

10.4: CP Minus CV

In Section 8.1 we pointed out that the heat capacity at constant pressure must be greater than the heat capacity at constant volume. We also showed that, for an ideal gas, $C_P = C_V + R$, where these refer to the molar heat capacities. We said that in Chapter 10 we would try and develop a more general expression for $C_P - C_V$, which was applicable in general and not only for an ideal gas. Some of the relations that we developed in Sections 10.2 and 10.3 give us the opportunity to try to do that now.

Let us consider an isobaric process and express the internal energy U as a function of V and T . (As we have pointed out, P , V and T are not independent variables because they are connected through the equation of state, so we may choose any two of them as independent variables.) Then, if the volume and temperature increase by infinitesimal amounts, the corresponding increase in the internal energy is given by

$$dU = \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT. \quad (10.4.1)$$

I.e.,

$$dU = \left(\frac{\partial U}{\partial V} \right)_T dV + C_V dT \quad (10.4.2)$$

Consider how the first law:

$$dU = dQ + dW. \quad (10.4.3)$$

In an isobaric process, $dQ = C_P dT$, and in a reversible process, $dW = -P dV$.

Therefore

$$C_P dT - P dV = \left(\frac{\partial U}{\partial V} \right)_T dV + C_V dT \quad (10.4.4)$$

Divide by dT , recalling that we are considering an isobaric process:

$$C_P - P \left(\frac{\partial V}{\partial T} \right)_P = \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P + C_V. \quad (10.4.5)$$

Hence

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P. \quad (10.4.6)$$

This is a useful general expression, as long as we know or can determine $(\partial U/\partial V)_T$. (Note that the extensive quantities can be total, specific or molar.)

Let us just test this by applying it to an ideal gas to see if it produces the result that it ought to produce. For an ideal gas, the internal energy at a given temperature is independent of the volume. This is because in an ideal gas there are no intermolecular forces, so that, as the volume increases and the intermolecular distances increase, there is no change in potential energy; and, if the temperature is constant, so is the kinetic energy. Thus, for an ideal gas, $\left(\frac{\partial U}{\partial V} \right)_T = 0$. The volume of a mole of ideal gas is $V = RT/P$, so that $\left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P}$.

Therefore

$$C_P - C_V = P \times \frac{R}{P} = R, \quad (10.4.7)$$

and all is well.

For any substance other than an ideal gas, we shall need to know $\left(\frac{\partial U}{\partial V} \right)_T$ before we can make use of equation 10.4.6. But equation 10.2.12, which we developed in Section 10.2 while analysing the Joule effect, enables us to do just this:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P. \quad (10.4.8)$$

On combining this with equation 10.4.6, we obtain

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \quad (10.4.9)$$

Depending on the equation of state, it may or may not be easy to evaluate these partial derivatives. For example, for the van der Waals equation of state (which is a cubic equation in V), it is not easy to evaluate $(\partial V/\partial T)_P$ directly, but one can then make use of $(\partial V/\partial T)_P = (\partial V/\partial T)_P$ or of $\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T = -1$ in order to get $C_P - C_V$ in terms of easily evaluable partial derivatives. For example

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \text{ or } -T\left(\frac{\partial P}{\partial T}\right)_V^2 \left(\frac{\partial P}{\partial V}\right)_T \quad (10.4.10)$$

or several other variants.

Any of equations 10.4.8 or 10.4.9 can be used to calculate $C_P - C_V$; it just depends on which of the derivatives, for a particular equation of state, are easiest to calculate.

The reader will easily be able to show that, for a mole of an ideal gas, this becomes just $C_P - C_V = R$. A little more algebra will be needed to show that, for a mole of a van der Waals gas,

$$C_P - C_V = \frac{R}{1 - 2a(V-b)^2/(RTV^3)} = R \cdot \frac{P + a/V^2}{P - a/V^2 + 2ab/V^3} \approx R \cdot \frac{(RT)^2 + aP}{(RT)^2 - aP}. \quad (10.4.11)$$

In the above analysis, we considered an isobaric process and we chose the internal energy as our function of state and we started by calculating the increment in U corresponding to increments dV and dT in the volume and temperature. It is tempting now to go through the same analysis, but this time to consider an isochoric process and to choose the enthalpy as our function of state. We start by calculating the increment in H corresponding to increments dP and dT in the pressure and temperature:

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT. \quad (10.4.12)$$

I.e.,

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + C_P dT. \quad (10.4.13)$$

Now

$$H = U + PV, \quad \therefore dH = dU + PdV + VdP = dQ + dW + PdV + VdP. \quad (10.4.14)$$

Provided that we include in dQ any irreversible work that is being done on the system (irreversible work has the same effect, as we have seen, as adding heat), so that $dW = -PdV$, then

$$dH = VdP + dQ = VdP + C_V dT. \quad (10.4.15)$$

On comparison of equations 10.4.11 and 10.4.12 we obtain

$$VdP + C_V dT = \left(\frac{\partial H}{\partial P}\right)_T dP + C_P dT. \quad (10.4.16)$$

Divide by dT , recalling that we are considering an isochoric process. From this, we obtain an alternative expression for the difference between the heat capacities:

$$C_P - C_V = \left[V - \left(\frac{\partial H}{\partial P}\right)_T \right] \left(\frac{\partial P}{\partial T}\right)_V. \quad (10.4.17)$$

This is quite analogous to equation 10.4.6. It is left to the reader to show that, for an ideal gas, this reduces to $C_P - C_V = R$. This will be easy if you recall equation 10.3.14, for an ideal gas: $\left(\frac{\partial H}{\partial P}\right)_T = 0$.

For any substance other than an ideal gas, we shall need to know $\left(\frac{\partial H}{\partial P}\right)_T$ before we can make use of equation 10.4.15. But equation 10.3.12, which we developed in Section 10.3 while analysing the Joule-Thomson effect, enables us to do just this:

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P. \quad (10.4.18)$$

On combining this with equation 10.4.15, we obtain again equation 10.4.8. We obtained no new result for $C_P - C_V$ (although we did obtain the important result 10.4.16 for an ideal gas), but it is satisfying and instructive to have obtained the same result via internal energy and via enthalpy.

After this, we can hardly resist the temptation to see what happens if we treat P and V as independent variables. Thus, if $U = U(P, V)$, then increases of dP and dV in the pressure and volume result in an increase dU of the internal energy given by

$$dU = \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV. \quad (10.4.19)$$

But we already know (equation 10.4.1), by choosing the independent variables to be T and V , that

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT. \quad (10.4.20)$$

And from the equation of state $T = T(P, V)$, we derive that

$$dT = \left(\frac{\partial T}{\partial P}\right)_V dP + \left(\frac{\partial T}{\partial V}\right)_P dV. \quad (10.4.21)$$

By elimination of dT from equations 10.4.1 and 10.4.18 we obtain

$$dU = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P dV + \left(\frac{\partial U}{\partial V}\right)_T dV. \quad (10.4.22)$$

On comparison of equations 10.4.17 and 10.4.19 we deduce the following relations, which are occasionally useful:

$$\left(\frac{\partial U}{\partial P}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V, \quad (10.4.23)$$

(which I hope we already knew!)

and

$$\left(\frac{\partial U}{\partial V}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P + \left(\frac{\partial U}{\partial V}\right)_T. \quad (10.4.24)$$

The first of these is, of course, trivial, and does not require this lengthy derivation. The second is a worthwhile relation, which we may occasionally find useful.

Summary:

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T \right] \left(\frac{\partial V}{\partial T}\right)_P = \left[V - \left(\frac{\partial H}{\partial P}\right)_T \right] \left(\frac{\partial P}{\partial T}\right)_V \quad (10.4.25)$$

$$C_P - C_V = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \text{ and variants.} \quad (10.4.26)$$

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