



# TEACHING THERMO WITH THE HELP OF FRIENDS

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Classical equilibrium thermodynamics is unique among the core courses in chemical engineering. It is uncommonly pervasive, for it addresses some of the deepest questions relating to the nature of the physical world and it lurks in the background of all disciplines (indeed, what but a departure from equilibrium drives transport, what but an approach toward chemical equilibrium is kinetics?). Yet it is also so plainly and tangibly applicable to real systems that, with a few well-placed comments, a teacher finds it quite unnecessary to apologize for any derivation, no matter how long, for there is always a *need to know* to act as a light at the end of the tunnel.

Most people either love or hate thermodynamics; it seems to evoke such strong emotions that there is little room for a middle ground. One sees people indifferent to (or mildly interested in or irritated by) transport, kinetics, control or design—but not so with thermo. And unlike other subjects, it seems not to be learned *per se*, but rather to be acquired by acclimation through repeated, deepening exposure in a sequence of courses that ostensibly cover the same material.

A teacher of thermodynamics makes a few inevitable observations. To wit: why is it that the student who professes most strongly to have studied for the first hour exam (and, in particular, claims to understand fully the difference between functions of state and path-dependent quantities) proudly recites the first law as  $U = \Delta Q - \Delta W$ ?

(Oh no!)

And why is it that at some time in every single semester somebody uses the ideal gas law to estimate the density of liquid water?

(NO! NO! NO!)

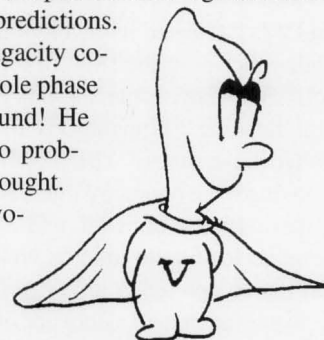
Actually, the purpose of these lines is not to belabor com-



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mon experiences but rather to record my acquaintance with two individuals who have profoundly affected the way in which I teach undergraduate thermodynamics, and the applied subject that rests so heavily upon it, separations. The first is a mysterious writer of urgent letters that always seem to arrive just before class and make me drop whatever I was "actually going to cover" in favor of working out his practical problem (which turns out to have considerable pedagogical value). Over time he has come to exude a real presence, despite the fact that he has never actually been seen by any student on or off campus. Rumor has it that he is quite incompetent (hence the need for all the help) and drinks copious amounts of organic liquids, apparently without ill effect. His name is Elroy Hutch.

The second is far more capable than Elroy, but more elusive. He is Virial Man, caped crusader against inaccuracies in physical property predictions. Faster than a speeding fugacity coefficient! Able to leap whole phase diagrams in a single bound! He solves really hard thermo problems without a second's thought. Unfortunately, his benevolent duties frequently require his presence else-



where, so he is rarely available.

## ENERGY

I had the privilege of dining with Elroy on March 3, 1990, and on that day he made a statement that puzzled me. He said, "the internal energy of gases depends only upon temperature." I corrected him by adding the qualification, *ideal* gases, but he was quite insistent and dismissed my protestations. Our conversation then turned to other things, but I was disturbed by his misconception, and slowly I began to realize why he'd said what he said.

In most courses the ideal gas is introduced immediately because of its key role as the simplest working fluid and a realizable limiting case of real gas behavior. Textbooks address all sorts of processes with ideal gases, which readily present themselves, and the first law is easy to apply because  $dU$  is indeed  $C_V dT$ . Soon it's off to the Carnot cycle, entropy, and the Maxwell relation leading to the identity

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \quad (1)$$

that finally allows one to ascertain the *volumetric* dependence of internal energy for real gases. But by then all the tough first-law problems with pistons and cylinders are forgotten, and they often go unrevisited because time is short and one must move on to the Gibbs energy and phase equilibria and mixtures and Raoult's law. So students can easily go on without being drilled in solving first-law problems with real gases using equations of state, and their first impulse is to write  $dU = C_V dT$  *always*.

By next morning I had come to the conclusion that I would have to change things. So I called Virial Man (who, thankfully, was available, albeit briefly for he soon had to be off to do battle against the Redlich-Kwong Invaders in the North). He thought for a moment and then responded with characteristic brevity and insight: Why not give students the identity, Eq. (1), at the start, promise them you will derive it later, quickly discuss the reversible and irreversible, isothermal and adiabatic processes with ideal gases (which they have inevitably seen before), and then concentrate on real gases? Virial Man suggested the following exercise.

► **PROBLEM** • One mol of ethylene gas is confined within an insulated, frictionless piston-and-cylinder assembly at 300K and 60 bar by a suitable weight *in vacuo* (Figure 1). If half the weight is suddenly removed so that the gas undergoes an irreversible adiabatic expansion, what will be the gas temperature when it finally settles down to equilibrium again? Data: the ideal gas heat capacity of ethylene is given by<sup>[1]</sup>

$$C_p^{ig}(T) = A + BT + CT^2 + DT^3$$

with

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$$\begin{aligned} A &= 38.06 \text{ bar cm}^3/\text{mol K} \\ B &= 1.566 \text{ bar cm}^3/\text{mol K}^2 \\ C &= -8.348 \times 10^{-4} \text{ bar cm}^3/\text{mol K}^3 \\ D &= 1.755 \times 10^{-7} \text{ bar cm}^3/\text{mol K}^4 \end{aligned}$$

and its PVT behavior may be assumed to be described by the Peng-Robinson<sup>[2]</sup> equation

$$P = \frac{RT}{V-b} - \frac{a\alpha(T_r)}{V^2 + 2bV - b^2}, \quad \alpha(T_r) = \left[1 + \kappa(1 - T_r^{1/2})\right]^2$$

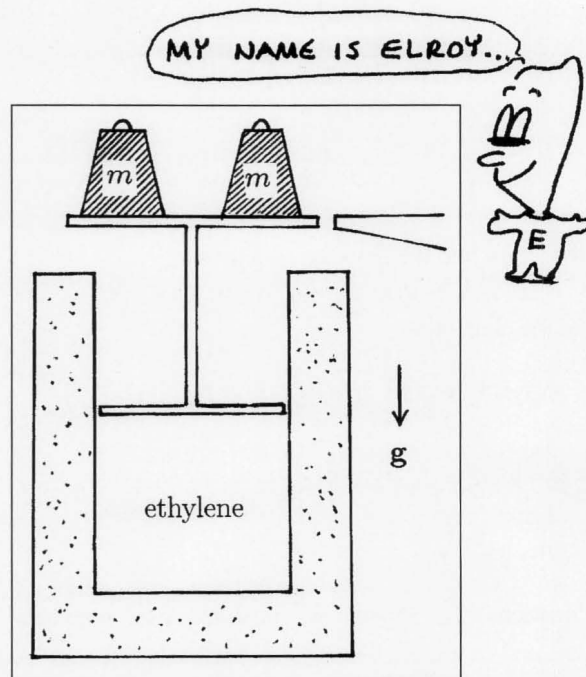
with

$$\begin{aligned} a &= 0.45724 R^2 T_c^2 / P_c = 5.001 \times 10^6 \text{ bar cm}^6/\text{mol}^2 \\ b &= 0.07780 RT_c / P_c = 36.24 \text{ cm}^3/\text{mol} \\ \kappa &= 0.37464 + 1.54226\omega - 0.26992\omega^2 = 0.5098^* \end{aligned}$$

**Elroy's (ideal gas) solution** • Assuming the piston to have negligible mass, the pressure has dropped by half in the final equilibrium state. The initial and final molar volumes are given by

$$V_i = \frac{RT_i}{P_i}, \quad V_f = \frac{RT_f}{P_f}$$

Note that the final temperature is unknown in the second equation. Assuming the heat capacity to be a constant, approximated by its value at 300K ( $C_V$  at 300 K = 354.3 bar cm<sup>3</sup>/mol K), application of the first law gives



**Figure 1.** Piston-and-cylinder assembly for carrying out an irreversible adiabatic expansion.

\* Critical constants and acentric factor  $T_c = 282.4\text{K}$ ,  $P_c = 50.4 \text{ bar}$ ,  $\omega = 0.089$ , from Reid, et al.<sup>[1]</sup>

$$C_V(T_f - T_i) = Q - W = 0 - P_f(V_f - V_i)$$

in which  $P_f(V_f - V_i)$  represents the work done by the gas in lifting the single weight remaining on the piston. It follows that

$$T_f = \frac{C_V + R(P_f/P_i)}{C_V + R} T_i = 271.5\text{K}$$

**Virial Man's solution** • The initial and final molar volumes are given by

$$60 \text{ bar} = P_i = \frac{RT_i}{V_i - b} - \frac{a\alpha(T_i)}{V_i^2 + 2bV_i - b^2} \quad (2)$$

$$30 \text{ bar} = P_f = \frac{RT_f}{V_f - b} - \frac{a\alpha(T_f)}{V_f^2 + 2bV_f - b^2} \quad (3)$$

Again, the final temperature,  $T_f$ , is unknown in Eq. (3).

Next, in applying the first law it will be necessary to ascertain the functional dependence of the internal energy  $U$  upon temperature  $T$  and molar volume  $V$ . By line integration from an arbitrary reference state at temperature  $T_0$  and effectively infinite molar volume,

$$\begin{aligned} U(T, V) &= U_0 + \int_{T_0}^T C_V^{ig}(T') dT' + \int_{\infty}^V \left( \frac{\partial U}{\partial V} \right)_T (T, V') dV' \\ &= U_0 + \int_{T_0}^T (C_P^{ig} - R) dT' + \int_{\infty}^V \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV' \\ &= (A - R)T + \frac{B}{2}T^2 + \frac{C}{3}T^3 + \frac{D}{4}T^4 \\ &\quad + \frac{a}{2\sqrt{2}b} \left[ \alpha(T_f) - T_f \alpha'(T_f) \right] \ln \left[ \frac{V + (1 - \sqrt{2})b}{V + (1 + \sqrt{2})b} \right] + \text{const.} \end{aligned}$$

Substitution into the first-law statement

$$U(T_f, V_f) - U(T_i, V_i) = Q - W = 0 - P_f(V_f - V_i)$$

gives the constraint

$$\begin{aligned} &(A - R)(T_f - T_i) + \frac{B}{2}(T_f^2 - T_i^2) + \frac{C}{3}(T_f^3 - T_i^3) + \frac{D}{4}(T_f^4 - T_i^4) \\ &+ \frac{a}{2\sqrt{2}b} \left\{ \left[ \alpha(T_f) - T_f \alpha'(T_f) \right] \ln \left[ \frac{V_f + (1 - \sqrt{2})b}{V_f + (1 + \sqrt{2})b} \right] - \left[ \alpha(T_i) - T_i \alpha'(T_i) \right] \ln \left[ \frac{V_i + (1 - \sqrt{2})b}{V_i + (1 + \sqrt{2})b} \right] \right\} \\ &= -(30 \text{ bar})(V_f - V_i) \quad (4) \end{aligned}$$

Equations (2), (3), and (4) constitute three nonlinear equations in the three un-



knowns  $V_i$ ,  $V_f$ , and  $T_f$ . (Actually, Eq. 2 can be solved first for  $V_i$  independently of Eqs. 3 and 4.) Solution by Newton's method (starting from Elroy's values as initial guesses) leads to the results

$$V_i = 210.1 \text{ cm}^3/\text{mol}$$

$$V_f = 367.2 \text{ cm}^3/\text{mol}$$

$$T_f = 251.1 \text{ K}$$

Work must be done to separate real molecules (which attract each other under these conditions), and the additional energy to do this work comes at the expense of a greater drop in temperature than would be observed with an ideal gas.

Examples where the temperature drop (and molar volume, for that matter) are off by fifty percent or more do wonders to convince students that the ideal gas law really wouldn't cut it in modeling supercritical extraction. If students are furnished with a nonlinear equation solver, they usually become quite agreeable to solving such problems (although I find surprising their initial reluctance to use the computer).

#### A Word About the Figures . . .

There are cases where the manuscript review process is a wholly rewarding experience, and this paper represents one of them, owing particularly to the input of Professor Kenneth R. Jolls, who served as one of the referees. In addition to suggesting numerous improvements now incorporated in the text, he kindly offered to make the figures with his unique expertise in thermodynamics and its graphical representation. This is embodied, in part, in his Equations of State (EOS) software [see K.R. Jolls, "Understanding Thermodynamics Through Interactive Computer Graphics," *Chem. Eng. Prog.*, **85**, 64 (1989)]. It is a pleasure to acknowledge Professor Jolls as the creator of Figures 2-5 as they appear here, far better than the author could have made them. They are, in fact, quantitative representations of the various processes discussed based on the Peng-Robinson equation, and not mere qualitative sketches.

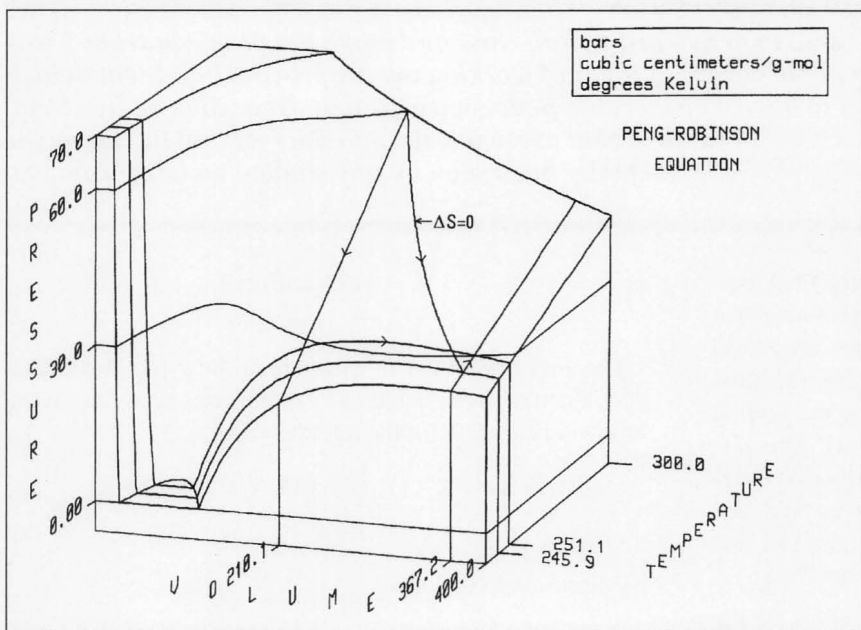


Figure 2. Two reversible paths between the initial state (300K, 60 bar) and the final state (251.1K, 30 bar). One path consists of a reversible adiabatic expansion followed by an isochoric heating step. The other consists of an isochoric cooling step followed by a reversible isothermal expansion.

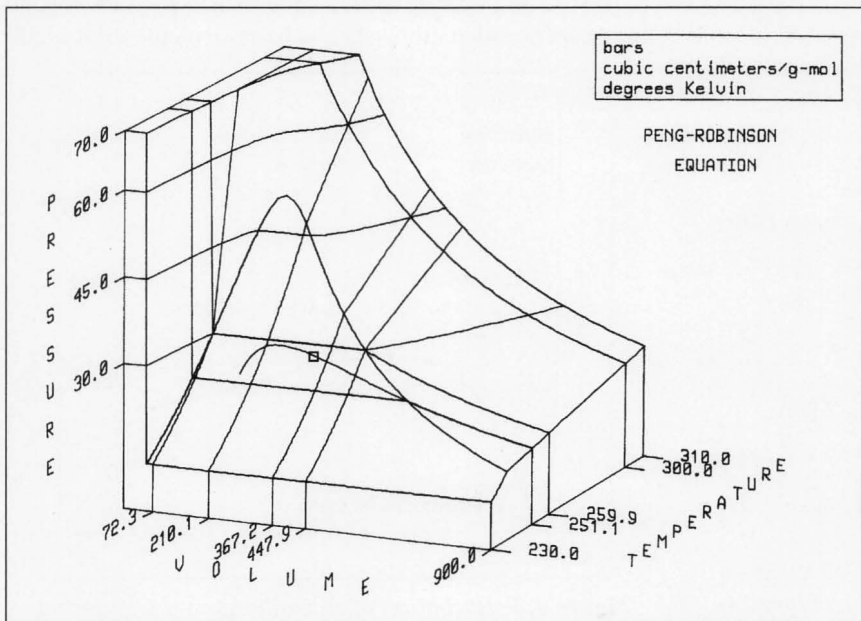
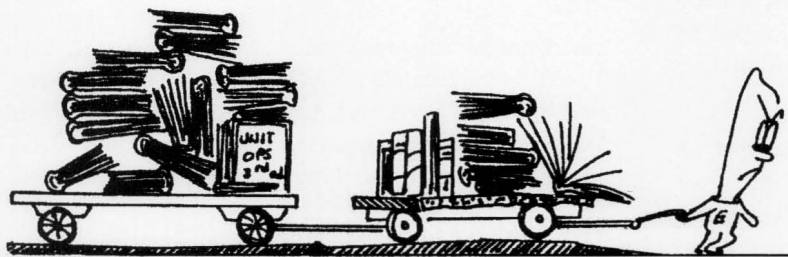


Figure 3. Final condition of the ethylene assuming the existence of only vapor (which turns out to be supersaturated vapor with molar volume 367.2 cm<sup>3</sup>/mol at 251.1 K, indicated by the small square box) or both vapor and liquid (with respective molar volumes 447.9 cm<sup>3</sup>/mol and 72.3 cm<sup>3</sup>/mol at 259.9 K).

## ENTROPY

For thorough practice in applying the first law and manipulating real gas properties, I have found it to be highly beneficial for students to calculate the line integral

$$\int \frac{dQ}{T}$$

between specified initial and final states by various reversible paths (e.g., the two paths in Figure 2). In the process, most students come to appreciate the following facts:

1. For a real gas, a reversible adiabatic expansion is governed by the differential equation

$$\frac{dT}{dV} \equiv \left( \frac{\partial T}{\partial V} \right)_S = -\frac{T \left( \frac{\partial P}{\partial T} \right)_V}{C_V(T, V)}$$

which generally must be solved numerically. The path  $PV^\gamma = \text{constant}$  is only a very special case. (Supplying a Runge-Kutta routine helps with the solution.) Of course,  $\Delta S = 0$  for the reversible adiabatic expansion marked in Figure 2, but it is necessary to perform a calculation to determine the temperature 245.9K at the start of the subsequent isochoric heating step for this path.

2. For a reversible isothermal expansion,  $Q$  is generally not equal to  $W$  but rather is given by

$$Q = T \int_{V_1}^{V_2} \left( \frac{\partial P}{\partial T} \right)_V dV$$

After a while the profound truth is driven home, by direct detailed calculation, that  $\int dQ/T$  is invariably independent of path for reversible processes carried out with any working fluid (not just ideal gases). The concept of entropy becomes downright palatable. Virial Man informs me that  $\Delta S$  for the irreversible expansion considered above comes out to be 6.537 bar cm<sup>3</sup>/mol K (by either reversible path marked with arrows in Figure 2). Unfortunately, Elroy doesn't believe in entropy and his remarks concerning  $\Delta S$  are quite unprintable.

## PHASE EQUILIBRIUM

The astute student will observe (and this sort of thing *has* happened!) that the vapor



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pressure of ethylene at the final temperature in our example is lower than the prescribed final pressure of 30 bar (or, equivalently, that the final temperature is lower than the boiling point of ethylene at 30 bar). This circumstance furnishes an excellent opportunity to discuss metastable states (for the outcome of the expansion as predicted above is, in fact, a supersaturated vapor), and the fact that alternatives to a single phase can exist (see Figure 3).

In the preceding problem we really ought to allow for the presence of two phases in equilibrium at the pressure  $P_f = 30$  bar. I mentioned this to Elroy, but his mind must have been on other things, for he responded only with the inexplicable statement, "two pints toluene, no ice," before rushing off. Predictably, the point was not overlooked by Virial Man, and it is worth considering somewhat later in the semester.

**Continuation of Virial Man's solution** • Allowing for the existence of both liquid and vapor, distinguished by  $\ell$  and  $v$  subscripts, the molar volumes of the final coexisting phases must satisfy

$$30 \text{ bar} = P_f = \frac{RT_f}{V_v - b} - \frac{a\alpha(T_{rf})}{V_v^2 + 2bV_v - b^2} \quad (5)$$

$$30 \text{ bar} = P_f = \frac{RT_f}{V_\ell - b} - \frac{a\alpha(T_{rf})}{V_\ell^2 + 2bV_\ell - b^2} \quad (6)$$

The condition of equality of chemical potential (molar Gibbs energy) leads to the additional constraint

$$\begin{aligned} & -RT \ln \left[ \frac{V_v - b}{V_\ell - b} \right] \\ & + \frac{a\alpha(T_{rf})}{2\sqrt{2}b} \left\{ \ln \left[ \frac{V_v + (1 - \sqrt{2})b}{V_v + (1 + \sqrt{2})b} \right] - \ln \left[ \frac{V_\ell + (1 - \sqrt{2})b}{V_\ell + (1 + \sqrt{2})b} \right] \right\} \\ & + 30 \text{ bar} (V_v - V_\ell) = 0 \end{aligned} \quad (7)$$

which is an algebraic statement of the Maxwell criterion. (This criterion will be discussed further below.) Equations (5) through (7) constitute three nonlinear equations in the three unknowns  $T_f$ ,  $V_v$ , and  $V_\ell$ , and one finds

$$T_f = 259.9 \text{ K}$$

$$V_v = 447.9 \text{ cm}^3/\text{mol}$$

$$V_\ell = 72.3 \text{ cm}^3/\text{mol}$$

The first law enters in ascertaining how the ethylene is distributed between liquid and vapor phases according to the following equation for the fraction vapor  $q$ :

$$\begin{aligned} qU(T_f, V_v) + (1-q)U(T_f, V_\ell) - U(T_i, V_i) \\ = -30 \text{ bar} (qV_v + (1-q)V_\ell - V_i) \end{aligned} \quad (8)$$

By direct computation,

$$U(T_i, V_i) = 1.92 \times 10^4 \text{ bar cm}^3/\text{mol}$$

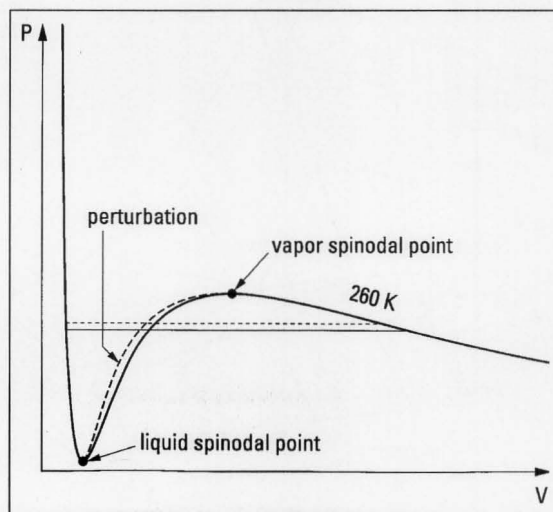
$$U(T_f, V_v) = 2.05 \times 10^4 \text{ bar cm}^3/\text{mol}$$

$$U(T_f, V_\ell) = -4.06 \times 10^4 \text{ bar cm}^3/\text{mol}$$

based on the reference value constant = 0 (*i.e.*,  $U_o = 0$ ,  $T_o = 0$ ) in the formula for  $U(T, V)$ . With these numbers, one finds  $q = 0.88$ . Needless to say, had the original problem not led to a final supersaturated vapor, the solution of Eq. (8) would not satisfy the requirement  $0 < q < 1$ .

## THE MAXWELL CRITERION

The reason I tolerate Elroy's antics and excursions beyond the realm of rationality is that he has rare moments of lucid-



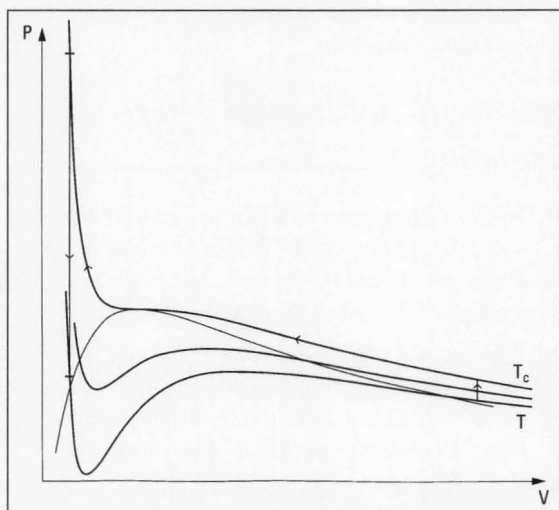
**Figure 4.** Perturbation of an isotherm in a manner that does not affect any measurable PVT properties. The perturbation should not have any effect, but according to the Maxwell equal-area construction, it changes the calculated vapor pressure.

ity in which he makes remarkably insightful observations. A case in point is an incident that occurred in late August of 1992 when Elroy woke me at 2:30 AM, pounding on my front door, and began a fit of unintelligible screaming at the top of his lungs that persisted for nearly four hours without interruption while I watched and wrung my hands. The blaring stopped only after he turned his head skyward, belted the words that I shall never forget, "Maxwell is a reptile!!!" and then toppled over backwards, landing with a thud, an exhausted silent heap. When Elroy came to, his mood was one of resignation. He withdrew a tattered sketch from his pocket (reproduced here as Figure 4) and asked quietly, "What do I do with *that*?" I stared at the figure for several minutes, and then I saw what was troubling Elroy so deeply.

According to standard practice, all thermodynamic functions (heat capacity  $C_V$ , Helmholtz energy  $A$ , etc.) are derived from the PVT equation of state together with ideal gas heat capacities by well-established integration procedures, and the formulas obtained are applied throughout the phase space. Thus, for instance, a liquid heat capacity at temperature  $T$  and molar volume  $V_\ell$  is computed from the formula

$$C_V(T, V_\ell) = C_V^{ig}(T) + T \int_{\infty}^{V_\ell} \frac{\partial^2 P}{\partial T^2}(T, V) dV \quad (9)$$

The trouble with Eq. (9) is that it tacitly makes use of the equation of state in the unstable interval between the spinodal points where it is devoid of significance. Adding a perturbation to the isotherms that is negligible outside the unstable region (Figure 4) should not affect the values of any measurable thermodynamic properties, but according to Eq. (9) it does. Similarly, in using Maxwell's equal-area construction, the calculated vapor pressure would be materially affected by the perturbation indicated in Figure 4.



**Figure 5.** Nonisothermal path between liquid and vapor states both at the same temperature  $T$ .

These types of concerns upon which Elroy stumbled were in fact enunciated many years ago in a short but profound article by G.D. Kahl<sup>[3]</sup> which unfortunately has gone almost unnoticed, being cited only three times since its publication in contexts removed from engineering VLE calculations. The conclusion to be drawn from Kahl's work is that calculations of thermodynamic functions must involve paths restricted to stable portions of the phase space. In particular, liquid properties at subcritical temperatures should be related to ideal gas properties *not* by isothermal integration but rather by using nonisothermal paths that go around the two-phase region (Figure 5). Recent work by the author<sup>[4]</sup> has shown that such a nonisothermal formalism offers distinct practical advantages in modeling phase equilibria. In particular, it furnishes an extra parameter for fitting vapor pressure data and enables the incorporation of liquid heat capacity data into algebraic representations of the free energy.

From the pedagogical perspective, the usual statement that all thermodynamic properties can be derived from (i) the ideal gas heat capacity and (ii) an equation of state, needs to be amended. One must also be in possession of (iii) liquid heat capacity data at subcritical temperatures. Students should be made suspicious of isothermal integration through the unstable region and be exposed to alternatives to this questionable procedure. They can derive considerable practice in the logical construction of nonisothermal computational paths between given initial and final states if they are forbidden to tread between the spinodal points.

## CONCLUDING REMARKS

The exercise considered here, spawned by Elroy's misconception and brought to a satisfactory resolution with Virial Man's assistance, shows that a simple-looking first-law problem can teach a lot about the calculation of thermodynamic properties with equations of state. There is value in revisiting a pithy example several times in a semester from increasingly advanced perspectives (*e.g.*, first law, second law, phase equilibrium), because this approach lends continuity and saves the time that would be spent in setting up several unrelated problems from scratch. Having friends to help (or hinder) you makes the teaching and learning process fun.

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