Math Diversion Problem 534: Use of Jacobians in Thermodynamics (E.T. Jaynes), Part 5

P. Reany

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> In a large class of problems, the objective is to express
> some quantity of interest, or some condition
> of interest, in terms of experimentally
> measurable quantities.
> — E. T. Jayne

1 Introduction

This is my fifth article explaining and demonstrating the revisions that physicist E.T. Jaynes[1] long ago proposed to the scientific community regarding how thermodynamics should be presented mathematically, especially with regard to partial derivatives and jacobians. I think it's probably necessary for the reader to have read and understood the previous papers in this series to understand this paper.

Note: The paper on Jaynes immediately preceding this one (Problem 516) contains some results necessary to understand a section of this paper. But, in theory, you could just take those results at face value and you'd still get something out of it.

2 From Last Time

We'll need this result:

$$[SX] = \frac{C_X}{T}[TX]\,, \tag{1}$$

which is Jaynes's Eq. (2-20).

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[1] Found in: "Use of Jacobians in Thermodynamics," available from on-line notes at https://bayes.wustl.edu/etj/thermo/stat.mech.2.pdf

3 Section 2.3 (Elementary Examples)

Jaynes has assured us that the experimentalist is always able to transform any given relation in thermodynamics variables into a relation that contains easy-to-measure variables. Those that aren't include S, U, H, F, G. He goes on to say:

> Thus, if the entropy appears in the combination $[TS]$, we can use the Maxwell relation to replace it with $[PV]$. If it appears in some other combination $[SX]$, we can use the identity (2-20).

After Jaynes explains how to deal with quantities like $[SX]$ and $[SX]$,, he defined the constituitive charcterizeind variable of

Isothermal Compressibility:

$$(2\text{-}27)\qquad K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_P = \frac{[TV]}{V[PT]}\,. \tag{2}$$

Thermal Expansion Coefficient:

$$(2\text{-}28)\qquad \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_T = \frac{[PV]}{V[PT]}\,. \tag{3}$$

Ratio of Specific Heats:

$$(2\text{-}29)\qquad \gamma = \frac{C_P}{C_V}\,. \tag{4}$$

And here's the fun part: Establish (2-31):

We'll start from the LHS, with help from Jaynes' (2-14) and then (2-16a):

$$\left(\frac{\partial U}{\partial P}\right)_S = \frac{[US]}{[PS]} = \frac{T[SX]_{X=S} - P[VX]_{X=S}}{[PS]} = \frac{T\cancel{[SS]} - P[VS]}{[PS]} = -P\frac{[VS]}{[PS]}\,. \tag{5}$$

Now for some intermediate results, using (1).

$$[SV] = \frac{C_V}{T}[TV]\,, \tag{6a}$$

$$[SP] = \frac{C_P}{T}[TP]\,. \tag{6b}$$

Then

$$\frac{[SV]}{[SP]} = \frac{C_V[TV]/T}{C_P[TP]/T} = \frac{C_V[TV]}{C_P[TP]}\,. \tag{7}$$

With the help of (2-27) and (2-29), we can write

$$\frac{C_V[TV]}{C_P[TP]} = \frac{C_V}{C_P}\frac{[TV]}{[TP]} = \gamma^{-1}KV\,. \tag{8}$$

On plugging this into (5), we get Jaynes' (2-31):

$$\left(\frac{\partial U}{\partial P}\right)_S = \frac{PVK}{\gamma} \tag{9}$$

And here's more of the fun part: Establish (2-35), using (2-16b):

$$\begin{aligned}
\left(\frac{\partial T}{\partial P}\right)_H &= \frac{[TH]}{[PH]} \\
&= \frac{-[HT]}{-[HP]} = \frac{[HT]}{[HP]} \\
&= \frac{T[SX]_{X=T} + V[PX]_{X=T}}{T[SX]_{X=P} + V[PX]_{X=P}} \\
&= \frac{T[ST] + V[PT]}{T[SP] + V\cancel{[PP]}} \\
&= \frac{T[VP] + V[PT]}{C_P[TP]} \qquad \text{(where } [ST] = [VP] \text{ \& we used (6b))} \\
&= \frac{V}{C_P}\frac{T[VP]/V + [PT]}{[TP]} \\
&= \frac{V}{C_P}\left(T\frac{[VP]}{V[TP]} - 1\right) \\
&= \frac{V}{C_P}\left(T\beta - 1\right)\,,
\end{aligned} \tag{10}$$

where we used (3).

And lastly, we identity $\left(\frac{\partial T}{\partial P}\right)_H$ as the Joule-Thomson coefficient μ, hence,

$$\mu = \frac{V}{C_P}\left(\beta T - 1\right)\,. \tag{11}$$

I just want to make a quick comment that Wikipedia gives the Joule-Thomson coefficient equation as

$$\mu_{JT} = \frac{V}{C_P}\left(\alpha T - 1\right)\,, \tag{12}$$

and leave it to my betters to resolve this discrepancy.