

Mathematical considerations for Thermodynamics. We have applied the differential and the cyclic rule. Now we want to use the chain rule as applied to equations where a function depends on more than 1 variable.

First review the chain rule for a function of one variable. If z is a function of y , $Z = Z(y)$ and y is a function of x , $y = y(x)$, evaluating $\frac{dZ}{dx}$ does not require substituting in and obtaining Z as a function of x directly. The chain rule of calculus can be applied here to evaluate this derivative as: $\frac{dZ}{dx} = \frac{dZ}{dy} \cdot \frac{dy}{dx}$. So now we extend the chain rule to understand how to obtain derivatives we do not know in terms of old ones we know.

A caution about mathematical notation in thermodynamics. The symbols, P,V,T, as well as S,U,H,G,A have well defined meaning. When we say that U is a function of V , and T and write $U = U(T, V)$, we could as easily write $U = U(V, T)$, but we would not be implying that we swap T and V in whatever equation U was. [A mathematician would object to this sort of sloppy use of notation; hopefully you are all comfortable with it by now.] Conversely, if we talk about U as a function of P and T , $U = U(P, T)$ we mean something quite different; the function is not the same at all. Because we work with differentials, and we integrate along certain paths, and we want the differentials to follow those paths. However, if we know the starting and ending points we can integrate over any path we choose as long as we start and end up at the same state.

Saying that $U = U(T, V)$ implies:

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

which means that the change of U over a path $T_i V_i \rightarrow T_f V_f$ is:

$$\Delta U = \int dU = \int_{T_i}^{T_f} \left(\frac{\partial U}{\partial T} \right)_{V_i} dT + \int_{V_i}^{V_f} \left(\frac{\partial U}{\partial V} \right)_{T_f} dV$$

Because these are the types of equations we deal with it follows that: $U(V, T) = U(T, V)$.

If we are given a path that goes along $T_i P_i \rightarrow T_f P_f$ and we want ΔU for that change this implies that we should know U as a function of P and T . This is not necessary. Because the integral is independent of path we can use the equation of state (EoS) to determine V_i and V_f and just go over the TV path to end up at the same place. Alternatively we can indeed relate the derivative of U as a function of P and T to those of V and T . This has much broader application in thermodynamics than just this example. So the method of transformation is worth knowing.

So we want to develop how to do a change of variables and use the chain rule for functions of two (or many) variables. How to extend the chain rule. From above we

have U as a function of T, and V means that we know the two derivatives in terms of P, V, T, and heat capacities:

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V \text{ and } \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

Now, how do we obtain

$$\left(\frac{\partial U}{\partial P}\right)_T \text{ and } \left(\frac{\partial U}{\partial T}\right)_P$$

To do this begin with what we know:

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

We want the derivatives of U which imply U is a function of P, and T: To do this begin with the fact that U is a function of V and T and, to obtain $\left(\frac{\partial U}{\partial P}\right)_T$, divide by ∂P to

have as an intermediate of where we need to be:

$$\frac{dU}{\partial P} = \left(\frac{\partial U}{\partial T}\right)_V \frac{dT}{\partial P} + \left(\frac{\partial U}{\partial V}\right)_T \frac{dV}{\partial P}, \text{ now convert to the partial differentials by noting that the}$$

derivatives are to be taken where T is held fixed:

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

We can evaluate the new partial derivatives using the EoS. The first one is particularly simple and independent of EoS: $\left(\frac{\partial T}{\partial P}\right)_T = 0$, by definition. In this case this simplifies

the connection that: $\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T$. This is the form we seek as we know everything on the r.h.s.

In a similar vein, if we want $\left(\frac{\partial U}{\partial T}\right)_P$, and it would be good to try this before looking at

the answer, which is:

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

Similarly other partial derivatives can be evaluated such as $\left(\frac{\partial T}{\partial T}\right)_P = 1$. The above simplifies to:

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

To practice other relations, derive $\left(\frac{\partial H}{\partial V}\right)_T$ and $\left(\frac{\partial H}{\partial T}\right)_V$ from the usual form that $H = H(P, T)$.