

15.1: The Chemical Potential and Fugacity of a Gas

The third law and the fugacity of a pure real gas.

In [Chapter 11](#), we introduce the fugacity as a measure of the difference between the molar Gibbs free energy of a real gas, $\bar{G}(P, T)$ at pressure P , and that of the pure gas in its hypothetical ideal-gas standard state at the same temperature. We choose the standard Gibbs free energy of formation, $\Delta_f G^\circ(HIG^\circ, T)$, to be the Gibbs free energy of the real gas in its hypothetical ideal-gas standard state. Letting the gas be A , we find

$$\bar{G}(P, T) = \Delta_f G^\circ(HIG^\circ, T) + RT \ln \left[\frac{f_A^\bullet(P)}{f_A(HIG^\circ)} \right]$$

(real gas)

where the fugacity depends on pressure according to

$$\ln \left[\frac{f_A^\bullet(P)}{f_A(HIG^\circ)} \right] = \ln \left[\frac{P}{P^\circ} \right] + \int_0^P \left[\frac{\bar{V}_A^\bullet}{RT} - \frac{1}{P} \right] dP$$

(real gas)

and \bar{V}_A^\bullet is the molar volume of the pure real gas. (In [Chapter 14](#), we introduce a solid-bullet superscript to indicate that a particular property is that of a pure substance.) Given $\Delta_f G^\circ(HIG^\circ, T)$ and an equation of state for the real gas, we can calculate the fugacity and molar Gibbs free energy of the real gas at any pressure.

The fugacity of a pure ideal gas

For a pure ideal gas, we have

$$\frac{\bar{V}_A^\bullet}{RT} - \frac{1}{P} = 0$$

(ideal gas)

The fugacity becomes equal to the ideal-gas pressure

$$f_A^\bullet(P) = P$$

(ideal gas)

and the Gibbs free energy relationship becomes

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

(ideal gas)

For pure gases, the system pressure that appears in these equations, P , is the same thing as the pressure of the gas.

The fugacity of an ideal gas in a mixture

In [Chapter 13](#), we find that the molar Gibbs free energy of a component of an ideal gas mixture is unaffected by the presence of the other gases. For an ideal gas, A , present at mole fraction x_A , in a system whose pressure is P , the partial pressure is $P_A = x_A P$. Since the partial pressure is the pressure that the system would exhibit if only ideal gas A were present, the molar Gibbs free energy of an ideal gas in a mixture is

$$\bar{G}_A(x_A, P, T) = \Delta_f G^\circ(A, P^\circ, T) + RT \ln \left[\frac{x_A P}{P^\circ} \right]$$

(ideal gas)

The chemical potential and fugacity of real gases

In [Chapter 14](#), we introduce the chemical potential as the partial molar Gibbs free energy. The defining relationship is

$$\mu_A = \bar{G}_A = \left(\frac{\partial G}{\partial n_A} \right)_{P, T, n_{i \neq A}}$$

(any substance in any system)

When the system is a pure substance, the chemical potential is identical to the Gibbs free energy per mole of the pure substance at the same temperature and pressure. For the chemical potential of A in a system comprised of pure A , we can write

$$\mu_A^\bullet = \bar{G}_A^\bullet = \frac{G^\bullet}{n_A} = \frac{dG^\bullet}{dn_A}$$

(any system comprised of pure A)

From Euler's theorem, we find that the Gibbs free energy of any system is the composition-weighted sum of the chemical potentials of the substances present:

$$G = \sum_{i=1}^{\omega} n_i \mu_i$$

For a pure real gas, the partial molar Gibbs free energy and the molar Gibbs free energy are the same thing; we also write

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

(pure real gas A)

and introducing $\mu_A^\circ(T) = \Delta_f G^\circ(A, HIG^\circ, T)$, we write

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

(pure real gas A)

Since μ_A° , $\Delta_f G^\circ(A)$, and $f_A(HIG^\circ)$ are defined to be properties of one mole of pure A , it is not necessary to include either the solid-bullet superscript or the solid over-bar in these symbols.

In [Section 14.11](#), we find that the partial molar Gibbs free energy of a component of a real-gas mixture is

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

(real gas A in a mixture)

where the fugacity of A , present at mole fraction x_A in a system whose pressure is P , is given by

$$RT \ln \left[\frac{f_A(P)}{f_A(HIG^\circ)} \right] = \ln \left[\frac{x_A P}{P^\circ} \right] + \int_0^P \left[\frac{\bar{V}_A}{RT} - \frac{1}{P} \right] dP$$

(real gas A in a mixture)

where $f_A(HIG^\circ) = P^\circ = 1 \text{ bar}$. The partial molar volume is a function of the system's pressure, temperature, and composition; that is,

$$\bar{V}_A(P) = \bar{V}_A(P, T, x_A, x_B, \dots, x_\omega)$$

and the fugacity depends on the same variables,

$$f_A(P) = f_A(P, T, x_A, x_B, \dots, x_\omega)$$

If the system is a mixture of ideal gases,

$$V = (n_A + n_B + \cdots + n_\omega) RT/P$$

and

$$\bar{V}_A = (\partial V / \partial n_A)_{PT, n_{m \neq A}} = RT/P$$

The integrand becomes zero, and the fugacity relationship reduces to the ideal-gas fugacity equation introduced in [Chapter 13](#) and repeated above.

The fugacity of a gas in any system is a measure of the difference between its chemical potential in that system and its chemical potential in its hypothetical ideal-gas standard state at the same temperature. The chemical potential of A in a particular system, μ_A , is the change in the Gibbs free energy when the amounts of the elements that form one mole of A pass from their standard states as elements into the (very large) system as one mole of substance A .

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