Hints for Finding Partial Derivatives

1. **Differentiate before doing algebra.** In many cases, you are given an equation which can be written \(f(w,x,y,z,\ldots) = 0\) and asked to calculate \((\partial w/\partial x)_{y,z,\ldots}\). The equations encountered in thermodynamics generally become simpler when a derivative is taken. Therefore, it is often better to differentiate the original equation \(f = 0\) rather than rearranging to obtain \(w = g(x,y,z,\ldots)\) before differentiating.

Example: Find \((\partial U/\partial V)_{S,N}\), given that
\[
S^4 = ANVU^2 \quad (A = \text{const}).
\] (1)

Longer:
\[
U = \sqrt{\frac{S^4}{ANV}} \Rightarrow \left(\frac{\partial U}{\partial V}\right)_{S,N} = -\frac{1}{2} \sqrt{\frac{S^4}{ANV^3}} = -\frac{U}{2V}.
\]

Shorter: Differentiate Eq. (1) directly with respect to \(V\) at constant \(S\) and \(N\):
\[
0 = ANU^2 + 2ANVU \left(\frac{\partial U}{\partial V}\right)_S \Rightarrow \left(\frac{\partial U}{\partial V}\right)_S = -\frac{U}{2V}.
\]

2. **Take logs before differentiating.** When products of powers are present, it can be quicker still to take logs before differentiating an equation.

Example: From Eq. (1),
\[
4 \ln S = \ln A + \ln N + \ln V + 2 \ln U.
\]

Now differentiate with respect to \(V\) at constant \(S\) and \(N\):
\[
0 = \frac{1}{V} + 2 \frac{U}{V} \left(\frac{\partial U}{\partial V}\right)_S \Rightarrow \left(\frac{\partial U}{\partial V}\right)_S = -\frac{U}{2V}.
\]

Note that in this method, the variables \(A\) and \(N\) are eliminated much sooner, saving effort and reducing the chances of making a mistake.

3. **Differentiate the entire equation.** In almost all situations where you need to calculate a partial derivative, you can get the answer by differentiating the entire equation.

Suppose you want to find \((\partial a/\partial b)_c\) given that you know
\[
z = f(x,y).
\] (2)

Here \(x, y,\) and \(z\) can be any permutation of \(a, b,\) and \(c,\) e.g., if \(x = c, y = a,\) and \(z = b,\) then Eq. (2) would say that \(b = f(c,a).\) (The reason for expressing the problem in this rather obscure notation is that it allows many different cases to be treated at once.)

Whatever the mapping from \((x,y,z)\) to \((a,b,c)\), you can find \((\partial a/\partial b)_c\) by differentiating Eq. (2) with respect to \(b\) at fixed \(c\), using the chain rule to handle the function \(f: \)
\[
\left(\frac{\partial z}{\partial b}\right)_c = \left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial b}\right)_c + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial b}\right)_c.
\] (3)
Equation (3) is completely general. To make it useful, you have to replace $x$, $y$, and $z$ everywhere by their values in terms of $a$, $b$, and $c$, and then apply two obvious truths:

$$
\left( \frac{\partial b}{\partial b} \right)_c = 1, \quad \left( \frac{\partial c}{\partial b} \right)_c = 0.
$$

The resulting equation can easily be rearranged in the form $(\partial a/\partial b)_c = \ldots$

Example: Let us try to find $(\partial u/\partial v)_s$ in a number of different cases:

(a) $u = f(s,v)$. This case is trivial:

$$
\left( \frac{\partial u}{\partial v} \right)_s = \left( \frac{\partial f}{\partial v} \right)_s.
$$

(b) $v = f(u,s)$. The procedure described above gives

$$
1 = \left( \frac{\partial f}{\partial u} \right)_s \left( \frac{\partial u}{\partial v} \right)_s \Rightarrow \left( \frac{\partial u}{\partial v} \right)_s = 1 / \left( \frac{\partial f}{\partial u} \right)_s = 1 / \left( \frac{\partial v}{\partial u} \right)_s.
$$

(c) $s = f(u,v)$. This time we get

$$
0 = \left( \frac{\partial f}{\partial u} \right)_v \left( \frac{\partial u}{\partial v} \right)_s + \left( \frac{\partial f}{\partial P} \right)_u \left( \frac{\partial P}{\partial v} \right)_s \Rightarrow \left( \frac{\partial u}{\partial v} \right)_s = - \left( \frac{\partial s}{\partial P} \right)_u / \left( \frac{\partial s}{\partial u} \right)_v.
$$

(d) The same general method works even if the partial derivative we want is defined implicitly by more than one equation. For example, suppose that

$$
v = f(u,P), \quad s = g(u,P).
$$

Then

$$
1 = \left( \frac{\partial f}{\partial u} \right)_P \left( \frac{\partial u}{\partial v} \right)_s + \left( \frac{\partial f}{\partial P} \right)_u \left( \frac{\partial P}{\partial v} \right)_s,
$$

and

$$
0 = \left( \frac{\partial g}{\partial u} \right)_P \left( \frac{\partial u}{\partial v} \right)_s + \left( \frac{\partial g}{\partial P} \right)_u \left( \frac{\partial P}{\partial v} \right)_s.
$$

We now have a pair of simultaneous equations for $(\partial u/\partial v)_s$ and $(\partial P/\partial v)_s$. It is straightforward to obtain

$$
\left( \frac{\partial u}{\partial v} \right)_s = \frac{\left( \frac{\partial s}{\partial P} \right)_u}{\left( \frac{\partial v}{\partial u} \right)_P \left( \frac{\partial s}{\partial P} \right)_u - \left( \frac{\partial v}{\partial P} \right)_u \left( \frac{\partial s}{\partial u} \right)_P}.
$$

Message: Don’t try to remember the formulae for cases (a)–(d). Just follow the general method described above, adapting it to the specifics of each situation.

4. **Write down the subscripts.** When finding partial derivatives, you have to pay careful attention to which variables are dependent and which are independent. (This is amply demonstrated in Hint 3.) To avoid errors, always write down explicitly the subscripts showing which variables are being held constant in any partial derivative.