10.9: The Relationship Between Cv and Cp for Any Substance

In Chapter 7, we derive the relationship between C_P and C_V for an ideal gas. It is useful to have a relationship between these quantities that is valid for any substance. We can derive this relationship from the equations for dS that we develop in Sections 10.4 and 10.5. If we apply the divide-through rule to dS expressed as a function of dT and dV, at constant pressure, we have

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_V}{T} + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

From dS expressed as a function of T and P,

$$dS = \frac{C_P}{T}dT + \left(\frac{\partial V}{\partial T}\right)_P dP$$

we have

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

so that

$$\frac{C_P}{T} = \frac{C_V}{T} + \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

and

$$C_P + C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \tag{10.9.1}$$

For an ideal gas, the right side of Equation 10.9.1 reduces to R, in agreement with our previous result. Note also that, for any substance, C_P and C_V become equal when the temperature goes to zero.

The partial derivatives on the right hand side can be related to the coefficients of thermal expansion, α, and isothermal compressibility, β. Using

$$\frac{\alpha}{\beta} = \left(\frac{\partial P}{\partial T}\right)_V$$

we can write the relationship between C_P and C_V as

$$C_P + C_V = \frac{VT\alpha^2}{\beta}$$