First: One variable:

Derivative \equiv \text{Slope}

\text{Average Slope} = \frac{\Delta y}{\Delta x}

\text{Exact Slope} = \frac{dy}{dx}

where \, d = \text{very small } \Delta

Calculus Review:

If \, y = Bx^n \quad (\text{where } B = \text{constant}) \quad \frac{dy}{dx} = \, ? \quad Bnx^{n-1}
Partial Derivatives  (Ideal Gas Law)
(needed if a function depends on more than one variable.)

\[ pV = nRT \text{ gives: } V = V(n, p, T) = \frac{nRT}{P} \]

If \( n \) and \( p \) are held constant, then \( V = B \ T \)

\[ \frac{dV}{dT} = B = \frac{nR}{P} \]

Cool way:

\[ \left( \frac{\partial V}{\partial T} \right)_{n,p} = \frac{nR}{P} = \text{the SLOPE of } V \text{ in the T direction} \]

The curly \( d \) is the same a the ordinary \( d \). The curliness just tells you that other variables besides \( T \) can affect \( V \), but are being held constant.

The subscripts further emphasize this by telling which variables are constant.
Similarly, if \( n \) and \( T \) are held constant

\[
V = \frac{nRT}{p}
\]

If \( n \) and \( T \) are held constant, then \( V = B' \, \frac{1}{p} \)

\[
\frac{dV}{dp} = B' \left( \frac{1}{p} \right) = nRT \, \frac{d}{dp} \left( \frac{1}{p} \right) = nRT \, \frac{dp^{-1}}{dp} = -\frac{nRT}{p^2}
\]

\[
\left( \frac{\partial V}{\partial p} \right)_{n,T} = -\frac{nR}{p^2}
\]

= the **SLOPE** of \( V \)

in the \( p \) direction

The *curly d* is the same as the ordinary \( d \). The *curliness just tells you that other variables besides \( T \) can affect \( V \), but are being held constant.

The subscripts further emphasize this by telling which variables are constant.
general change in $V$:

$$dV = \left( \frac{\partial V}{\partial T} \right)_{n,p} \, dT + \left( \frac{\partial V}{\partial P} \right)_{n,T} \, dP + \left( \frac{\partial V}{\partial n} \right)_{P,T} \, dn$$

If $n$ not constant

$$dV = \text{Slope in } T \text{ direction} \times \text{Change in } T$$
$$+ \text{Slope in } P \text{ direction} \times \text{Change in } P$$
$$+ \text{Slope in } n \text{ direction} \times \text{Change in } n$$
Slopes are not independent !!!

\[ dV = \text{Slope in } T \text{ direction } \times \text{Change in } T + \text{Slope in } P \text{ direction } \times \text{Change in } P + \text{Slope in } n \text{ direction } \times \text{Change in } n \]

Now, for simplicity keep \( n \) constant, so that \( V = V(P,T) \)

Two paths from 1 \( \rightarrow \) 2
Steep up \( T \), steep down \( p \), or less steep down \( p \), less steep up \( T \)

This is a way of saying the order of differentiation does not matter.
Slopes are not independent: Maxwell’s Relations

\[ dV = \left( \frac{\partial V}{\partial T} \right)_P \, dT + \left( \frac{\partial V}{\partial P} \right)_T \, dP \]

\[ \frac{nR}{P} \, dT - \frac{nRT}{P^2} \, dP \]

because \[ V = \frac{nRT}{P} \]

Maxwell: \[ \frac{\partial}{\partial P} \left( \frac{\partial V}{\partial T} \right)_P = \frac{\partial}{\partial T} \left( \frac{\partial V}{\partial P} \right)_V \]

\[ = -\frac{nR}{P^2} \quad = -\frac{nR}{P^2} \]

i.e., the T slope changes with p exactly as the p slope changes with T
The **Maxwell Relations** apply to all such equations:

Applied to the Fundamental Equation:

\[
dU = TdS - pdV \text{ is also } \left( \frac{\partial U}{\partial S} \right)_V dS + \left( \frac{\partial U}{\partial V} \right)_S dV
\]

Recall this means that \( T = ? \) and \( p = ? \)

\[
\left( \frac{\partial U}{\partial S} \right)_V = T \text{ and } \left( \frac{\partial U}{\partial V} \right)_S = -p
\]

Therefore implies:

\[
\left( \frac{\partial T}{\partial V} \right)_S = -\left( \frac{\partial p}{\partial S} \right)_V
\]

Because:

\[
\frac{\partial}{\partial V} \left( \frac{\partial U}{\partial S} \right)_V = \frac{\partial}{\partial S} \left( \frac{\partial U}{\partial V} \right)_S
\]

The V slope of the S slope of U = The S slope of the V slope of U
Similar relationships come from definitions of $H$, $G$, and $A$

IF we add $d(PV)$ to both sides of the Fundamental Equation, we magically transform it into a similar equation for $dH$:

$$dU = TdS - PdV = dq_{\text{rev}} + dW_{\text{rev}}$$

$$dU + d(PV) = dH$$

$$dH = TdS - PdV + PdV + VdP$$

$$dH = TdS + VdP$$

Then it follows that: $$\left( \frac{\partial H}{\partial S} \right)_P = T \text{ and } \left( \frac{\partial H}{\partial P} \right)_S = V$$

and $$\left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial S} \right)_P$$

The last 3 lines show how to answer problem S4 on homework but how do we get to something useful?
Generalize
Let $Z$ be anything that depends on $X$ and $Y$, i.e., $Z = Z(X,Y)$

$X$, $Y$, and $Z$ are any state functions whatsoever.

For example:
$Z = \text{elevation above sea level}$
$X = \text{distance heading EAST}$
$Y = \text{distance heading NORTH}$

Then it is \text{ALWAYS TRUE} that:

$$dZ = \left( \frac{\partial Z}{\partial X} \right)_Y dX + \left( \frac{\partial Z}{\partial Y} \right)_X dY$$

If changes are small, but not infinitely small, it is true that:

$$\Delta Z = \left( \frac{\Delta Z}{\Delta X} \right)_Y \Delta X + \left( \frac{\Delta Z}{\Delta Y} \right)_X \Delta Y$$
Compare:

\[ dZ = \left( \frac{\partial Z}{\partial X} \right)_Y dX + \left( \frac{\partial Z}{\partial Y} \right)_X dY \]

With:

Given that \( q_{\text{rev}} + w_{\text{rev}} = dU = T \ dS - P \ dV \),

adding \( d(PV) \) to \( dU \) gives:

\[ dH = T \ dS + V \ dP = \left( \frac{\partial H}{\partial S} \right)_V dS + \left( \frac{\partial H}{\partial P} \right)_S dP \]

subtract \( d(TS) \) from \( dU \) gives:

\[ dA = -S \ dT - P \ dV = \left( \frac{\partial A}{\partial T} \right)_V dT + \left( \frac{\partial A}{\partial V} \right)_T dV \]

subtract \( d(TS) \) from \( dH \) gives:

\[ dG = -S \ dT + V \ dP = \left( \frac{\partial G}{\partial T} \right)_P dT + \left( \frac{\partial G}{\partial P} \right)_T dP \]

Conclude that:

\[ \left( \frac{\partial U}{\partial S} \right)_V = T \text{ and } \left( \frac{\partial U}{\partial V} \right)_S = -P \text{ and } \left( \frac{\partial T}{\partial V} \right)_S = -\left( \frac{\partial P}{\partial S} \right)_V \]

\[ \left( \frac{\partial H}{\partial S} \right)_P = T \text{ and } \left( \frac{\partial H}{\partial P} \right)_S = V \text{ and } \left( \frac{\partial T}{\partial P} \right)_S = -\left( \frac{\partial V}{\partial S} \right)_P \]

\[ \left( \frac{\partial A}{\partial T} \right)_V = -S \text{ and } \left( \frac{\partial A}{\partial V} \right)_T = -P \text{ and } \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \]

\[ \left( \frac{\partial G}{\partial T} \right)_P = -S \text{ and } \left( \frac{\partial G}{\partial P} \right)_T = V \text{ and } -\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial V}{\partial T} \right)_P \]

This matrix of information surprisingly leads to something of great practical value.

CAN YOU SEE IT?
First and Second Laws combined to give $U = U(S,V)$

$$dU = TdS - PdV$$ (the “Fundamental Equation”).

But we talk a lot about $U=U(T,V)$. This is more useful because we know how to change $T$ and $V$ and how to keep $T$ and $V$ constant.

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

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

What is $\left( \frac{\partial U}{\partial V} \right)_T$ for an ideal gas? 0, of course

What is $\left( \frac{\partial U}{\partial V} \right)_T$ for any material?
What is \( \left( \frac{\partial U}{\partial V} \right)_T \) for any material?

\[ dU = TdS - PdV \]

Divide by \( dV \) and hold \( T \) constant

\[ \left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial S}{\partial V} \right)_T - P \]

But, there is no entropy meter. 😞

However, from:

\[ dA = -S \, dT - P \, dV \]

\[ \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \]

\[ \left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P \]

Encase the material in a rigid constant \( V \) container equipped with a PRESSURE GAUGE.

Measure \( P \) as you raise the \( T \)

Good that it is all in terms of MEASUREABLE variables.

How do you experimentally determine \( \left( \frac{\partial U}{\partial V} \right)_T \)?
Does this give zero for an ideal gas?

\[
\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P
\]

For ANYTHING!!

\[
P = \frac{nRT}{V}
\]

\[
\left( \frac{\partial P}{\partial T} \right)_V = \frac{nR}{V}; \quad T \left( \frac{\partial P}{\partial T} \right)_V = \frac{nRT}{V} = +P
\]

\[
T \left( \frac{\partial P}{\partial T} \right)_V - P = P - P = 0
\]
Use a Volume Meter at different temperatures

Getting how $E$ changes with $V$ and how $H$ changes with $P$ for anything

Use a Pressure Meter at different temperatures