A brief (and possibly helpful) note on calculus

Consider a function of some thermodynamic quantities, say $f(P,V,T) = PV - NkT$. Now, consider a process where P, V and T are all changing. Let P change first and the change in P be ΔP. This changes f by an amount equal to

$$\Delta f \approx \left.\frac{\partial f}{\partial P}\right|_{V,T} \Delta P$$

where I have indicated that V and T are to be treated as constants for the purpose of differentiation (n and R are constants as well, of course). Taking a derivative, we easily get that

$$\Delta f = V\Delta P$$

Next, we allow V to change by ΔV while holding P and T constant. The change in f (do it for yourself!) is now

$$\Delta f \approx P\Delta V$$

Finally, change T by ΔT to get

$$\Delta f \approx -Nk\Delta T$$

The total change in f, from these three steps one after another is

$$\Delta f \approx V\Delta P + P\Delta V - Nk\Delta T$$

However, the ideal gas law says that f is always **zero**: it cannot change at all. Thus, for a substance that follows the ideal gas law, we obtain

$$V\Delta P + P\Delta V - Nk\Delta T \approx 0$$

We can also write it as

$$VdP + PdV - NkdT = 0$$

The notation dP implies an infinitesimal (very small) change in P, such that the linear approximations we used above are basically exact, so I replaced $\approx$ with $=$.

The equation $VdP + PdV - NkdT = 0$ is a relationship between changes in the thermodynamic variables T, P and V.

There are several ways in which this statement should be familiar to you. Let P, V and T all be functions of some other variable, such as time, t. Then, I can divide by a small increment in the time variable, dt, to get

$$V\frac{dP}{dt} + P\frac{dV}{dt} - Nk\frac{dT}{dt} = 0$$

This is just 'related rates,' which you are familiar with from MATH 100. For example, if you are given the values of T, V and P and the rate of change of V and T, you can compute the rate of change of P.

$$\frac{dP}{dt} = -\frac{P}{V}\frac{dV}{dt} + \frac{Nk}{V}\frac{dT}{dt}$$

We can also do this computation for the infinitesimal changes themselves: If you know the change in, say, T and V, you can solve for a change in P:

$$dP = -\frac{P}{V}dV + \frac{Nk}{V}dT = -\frac{NkT}{V^2}dV + \frac{Nk}{V}dT$$

where on the last line I used the ideal gas law (P=NkT/V) to get rid of P. Now, we have an equation that tells us how much P changes if we know T and V and their change. This allows us to think of P as a function of T and V.

The equation $VdP + PdV - NkdT = 0$ can be thought of another way: since the ideal gas law says, for example, that T is a function of V and P, I can ask questions like: holding T constant, what is the derivative dP/dV. This, in MATH 100, was called implicit differentiation. In $VdP + PdV - NkdT = 0$, I can set $dT = 0$ (since T is now a constant), then divide by dV to get

$$VdP + PdV = 0 \quad \Rightarrow \quad V\frac{dP}{dV} + P = 0 \quad \Rightarrow \quad \frac{dP}{dV} = -\frac{P}{V} \quad \text{if } T = \text{const.}$$

Consider an adiabatic process (like in worksheet 3). We want no heat flow, so $dU = W + Q = W$. Since $U = (f/2)NkT$, $dU = (f/2)NkdT$ (f, k and N are all constants). Together with $W = -PdV$, we have

$$(f/2)NkdT + PdV = 0$$

or

$$(f/2)NkdT = -PdV = -\frac{NkT}{V}dV$$

so that

$$\frac{dT}{dV} = -\frac{NkT}{V(f/2)Nk} = -\frac{2T}{fV}$$

This is the derivative of T w.r.t. V along the adiabatic curve, i.e., an example of implicit differentiation in which the curve was only given to us in an infinitesimal form ($Q = 0$ so $(f/2)NkdT + PdV = 0$) and not in a form of 'this function is constant' because heat is not a function of state! This is why we need to get comfortable with differentials.

We already introduced two different things you can do with the infinitesimals such as dV and dT: you can divide them by an infinitesimal change dt in an independent variable such as time to obtain related rates from an equation of motion; you can divide them by each other to obtain derivatives such as $\frac{dT}{dV}$, **along a path** (such as the adiabatic curve above).

The last thing we can do with differentials is integrals. Separate the variables in the last equation we wrote down:

$$\frac{f}{2}\frac{1}{T}dT = -\frac{1}{V}dV$$

For a finite change, say from V_i to V_f, we need to sum up a large number of infinitesimal changes. This is what an integral is, as you learned in MATH 101. We can write

$$\int_{T_i}^{T^f} \frac{f}{2}\frac{1}{T}dT = -\int_{V_i}^{V^f} \frac{1}{V}dV$$

Computing the integral yields an equation for the adiabatic curve.