

## 13.1: The Gibbs Free Energy of an Ideal Gas

In Chapter 11, we find a general equation for the molar Gibbs free energy of a pure gas. We adopt the Gibbs free energy of formation of the hypothetical ideal gas, in its standard state at 1 bar,  $P^\circ$ , as the reference state for the Gibbs free energy of the gas at other pressures and the same temperature. Then, the molar Gibbs free energy of pure gas  $A$ , at pressure  $P$ , is

$$\bar{G}_A(P) = \Delta_f G^\circ(A, HIG^\circ) + RT \ln\left(\frac{P}{P^\circ}\right) + RT \int_0^P \left(\frac{\bar{V}}{RT} - \frac{1}{P}\right) dP$$

(any pure gas)

$\bar{G}_A(P)$  is the difference between the Gibbs free energy of the gas at pressure  $P$  and that of its constituent elements at 1 bar and the same temperature. If gas  $A$  is an ideal gas, the integral is zero, and the standard-state Gibbs free energy of formation is that of an “actual” ideal gas, not a “hypothetical state” of a real gas. To recognize this distinction, let us write  $\Delta_f G^\circ(A, P^\circ)$ , rather than  $\Delta_f G^\circ(A, HIG^\circ)$ , when the gas behaves ideally. In a mixture of ideal gases, the partial pressure of gas  $A$  is given by  $P_A = x_A P$ , where  $x_A$  is the mole fraction of  $A$  and  $P$  is the pressure of the mixture. In §3, we find that the Gibbs free energy of one mole of pure ideal gas  $A$  at pressure  $P_A$  has the same Gibbs free energy as one mole of gas  $A$  in a gaseous mixture in which the partial pressure of  $A$  is  $P_A = x_A P$ . Recognizing these properties of an ideal gas, we can express the molar Gibbs free energy of an ideal gas—pure or in a mixture—as

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

(ideal gas)

Note that we can obtain this result for pure gas  $A$  directly from  $\left(\partial \bar{G} / \partial P\right)_T = \bar{V} = RT/P$  by evaluating the definite integrals

$$\int_{\Delta_f G^\circ(A, P^\circ)}^{\bar{G}_A(P_A)} d\bar{G} = \int_{P^\circ}^{P_A} \frac{RT}{P} dP$$

Including the constant,  $P^\circ$ , in these relationships is a useful reminder that  $RT \ln(P_A/P^\circ)$  represents a Gibbs free energy difference. Including  $P^\circ$  makes the argument of the natural-log function dimensionless; if we express  $P$  in bars, including  $P^\circ = 1$  bar leaves the numerical value of the argument unchanged. If we express  $P$  in other units,  $P^\circ$  becomes the conversion factor for converting those units to bars; if we express  $P$  in atmospheres, we have  $P^\circ = 1 \text{ bar} = 0.986923 \text{ atm}$ .

However, including the “ $P^\circ$ ” is frequently a typographical nuisance. Therefore, let us introduce another bit of notation; we use a lower-case “ $p$ ” to denote the ratio “ $P/P^\circ$ ”. That is,  $p_A$  is a dimensionless quantity whose numerical value is that of the partial pressure of  $A$ , expressed in bars. The molar Gibbs free energy becomes

$$\bar{G}_A(P_A) = \Delta_f G^\circ(A, P^\circ) + RT \ln p_A$$

(ideal gas)

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