

3.2: Heat Capacities

At this point we have enough thermodynamic variables to derive more complex relationships. For example, we have shown that $\partial H = \partial q$ at constant pressure. Since $\partial q = C_P \partial T$ at constant P, then $\partial H = C_P \partial T$ which allows us to define heat capacity at constant pressure as $C_P = \left(\frac{\partial H}{\partial T} \right)_P$. We have also shown above that $\partial H = (C_V + nR) \partial T$, which must mean that the two forms of heat capacity are related via $C_P = C_V + nR$, which is consistent with the data in Table 2.2 of Chapter 2. Here we present an exact proof of this relationship. In fact, there are two derivational routes to do so, and both are shown. It is also instructive to see that there are multiple methods to demonstrate thermodynamic relationships.

Method 1: We have already shown that $\partial U = \partial w + \partial q = -P \partial V + \partial q$, which is due to the exactness of internal energy. If we bring ∂q to the left side of the equation:

$$\partial q = C_V \partial T + P \partial V$$

and divide by ∂T : $\frac{\partial q}{\partial T} = C_V \frac{\partial T}{\partial T} + P \frac{\partial V}{\partial T}$, and then keep P constant:

$$\left(\frac{\partial q}{\partial T} \right)_P = C_P = C_V \left(\frac{\partial T}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P$$

Clearly $\left(\frac{\partial T}{\partial T} \right)_P = 1$ and $P \left(\frac{\partial V}{\partial T} \right)_P = P \left(\frac{\partial \frac{nRT}{P}}{\partial T} \right)_P = P \frac{nR}{P} = nR$. Thus, $C_P = C_V + nR$.

Method 2: This derivation is unfortunately more complex. Starting with:

$$\partial H = \partial U + \partial(PV) = \partial U + V \partial P + P \partial V$$

we divide by ∂T :

$$\frac{\partial H}{\partial T} = \frac{\partial U}{\partial T} + V \frac{\partial P}{\partial T} + P \frac{\partial V}{\partial T}$$

Note that we haven't made anything constant yet. We can set anything we want to be constant, but we should choose something that makes sense like pressure:

$$\left(\frac{\partial H}{\partial T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_P + V \left(\frac{\partial P}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P$$

Since $\left(\frac{\partial H}{\partial T} \right)_P = C_P$ by definition and $V \left(\frac{\partial P}{\partial T} \right)_P = 0$ since $\partial P = 0$ at constant pressure:

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

Using the perfect gas law: $P \left(\frac{\partial V}{\partial T} \right)_P = P \frac{\partial \frac{nRT}{P}}{\partial T} = P \frac{nR}{P} = nR$, leaving us with:

$$C_P = \left(\frac{\partial U}{\partial T} \right)_P + nR$$

We are so close to proving $C_P = C_V + nR$, but we can't just state $\left(\frac{\partial U}{\partial T} \right)_P = C_V$ out of thin air (but we can already see $\left(\frac{\partial U}{\partial T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_V = C_V$ must be true!). Let's show this with another proof by deriving ∂U with changing T and V:

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

(recall that this is the proper form for the change of a multivariable function, Equation 2.7). Next, we divide by ∂T :

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

Setting pressure constant moves things along nicely:

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

And now we can make several simplifications. For one, $\left(\frac{\partial T}{\partial T} \right)_P = 1$, $\left(\frac{\partial U}{\partial T} \right)_V = C_V$ (by definition), and

$\left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P = 0 \text{ J/K}$ because $\left(\frac{\partial U}{\partial V} \right)_T = 0 \text{ J/m}^3$. Why is that? Because we can infer $\partial U = 0 \text{ J}$ since T is constant; as always, there is no change in internal energy at constant temperature due to the Equipartition theorem. We are left with:

$\left(\frac{\partial U}{\partial T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_V = C_V$, and going back to: $C_P = \left(\frac{\partial U}{\partial T} \right)_P + nR$, we can finally finish the proof:

$$C_P = C_V + nR \quad (3.2.1)$$

To summarize, we have defined a new type of energy, called enthalpy, via $H = U + PV$. The change in enthalpy is the heat exchange under constant pressure conditions. Enthalpy also provides a definition for C_P and explains why the heat capacity is highest under constant pressure conditions. Overall, it appears that there is a special relationship between pressure and enthalpy, just as we saw with volume and internal energy. The next section will shed light on this fact.

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