bar{V}_A is the partial molar volume of A in the system, and P is the pressure of the system. Let us find μ_A in a binary mixture that contains one mole of A and n_B moles of a second component, B . Let the partial molar volume of B be \bar{V}_B . The system volume is $V = \bar{V}_A + n_B \bar{V}_B$. The mole fractions of A and B are $x_A = 1/(n_B + 1)$ and $x_B = n_B/(n_B + 1)$.

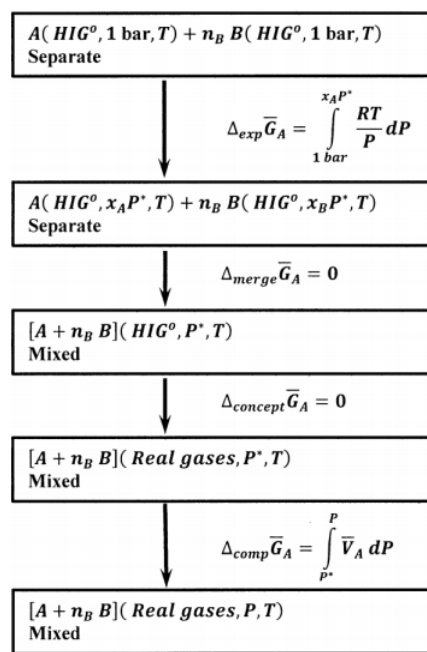


Figure 1. Finding the Gibbs free energy of a real gas in a mixture.

To find the change in μ_A , we need a reversible process that takes one mole of A in its standard state to a mixture of one mole A with n_B moles of B , in which the pressure of the mixture is P . The four-step process described in Figure 1 answers our requirements: One mole of A and n_B moles of B are separately expanded from their hypothetical ideal gas standard states, at P° , to the arbitrary low pressures $x_A P^*$ and $x_B P^*$, respectively. For this expansion, the change in the Gibbs free energy of one mole of A , which remains in its hypothetical ideal gas state, is

$$\Delta_{\text{exp}} \bar{G}_A = \int_{P^\circ}^{x_A P^*} \bar{V}_A dP = \int_{P^\circ}^{x_A P^*} \frac{RT}{P} dP = RT \ln \left(\frac{x_A P^*}{P^\circ} \right)$$

Next, these low-pressure ideal gases are merged to form a mixture of one mole of A with n_B moles of B at the total pressure P^* . For this merging process, $\Delta_{\text{merge}} \bar{G}_A = 0$. Then, we suppose that the ideal gases become real gases in a mixture whose pressure is P^* . Since this is merely a conceptual change, we have $\Delta_{\text{concept}} \bar{G}_A = 0$. Finally, we compress the mixture of real gases from P^* to an arbitrary pressure, P . Since the volume of the mixture is $V = \bar{V}_A + n_B \bar{V}_B$, the Gibbs free energy change for this compression of the mixture is

$$\Delta_{\text{comp}} G_{\text{mixture}} = \int_{P^*}^P V dP = \int_{P^*}^P \bar{V}_A dP + n_B \int_{P^*}^P \bar{V}_B dP$$

We see that the Gibbs free energy change for the real-gas system is the sum of the Gibbs free energy changes for the components; we have

$$\Delta_{\text{comp}} \bar{G}_A = \int_{P^*}^P \bar{V}_A dP$$

For this process, we have

$$\begin{aligned} \mu_A - \mu_A^\circ &= RT \ln \left[\frac{f_A(P)}{f_A(HIG^\circ)} \right] \\ &= \Delta_{\text{exp}} \bar{G}_A + \Delta_{\text{merge}} \bar{G}_A + \Delta_{\text{concept}} \bar{G}_A + \Delta_{\text{comp}} \bar{G}_A \\ &= RT \ln \left[\frac{x_A P^*}{P^\circ} \right] + \int_{P^*}^P \bar{V}_A dP - \int_{P^*}^P \frac{RT}{P} dP + \int_{P^*}^P \frac{RT}{P} dP \end{aligned}$$

where we have added and subtracted the quantity

$$\int_{P^*}^P \frac{RT}{P} dP$$

Dividing by RT and evaluating the last integral, we find

$$\begin{aligned} \frac{\mu_A - \mu_A^o}{RT} &= \ln \left[\frac{f_A(P)}{f_A(HIG^o)} \right] \\ &= \ln x_A + \ln P^* - \ln P^o + \int_{P^*}^P \left(\frac{\bar{V}_A}{RT} - \frac{1}{P} \right) dP + \ln P - \ln P^* \end{aligned}$$

P^* is a finite pressure arbitrarily near zero. At very low pressures, real gas A behaves as an ideal gas; hence, at very low pressures, the partial molar volume of the real gas is well approximated by the partial molar volume of pure gas A . That is, we have $\bar{V}_A \approx \bar{V}_A^*$, and

$$\begin{aligned} \int_0^{P^*} \left(\frac{\bar{V}_A}{RT} - \frac{1}{P} \right) dP &\approx \int_0^{P^*} \left(\frac{\bar{V}_A^*}{RT} - \frac{1}{P} \right) dP \\ &\approx 0 \end{aligned}$$

where the approximation becomes exact in the limit as $P^* \rightarrow 0$. Simplifying the natural logarithm terms and expanding the integral, we obtain

$$\begin{aligned} \frac{\mu_A - \mu_A^o}{RT} &= \ln \left[\frac{f_A(P)}{f_A(HIG^o)} \right] \\ &= \ln \frac{x_A P}{P^o} + \int_0^P \left(\frac{\bar{V}_A}{RT} - \frac{1}{P} \right) dP - \int_0^{P^*} \left(\frac{\bar{V}_A}{RT} - \frac{1}{P} \right) dP \\ &= \ln \frac{x_A P}{P^o} + \int_0^P \left(\frac{\bar{V}_A}{RT} - \frac{1}{P} \right) dP \end{aligned}$$

Defining the fugacity coefficient for A in this mixture, γ_A , by

$$\gamma_A = \frac{f_A(P)}{x_A P}$$

and recalling that $f_A(HIG^o) = P^o$, we use this result to find

$$\ln \gamma_A = \ln \left(\frac{f_A(P)}{x_A P} \right) = \int_0^P \left(\frac{\bar{V}_A}{RT} - \frac{1}{P} \right) dP$$

This differs from the corresponding relationship for the fugacity of a pure gas only in that the partial molar volume is that of gas A in a mixture with other gases. This is a trifling difference in principle, but a major difference in practice. To find the fugacity of pure A , we use the partial molar volume of the pure gas, which is readily calculated from any empirical pure-gas equation of state. However, to experimentally obtain the partial molar volume of gas A in a gas mixture, we must collect pressure–volume–temperature data as a function of the composition of the system. If we contemplate creating a catalog of such data for the mixtures of even a modest number of compounds, we see that an enormous amount of data must be collected. Just the number of systems involving only binary mixtures is large. For N compounds, there are $N(N-1)/2$ binary mixtures—each of which would have to be studied at many compositions in order to develop good values for the partial molar volumes.

Fortunately, practical experience shows that a simple approximation often gives satisfactory results. In this approximation, we assume that the partial molar volume of gas A —present at mole fraction x_A in a system whose pressure is P —is equal to the partial molar volume of the pure gas at the same pressure. That is, for a binary mixture of gases A and B , we assume

$$\bar{V}_A(P, x_A, x_B) = \bar{V}_A^*(P)$$

In this approximation, we have

$$\frac{\mu_A - \mu_A^o}{RT} = \ln \frac{x_A P}{P^o} + \int_0^P \left(\frac{\bar{V}_A^\bullet}{RT} - \frac{1}{P} \right) dP$$

and

$$\ln \gamma_A = \ln \left(\frac{f_A(P)}{x_A P} \right) = \int_0^P \left(\frac{\bar{V}_A^\bullet}{RT} - \frac{1}{P} \right) dP$$

We make the same assumption for gas B . From Euler's theorem on homogeneous functions, we have $\bar{V} = x_A \bar{V}_A + x_B \bar{V}_B$. Therefore, in this approximation, we have

$$\bar{V} = x_A \bar{V}_A + x_B \bar{V}_B \approx x_A \bar{V}_A^\bullet + x_B \bar{V}_B^\bullet$$

The last sum is the Amagat's law representation of the molar volume of the gas mixture. We see that our approximation is equivalent to assuming that the system obeys Amagat's law. Physically, this assumes that the gas mixture is an ideal (gaseous) solution. We discuss ideal solutions in Chapter 16. In an ideal solution, the intermolecular interactions between an A molecule and a B molecule are assumed to have the same effect as the interactions between two A molecules or between two B molecules. This differs from the ideal-gas assumption; there is no effect from the interactions between any two ideal-gas molecules.

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