

CONFIRMING THERMODYNAMIC STABILITY

A Classroom Example

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Stability theory is a topic that has begun to appear more frequently in modern thermodynamics courses. The recent chemical engineering texts by Sandler^[1] and Kyle^[2] and the mechanical engineering text by Bejan^[3] discuss the subject briefly, and the more advanced monographs by Glansdorff and Prigogine,^[4] Callen,^[5] and Modell and Reid^[6] treat it in greater depth. Stability considerations underlie much of the thinking in classical thermodynamics and are essential to any thorough understanding of processes involving phase change.

Teaching stability theory, however, is hampered by a lack of practical examples. Students are accustomed to systems that are presumed to be in stable equilibrium, and they have little experience with states removed from that condition. While one may memorize stability precepts formally—entropy maximization under isolation or other potential minimizations under corresponding constraints—translating such notions into an understanding of their significance is not easy. Thermodynamics has its share of skeptics among students, both in regard to its content and to its conventional pedagogy. Expecting such individuals to give serious thought to a difficult theory describing states rarely (or never) observed is naive at best.

But everyday examples certainly exist. Common among these are supersaturated solutions and superheated liquids, both predictably metastable and both primed to revert to the more stable, two-phase conditions in response to nucleating stimuli. Experiments involving superheated liquids have been performed by Patrick-Yeboah and Reid,^[7] and classroom demonstrations have been developed by Jolls and Prausnitz.^[8] Still more deeply metastable liquid states were discussed in the interesting articles by

Hayward^[9] and Scholander^[10] on "negative pressure" and "tensile water."

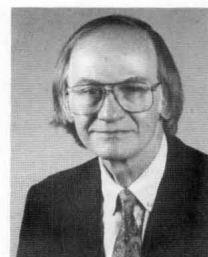
In the absence of such experiments, however, one must develop descriptions of stability-related phenomena that are sufficiently concrete to be convincing. Students must be persuaded that these ideas are real and merit the same level of attention as the more tangible aspects of thermodynamic analysis.

INTRODUCTION

We have found a way to reinforce stability concepts that both satisfies the pragmatist and retains theoretical rigor. We use the tabulations of stable and metastable states for water and steam found in the well-known *Steam Tables* by Keenan, Keyes, Hill, and Moore (KKHM^[11]). Students use these data to locate pairs of matched states in stable-metastable combinations. Then, using the appropriate thermodynamic potential for a given pair, they compare the stability levels of the states and confirm the rankings.

In this paper we show a typical set of comparisons for the five potentials customarily applied to pure fluids. Before proceeding, however, we give a brief review of the principles of stability analysis, presented in the style of Modell and Reid.^[6]

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The following inequalities are associated with the stable equilibrium states of variously constrained systems:

$$\Delta \underline{S}_{U,V,M} < 0 \quad (1a)$$

$$\Delta \underline{U}_{S,V,M} > 0 \quad (2a)$$

$$\Delta \underline{A}_{T,V,M} > 0 \quad (3a)$$

$$\Delta \underline{H}_{S,P,M} > 0 \quad (4a)$$

$$\Delta \underline{G}_{T,P,M} > 0 \quad (5a)$$

In these expressions the underbar signifies an extensive property, subscripts specify the constraints imposed for a given comparison, and the symbolism is conventional.

Inequality (1a) expresses the entropy-maximum principle: *for an isolated system, unconstrained internally and in a stable equilibrium state, the entropy decreases in response to all perturbations that preserve isolation.* One tests this idea through a so-called "thought" experiment in which an isolated system in a stable equilibrium state is partitioned into two contiguous sections and perturbed by means of a "virtual" process. The two (intensively) identical parts provide the mutual "give" needed for the thermodynamic properties to change locally while overall isolation is maintained. Kyle's discussion^[2] provides a helpful background for conceptualizing such processes.

Inequality (2a) reflects the duality of the entropy and energy representations of the fundamental equation—the entropy maximum *implies* an energy minimum.* Inequalities (3a), (4a), and (5a) follow from (2a) and are derived by contriving a subsystem within the (S,V,M)-fixed composite whose temperature and/or pressure may be held constant during the perturbation process.

Paraphrasing inequality (3a), for example, we note that any extensive state, known to represent a stable equilibrium condition, will possess a value for the Helmholtz energy less than that of a second state, remote from the first but having the same temperature, mass, and total volume. Analogous statements characterize the comparisons implied by the other four constrained inequalities.

For single-phase states well removed from any phase-change boundary, verifying in-

Paraphrasing inequality, we note that any extensive state, known to represent a stable equilibrium condition, will possess a value for the Helmholtz energy less than that of a second state, remote from the first but having the same temperature, mass, and total volume.

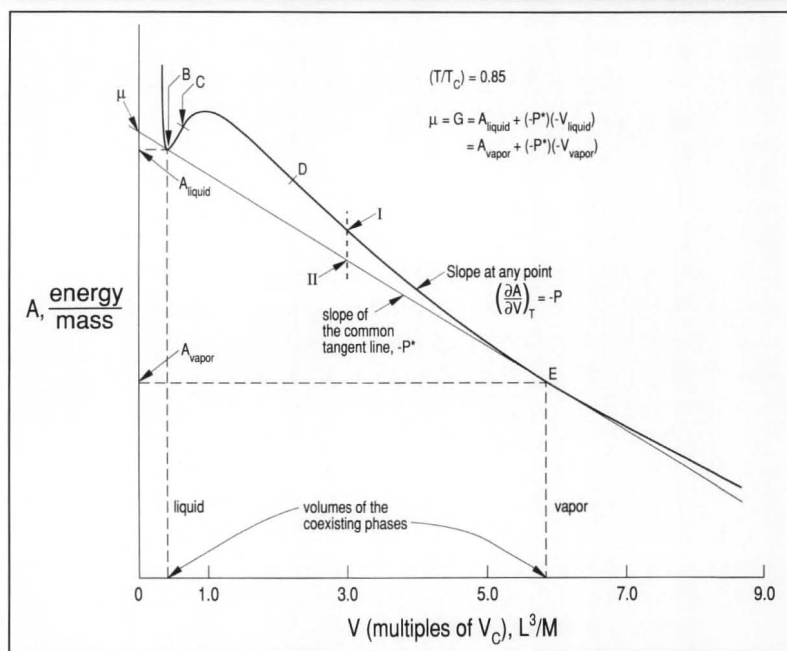


Figure 1. Subcritical isotherm of the Helmholtz energy from the Peng-Robinson equation (P^* denotes vapor pressure).

equalities (1a) through (5a) can be carried out only through statistical reasoning—examination of molecular configurations that are allowed but less probable. (Balzhiser^[12] presents simple but effective examples of these.) For two-phase conditions, however, particularly where the equilibrium state lies only a short distance inside the coexistence boundary, more tangible comparisons are possible.

In Figure 1 we show a typical isotherm of the specific Helmholtz energy* for a temperature below the fluid-phase critical point in a pure system. Intrinsic stability is guaranteed for states where $(\partial^2 A / \partial V^2)_T$ is positive (volumes to the left of point C and to the right of point D). The line tangent to the two lobes of the curve identifies states B and E that have the same temperature, pressure, and chemical potential. These states can thus coexist in equilibrium at any fraction vapor so as to yield (through lever-rule proportioning) values of A and V for the two-phase mixture intermediate to those for the individual states.

The dotted line in Figure 1 intersects the metastable, single-phase state I and the stable, two-phase state II—each at the same temperature and volume but with the latter possessing a lower value of A to coincide with its more stable condition. Similar arguments applied to a subcritical *isobar* on H-S coordinates show that the more stable state has a lower value of H when entropy and pressure are the constraints.

* Page 126 of Reference 6.

* Based on a cubic equation of state.

In the following sections we will quantify these comparisons for inequalities (1a) through (4a) and show analogous stable/metastable pairs for inequality (5a).

THE KKHM TABLES

The data tabulated in the *Steam Tables*^[11] are based on an empirically determined expression for the Helmholtz energy per unit mass of water substance $A(T,V)$.* The form of this function is shown in the Appendix of the *Steam Tables*, which also includes tabulated values of the sixty-one constants used and discussions of the supporting experimental data. In addition to the usual coverage of properties in the fully stable regions, data for the metastable, single-phase states that lie just inside the saturation curves are given for both the liquid and vapor phases. In compiling the *Steam Tables* this information was generated by extrapolating the fundamental equation inside the coexistence boundary and tabulating property values as continuous extensions of the fully stable iso-lines outside. (Italics are used to designate metastable conditions.) While no experimental values were used to control these extensions, the authors refer to them as "reasonable" and as providing "the best values available" (ca. 1978).

* Given in the *Steam Tables* as $\Psi(T,\rho)$.

In Table 1 we reproduce a small portion of the data for saturated and superheated steam (regular face) and for subcooled steam (italic) in the vicinity of the normal condensation point for a pressure of 0.38 MPa. The actual condensation temperatures are shown in parentheses, and a dashed line is drawn in each column to separate data for the two kinds of stability.

It is thus possible to identify properties and property changes in the metastable regions and also to expect that conventional thermodynamic operations will be borne out using those data. For example, one might use numerical differentiation to verify the following Maxwell relation:

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

Substituting property values centered around the metastable condition $t = 95^\circ\text{C}$, $P = 0.38 \text{ MPa}$, into the finite-difference approximations of the derivatives, we obtain

$$\left(\frac{\Delta S}{\Delta P}\right)_T = \frac{(6.5972 - 6.6600)(10^{-3})}{0.04} = -1.57 \times 10^{-3} (\text{m}^3 / \text{kg} \cdot \text{K})$$

$$-\left(\frac{\Delta V}{\Delta T}\right)_P = \frac{(408.9 - 424.5)(10^{-3})}{10} = -1.56 \times 10^{-3} (\text{m}^3 / \text{kg} \cdot \text{K})$$

The small error results from simple finite differencing

TABLE 1
Vapor-Phase Data (*Steam Tables*,^[11] pages 28-29)

P(t Sat.)	0.36 (139.87)				0.38 (141.79)				0.40 (143.63)			
t	V × 10 ³	U	H	S	V × 10 ³	U	H	S	V × 10 ³	U	H	S
Sat	510.6	2549.9	2733.7	6.9311	485.3	2551.8	2736.2	6.9130	462.5	2553.6	2738.6	6.8959
75	<i>407.9</i>	<i>2429.2</i>	<i>2576.1</i>	<i>6.5148</i>	<i>384.1</i>	<i>2425.9</i>	<i>2571.9</i>	<i>6.4800</i>	<i>362.6</i>	<i>2422.6</i>	<i>2567.6</i>	<i>6.4463</i>
80	<i>416.7</i>	<i>2439.4</i>	<i>2589.4</i>	<i>6.5528</i>	<i>392.5</i>	<i>2436.4</i>	<i>2585.5</i>	<i>6.5189</i>	<i>370.8</i>	<i>2433.2</i>	<i>2581.5</i>	<i>6.4860</i>
85	<i>425.2</i>	<i>2449.5</i>	<i>2602.5</i>	<i>6.5897</i>	<i>400.8</i>	<i>2446.6</i>	<i>2598.9</i>	<i>6.5564</i>	<i>378.7</i>	<i>2443.7</i>	<i>2595.2</i>	<i>6.5243</i>
90	<i>433.6</i>	<i>2459.3</i>	<i>2615.4</i>	<i>6.6254</i>	<i>408.9</i>	<i>2456.6</i>	<i>2612.0</i>	<i>6.5928</i>	<i>386.6</i>	<i>2453.9</i>	<i>2608.5</i>	<i>6.5614</i>
95	<i>441.8</i>	<i>2469.0</i>	<i>2628.1</i>	<i>6.6600</i>	<i>416.8</i>	<i>2466.5</i>	<i>2624.9</i>	<i>6.6280</i>	<i>394.2</i>	<i>2464.0</i>	<i>2621.6</i>	<i>6.5972</i>
100	<i>449.9</i>	<i>2478.5</i>	<i>2640.5</i>	<i>6.6935</i>	<i>424.5</i>	<i>2476.2</i>	<i>2637.5</i>	<i>6.6621</i>	<i>401.7</i>	<i>2473.8</i>	<i>2634.5</i>	<i>6.6319</i>
110	<i>465.7</i>	<i>2497.1</i>	<i>2664.8</i>	<i>6.7578</i>	<i>439.7</i>	<i>2495.1</i>	<i>2662.2</i>	<i>6.7273</i>	<i>416.3</i>	<i>2493.0</i>	<i>2659.5</i>	<i>6.6981</i>
120	<i>481.0</i>	<i>2515.2</i>	<i>2688.4</i>	<i>6.8187</i>	<i>454.4</i>	<i>2513.4</i>	<i>2686.1</i>	<i>6.7890</i>	<i>430.4</i>	<i>2511.6</i>	<i>2683.8</i>	<i>6.7605</i>
130	<i>496.0</i>	<i>2532.9</i>	<i>2711.5</i>	<i>6.8765</i>	<i>468.8</i>	<i>2531.3</i>	<i>2709.4</i>	<i>6.8475</i>	<i>444.2</i>	<i>2529.7</i>	<i>2707.3</i>	<i>6.8197</i>
140	<i>510.8</i>	<i>2550.1</i>	<i>2734.0</i>	<i>6.9318</i>	<i>482.8</i>	<i>2548.7</i>	<i>2732.2</i>	<i>6.9033</i>	<i>457.6</i>	<i>2547.3</i>	<i>2730.3</i>	<i>6.8761</i>
150	525.2	2567.0	2756.1	6.9847	496.6	2565.8	2754.5	6.9567	470.8	2564.5	2752.8	6.9299
160	539.4	2583.7	2777.9	7.0355	510.2	2582.6	2776.4	7.0079	483.8	2581.4	2774.9	6.9815
170	553.5	2600.1	2799.4	7.0846	523.6	2599.1	2798.0	7.0573	496.6	2598.1	2796.7	7.0312
180	567.4	2616.3	2820.6	7.1320	536.8	2615.4	2819.4	7.1049	509.3	2614.5	2818.2	7.0792
190	581.2	2632.4	2841.7	7.1779	550.0	2631.6	2840.6	7.1511	521.8	2630.7	2839.5	7.1256

Properties at conditions below the saturation temperature for each pressure are italicized and correspond to metastable (subcooled) states.

Symbol and Meaning	Units	Symbol and Meaning	Units	Symbol and Meaning	Units
P pressure	MPa	V specific volume	m ³ /kg	H specific enthalpy	kJ/kg
t temperature	°C	U specific energy	kJ/kg	S specific entropy	kJ/kg·K

Energy and entropy are each taken to be zero for the saturated liquid phase at the triple point.

of these nonlinear functions.

Because the *Steam Tables* present data on a per-unit-mass basis, we need not be concerned with the fixed-mass constraint. Thus we can express each of the conditions we wish to confirm in the simpler, doubly subscripted form involving specific properties only:

$$\Delta S_{U,V} < 0 \quad (1b)$$

$$\Delta U_{S,V} > 0 \quad (2b)$$

$$\Delta A_{T,V} > 0 \quad (3b)$$

$$\Delta H_{S,P} > 0 \quad (4b)$$

$$\Delta G_{T,P} > 0 \quad (5b)$$

Inequalities (3b), (4b), and (5b) are the easiest to verify because one or both constraints conform to the temperature and pressure indexing of the data.^[11] We show these calculations first.

Helmholtz Energy

To confirm inequality (3b), we must find two states at the same temperature and volume—one that represents stable equilibrium conditions and the other metastable. In Figure 2 we show the two-phase region in the vicinity of the 95°C isotherm on pressure-volume coordinates. (Note the difference in volume scales for liquid and vapor.) Let us consider the metastable (subcooled) vapor state at 95°C, 0.38 MPa, as our base point. From Table 1 we have the following properties:

$$V = 0.4168 \text{ m}^3/\text{kg}$$

$$U = 2466.5 \text{ kJ/kg}$$

$$S = 6.6280 \text{ kJ}/(\text{kg} \cdot \text{K})$$

Liquid water and steam at 95°C will coexist in

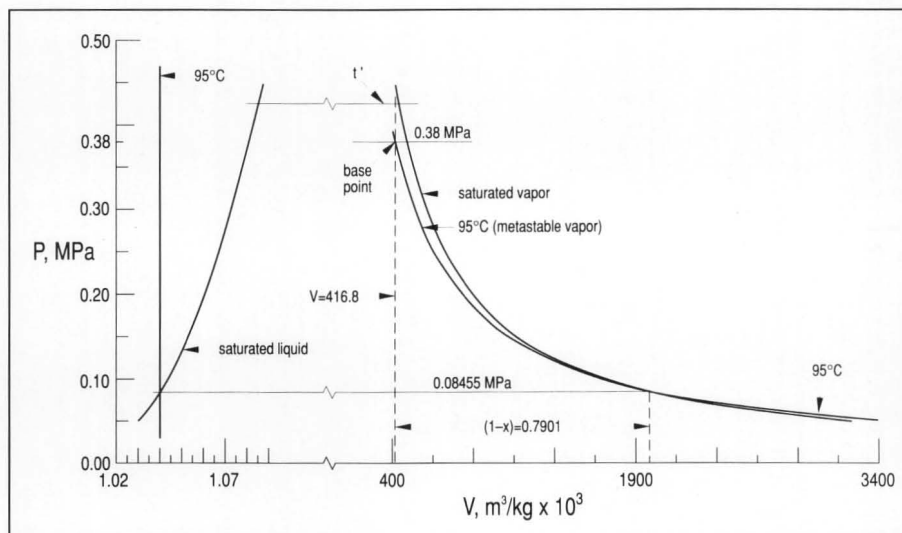


Figure 2. Pressure-volume diagram, low-pressure range (volume scales differ for liquid and vapor).

stable equilibrium under a vapor pressure of 0.08455 MPa¹ and with any fraction vapor. To find a temperature-volume match for the base point, we need only compute the fraction vapor in the two-phase state that gives the same overall specific volume as in the metastable state (0.4168 m³/kg). Noting that the saturated-state liquid and vapor volumes at this temperature are 1.0397 × 10⁻³ and 1.9819 m³/kg, respectively, we solve for the desired fraction.

$$x = \frac{416.8 - 1.0397}{1981.9 - 1.0397} = 0.2099$$

Thus, the stable, two-phase state at 95°C (0.08455 MPa) and with vapor fraction 0.2099 has the same temperature and volume as the metastable, single-phase state at 95°C and 0.38 MPa, and we can proceed to compare the Helmholtz energies.

• *metastable state:*

$$A = U - TS = 2466.5 - (95 + 273.15)(6.6280) = 26.4 \text{ kJ/kg}$$

• *stable state:*

	saturated phases at 95°C	
	liquid	vapor
U	397.88	2500.6
S	1.2500	7.4159

from which

$$A = x[U - TS]_{\text{vapor}} + (1-x)[U - TS]_{\text{liquid}} = -97.4 \text{ kJ/kg} \quad (6)$$

and

$$A_{\text{stable}} < A_{\text{metastable}}$$

Enthalpy

Confirming inequality (4b) requires a stable-metastable pair at the same entropy and pressure. Figure 3 shows the two-phase region in the vicinity of the 0.38 MPa isobar on t-S coordinates. Again we choose the metastable (subcooled vapor) base state along the 0.38 MPa isobar at 95°C [where S = 6.6280 kJ/(kg·K) and H = 2624.9 kJ/kg]. From entropy-matching calculations analogous to the volume-matching calculations in the previous case, we find that the stable, two-phase state at 0.38 MPa (t = 141.79°C) and vapor fraction x = 0.9447 has the same entropy.² With saturation properties

$$H_{\text{liquid}} = 596.83$$

and

¹ Reference 11, page 3.

² Reference 11, page 10.

$$H_{\text{vapor}} = 2736.2$$

the enthalpy of the two-phase state is given by

$$H_{\text{stable}} = xH_{\text{vapor}} + (1-x)H_{\text{liquid}} = 2617.94 \text{ kJ/kg} \quad (7)$$

and

$$H_{\text{stable}} < H_{\text{metastable}}$$

Gibbs Energy

Stable-metastable pairs that confirm inequality (5b) involve liquid states that are either stably compressed above or metastably expanded below saturation. The limited amount of data for such states in the *Steam Tables* requires that we move the region of interest to a higher temperature. Figure 4 shows the liquid and vapor branches of the 260°C isotherm with the saturation points (at 4.688 MPa) dividing each branch into stable and metastable sections. Numerical data appear in Table 2.

Two Gibbs energy comparisons are possible from these data. At 2.5 MPa the liquid state (○) is metastable:

$$G = H - TS = 1134.8 - (533.15)(2.8898) = -405.9 \text{ kJ/kg}$$

whereas for the stable (superheated) vapor at this pressure (□)

$$G = 2907.4 - (533.15)(6.4601) = -536.8 \text{ kJ/kg}$$

and

$$G_{\text{stable}} < G_{\text{metastable}}$$

At 5.1 MPa the situation is reversed. For the metastable (supercompressed or subcooled) vapor (△)

$$G = 2770.4 - (533.15)(5.9214) = -386.6$$

and for the stable (compressed or subcooled) liquid (◇)

$$G = 1134.3 - (533.15)(2.8827) = -402.6$$

Again the inequality is confirmed. Re-

peating the calculation at the exact saturation pressure confirms the equality of G for phases coexisting at equilibrium.*

$$G_{\text{liquid}} = -403.1$$

$$G_{\text{vapor}} = -403.0$$

Entropy and Energy

Inequalities (1b) and (2b) are more difficult to confirm because the two-phase state in each case must satisfy two nonindexed constraints. For the entropy comparison one must find a stable-metastable pair with the same volume and energy. Re-

* Properties of coexisting states are obtained from the fundamental equation at the observed vapor pressure for a given temperature—thus the insignificant difference in G -values for saturated liquid and vapor phases (Ref. 11, p. 135).

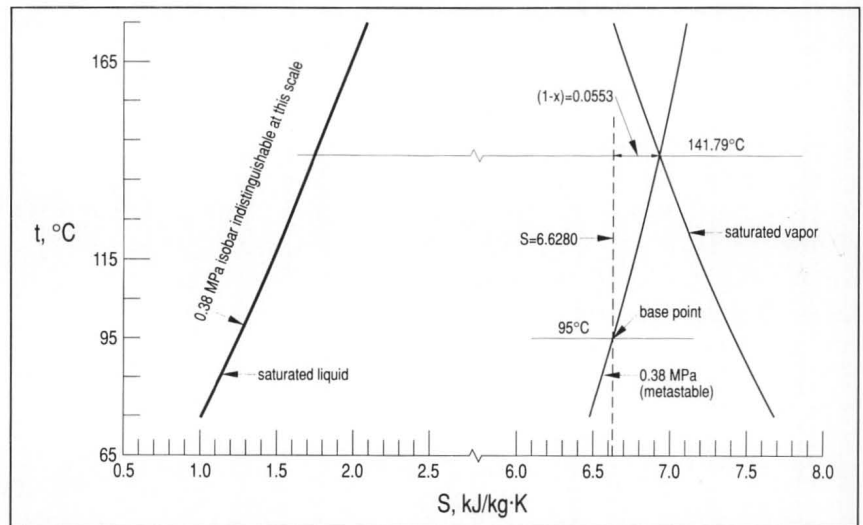


Figure 3. Temperature-entropy diagram.

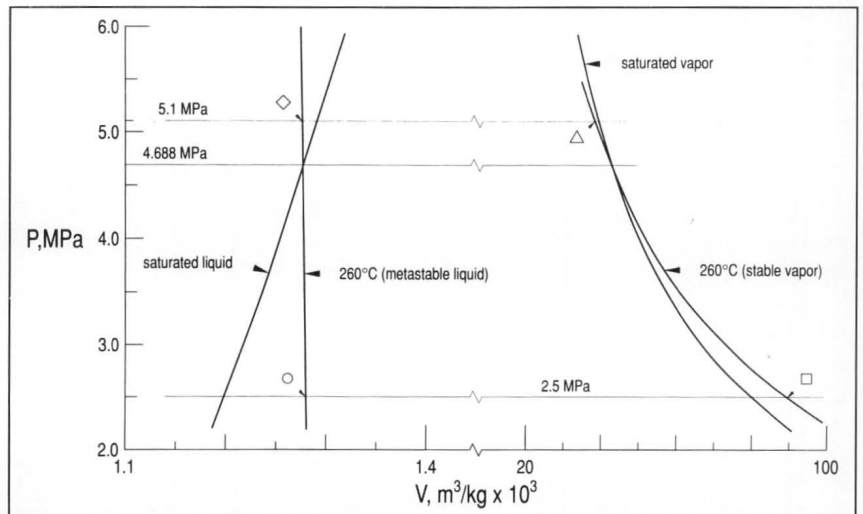


Figure 4. Pressure-volume diagram, high-pressure range (volume scales differ.)

TABLE 2			
Data at 260°C			
(Steam Tables, ¹¹ pages 6, 49, 63, 104)			
P, MPa		Liquid	Vapor
2.5	H	1134.8	2907.4
	S	2.8898	6.4601
4.688	H	1134.37	2796.9
	S	2.8838	6.0019
5.1	H	1134.3*	2770.4
	S	2.8827*	5.9214

* Interpolated

turning to Figure 2 and to the original metastable base point, we search for a two-phase state with a temperature and fraction vapor such that

$$xU_{\text{vapor}}(t) + (1-x)U_{\text{liquid}}(t) = U_{\text{metastable}} = 2466.5 \quad (8)$$

and

$$xV_{\text{vapor}}(t) + (1-x)V_{\text{liquid}}(t) = V_{\text{metastable}} = 0.4168 \quad (9)$$

Trial-and-error solution of these equations (using linear interpolation for saturation properties between tabulated points) yields

$$t = 145.84^\circ\text{C} \quad x = 0.9541 \quad (P = 0.4251 \text{ MPa})$$

with saturation values at this temperature*

	liquid	vapor
U	613.78	2555.7
10^3V	1.0859	436.8
S	1.7992	6.8756

Thus, the entropy of the stable, two-phase state is

$$S_{\text{stable}} = xS_{\text{vapor}} + (1-x)S_{\text{liquid}} = 6.6426$$

This exceeds the entropy of the metastable state (6.6280), and we conclude

$$S_{\text{stable}} > S_{\text{metastable}}$$

For the energy comparison we must match the volume and entropy of the base state. We replace Eq. (8) with the analogous expression for entropy

$$xS_{\text{vapor}}(t) + (1-x)S_{\text{liquid}}(t) = S_{\text{metastable}} = 6.6280 \quad (10)$$

and solve as before through linear interpolation

$$t = 145.71^\circ\text{C} \quad x = 0.9510 \quad (P = 0.4236 \text{ MPa})$$

with saturation properties

	liquid	vapor
S	1.7979	6.8768
10^3V	1.0858	438.3
U	613.24	2555.5

From these data we determine $U_{\text{stable}} = 2460.3$ and

$$U_{\text{stable}} < U_{\text{metastable}}$$

The two-phase states for these latter comparisons are indistinguishable at the scale of Figure 2, and we represent both on the single horizontal line t' .

CLOSING REMARKS

The significance of these comparisons must be explained carefully. They must not be characterized as any form of proof of the validity of stability theory. Indeed, they are not that at all. The principles of stability theory are no more capable of proof than are the Laws of Thermodynamics themselves. Given our acceptance of the Laws (or of the Postulates that

underlie the Laws in the neo-Gibbsian tradition^[13]), stability criteria follow logically. Thus, material behavior in violation of any criterion of thermodynamic stability is in *de facto* violation of the Second Law.

These examples do, however, offer a tangible link between real systems and abstract models. They reveal the thermodynamic consistency of an empirically fashioned fundamental equation (the basis for the KKHM *Steam Tables*), and they give support to the too often rote-learned precepts of entropy maximization and Gibbs energy minimization.

We offer these exercises as a way to give students a semiquantitative feeling for concepts usually relegated to pure abstraction. They may be understood even better when accompanied by descriptions of "familiar" metastable-stable transitions—crystallization from a supersaturated solution or the explosive (and potentially dangerous) vaporization of a superheated liquid. Reid's series on the latter subject^[14] provides excellent background reading.

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* Reference 11, page 4.