Introduction to Physical Chemistry – Lecture 7 Supplement: Computing $C_P - C_V$ For Any Material

Earlier in the course, we showed that, for an ideal gas, $C_P - C_V = nR$, or equivalently, that $\bar{C}_P - \bar{C}_V = R$. We can use the Maxwell relations to compute the general expression for $C_P - C_V$.

Beginning with a process at constant volume, so $dV = 0$, the First Law reads, $dU = \delta Q = C_V dT = TdS$, so that,

$$C_V = T(\frac{\partial S}{\partial T})_V \tag{1}$$

Now, we have,

$$dH = TdS + VdP \tag{2}$$

If we regard S as a function of T and V, then,

$$dS = (\frac{\partial S}{\partial T})_V dT + (\frac{\partial S}{\partial V})_T dV \tag{3}$$

If we regard P as a function of T and V, then,

$$dP = (\frac{\partial P}{\partial T})_V dT + (\frac{\partial P}{\partial V})_T dV \tag{4}$$

From Lecture 7, we have,

$$(\frac{\partial P}{\partial T})_V = (\frac{\partial S}{\partial V})_T = \frac{\alpha}{\kappa} \tag{5}$$

and

$$(\frac{\partial P}{\partial V})_T = 1/(\frac{\partial V}{\partial P})_T = -\frac{1}{V\kappa} \tag{6}$$

Putting everything together gives,

$$\begin{aligned} dH &= (T(\frac{\partial S}{\partial T})_V + V(\frac{\partial P}{\partial T})_V)dT + (T(\frac{\partial S}{\partial V})_T + V(\frac{\partial P}{\partial V})_T)dV \\ &= (C_V + V\frac{\alpha}{\kappa})dT + (T\frac{\alpha}{\kappa} - \frac{1}{\kappa})dV \end{aligned} \tag{7}$$

If we regard V as a function of T and P, then,

$$\begin{aligned} dV &= (\frac{\partial V}{\partial T})_P dT + (\frac{\partial V}{\partial P})_T dP \\ &= V\alpha dT - V\kappa dP \end{aligned} \tag{8}$$

Therefore,

$$\begin{aligned} dH &= (C_V + V\frac{\alpha}{\kappa} + V\alpha(T\frac{\alpha}{\kappa} - \frac{1}{\kappa}))dT - V\kappa(T\frac{\alpha}{\kappa} - \frac{1}{\kappa})dP \\ &= (C_V + V\frac{\alpha}{\kappa} + TV\frac{\alpha^2}{\kappa} - V\frac{\alpha}{\kappa})dT - V(T\alpha - 1)dP \\ &= (C_V + TV\frac{\alpha^2}{\kappa})dT - V(T\alpha - 1)dP \end{aligned} \tag{9}$$

and so,

$$C_P = (\frac{\partial H}{\partial T})_P = C_V + TV\frac{\alpha^2}{\kappa} \tag{10}$$

which gives, finally,

$$C_P - C_V = TV\frac{\alpha^2}{\kappa} \tag{11}$$

or equivalently,

$$\bar{C}_P - \bar{C}_V = C_{P,m} - C_{V,m} = T\bar{V}\frac{\alpha^2}{\kappa} = TV_m\frac{\alpha^2}{\kappa} \tag{12}$$

For an ideal gas, $\alpha = 1/T$, $\kappa = 1/P$, so $\bar{C}_P - \bar{C}_V = P\bar{V}/T = R$.