minus

Here we identify the multiplier of dT as the constant-volume heat capacity, that is,

$$C_V^{\text{ig}} = C_P^{\text{ig}} + R. \qquad [3.35]$$

Thus we have recovered all the results obtained previously by independent methods. The ideal-gas properties are summarized in Table 5-2.

5.6 Incompressible Phases

The effect of pressure on enthalpy and entropy is described by the dP term in eqs. (5.37) and (5.40). The partial derivative that appears in this term can be expressed in terms of the coefficient of thermal expansion as follows,

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \Rightarrow \quad \left(\frac{\partial V}{\partial T}\right)_P = \beta V.$$

With this result, the equations for enthalpy and entropy become

$$dH = C_P\,dT + V(1-\beta T)\,dP \qquad (5.29)$$

$$dS = C_P\frac{dT}{T} - \beta V dP. \qquad (5.30)$$

For condensed phases (solids, liquids away from the critical point), both β and V are small. Accordingly, the contribution of the terms $V(1-\beta T)dP$ and $-\beta V dP$ to the enthalpy and entropy is generally negligible when compared to the contribution of the temperature term. This is the reason that we often take the enthalpy and entropy of compressed liquids to be independent of pressure. This accuracy of this approximation is tested in the example below.

Example 5.6: Effect of Pressure and Temperature on the Enthalpy and Entropy of Liquid

The volume-temperature relationship for liquid acetone is (see *Perry's Chemical Engineers' Handbook*, 7th ed., p. 2-131)

$$V = V_0\left(1 + a_1 t + a_2 t^2 + a_3 t^3\right),$$

where $V_0 = 1.228 \times 10^{-3}$ m^3/kg, V is the volume at temperature t (in °C), and the parameters a_1, a_2, a_3, are

$$a_1 = 1.3240 \times 10^{-3}, \quad a_2 = 3.8090 \times 10^{-6}, \quad a_3 = -0.87983 \times 10^{-8}.$$

Determine the sensitivity of enthalpy and entropy to pressure by calculating the partial derivatives,

$$\left(\frac{\partial H}{\partial P}\right)_T \quad \text{and} \quad \left(\frac{\partial S}{\partial P}\right)_T.$$