

3.5 HOW ARE C_P AND C_V RELATED?

To this point, two separate heat capacities, C_P and C_V , have been defined. Are these quantities related? To answer this question, the differential form of the first law is written as

$$\delta q = C_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV + P_{\text{external}} dV \quad (3.35)$$

Consider a process that proceeds at constant pressure for which $P = P_{\text{external}}$. In this case, Equation (3.35) becomes

$$\delta q_P = C_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV + P dV \quad (3.36)$$

Because $\delta q_P = C_P dT$,

$$\begin{aligned} C_P &= C_V + \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \\ &= C_V + \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] \left(\frac{\partial V}{\partial T} \right)_P = C_V + T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P \end{aligned} \quad (3.37)$$

To obtain Equation (3.37), both sides of Equation (3.36) have been divided by dT , and the ratio dV/dT has been converted to a partial derivative at constant P . Equation 3.19 has been used in the last step. Using Equation (3.9) and the cyclic rule, one can simplify Equation (3.37) to

$$\begin{aligned} C_P &= C_V + T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P = C_V - T \frac{\left(\frac{\partial V}{\partial T} \right)_P^2}{\left(\frac{\partial P}{\partial V} \right)_T} \\ C_P &= C_V + TV \frac{\beta^2}{\kappa} \quad \text{or} \quad C_{P,m} = C_{V,m} + TV_m \frac{\beta^2}{\kappa} \end{aligned} \quad (3.38)$$

Equation (3.38) provides another example of the usefulness of the formal theory of thermodynamics in linking seemingly abstract partial derivatives with experimentally available data. The difference between $C_{P,m}$ and $C_{V,m}$ can be determined at a given temperature knowing only the molar volume, the coefficient for thermal expansion, and the isothermal compressibility.

Equation (3.38) is next applied to ideal and real gases as well as for liquids and solids, in the absence of phase changes and chemical reactions. Because β and κ are always positive for real and ideal gases, $C_P - C_V > 0$ for these substances. First, $C_P - C_V$ is calculated for an ideal gas, and then it is calculated for liquids and solids. For an ideal gas, $(\partial U/\partial V)_T = 0$ as shown in Example Problem 3.3, and $T(\partial P/\partial T)_V(\partial V/\partial T)_P = T(nR/V)(nR/P) = nR$ so that Equation (3.37) becomes

$$C_P - C_V = nR \quad (3.39)$$

This result was stated without derivation in Section 2.4. The partial derivative $(\partial V/\partial T)_P = V\beta$ is much smaller for liquids and solids than for gases. Therefore, generally

$$C_V \gg \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] \left(\frac{\partial V}{\partial T} \right)_P \quad (3.40)$$

so that $C_P \approx C_V$ for a liquid or a solid. As shown earlier in Example Problem 3.2, it is not feasible to carry out heating experiments for liquids and solids at constant volume because of the large pressure increase that occurs. Therefore, tabulated heat capacities for liquids and solids list $C_{P,m}$ rather than $C_{V,m}$.

3.6 THE VARIATION OF ENTHALPY WITH PRESSURE AT CONSTANT TEMPERATURE

In the previous section, we learned how H changes with T at constant P . To calculate how H changes as both P and T change, $(\partial H/\partial P)_T$ must be calculated. The partial derivative $(\partial H/\partial P)_T$ is less straightforward to determine in an experiment than $(\partial H/\partial T)_P$. As will be seen, for many processes involving changes in both P and T , $(\partial H/\partial T)_P dT \gg (\partial H/\partial P)_T dP$ and the pressure dependence of H can be neglected relative to its temperature dependence. However, the knowledge that $(\partial H/\partial P)_T$ is not zero is essential for understanding the operation of a refrigerator and the liquefaction of gases. The following discussion is applicable to gases, liquids, and solids.

Given the definition $H = U + PV$, we begin by writing dH as

$$dH = dU + P dV + V dP \quad (3.41)$$

Substituting the differential forms of dU and dH ,

$$\begin{aligned} C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP &= C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + P dV + V dP \\ &= C_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV + V dP \end{aligned} \quad (3.42)$$

For isothermal processes, $dT = 0$, and Equation (3.42) can be divided by dP and rearranged to

$$\left(\frac{\partial H}{\partial P}\right)_T = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \left(\frac{\partial V}{\partial P}\right)_T + V \quad (3.43)$$

Using Equation (3.19) for $(\partial U/\partial V)_T$,

$$\begin{aligned} \left(\frac{\partial H}{\partial P}\right)_T &= T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T + V \\ &= V - T \left(\frac{\partial V}{\partial T}\right)_P = V(1 - T\beta) \end{aligned} \quad (3.44)$$

The second formulation of Equation (3.44) is obtained through application of the cyclic rule [Equation (3.7)]. This equation is applicable to all systems containing pure substances or mixtures at a fixed composition, provided that no phase changes or chemical reactions take place. The quantity $(\partial H/\partial P)_T$ is evaluated for an ideal gas in Example Problem 3.8.

EXAMPLE PROBLEM 3.8

Evaluate $(\partial H/\partial P)_T$ for an ideal gas.

Solution

$(\partial P/\partial T)_V = (\partial[nRT/V]/\partial T)_V = nR/V$ and $(\partial V/\partial P)_T = (d[nRT/P]/dP)_T = -nRT/P^2$ for an ideal gas. Therefore,

$$\left(\frac{\partial H}{\partial P}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T + V = T \frac{nR}{V} \left(-\frac{nRT}{P^2}\right) + V = -\frac{nRT}{P} \frac{nRT}{nRT} + V = 0$$

This result could have been derived directly from the definition $H = U + PV$. For an ideal gas, $U = U(T)$ only and $PV = nRT$. Therefore, $H = H(T)$ only for an ideal gas and $(\partial H/\partial P)_T = 0$.

Because Example Problem 3.8 shows that H is a function of T only for an ideal gas,

$$\Delta H = \int_{T_i}^{T_f} C_P(T) dT = n \int_{T_i}^{T_f} C_{P,m}(T) dT \quad (3.45)$$

for an ideal gas. Because H is a function of T only, Equation (3.45) holds for an ideal gas even if P is not constant. This result is also understandable in terms of the potential function of Figure 1.7. Because ideal gas molecules do not attract or repel one another, no energy is required to change their average distance of separation (increase or decrease P).

Equation (3.44) is next applied to several types of systems. We have seen that $(\partial H/\partial P)_T = 0$ for an ideal gas. For liquids and solids, $1 \gg T\beta$ for $T < 1000$ K as can be seen from the data in Table 3.1. Therefore, for liquids and solids, $(\partial H/\partial P)_T \approx V$ to a good approximation, and dH can be written as

$$dH \approx C_P dT + V dP \quad (3.46)$$