Math Diversion Problem 516: Use of Jacobians in Thermodynamics (E.T. Jaynes), Part 4

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Thermodynamics is Nature's way of balancing
entropy with enthalpy.
— Rafael Jaramillo

1 Introduction

This is my fourth 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 first two papers in this series to understand this paper.

Note: The paper on Jaynes immediately preceding this one (Problem 509) 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.

This time we have two equations to establish: Jaynes's (2-22) and (2-23):

$$TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP\,, \tag{1a}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P\,. \tag{1b}$$

We'll soon find a reference to Eq. (2-14), so here it is:

$$\left(\frac{\partial A}{\partial B}\right)_C = \frac{[AC]}{[BC]} = \frac{[CA]}{[CB]}\,. \tag{2}$$

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

2 Continuing the discussion

We'll begin by moving on to page 6 of Jaynes's paper. Next, we come across the definition of heat capacity at constant X:

$$\text{(2-19)} \qquad C_X = T\left(\frac{\partial S}{\partial T}\right)_X \,. \tag{3}$$

Using this last equation and Jaynes's (2-14), we have that

$$\text{(2-20)} \qquad [SX] = \frac{C_X}{T}\,[TX]\,. \tag{4}$$

Establishing Eq. (2-21)

We start with Jaynes's (2-9):

$$\text{(2-9)} \qquad [AB]dC + [BC]dA + [CA]dB = 0\,, \tag{5}$$

Theorem:

Using Jaynes's (2-9), show that

$$TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV\,, \tag{6}$$

where the independent variables are chosen as $\eta = \{T, V\}$.[2]

Proof:

We make the carefully chosen replacements into (**??**):

$$A \to T\,, \quad B \to V\,, \quad C \to S\,, \tag{7}$$

which gives us

$$[TV]dS + [VS]dT + [ST]dV = 0\,. \tag{8}$$

Now we expand this in the method we were told, to get

$$\begin{aligned}\Big[\left(\frac{\partial T}{\partial T}\right)_V\left(\frac{\partial V}{\partial V}\right)_T - \left(\frac{\partial T}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_V\Big]dS \\ + \Big[\left(\frac{\partial V}{\partial T}\right)_V\left(\frac{\partial S}{\partial V}\right)_T - \left(\frac{\partial V}{\partial V}\right)_T\left(\frac{\partial S}{\partial T}\right)_V\Big]dT \\ + \Big[\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_T - \left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial T}{\partial T}\right)_V\Big]dV = 0\,.\end{aligned} \tag{9}$$

[2] In SD, I usually use the symbol η to represent the fundamental, or the listing of the independent variables. When they are delimited by parentheses, it refers to a vector. When delimited by curly braces, it refers to an ordered list. And since we are not going to take derivatives by the fundamental vector, per se (SD style), I chose the set delimiters.

At a first simplification, we get

$$\Big[1 - 0\Big]\, dS + \left[0 - \left(\frac{\partial S}{\partial T}\right)_V\right] dT + \left[0 - \left(\frac{\partial S}{\partial V}\right)_T\right] dV = 0\,, \tag{10}$$

or more simply yet,

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV\,. \tag{11}$$

On applying (**??**) with $X = V$, we have that

$$dS = \frac{C_V}{T}\, dT + \left(\frac{\partial S}{\partial V}\right)_T dV\,. \tag{12}$$

Multiplying through by T we get

$$T dS = C_V\, dT + T \left(\frac{\partial S}{\partial V}\right)_T dV\,. \tag{13}$$

On applying a Maxwell relation,[3] we end up with Jaynes's (2-21):

$$T dS = C_V\, dT + T \left(\frac{\partial P}{\partial T}\right)_V dV\,. \tag{14}$$

To get Jaynes's (2-22), we go back to Eq. (**??**), we make the assignments:

$$A \to T\,, \quad B \to V\,, \quad C \to S\,, \tag{15}$$

but this time $\eta = \{T, P\}$, we eventually get

$$T dS = C_P\, dT - T \left(\frac{\partial V}{\partial T}\right)_P dP\,. \tag{16}$$

[As a heads-up, I think Jaynes's department secretary missed hitting the shift key a couple times when typing this paper.]

Theorem:

Using Jaynes's (2-14) and others, show that

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P\,, \tag{17}$$

which Eq. (2-23), Jaynes's 'energy equation'.

Proof:

[3] See page 5 of Jaynes's paper.

Jaynes has us invoking (2-14):

$$\left(\frac{\partial A}{\partial B}\right)_C = \frac{[AC]}{[BC]}\,. \tag{18}$$

Into this we make the replacements:

$$A \to S\,, \quad B \to T\,, \quad C \to X\,, \tag{19}$$

to get

$$\left(\frac{\partial S}{\partial T}\right)_X = \frac{[SX]}{[TX]}\,, \tag{20}$$

or

$$[SX] = \left(\frac{\partial S}{\partial T}\right)_X [TX] = \frac{C_X}{T}[TX]\,, \tag{21}$$

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

Next, Eq. (2-13):

$$[AX] = b[BX] + c[CX]\,. \tag{22}$$

The differential energy equation:

$$dU = TdS - PdV\,. \tag{23}$$

So, we divide through by dV,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P\,. \tag{24}$$

On using anther Maxwell relation, have (2-23):

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P\,. \tag{25}$$

Establish (2-24):

$$dA = bdB + cdC\,, \tag{26}$$

$$[AX] = b[BX] + c[CX]\,, \tag{27}$$

Pattern-matching these to

$$dU = T\,dS - P\,dV\,, \tag{28}$$

and

$$[UX] = T[SX] - P[VX]\,, \tag{29}$$

and then letting $X \to T$:

$$[UT] = T[ST] - P[VT]\,, \tag{30}$$

etc, which Jaynes refers to as the energy equation in jacobian notation.