5.12 USING THE FACT THAT S IS A STATE FUNCTION TO DETERMINE THE DEPENDENCE OF S ON V AND T

Section 5.4 showed how the entropy varies with P, V, and T for an ideal gas. In this section, we derive general equations for the dependence of S on V and T that can be applied to solids, liquids, and real gases. We do so by using the property that dS is an exact differential. A similar analysis of S as a function of P and T is carried out in Section 5.13. Consider Equation (5.30), rewritten in the form

$$dS = \frac{1}{T} dU + \frac{P}{T} dV \qquad (5.54)$$

Because $1/T$ and P/T are greater than zero, the entropy of a system increases with the internal energy at constant volume, and increases with the volume at constant internal energy. However, because internal energy is not generally a variable under experimental control, it is more useful to obtain equations for the dependence of dS on V and T.

We first write the total differential dS in terms of the partial derivatives with respect to V and T:

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \qquad (5.55)$$

To evaluate $(\partial S/\partial T)_V$ and $(\partial S/\partial V)_T$, Equation (5.54) for dS is rewritten in the form

$$dS = \frac{1}{T}\left[C_V\, dT + \left(\frac{\partial U}{\partial V}\right)_T dV\right] + \frac{P}{T} dV = \frac{C_V}{T} dT + \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV \qquad (5.56)$$

Equating the coefficients of dT and dV in Equations (5.55) and (5.56),

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \qquad (5.57)$$

The temperature dependence of entropy at constant volume can be calculated straightforwardly using the first equality in Equation (5.57):

$$dS = \frac{C_V}{T} dT, \text{ constant } V \qquad (5.58)$$

The expression for $(\partial S/\partial V)_T$ in Equation (5.57) is not in a form that allows for a direct comparison with experiment to be made. To develop a more useful relation, the property is used (see Section 3.1) that because dS is an exact differential, then

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T\right)_V = \left(\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_V\right)_T \qquad (5.59)$$

Taking the mixed second derivatives of the expressions in Equation (5.57),

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_V\right)_T = \frac{1}{T}\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right)_T$$

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T\right)_V = \frac{1}{T}\left[\left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V\right] - \frac{1}{T^2}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \qquad (5.60)$$

Substituting the expressions for the mixed second derivatives in Equation 5.60 into Equation 5.59, canceling the double mixed derivative of U that appears on both sides of the equation, and simplifying the result, the following equation is obtained:

$$P + \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V \qquad (5.61)$$

This equation provides the expression for $(\partial U/\partial V)_T$ that was used without a derivation in Section 3.2. It provides a way to calculate the internal pressure of the system if the equation of state for the substance is known.

Comparing the result in Equation (5.61) with the second equality in Equation (5.57), a practical equation is obtained for the dependence of entropy on volume under constant temperature conditions:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T} = \frac{\beta}{\kappa} \qquad (5.62)$$

where β is the coefficient for thermal expansion at constant pressure, and κ is the isothermal compressibility coefficient. Both of these quantities are readily obtained from experiments. In simplifying this expression, the cyclic rule for partial derivatives, Equation (3.7), has been used.

The result of these considerations is that dS can be expressed in terms of dT and dV as

$$dS = \frac{C_V}{T} dT + \frac{\beta}{\kappa} dV \qquad (5.63)$$

Integrating both sides of this equation along a reversible path,

$$\Delta S = \int_{T_i}^{T_f} \frac{C_V}{T} dT + \int_{V_i}^{V_f} \frac{\beta}{\kappa} dV \qquad (5.64)$$

This result applies to a single-phase system of a liquid, solid, or gas that undergoes a transformation from the initial result T_i, V_i to T_f, V_f, provided that no phase changes or chemical reactions occur in the system.

5.13 THE DEPENDENCE OF S ON T AND P

Because chemical transformations are normally carried out at constant pressure rather than constant volume, we need to know how S varies with T and P. The total differential dS is written in the form

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \tag{5.65}$$

Starting from the relation $U = H - PV$, we write the total differential dU as

$$dU = T\,dS - P\,dV = dH - P\,dV - V\,dP \tag{5.66}$$

This equation can be rearranged to give an expression for dS:

$$dS = \frac{1}{T}dH - \frac{V}{T}dP \tag{5.67}$$

The previous equation is analogous to Equation (5.54), but contains the variables H and P rather than U and V.

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = C_P\,dT + \left(\frac{\partial H}{\partial P}\right)_T dP \tag{5.68}$$

Substituting this expression for dH into Equation (5.67),

$$dS = \frac{C_P}{T}dT + \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]dP = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \tag{5.69}$$

Because the coefficients of dT and dP must be the same on both sides of Equation (5.69),

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] \tag{5.70}$$

The ratio C_P/T is positive for all substances, allowing one to conclude that S is a monotonically increasing function of the temperature.

Just as for $(\partial S/\partial V)_T$ in Section 5.12, the expression for $(\partial S/\partial P)_T$ is not in a form that allows a direct comparison with experimental measurements to be made. Just as in our evaluation of $(\partial S/\partial V)_T$, we equate the mixed second partial derivatives of S with respect to T and P:

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial P}\right)_T\right)_P = \left(\frac{\partial}{\partial P}\left(\frac{\partial S}{\partial T}\right)_P\right)_T \tag{5.71}$$

These mixed partial derivatives can be evaluated using Equation (5.70):

$$\left(\frac{\partial}{\partial P}\left(\frac{\partial S}{\partial T}\right)_P\right)_T = \frac{1}{T}\left(\frac{\partial C_P}{\partial P}\right)_T = \frac{1}{T}\left(\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial T}\right)_P\right)_T \tag{5.72}$$

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial P}\right)_T\right)_P = \frac{1}{T}\left[\left(\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right)_T\right)_P - \left(\frac{\partial V}{\partial T}\right)_P\right] - \frac{1}{T^2}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] \tag{5.73}$$

Equating Equations 5.72 and 5.73,

$$\frac{1}{T}\left(\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right)_T\right)_P = \frac{1}{T}\left[\left(\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right)_T\right)_P - \left(\frac{\partial V}{\partial T}\right)_P\right] - \frac{1}{T^2}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] \tag{5.74}$$

Simplifying this equation results in

$$\left(\frac{\partial H}{\partial P}\right)_T - V = -T\left(\frac{\partial V}{\partial T}\right)_P \tag{5.75}$$

Using this result and Equation 5.70, the pressure dependence of the entropy at constant temperature can be written in a form that easily allows an experimental determination of this quantity to be made:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -V\beta \tag{5.76}$$

Using these results, the total differential dS can be written in terms of experimentally accessible parameters as

$$dS = \frac{C_P}{T}dT - V\beta\,dP \tag{5.77}$$

Integrating both sides of this equation along a reversible path,

$$\Delta S = \int_{T_i}^{T_f}\frac{C_P}{T}dT - \int_{P_i}^{P_f}V\beta\,dP \tag{5.78}$$

This result applies to a single-phase system of a pure liquid, solid, or gas that undergoes a transformation from the initial result T_iP_i to T_f, P_f, provided that no phase changes or chemical reactions occur in the system.