We have

$$C_{P,\mathrm{m}} \equiv C_P/n \qquad \text{pure substance} \tag{2.54}^*$$

$$c_P \equiv C_P/m \qquad \text{one-phase system} \tag{2.55}^*$$

$C_{P,\mathrm{m}}$ and c_P are functions of T and P. Figure 2.5 plots some data for $H_2O(g)$. These curves are discussed in Sec. 8.5.

One can prove from the laws of thermodynamics that C_P and C_V must both be positive. (See *Münster*, sec. 40.)

$$C_P > 0, \qquad C_V > 0 \tag{2.56}$$

What is the relation between C_P and C_V? We have

$$C_P - C_V = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial (U + PV)}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

$$C_P - C_V = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V \tag{2.57}$$

We expect $(\partial U/\partial T)_P$ and $(\partial U/\partial T)_V$ in (2.57) to be related to each other. In $(\partial U/\partial T)_V$, the internal energy is taken as a function of T and V; $U = U(T, V)$. The total differential of $U(T, V)$ is [Eq. (1.30)]

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{2.58}$$

Equation (2.58) is valid for any infinitesimal process, but since we want to relate $(\partial U/\partial T)_V$ to $(\partial U/\partial T)_P$, we impose the restriction of constant P on (2.58) to give

$$dU_P = \left(\frac{\partial U}{\partial T}\right)_V dT_P + \left(\frac{\partial U}{\partial V}\right)_T dV_P$$

where the P subscripts indicate that the infinitesimal changes dU, dT, and dV occur at constant P. Division by dT_P gives

$$\frac{dU_P}{dT_P} = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \frac{dV_P}{dT_P}$$

The ratio of infinitesimals dU_P/dT_P is the partial derivative $(\partial U/\partial T)_P$, so

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \tag{2.59}$$

Substitution of (2.59) into (2.57) gives the desired relation:

$$C_P - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P \tag{2.60}$$

What is the physical reason for the fact that $C_P \neq C_V$? The definitions $C_P = dq_P/dT$ and $C_V = dq_V/dT$ show that the origin of the difference lies in the difference between dq_P and dq_V, the heats added at constant pressure and at constant volume. The first law $dU = dq + dw$ gives $dq = dU - dw = dU + P\,dV$ for a closed system with only P-V work. It follows that $dq_P = dU_P + P\,dV_P$ and $dq_V = dU_V$, where the subscripts indicate constant P or V. Therefore,

$$dq_P - dq_V = dU_P - dU_V + P\,dV_P \tag{2.61}$$

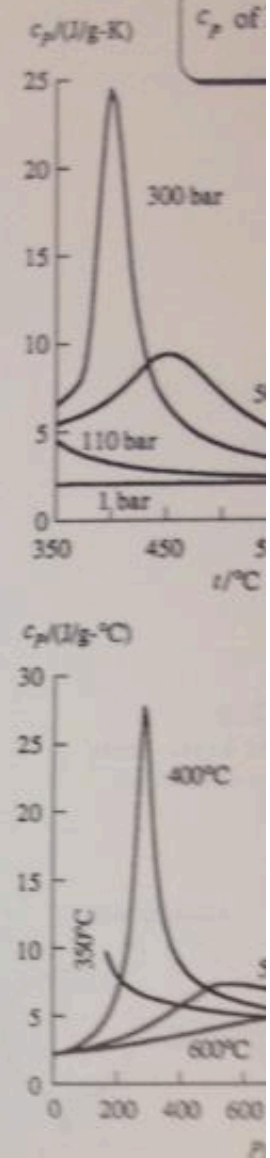

FIGURE 2.5
Specific heat of H_2O(g versus T and versus P.