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The Legendre Transformation for beginning Thermodynamics students

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The Legendre Transform, as traditionally taught in introductory Physical Chemistry classes, can be better understood with some simple examples, which are discussed herein,

I. INTRODUCTION

The student who reads the equation creating the Enthalpy from the internal Energy:

$$dH = dE + d(pV) \qquad (1)$$

and understands that E is a function V while H is a function of p (both are functions of S) is truly lucky, since s/he need not read this paper.
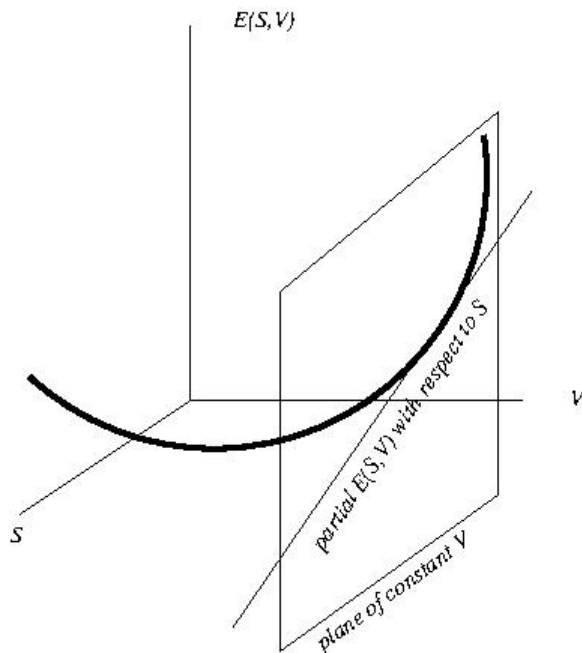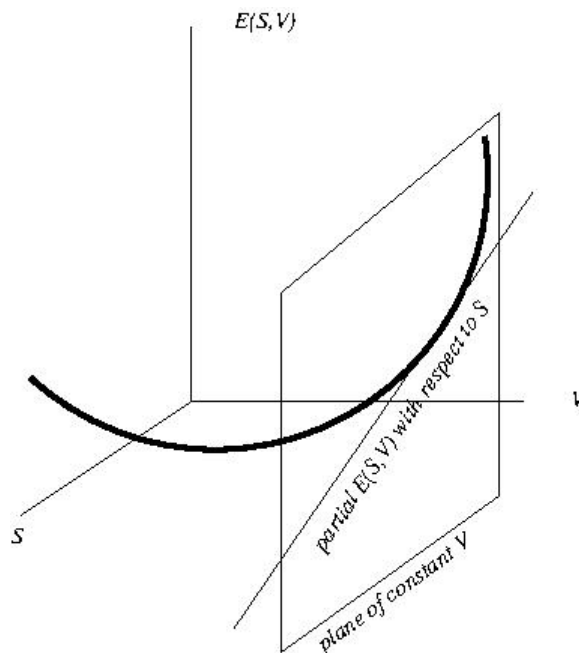
II. $dE = dq + dw$

FIG. 1. partial derivative with respect to S

Depending on how one was educated, the First Law $dE = dq + dw$ can be re-written as

$$dE = TdS - pdV$$

which means that E is a function of S and V, i.e., $E(S, V)$. Thus

$$\left(\frac{\partial E}{\partial S}\right)_V = T$$

and

$$\left(\frac{\partial E}{\partial V}\right)_S = -p$$

since

$$dE = \left(\frac{\partial E}{\partial S}\right)_V + \left(\frac{\partial E}{\partial V}\right)_S$$

The question asked in this piece is, how does it happen that when one invokes the "classical" Legendre Transformation:

$$dE + d(pV) \equiv dH = TdS - pdV + (pdV + Vdp) = TdS + Vdp$$

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H turns out to be a function of S and p, i.e. $H(S, p)$! Why does this work? The answer is, of course, that the Legendre Transformation is more than meets the eye (above).

Why do we care? Although most chemistry students get to run a reaction at constant volume, i.e., employing a bomb calorimeter, they also understand that most reactions are carried out at constant pressure, i.e., the external pressure of the atmosphere which surrounds us. Further, although reactions can be carried out adiabatically, i.e., at constant entropy, very often they are run under thermostatic control of the temperature, i.e., isothermally. So, we want to have variables T and p, not S and V!

Parenthetically, we note that in physics, the change from the Lagrangian to the Hamiltonian involves changing canonical variables in the same manner as we've been doing here in thermodynamics.

1. Classical Derivation

Recall

$$dE = dq + dw$$

or

$$dE = TdS - pdV$$

which are statements of the First Law.

Then

$$dE + d(pV) = TdS - pdV + d(pV) \rightarrow dH$$

$$dH = TdS - p\!\!\!/dV + p\!\!\!/dV + Vdp$$

$$Vdp - SdT - TdS \rightarrow dA$$

which yields

$$dH - d(TS) = \cancel{TdS} + Vdp - SdT - \cancel{TdS} \rightarrow A(T, V)$$

(We omit the Gibbs Free Energy equivalent derivation) So, these manipulations do not seem, to me, to be convincing that we are changing the independent variables. Again, if you are convinced of the opposite, you need not read further!

III. $y[x]$ AS AN EXAMPLE

Consider a function $y(x)$. For the rest of this discussion we will write $y[x]$ rather than $y(x)$ to emphasize the functionality, and y will be analogous to E, and x will be analogous to V or S, so that we are doing the constant entropy or constant volume part of the transformation from dE to dH or dA.

We wish to recast the form $y[x]$ into a new form, $\beta[y']$, where β is some new function, and y' is $\frac{dy}{dx}$ This will encode the information about $y[x]$ in terms of the slope of $y[x]$ and the intercept of the tangent (β) to the curve $y[x]$ with the $y[x]$ axis.
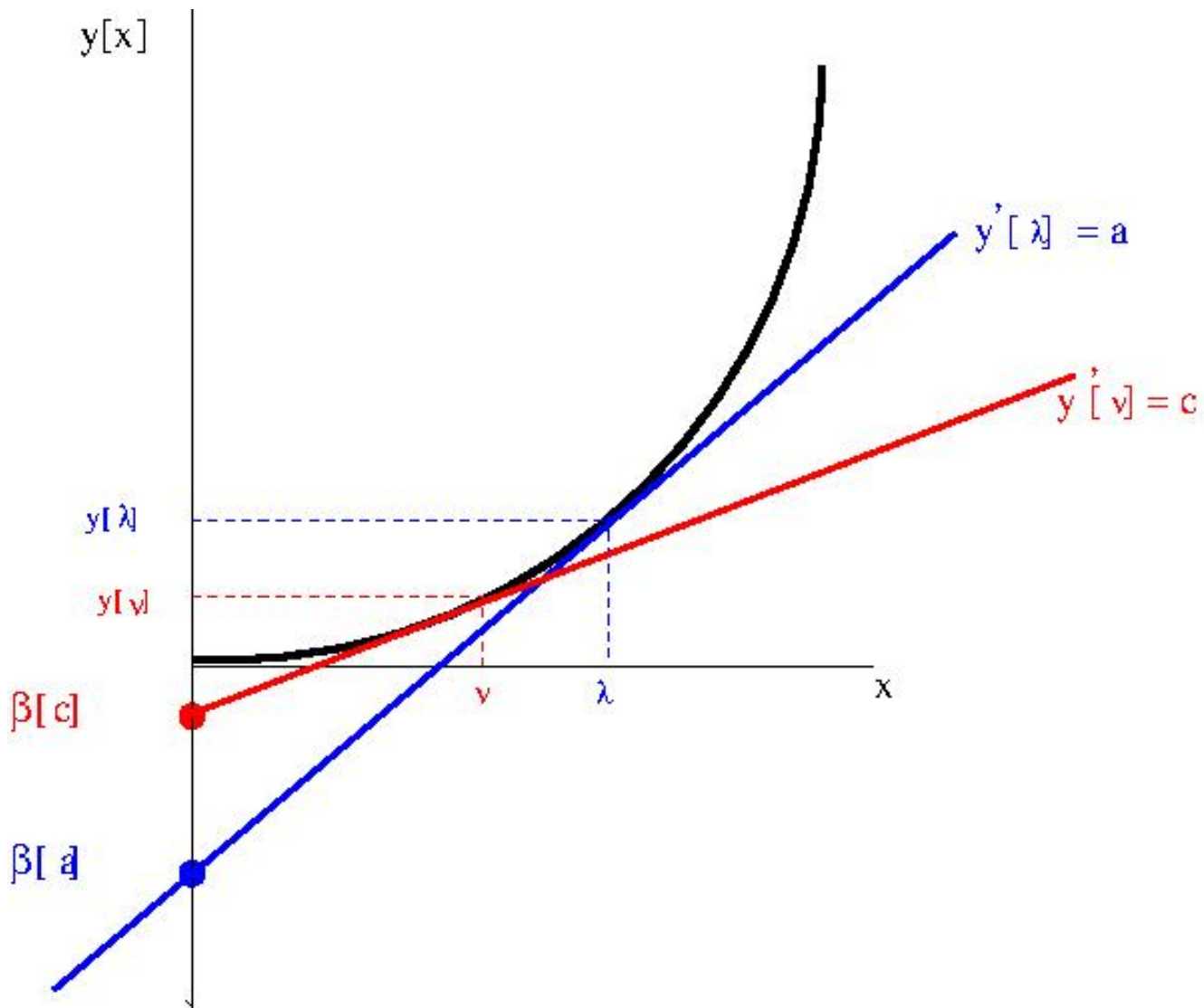
FIG. 2. First illustration of Legendre Transformation. The slope $y'[x]$ in blue, for $x = \lambda$, and the slope $y'[x]$ in red, for $x = \nu$ are shown explicitly. The intercepts are shown as $\beta[a]$ and $\beta[c]$ respectively (mnemonically to remind us of $y = mx + b$). The trick is to represent the same function $y[x]$ in terms of β and y'. Thus, $y[\lambda] = \beta[a] + a * \lambda$, and $y[\nu] = \beta[c] + c * \nu$

Defining $y[x]$ as a function of x and then forcing a representation of this same function in the form $$y[x] = mx + b$$ where $$m = \frac{dy}{dx} = y'$$	If, for example $$y[x] = ax^2 + bx$$ so that $$\frac{dy}{dx} = 2ax + b = y'$$ then, solving for x in terms of the slope, we obtain $$x = \frac{(y' - b)}{2a}$$ where, defining β as the intercept, we have:	If, for example $$E[V] = aV^2 + bV$$ so that $$\frac{dE}{dV} = 2aV + b = E'$$ then, solving for V in terms of the slope, we obtain $$V = \frac{(E' - b)}{2a}$$ where, defining β as the intercept, we have:
$$y[x] = \frac{dy}{dx} \times x + \beta$$ i.e., $$y[x] = y' \times x + \beta[y']$$ where $\beta[y']$ is the intercept.	$$y = y' \times x + \beta[y']$$ which is, rearranging: $$\beta[y'] = y[x] - xy'$$	$$E = E' \times V + \beta[E']^{-p}$$ which is, rearranging: $$\beta[E']^{-p} = E[V] - VE'^{-p}$$ Thus $H(S, p) \equiv \beta = E(S, V) + pV$
This provides a vehicle for obtaining x, i.e. $$x = \frac{[y'] - \beta[y']}{[y']}$$	Substituting $$y = ax^2 + bx = slope \times x$$ $$+ intercept$$ for x on the left hand side we have: $$a\left(\frac{y' - b}{2a}\right)^2 + b\left(\frac{y' - b}{2a}\right) =$$ $$y' \times x + \beta$$ and substituting for x on the right hand side we have: $$a\left(\frac{y' - b}{2a}\right)^2 + b\left(\frac{y' - b}{2a}\right) =$$ $$y' \times \left(\frac{y' - b}{2a}\right) + \beta$$	Substituting $$E = aV^2 + bV = slope \times V$$ $$+ intercept$$ for V on the left hand side we have: $$a\left(\frac{E' - b}{2a}\right)^2 + b\left(\frac{E' - b}{2a}\right) =$$ $$E' \times V + \beta$$ and substituting for V on the right hand side we have: $$a\left(\frac{E' - b}{2a}\right)^2 + b\left(\frac{E' - b}{2a}\right) =$$ $$E' \times \left(\frac{E' - b}{2a}\right) + \beta$$

$$\dfrac{\partial \beta}{\partial y\prime} \equiv \beta'$$	Solving for β we have $$\beta = (b - y')\left(\frac{y' - b}{2a}\right) + a\left(\frac{y' - b}{2a}\right)^2$$ which is $$\beta = \\ 2a(b - y')\left(\frac{y' - b}{2a}\right)\left(\frac{b - y'}{2a}\right) \\ + a\left(\frac{y' - b}{2a}\right)^2$$ and $$\beta = -a\left(\frac{y' - b}{2a}\right)^2$$ where we have expressed β as a function of y', which happens to be $-x$ (see above). This means $\beta(-x)$.	Solving for β we have $$\beta = (b - E')\left(\frac{E' - b}{2a}\right) + a\left(\frac{E' - b}{2a}\right)^2$$ which is $$\beta = \\ 2a(b - E')\left(\frac{E' - b}{2a}\right)\left(\frac{b - E'}{2a}\right) \\ + a\left(\frac{E' - b}{2a}\right)^2$$ and $$\beta = -a\left(\frac{E' - b}{2a}\right)^2$$ where we have expressed β as a function of E', which happens to be $-p$ (see above). This means $\beta(-p)$. $\quad^{H(p)}$

Proof that $\beta' = -x$:

$$\frac{\partial \left(\beta = y[x] - x\frac{\partial y}{\partial x} \right)}{\partial x}$$

and since

$$\frac{\partial \beta}{\partial x} = \frac{\partial \beta}{\partial y'} \frac{\partial y'}{\partial x}$$

one has

$$\beta' \frac{\partial y'}{\partial x} = y' - y' - x\frac{\partial y'}{\partial x}$$

i.e., $\beta' = -x$ and therefore

$$\frac{\partial \beta}{\partial y'} = \frac{y' - b}{2a} \equiv \beta' = -x$$

Q.E.D.

Choosing again to write β in an alternate format using a straight line (slope and intercept, i.e. performing another Legendre Transformation) we have

$$\beta = slope \times y' + intercept$$

which is

$$\beta = -x \times y' + intercept$$

where the intercept is called "y". Thus, we have

$$\beta = -x \times y' + y$$

so

$$y = \beta + y' \times \beta'$$

$$\beta = \beta' \times y' + intercept$$

$$\beta = -x \times y' + intercept$$

where the intercept is called y Then we have

$$\beta = -x \times y' + y$$

$$-a\left(\frac{y' - b}{2a}\right)^2 = -x \times (2ax + b) + y$$

$$-ax^2 = -x \times (2ax + b) + y$$

which is exactly the original defining equation for $y[x]$!

$$\beta = \beta' \times E' + intercept$$

$$\beta = -V \times E' + intercept$$

where the intercept is called E Then we have

$$\beta = -V \times E' + E$$

$$-a\left(\frac{E' - b}{2a}\right)^2 = -V \times (2aV + b) + E$$

$$-aV^2 = -V \times (2aV + b) + E$$

which is exactly the original defining equation for $E[V]$!

IV. AN EXAMPLE (SEE WIKIPEDIA ON THIS SUBJECT)

Let

$$y(x) = e^x$$

and

$$\frac{dy}{dx} = e^x = y'$$

Now

$$y \equiv y'x + \beta$$

is the desired replacement, so that

$$\beta = y - y'x$$

which is

$$\beta = y - y'\ell n y$$

Oddly enough, this form is equivalent to

$$\beta[y'] = y' - y'\ell n y'$$

which is amazing.

V. ANOTHER EXAMPLE (THIS TIME IN THERMODYNAMIC LANGUAGE)

We wish to perform a Legendre Transformation on $E(S, V)$ to change the S variable to something else (it's going to be the temperature).
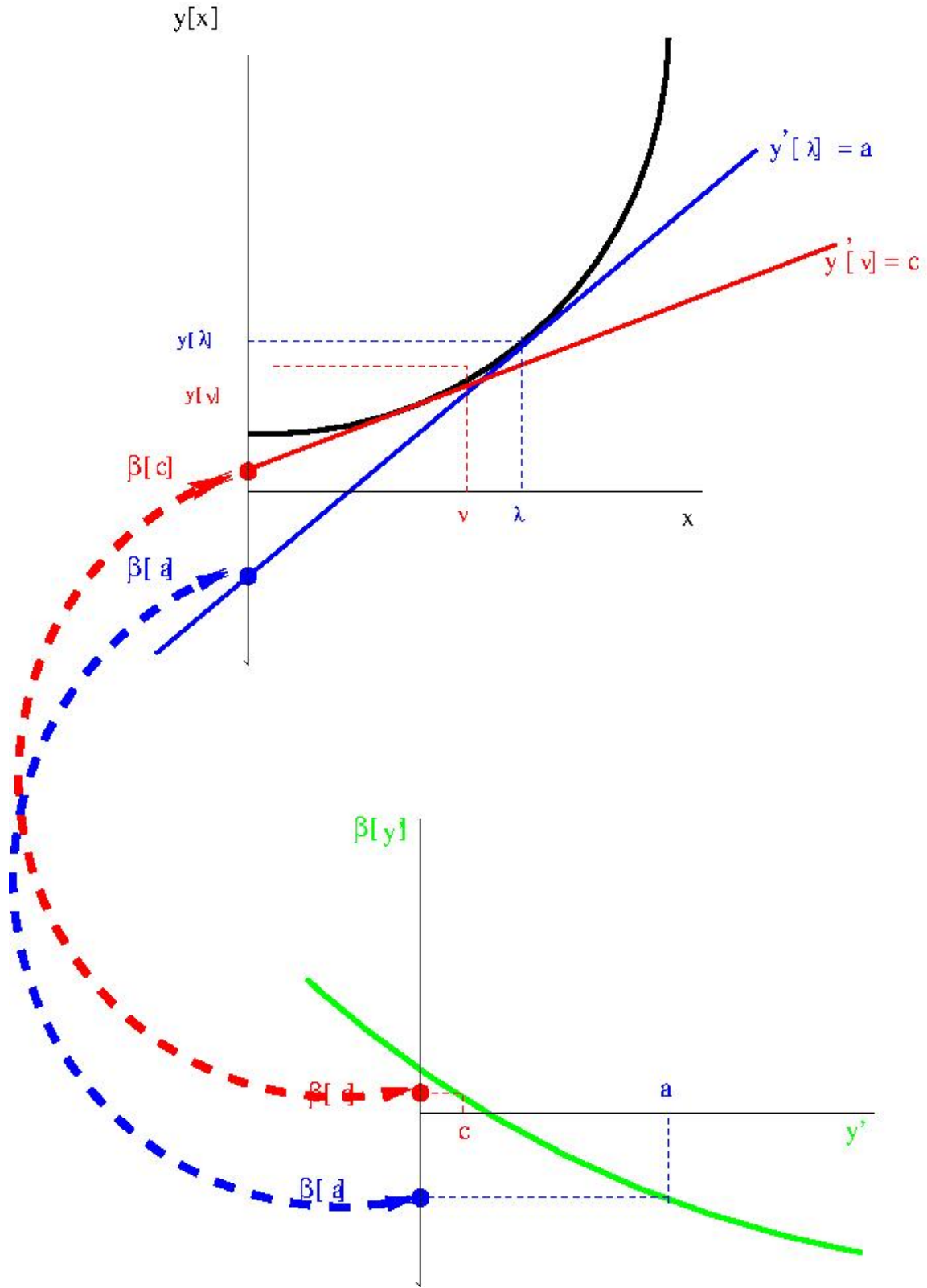
FIG. 3. The construction of the Legendre Transformation

Consider a system whose energy has the form:

$$E = 2S^2 + 4 + V^2 = E(S, V) \qquad (2)$$

where E is an explicit function of S and V (as required in elementary thermo. Note that this function is completely invented, arbitrary, and not meant to mimic or represent any real system in this or any other universe.).

We wish to couch this function in the Legendre form:

$$E = slope \times (S - 0) + intercept \qquad (3)$$

At constant V, we have

$$\left(\frac{\partial E}{\partial S}\right)_V = 4S = slope$$

Since the slope is $4S$ (see above) we have $S = \frac{slope}{4}$, so that, by substituting into Equation 3 we have

$$E = slope \times (S-0) + intercept = slope \times \frac{slope}{4} + intercept$$

so that

$$2S^2 + 4 + V^2 = \frac{slope^2}{4} + intercept$$

which is, substituting $(\frac{slope}{4})$ for S on the left hand side

$$2\left(\frac{slope}{4}\right)^2 + 4 + V^2 = \frac{slope^2}{4} + intercept$$

which is an equation for the intercept as a function of the slope (and V which is being carried along here):

$$intercept = V^2 + 4 - \frac{slope^2}{8}$$

If we call the intercept A, the Helmholtz Free Energy, and the slope we call T, the temperature, then we have

$$A(T, V) = V^2 + 4 - \frac{T^2}{8}$$

which is the desired result. That is, we have started with a function of S and V and ended up with a function of T and V. Just to prove that we know what we're doing, we will do it again, this time transforming $A(T, V)$ into $E(S, V)$. We start with desiring a representation of $A(T, V)$ of the form:

$$A = slope' \times T + intercept'$$

Then

$$\left(\frac{\partial A}{\partial T}\right)_V = -2T/8 = slope' \qquad (4)$$

i.e., $T = -4 \times slope'$. Substituting for T in Equation 4

$$A = slope' \times T + intercept' = slope' \times (-4 \times slope') + intercept'$$

which is, substituting on the l.h.s.

$$V^2 + 4 - \frac{T^2}{8} = slope' \times (-4 \times slope') + intercept'$$

which is, again substituting for T,

$$V^2 + 4 - \frac{(-4 \times slope')^2}{8} = slope' \times (-4 \times slope') + intercept'$$

which rearranges to

$$V^2 + 4 + 2 \times slope'^2 = intercept'$$

i.e.

$$V^2 + 4 + 2 \times S^2 = E$$

which is what we started with (sorry about the sentence construction).

VI. THE SACKUR-TETRODE EXAMPLE

When one writes

$$E = \frac{3}{2} N k_B T \qquad (5)$$

for an ideal (monatomic) gas, where k_B is the Boltzmann constant, it certainly looks like the energy is a function of T, the temperature. (N is the number of molecules, and E is the first law thermodynamic energy.) But we are taught that $E = E(S, V)$, and while it is true (from the Joule expansion argument), that for an ideal gas, $E = E(S)$ alone, i.e., the energy does not depend on the volume, never the less, one wonders how to reconcile these two views, that on the one hand, the energy should be a function of S, and yet it explicitly is written as a function of T in Equation 5. How is one to write

$$dE = TdS - pdV = TdS (for\ an\ ideal\ gas, V = fixed)$$

using Equation 1 above? Even if one were willing to say that E is a function of T through S, i.e., $S = S(T, V)$ and $E = E(S)$, what are we to do with Equation 5 to construct the Helmholtz free energy (and the Gibbs)?

The Sackur-Tetrode Equation gives us some insight into this problem. Specifically, this equation is

$$\frac{S}{k_B N} = \ln\left[\frac{V}{N}\left(\frac{4\pi m}{3h^2}\frac{E}{N}\right)^{3/2}\right] + \frac{5}{2} \qquad (6)$$

i.e., $S = S(E, V)$ and assorted atomic constants. For clarity, we absorb these constants (lump them) so the Sackur-Tetrode Equation becomes

$$S = N k_B \ell n \left(E^{3/2} V\right) + \beta \qquad (7)$$

where β absorbs Planck's constant, the mass of the atomic constituent of the ideal gas, π, etc.. We can invert Equation 7 solving for E in terms of S and V, obtaining

$$E = \left(\frac{e^{(S-\beta)/Nk_B}}{V} \right)^{3/2}$$

which surely reflects the desired dependency on S and V. This form begs us to take the partial derivative of E with respect to S at constant V, to see what happens. Thus

$$\left(\frac{\partial E}{\partial S} \right)_V = \frac{2}{3} \frac{E}{Nk_B} \equiv T$$

which recovers $E = \frac{3}{2}Nk_BT$ (Equation 1). As an aside, we obtain the other partial derivative

$$\left(\frac{\partial E}{\partial V} \right)_S = -\frac{2}{3} \frac{E}{V} \equiv -p$$

which recovers a well known result for ideal gases. In the set of variables S, T, p, and V the form of the partial derivatives is simplest if one chooses two of them appropriately, the so called canonical variables.

Choosing $E(T, V)$ is not useful, since the partial of E with T at constant V has no special meaning, i.e., does not lead to another member of the set. Choosing

$E = E(S, V)$, on the other hand, leads to something wonderful since the partial of E with respect to S leads to T, a member of the set. The variable pairs S and T on the one hand, and p and V on the other are known as canonically conjugate variables. Posing thermodynamic equations in properly chosen canonical pairs (one from each pair) results in equations whose information content is maximum, and whose applicable partial derivatives are themselves canonically conjugate opposites.

VII. APOLOGIA

I'm reluctant to close the file on this paper, since the words are not flowing well, but at the age of 81, I can't dawdle too long. The original web pages from which the above is drawn and re-worked, were written 20+ years ago. I've attempted to clean the words and equations but feel some misgivings that the structure of the discussion is somehow wrong. Perhaps the reader will find a better way to express these thoughts. But the take away, about changing variables, I still think is important for chemistry students to understand.

Many others [1–3] have written about the Legendre transformation. And, of course, Wikipedia has an article on it.

[1] R. K. P. Zia, E. F. Redish, and S. R. McKay, American Journal of Physics **77**, 614 (2009), https://doi.org/10.1119/1.3119512.

[2] N. Čutić, This is an anonymous paper posted by the cited author. In case the link fails sometime in the future, I've got a local copy here: https://drive.google.com/file/d/1T8UuVAkDjzllk7M-2Gn7WhKzsfxL937o/view?usp=sharing. Otherwise, the original link is, http://mafija.fmf.uni-lj.si/seminar/files/2002_2003/legendre6.pdf.

[3] C. E. Mungan, https://www.aapt.org/docdirectory/meetingpresentations/sm14/mungan-poster.pdf.