Math Diversion Problem 489: Jacobians in Thermodynamics, Part 2

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March 30, 2025

> There is general agreement that a procedure for deriving relations among the thermodynamic derivatives without resorting to the Bridgman tables is highly desirable. The use of Jacobians makes for directness and speed.
>
> — Benjamin Carroll [1]

> Furthermore, it is not possible in thermodynamics to hold all other variables constant. These practices do not always match how partial derivatives are first introduced in multivariable calculus.
>
> — Paul J. Emigh and Corinne A. Manogue [2]

1 Introduction

This is my second (and I think final) paper on an article by Benjamin Carroll. Unlike in the last article, this time I shall definitely be using the techniques of structured differentiation (SD) throughout to perform and explain what Carroll has done in this section of his article.

Note: In SD, an expression like

$$\frac{\partial(W,X)}{\partial(Y,Z)} \tag{1}$$

is a matrix (the jacobian matrix), and the 'jacobian' derived from it as

$$\det\left[\frac{\partial(W,X)}{\partial(Y,Z)}\right] = \left|\frac{\partial(W,X)}{\partial(Y,Z)}\right| . \tag{2}$$

However, in conventional thermodynamics, an expression like (1) is a determinant already.

[1] Found in: "On the Use of Jacobians in Thermodynamics," Benjamin Carroll, J. of Chem. Ed., Vol. 42, No. 4, 1965, pp 218–221.

[2] Found in: "Student interpretations of partial derivatives,' Paul J. Emigh and Corinne A. Manogue. PERC Proceedings, 2017, p. 120.

The point of this article is to prove the Joule-Thompson expansion equation that Carroll proved, but using the SD calculus:

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right] . \tag{3}$$

2 The Lemma from the last time

The purpose of the previous article in this two-article series was to establish Carroll's enigmatic 'muffin-top' pseudo-equation:

$$J(T, S) = J(P, V)\,, \tag{4}$$

of which he then used to produce the relation

$$\left|\frac{\partial(T,S)}{\partial(T,P)}\right| = \left|\frac{\partial(P,V)}{\partial(T,P)}\right| . \tag{5}$$

This last equation together with the following equations will be our starting points for the demonstration:

$$\frac{C_P}{T} = \left(\frac{\partial S}{\partial T}\right)_P , \tag{6}$$

and

$$dH = T\,dS + V\,dP\,. \tag{7}$$

3 The Proof

We'll begin by expanding the LHS of (5):

$$\left|\frac{\partial(T,S)}{\partial(T,P)}\right| = \begin{vmatrix} \left(\frac{\partial T}{\partial T}\right)_P & \left(\frac{\partial T}{\partial P}\right)_T \\ \left(\frac{\partial S}{\partial T}\right)_P & \left(\frac{\partial S}{\partial P}\right)_T \end{vmatrix} = \begin{vmatrix} 1 & 0 \\ \left(\frac{\partial S}{\partial T}\right)_P & \left(\frac{\partial S}{\partial P}\right)_T \end{vmatrix} = \left(\frac{\partial S}{\partial P}\right)_T . \tag{8}$$

Next, we expand the RHS of (5):

$$\left|\frac{\partial(P,V)}{\partial(T,P)}\right| = \begin{vmatrix} \left(\frac{\partial P}{\partial T}\right)_P & \left(\frac{\partial P}{\partial P}\right)_T \\ \left(\frac{\partial V}{\partial T}\right)_P & \left(\frac{\partial V}{\partial P}\right)_T \end{vmatrix} = \begin{vmatrix} 0 & 1 \\ \left(\frac{\partial V}{\partial T}\right)_P & \left(\frac{\partial V}{\partial P}\right)_T \end{vmatrix} = -\left(\frac{\partial V}{\partial T}\right)_P . \tag{9}$$

On setting these last two result equal, we have that

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P . \tag{10}$$

Next, we need the generic result that

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1\,. \tag{11}$$

From this we have that

$$\left(\frac{\partial x}{\partial y}\right)_z = -\frac{1}{\left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y}\,. \tag{12}$$

But since

$$\frac{1}{\left(\frac{\partial y}{\partial z}\right)_x} = \left(\frac{\partial z}{\partial y}\right)_x\,, \tag{13}$$

then (11) becomes

$$\left(\frac{\partial x}{\partial y}\right)_z = -\frac{\left(\frac{\partial z}{\partial y}\right)_x}{\left(\frac{\partial z}{\partial x}\right)_y}\,. \tag{14}$$

On making the substitutions $x = T$, $y = P$, and $z = H$, we get[3]

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P}\,. \tag{15}$$

Now, we let H be dependent on S and P, that is

$$H = H(S, P)\,. \tag{16}$$

On taking the differential of this, we have that

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial S}\right)_P dP\,. \tag{17}$$

Next, we compare (7) and (17), to get

$$\left(\frac{\partial H}{\partial S}\right)_P = T, \quad \left(\frac{\partial H}{\partial P}\right)_S = V\,. \tag{18}$$

Now we're going to dip once more into the wellspring called (7), and divide through by dP while holding T constant:

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V\,. \tag{19}$$

[3] An alternative proof of this, that does not depend on the previous generic computations, can be found in the Appendix.

Likewise,

$$\left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P + V\cancelto{0}{\left(\frac{\partial P}{\partial T}\right)_P} = T\left(\frac{\partial S}{\partial T}\right)_P . \tag{20}$$

It's time to return to (15) and use (19) and (20):

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} = -\frac{T\left(\frac{\partial S}{\partial P}\right)_T + V}{T\left(\frac{\partial S}{\partial T}\right)_P} = -\frac{T\left(\frac{\partial S}{\partial P}\right)_T + V}{C_P} , \tag{21}$$

where we also used (6). But we still haven't used (10), and when we do this last equation becomes:

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] , \tag{22}$$

and this brings as far as Carroll brought us. But we can go the extra mile.

Introducing the coefficient of thermal expansion,

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial P}\right)_H , \tag{23}$$

and the volumetric coefficient of expansion,

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P , \tag{24}$$

then (22) becomes

$$\mu_{JT} = \frac{V}{C_P}\left[\,\alpha T - 1\,\right] . \tag{25}$$

The point of deriving (22) is that it is in terms of variables which are more easily measured than those we started with in (15).

4 Appendix

This is Carroll's proof of (15):

$$\left(\frac{\partial T}{\partial P}\right)_H = \left|\frac{\partial(T,H)}{\partial(P,H)}\right| = \frac{\left|\frac{\partial(T,H)}{\partial(T,P)}\right|}{\left|\frac{\partial(P,H)}{\partial(T,P)}\right|} = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} . \tag{26}$$