10.10: The Dependence of Cv on Volume and of Cp on Pressure

The heat capacities of a substance increase with temperature. The rate of increase decreases as the temperature increases. To achieve adequate accuracy in calculations, we often need to know how heat capacities depend on temperature. In contrast, the dependence of heat capacities on pressure and volume is usually negligible; that is, the dependence of C_V on V and the dependence of C_P on P can usually be ignored. Nevertheless, we need to know how to find them.

An exact equation for the dependence of C_V on V follows readily from dS expressed as a function of dT and dV

$$dS=\frac{C_V}{T}dT+\left(\frac{\partial P}{\partial T}\right)_VdV$$

Since the mixed second-partial derivatives must be equal, we have

$$\left[\frac{\partial}{\partial V}\left(\frac{C_V}{T}\right)\right]_T=\left[\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial T}\right)_V\right]_V$$

and thus

$$\left(\frac{\partial C_V}{\partial V}\right)_T=T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

Similarly, the dependence of C_P on P follows from dS expressed as a function of dT and dP,

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

Equating the mixed second-partial derivatives, we have

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

and thus

$$\left(\frac{\partial C_P}{\partial P}\right)_T=-T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

For an ideal gas, it follows that C_V is independent of V, and C_P is independent of P.

When we use the coefficient of thermal expansion to describe the variation of volume with temperature, we have

$$\left(\frac{\partial V}{\partial T}\right)_P=\alpha V$$

When it is adequate to approximate α as a constant, another partial differentiation with respect to temperature gives

$$\left(\frac{\partial C_P}{\partial P}\right)_T=-T\left(\frac{\partial\left(\alpha V\right)}{\partial T}\right)_P=-\alpha^2TV$$

Since α is normally small, this result predicts weak dependence of C_P on P. If α and β are both adequately approximated as constants, we have from

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

that

$$\left(\frac{\partial C_V}{\partial V}\right)_T=T\left(\frac{\partial\left(\alpha/\beta\right)}{\partial T}\right)_V=0$$