6.8: The Difference between Cp and Cv

Constant volume and constant pressure heat capacities are very important in the calculation of many changes. The ratio $C_p/C_V = \gamma$ appears in many expressions as well (such as the relationship between pressure and volume along an adiabatic expansion.) It would be useful to derive an expression for the difference $C_p - C_V$ as well. As it turns out, this difference is expressible in terms of measureable physical properties of a substance, such as α, κ_T, p, V, and T.

In order to derive an expression, let's start from the definitions.

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

and

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

The difference is thus

$$C_p - C_v = \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V$$

In order to evaluate this difference, consider the definition of enthalpy:

$$H = U + pV$$

Differentiating this yields

$$dH = dU + pdV + Vdp$$

Dividing this expression by dT and constraining to constant p gives

$$\left.\frac{dH}{dT}\right|_p = \left.\frac{dU}{dT}\right|_p + p\left.\frac{dV}{dT}\right|_p + V\left.\frac{dp}{dT}\right|_p$$

The last term is kind enough to vanish (since $dp = 0$ at constant pressure). After converting the remaining terms to partial derivatives:

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p \tag{6.8.1}$$

This expression is starting to show some of the players. For example,

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p$$

and

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

So Equation 6.8.1 becomes

$$C_p = \left(\frac{\partial U}{\partial T}\right)_p + pV\alpha \tag{6.8.2}$$

In order to evaluate the partial derivative above, first consider $U(V,T)$. Then the total differential du can be expressed

$$du = \left(\frac{\partial U}{\partial V}\right)_T dV - \left(\frac{\partial U}{\partial T}\right)_V dT$$

Dividing by dT and constraining to constant p will generate the partial derivative we wish to evaluate:

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

The last term will become unity, so after converting to partial derivatives, we see that

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial U}{\partial T}\right)_V \tag{6.8.3}$$

(This, incidentally, is an example of partial derivative transformation type III.) Now we are getting somewhere!

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V$$

and

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

So the Equation 6.8.3 can be rewritten

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

If we can find an expression for

$$\left(\frac{\partial U}{\partial V}\right)_T$$

we are almost home free! Fortunately, that is an easy expression to derive. Begin with the combined expression of the first and second laws:

$$d = TdS - pdV$$

Now, divide both sides by dV and constrain to constant T.

$$\left.\frac{dU}{dV}\right|_T = T\left.\frac{dS}{dV}\right|_T - p\left.\frac{dV}{dV}\right|_T$$

The last term is unity, so after conversion to partial derivatives, we see

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p \tag{6.8.4}$$

A Maxwell relation (specifically the Maxwell relation on A) can be used

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

Substituting this into Equation 6.8.4 yields

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

and since

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$$

then

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{\alpha}{\kappa_T} - p$$

Now, substituting this into the expression into Equation 6.8.3 to get

$$\begin{aligned}\left(\frac{\partial U}{\partial T}\right)_p &= \left[T\frac{\alpha}{\kappa_T} - p\right]V\alpha + C_V \\ &= \frac{TV\alpha^2}{\kappa_T} - pV\alpha + C_V\end{aligned}$$

This can now be substituted into the Equation 6.8.2 yields

$$C_p = \left[\frac{TV\alpha^2}{\kappa_T} - \cancel{pV\alpha} + C_V\right] + \cancel{pV\alpha}$$

The $pV\alpha$ terms will cancel. And subtracting C_V from both sides gives the desired result:

$$C_p - C_V = \frac{TV\alpha^2}{\kappa_T} \tag{6.8.5}$$

And this is a completely general result since the only assumptions made were those that allowed us to use the combined first and second laws in the form

$$dU = TdS - pdV.$$

That means that this expression can be applied to any substance whether gas, liquid, animal, vegetable, or mineral. But what is the result for an ideal gas?

Since we know that for an ideal gas

$$\alpha = \frac{1}{T}$$

and

$$\kappa_T = \frac{1}{p}$$

Substitution back into Equation 6.8.5 yields

$$\begin{aligned}C_p - C_V &= \frac{TV\left(\frac{1}{T}\right)^2}{\left(\frac{1}{p}\right)} \\ &= \frac{pV}{T} \\ &= R\end{aligned}$$

So for an ideal gas, $C_p - C_V = R$. That is good to know, no?

Example 6.8.1

Derive the expression for the difference between C_p and C_V by beginning with the definition of H, differentiating, dividing by dV (to generate the partial derivative definition of C_V). In this approach, you will need to find expressions for

$$\left(\frac{\partial H}{\partial T}\right)_V$$

and

$$\left(\frac{\partial U}{\partial p}\right)_T$$

and also utilize the Maxwell-Relation on G.

Solution

Begin with the definition of enthalpy.

$$H = U + pV$$

Differentiate the expression.

$$dH = dU + pdV + Vdp$$

Now, divide by dV and constrain to constant T (as described in the instructions) to generate the partial derivative definition of C_V

$$\left.\frac{dH}{dT}\right|_V = \left.\frac{dU}{dT}\right|_V + p\left.\frac{dV}{dT}\right|_V + V\left.\frac{dp}{dT}\right|_V$$

$$\left(\frac{dH}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V + V\left(\frac{dp}{dT}\right)_V \tag{6.8.6}$$

Now what is needed is an expression for

$$\left(\frac{dH}{dT}\right)_V.$$

This can be derived from the total differential for $H(p,T)$ by dividing by dT and constraining to constant V.

$$dH = \left(\frac{dH}{dp}\right)_T dp + \left(\frac{dH}{dT}\right)_p dT$$

$$\left(\frac{dH}{dT}\right)_V = \left(\frac{dH}{dp}\right)_T \left(\frac{dp}{dT}\right)_V + \left(\frac{dH}{dT}\right)_p \tag{6.8.7}$$

This again is an example of partial derivative transformation type III. To continue, we need an expression for

$$\left(\frac{dH}{dp}\right)_T.$$

This can be quickly generated by considering the total differential of $H(p,S)$, its natural variables:

$$dH = TdS + Vdp$$

Dividing by dp and constraining to constant T yields

$$\left.\frac{dH}{dp}\right|_T = T\left.\frac{dS}{dp}\right|_T + V\left.\frac{dp}{dp}\right|_T$$

$$\left(\frac{dH}{dp}\right)_T = T\left(\frac{dS}{dp}\right)_T + V \tag{6.8.8}$$

Using the Maxwell Relation on G, we can substitute

$$-\left(\frac{dV}{dT}\right)_p = \left(\frac{dS}{dp}\right)_T$$

So Equation 6.8.8 becomes

$$\left(\frac{dH}{dp}\right)_T = -T\left(\frac{dV}{dT}\right)_p + V$$

Now, substitute this back into the expression for (Equation 6.8.7):

$$\left(\frac{dH}{dT}\right)_V = \left[-T\left(\frac{dV}{dT}\right)_p + V\right]\left(\frac{dp}{dT}\right)_V + \left(\frac{dH}{dT}\right)_p$$

$$\left(\frac{dH}{dT}\right)_V = -T\left(\frac{dV}{dT}\right)_p\left(\frac{dp}{dT}\right)_V + V\left(\frac{dp}{dT}\right)_V + \left(\frac{dH}{dT}\right)_p$$

This can now substituted for the right-hand side of the initial expression for $\left(\frac{dH}{dT}\right)_V$ back into Equation 6.8.6:

$$-T\left(\frac{dV}{dT}\right)_p\left(\frac{dp}{dT}\right)_V + \cancel{V\left(\frac{dp}{dT}\right)_V} + \left(\frac{dH}{dT}\right)_p = \left(\frac{dU}{dT}\right)_V + \cancel{V\left(\frac{dp}{dT}\right)_V} \tag{6.8.9}$$

Several terms cancel one another. Equation 6.8.9 can then be rearranged to yield

$$\left(\frac{dH}{dT}\right)_p - \left(\frac{dU}{dT}\right)_V = T\left(\frac{dV}{dT}\right)_p\left(\frac{dp}{dT}\right)_V$$

or

$$C_p - C_V = \frac{TV\alpha^2}{\kappa_T}$$

which might look familiar (Equation 6.8.5)!