CHAPTER IX

FUGACITY AND ACTIVITY

Introduction

It was shown earlier that the molar Gibbs energy of an ideal gas can be obtained by integrating \( dG = V \, dP = RT \, d\ln P \) at constant temperature; the result is

\[
G = G^o(T) + RT \ln P; \quad [G^o(T) = G^o(P = 1, T)]
\]

where \( G \) is a function of both temperature and pressure but \( G^o \) is only a function of temperature at a fixed standard pressure of one bar (one atm in older publications). The value of \( G \) cannot be determined experimentally but \( G - G^o \) can be obtained from \( G - G^o = RT \ln P \). The relationship \( dG = RT \, d\ln P \) is not applicable to real gases, but a purely convenient function called the fugacity, \( f \), was first introduced by G. N. Lewis in 1901 so that for real gases

\[
dG = RT \, d\ln f, \quad \text{(constant \( T \))}
\]

This equation is the formal definition of fugacity. Both \( f \) and \( P \) are expressed in the same units. Integration of (9.2) gives

\[
G(P, T) - G(P_o, T) = RT \ln f - RT \ln P_o
\]

where \( P_o \rightarrow 0 \), or \( P_o \) is sufficiently low in order that \( f \) can be set equal to \( P_o \) as shown by the second term on the right side. Summation of the preceding equation and \( G(P_o, T) = G^o(P = 1, T) + RT \ln P_o \) from (9.1) gives

\[
G(P, T) = G^o(P = 1, T) + RT \ln f
\]

where \( G^o(P = 1, T) \) is the standard Gibbs energy of the same gas as a hypothetically existing ideal gas at one bar. This is evident from \( G^o(P = 1, T) - G(P_o, T) = RT \ln(1/P_o) \), which is the change in \( G \) for compressing the gas from \( P_o \) where it is ideal to 1 bar by assuming that it follows the ideal behavior.

A real gas becomes ideal with decreasing pressure and in the limit \( f \rightarrow P \), when \( P_o = P \rightarrow 0 \), and the state of \( f \rightarrow P \) defines the reference state for the fugacity of a real gas. A term defined by \( \phi = f/P \) for any pressure is called the fugacity coefficient.*

Fugacity of Pure Gases

For a real or ideal gas at constant temperature, \( dG = V \, dP \) where \( V \) is the real or actual molar volume, and from \( dG = V \, dP \) and (9.2),

\[
RT \, d \ln f = V \, dP, \quad \text{(constant } T) \tag{9.4}
\]

Integration of the right side requires an equation of state from which \( V \) can be expressed as a function of pressure. For this purpose, the virial equation of state, first proposed by Kammerlingh Onnes (1901) is useful. The virial equation in terms of pressure is

\[
Z = PV/RT = 1 + (B_2/RT)P + \left[ \left( \frac{B_3 - B_2^2}{R^2T^2} \right) P^2 \right] \tag{9.5}
\]

[cf. (3.52a)]. \( B_2 \) and \( B_3 \) are functions of \( T \) only. \( (B_1 = RT) \). Substitution of \( V \) from (9.5) into \( RT \, d \ln f = V \, dP \) gives

\[
RT \, d \ln f - RT \, d \ln P = B_2 \, dP + \left[ \left( \frac{B_3 - B_2^2}{RT} \right) P \, dP \right]
\]

Integration of the left side from \( P_o = P \to 0 \) to \( P \) gives \( RT \ln(f/P) - RT \ln(f_o/P_o) \), because, at \( P_o \), \( (f_o/P_o) \) is unity; hence,

\[
RT \ln f = RT \ln P + B_2P + 0.5 \left( B_3 - B_2^2 \right) P^2/RT \tag{9.6}
\]

The virial coefficients \( B_2, B_3, \ldots \) are related to the interactions in clusters of 2, 3, \ldots molecules respectively as signified by the subscripts. At about 50 bars of pressure at ordinary temperatures, or when the deviation from ideality is on the order of 2 percent, the terms beyond \( B_2P \) may be neglected, and then (9.6) becomes

\[
RT \ln f = RT \ln P + B_2P \tag{9.7}
\]

Combination of (9.7) with (9.3) gives

\[
G(P, T) = G^\circ(T) + RT \ln P + B_2P \tag{9.8}
\]

The second virial coefficient \( B_2 \), whose dimensions are volume per mole varies with temperature according to the empirical equation

\[
B_2 = B_o - \frac{\alpha}{T} - (\beta/T^2) \tag{9.9}
\]

where \( B_o, \alpha, \) and \( \beta \) are purely empirical constants. When \( P \) is in bars then \( B_2 \) has to be in \( 10 \times \text{cm}^3 \). Thus, for Ar and N\(_2\), we have

\[
B_2 = 357.3 - \frac{128,500}{T} - \frac{7.55 \times 10^6}{T^2}; \quad \text{(Ar)} \tag{9.9a}
\]

\[
B_2 = 423.8 - \frac{108,900}{T} - \frac{9.25 \times 10^6}{T^2}; \quad \text{(N\(_2\))} \tag{9.9b}
\]

Equation (9.9b) yields 324.27 K for the Boyle temperature, at which \( B_2 \) is zero, and within the validity of this equation, usually a few bars, \( PV = RT \text{(Boyle)} \).