7.9: Standard Molar Quantities of a Gas

A **standard molar quantity** of a substance is the molar quantity in the standard state at the temperature of interest. We have seen (Sec. 7.7) that the standard state of a pure *liquid* or *solid* is a real state, so any standard molar quantity of a pure liquid or solid is simply the molar quantity evaluated at the standard pressure and the temperature of interest.

The standard state of a *gas*, however, is a hypothetical state in which the gas behaves ideally at the standard pressure without influence of intermolecular forces. The properties of the gas in this standard state are those of an ideal gas. We would like to be able to relate molar properties of the real gas at a given temperature and pressure to the molar properties in the standard state at the same temperature.

We begin by using Eq. 7.8.7 to write an expression for the chemical potential of the real gas at pressure p':

$$\mu(p') = \mu°(g) + RT \ln \frac{f(p')}{p°} = \mu°(g) + RT \ln \frac{p'}{p°} + RT \ln \frac{f(p')}{p'} \tag{7.9.1}$$

We then substitute from Eq. 7.8.14 to obtain a relation between the chemical potential, the standard chemical potential, and measurable properties, all at the same temperature:

$$\mu(p') = \mu°(g) + RT \ln \frac{p'}{p°} + \int_0^{p'} \left(V_m - \frac{RT}{p} \right) dp \tag{7.9.2}$$
$$\text{(pure gas)}$$

Note that this expression for μ is not what we would obtain by simply integrating $d\mu = V_m\, dp$ from $p°$ to p', because the real gas is not necessarily in its standard state of ideal-gas behavior at a pressure of 1 bar.

Recall that the chemical potential μ of a pure substance is also its molar Gibbs energy $G_m = G/n$. The standard chemical potential $\mu°(g)$ of the gas is the standard molar Gibbs energy, $G_m°(g)$. Therefore Eq. 7.9.2 can be rewritten in the form

$$G_m(p') = G_m°(g) + RT \ln \frac{p'}{p°} + \int_0^{p'} \left(V_m - \frac{RT}{p} \right) dp \tag{7.9.3}$$

The middle column of Table 7.5 contains an expression for $G_m(p') - G_m°(g)$ taken from this equation. This expression contains all the information needed to find a relation between any other molar property and its standard molar value in terms of measurable properties. The way this can be done is as follows.

The relation between the chemical potential of a pure substance and its molar entropy is given by Eq. 7.8.3:

$$S_m = -\left(\frac{\partial \mu}{\partial T} \right)_p \tag{7.9.4}$$

The standard molar entropy of the gas is found from Eq. 7.9.4 by changing μ to $\mu°(g)$:

$$S_m°(g) = -\left(\frac{\partial \mu°(g)}{\partial T} \right)_p \tag{7.9.5}$$

By substituting the expression for μ given by Eq. 7.9.2 into Eq. 7.9.4 and comparing the result with Eq. 7.9.5, we obtain

$$S_m(p') = S_m°(g) - R \ln \frac{p'}{p°} - \int_0^{p'} \left[\left(\frac{\partial V_m}{\partial T} \right)_p - \frac{R}{p} \right] dp \tag{7.9.6}$$

The expression for $S_m - S_m°(g)$ in the middle column of Table 7.5 comes from this equation. The equation, together with a value of S_m for a real gas obtained by the calorimetric method described in Sec. 6.2.1, can be used to evaluate $S_m°(g)$.

Now we can use the expressions for G_m and S_m to find expressions for molar quantities such as H_m and $C_{p,m}$ relative to the respective standard molar quantities. The general procedure for a molar quantity X_m is to write an expression for X_m as a function of G_m and S_m and an analogous expression for $X_m°(g)$ as a function of $G_m°(g)$ and $S_m°(g)$. Substitutions for G_m and S_m from Eqs. 7.9.3 and 7.9.6 are then made in the expression for X_m, and the difference $X_m - X_m°(g)$ taken.

For example, the expression for $U_m - U_m°(g)$ in the middle column Table 7.5 was derived as follows. The equation defining the Gibbs energy, $G = U - TS + pV$, was divided by the amount n and rearranged to

$$U_{\mathrm{m}} = G_{\mathrm{m}} + TS_{\mathrm{m}} - pV_{\mathrm{m}} \tag{7.9.7}$$

The standard-state version of this relation is

$$U_{\mathrm{m}}^{\circ}(\mathrm{g}) = G_{\mathrm{m}}^{\circ}(\mathrm{g}) + TS_{\mathrm{m}}^{\circ}(\mathrm{g}) - p^{\circ}V_{\mathrm{m}}^{\circ}(\mathrm{g}) \tag{7.9.8}$$

where from the ideal gas law $p^{\circ}V_{\mathrm{m}}^{\circ}(\mathrm{g})$ can be replaced by RT. Substitutions from Eqs. 7.9.3 and 7.9.6 were made in Eq. 7.9.7 and the expression for $U_{\mathrm{m}}^{\circ}(\mathrm{g})$ in Eq. 7.9.8 was subtracted, resulting in the expression in the table.

For a real gas at low to moderate pressures, we can approximate V_{m} by $(RT/p) + B$ where B is the second virial coefficient (Eq. 7.8.17). Equation 7.9.2 then becomes

$$\mu \approx \mu^{\circ}(\mathrm{g}) + RT \ln \frac{p}{p^{\circ}} + Bp \tag{7.9.9}$$

The expressions in the last column of Table 7.5 use this equation of state. We can see what the expressions look like if the gas is ideal simply by setting B equal to zero. They show that when the pressure of an ideal gas increases at constant temperature, G_{m} and A_{m} increase, S_{m} decreases, and U_{m}, H_{m}, and $C_{p,\mathrm{m}}$ are unaffected.