

III. States of Pure Substances in Terms of Measurables

I. Getting Started

III. Models for PvT Behavior of Pure Substances

IV. Work

V. First Law for Closed Systems

VI. Heat Effects from Property Changes

VII. First Law for Open Steady-Flow Systems

VIII. The Second Law

IX. Heat Engines and Heat Pumps

Lecture 4

PvT Surfaces for Pures

A principal use of thermodynamics is in determining the energy transfers associated with changing the state of a system. But before discussing changes of state, we must be aware of what kinds of states are available, what properties are typically used to characterize states, and how numerical values are usually obtained for those properties. These issues claim our attention for the next several lectures. However, in these lectures, our attention is limited in two ways: (i) we restrict the discussions to states of pure substances, and (ii) of the many possible properties that could be used to identify states, we restrict the discussions to the measurables P , v , and T .

4.1 Possible States for Pures

For a known amount of a pure substance confined to a closed vessel, Duham's theorem (3.1) asserts that the state depends on the values of two additional properties. Thus, the molar volume v of the substance could be expressed as a function of the temperature T and pressure P ,

$$v = v(T, P) \quad (4.1)$$

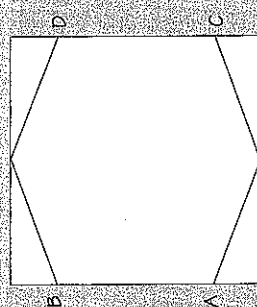
or the pressure could be expressed as a function of T and v ,

$$P = P(T, v) \quad (4.2)$$

Of course, we could also imagine writing $T = T(P, v)$, but in practice this is rarely done, because temperature is usually the easiest property to measure and manipulate, so we prefer to have T as an independent variable. The equations of state (4.1) and (4.2) represent three-dimensional (3D) surfaces with P , v , and T each plotted along one of three mutually orthogonal Cartesian axes. The goal of this lecture is to describe such 3D surfaces.

Step 2

On your square, locate the midpoint M of base and midpoint N of top. On left edge, mark point A about $1/6$ distance from bottom and point B about $1/6$ distance from top. Likewise, mark C and D on right edge. Draw lines MA , MC , NB , and ND .



We want our 3D picture to represent all the commonly observed phase behavior for our pure substance, so let's ask, what kinds of phase behavior does a pure substance normally display? Here they are:

- (a) At least three one-phase situations: solid (S), liquid (L), and vapor (V).
- (b) At least three two-phase equilibrium situations: solid-liquid (SL), vapor-liquid (VL), and solid-vapor (SV), as in Figure 4.1.
- (c) At least one three-phase equilibrium situation in which solid, liquid, and vapor are all in equilibrium; this is called a *triple point*. See the right-most illustration in Figure 4.1.

We will be content to study a *P-T* surface that contains these seven kinds of phase behavior, but we note that many pure substances can have more than this. For example, many pure substances have several distinct solid phases (ice has more than half a dozen [1]), and such substances can exhibit several different SL and SV equilibria, as well as multiple triple points.

4.2 Gibbs Phase Rule

We have asserted that Duhem's theorem tells us the number of independent properties on which the state depends, but many situations arise in which we don't know the total amounts of all components present or further we don't need to know those amounts (see § 3.1). That is, Duhem's theorem helps us identify the *extensive* state, but in many situations we only need the *intensive* state. The *intensive* state is independent of the total amount of material contained in the system.

In general, the number of independent properties \mathcal{F} is obtained by counting the total number of interactions available to the system and subtracting the total number of constraints imposed [2].

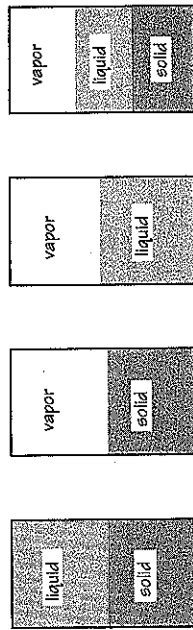


Figure 4.1 Common phase-equilibrium situations for a pure substance.

$$\mathcal{F} = \left(\begin{array}{c} \text{total number of interactions} \\ \text{available to all phases} \end{array} \right) - \left(\begin{array}{c} \text{total number of} \\ \text{constraints imposed} \end{array} \right) \quad (4.3)$$

The standard situation is to consider a system that contains C components (such as water, ethanol, and benzene) distributed among \mathcal{P} phases. The phases may be solids, liquids, vapors, or any combinations of these; for example, if the system were oil-and-vinegar salad dressing, then $\mathcal{P} = 2$ because we have two liquid phases. Next we assume each phase has $(C+2)$ interactions: one to change the amount of each component, one P - V work mode, and one thermal interaction by conduction. Thus, we have $\mathcal{P}(C+2)$ interactions.

Now let's count the number of constraints. First, we want only the intensive state; therefore, we need one constraint per phase to remove the total amount of material in each phase as a variable. This gives \mathcal{P} constraints. Second, we have $(\mathcal{P}-1)$ phases in equilibrium and, according to § 2.3, each equilibrium situation involves one mechanical-equilibrium constraint, one thermal-equilibrium constraint, and one diffusional-equilibrium constraint for each component. These give $(\mathcal{P}-1)(C+2)$ additional constraints; thus, we have a total of $[\mathcal{P} + (\mathcal{P}-1)(C+2)]$ constraints, and (4.3) becomes

$$\mathcal{F} = \mathcal{P}(C+2) - [\mathcal{P} + (\mathcal{P}-1)(C+2)] \quad (4.4)$$

$$= \mathcal{P}C + 2\mathcal{P} - \mathcal{P} - \mathcal{P}C - 2\mathcal{P} + C + 2 \quad (4.5)$$

$$\mathcal{P} + \mathcal{F} = C + 2 \quad (4.6)$$

This is called the *Gibbs phase rule*. It tells us that, when we have C components distributed among \mathcal{P} phases in equilibrium, the state depends on \mathcal{F} independent intensive properties. This version of the phase rule is special in that it assumes only certain interactions and certain constraints. If we have other interactions (such as electrical work) or additional constraints (such as a semipermeable membrane that prevents some components from entering some phases), then the Gibbs version of the phase rule must be modified.

4.3 The 3D Surface for a Pure

For a pure substance, $C=1$ and the Gibbs phase rule (4.6) reduces to

$$\mathcal{F} = 3 - \mathcal{P} \quad \text{pure} \quad (4.7)$$

To obtain the kinds of phase behavior cited in § 4.1, we have three possibilities: $\mathcal{P}=1$ for one-phase situations, $\mathcal{P}=2$ for two-phase equilibria, and $\mathcal{P}=3$

Table 4.1

Kinds of Objects Created on a 3D PvT Surface
by P Phases of a Pure Substance

# phases P	# properties f	object
1	2	area
2	1	line
3	0	point

for triple points. For each of these situations, the resulting value of f gives the dimension of an object on a three-dimensional plot of P , v , and T , such as in Figure 4.2. The possibilities are listed in Table 4.1.

Areas. On the PvT diagram, one-phase situations—solid (S), liquid (L), or vapor (V)—appear as areas; that is, we need values for two of the three properties (P and v) or (P and T) or (T and v) to locate a one-phase state. In addition to S , L , and V , the diagram has areas labeled *fluid* and *gas*. These are liquid and vapor states extended to high temperatures; they will be defined in the next lecture.

Lines. The two-phase lines for SL , SV , and VL appear in pairs in Figure 4.2. The lines for SL equilibrium are the *melting* curves and are separated by the region marked ($S + L$). The two melting lines are parallel and never intersect. The lines for SV equilibrium are the *sublimation* curves and are separated by a region marked ($S + V$). The lines for VL equilibrium are branches of the *vapor pressure* curve and are separated by a region marked ($L + V$). States in the regions marked ($S + L$), ($S + V$), and ($L + V$) are *not* stable one-phase states; instead, any attempt to form a single phase in those regions is generally frustrated by the substance splitting into two phases.

Note that, unlike the melting and sublimation curves, the two branches of the vapor-pressure curve intersect. Along either branch, as temperature is increased, the vapor pressures increase; but simultaneously, the molar volume of the liquid increases while that of the vapor decreases. The liquid and vapor molar volumes coincide at the *gas-liquid critical point* (labeled cp in the figure). Thus at the critical point, the vapor and liquid phases are indistinguishable, and the critical point is actually a one-phase equilibrium situation. For a pure, it is usually identified by giving values for any two of these three: the critical temperature T_c , the critical pressure P_c , and the critical molar volume v_c . The *critical isotherm* is labeled T_c on Figure 4.2.

Triple Point. The line of constant T and constant P , common to the three two-phase areas ($S + L$), ($S + V$), and ($L + V$), identifies the *SLV triple point*. Thus, the melting curves, sublimation curves, and vapor-pressure curve all coincide at the triple-point temperature and pressure. However, the molar volumes of the three phases differ, so on the PvT diagram, the SLV triple

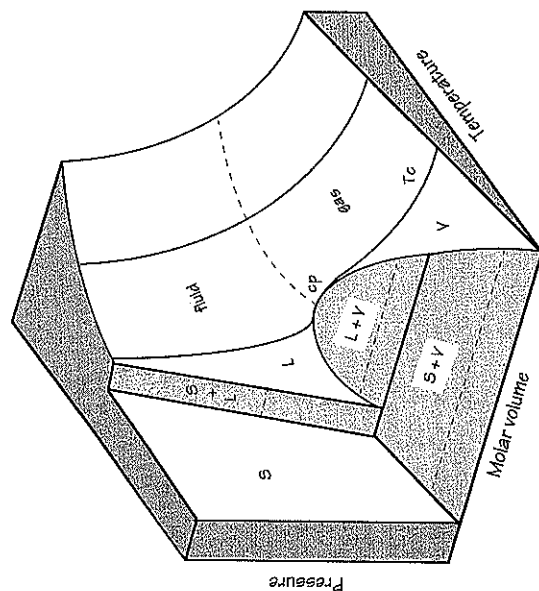


Figure 4.2 Schematic PvT surface for a pure substance (like ethanol) that expands on melting ($v_{liq} > v_{sol}$), so the solid sinks in its own liquid.

point actually appears as three points. A relatively inexpensive procedure for measuring the triple point of water is given in an article in *Scientific American* [3]. Values for the triple point, critical point, and normal boiling point of water are presented in Table 4.2.

The three-dimensional surface in Figure 4.2 applies to most pure substances. These materials expand when the solid phase melts to liquid, so the solid sinks in its own liquid. Thus, benzene sinks in pure liquid benzene and ethanol sinks in pure liquid ethanol. But water is an exception: water contracts when ice melts,

$$v_{liq} < v_{sol} \quad \text{water} \quad (4.8)$$

so ice floats on its liquid. Because of this, the PvT diagram for water is not like Figure 4.2; instead, it has a PvT diagram like that in Figure 4.3.

Table 4.2

Triple Point (TP), Normal Boiling Point (NBP), and Critical Point (CP) for Water. (Values from the NIST webbook [10])

	T (°C)	P (bar)	v (liter/mol)		
			vapor	liquid	solid
TP	0.01	0.00612	371.0	0.01802	0.0196
NBP	99.974	1.01325	30143	0.01680	...
CP	373.95	220.64	0.05556	0.05556	...

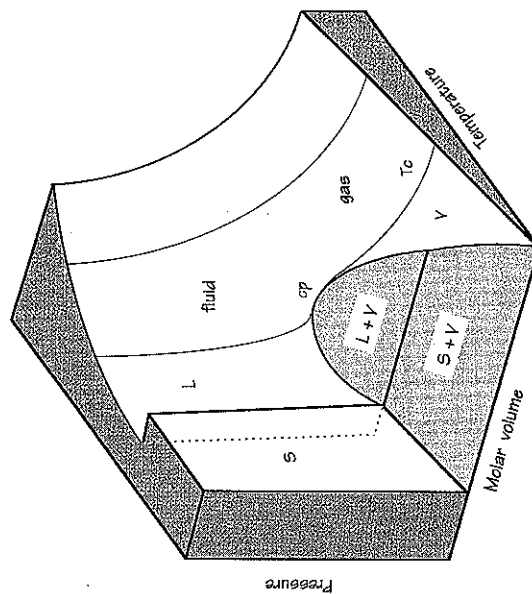


Figure 4.3 Schematic P - v - T surface for a pure substance (like water) that contracts on melting ($v_{liq} < v_{sol}$), so the solid floats on its own liquid.

4.4 Thermodynamic Tables

Experimental P - v - T data have been tabulated for many common substances, including nitrogen, oxygen, carbon dioxide, ammonia, low molecular weight hydrocarbons, refrigerants, and water. In the case of water, the tabulations are called steam tables. Many sets of steam tables are available [4-6]; excerpts are provided in Appendix I. In addition to values for the measurable P , v , and T , such tables also contain computed values for important conceptuals; these will be discussed as they arise in later lectures. In using any such table, you can expect to have to interpolate among tabulated entries to find the state you need. Most tables use T and P as the independent variables, and good tables will have entries of P , v , and T closely enough spaced so that linear interpolation is sufficient. However, you should not extrapolate any values to states beyond the bounds of a table.

You can find books of these tables by searching in your local (technical) library. A review of the experimental literature published between 1950 and 1971 for pure substances is available [7]; also available is an abbreviated bibliography that will direct you to data for 40 pure fluids [8]. A convenient collection for many pure fluids is contained in a book by Vargaftik [9]. Data for a few pure fluids are available on the web-site maintained by NIST (the National Institute for Standards and Technology): search for [10]

<http://webbook.nist.gov/>

But in spite of the huge experimental effort that has been made over the last 100 years, reliable thermodynamic data are available for relatively few pure fluids. Thus, we need ways to extend existing data to unmeasured states and unmeasured fluids. One way to do so is via corresponding states, which is discussed in Lectures 10 and 11. Other ways for estimating properties of fluids are described in the book by Poling, *et al.* [11].

Literature Cited

- [1] D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water*, Oxford University Press, New York, 1969.
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- [11] B. E. Poling, J. M. Prausnitz, and J. P. O'Connell, *The Properties of Gases and Liquids*, 5th ed., McGraw-Hill, New York, 2000.

Problems

- 4.1 For each of the following situations, determine the number of independent intensive properties on which the intensive state depends:
 - (a) ethanol and water in vapor-liquid equilibrium
 - (b) benzene and water in vapor-liquid-liquid equilibrium
 - (c) carbon dioxide in solid-vapor equilibrium
 - (d) carbon dioxide dissolved in water
- 4.2 When water freezes at 0°C, by what % does the molar volume change? Does it increase or decrease? Does the picture for a triple point in Figure 4.1 apply to water? If not, how should that picture appear?
- 4.3 Using data in Table 4.2, determine the change in molar volume between the triple point and normal boiling point for water vapor and compare with the corresponding value for the liquid. Conclusion?
- 4.4 The pictures of phase separation in Figure 4.1 represent artifacts caused by the earth's gravitational field. Sketch a corrected picture of VLE for situations in which gravity is absent—for example, say the sample were on a space station.

Lecture 5

States on PT and Pv Diagrams

The three-dimensional PvT diagrams shown in the previous lecture are informative, but not particularly useful in practice. More useful are two-dimensional projections; two are commonly used— P vs T and P vs v . They are described here.

5.1 PT Projections

If we project from the three-dimensional surface in Figure 4.2 onto a two-dimensional plot of P vs T , we obtain a PT diagram such as appears in Figure 5.1. The Gibbs phase rule is still obeyed, so one-phase states occupy areas, two-phase states fall on lines, and triple points project as points. These all appear in Figure 5.1; for example, one-phase solid states occupy an area that starts at low temperatures and pressures and extends to high temperatures. One-phase vapor states span an area from low T and P to high temperatures, and one-phase liquids occupy the area between solid and vapor.

Since the phase-equilibrium criteria (§2.3) require two phases in equilibrium to have the same T and P , each pair of two-phase lines on the 3D figure projects as a single line on the PT diagram. Hence, the sublimation curve (SV equilibrium) starts at low T and P and ends at the SLV triple point; the vapor-pressure curve starts at the triple point (tp) and ends at the critical point (cp); the melting curve starts at the triple point and continues, without end, to high pressures. Note that the sublimation and vapor-pressure curves always have positive slopes,

$$\left(\frac{\partial P}{\partial T}\right)_{eq} > 0 \quad (5.1)$$

where the subscript eq reminds us that the derivative is evaluated along a two-phase equilibrium curve. However, the melting line can have a slope of

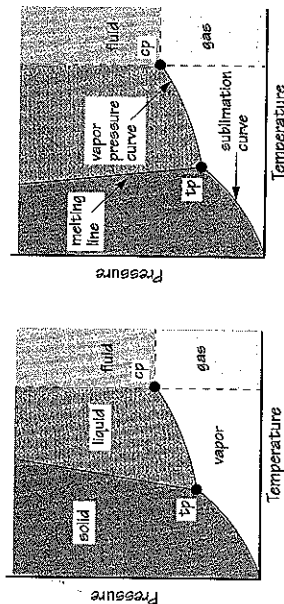


Figure 5.1 Schematic PT projections from the three-dimensional $P-v-T$ surfaces shown in the previous lecture. That on the left is from Figure 4.2; it applies to a material that expands on melting (its melting line has a positive slope). That on the right is from Figure 4.3; it applies to a material (such as water) that contracts on melting (its melting line has a negative slope). The SLV triple point is marked tp and the gas-liquid critical point is marked cp . Slopes of melting lines are exaggerated; on the scales of these plots, both melting lines would appear nearly vertical.

either sign. The slope is positive for materials that expand on melting (as in Figure 4.2), but it is negative for materials (like water) that contract on melting (as in Figure 4.3). Both possibilities are shown in Figure 5.1.

We also show on Figure 5.1 the areas for one-phase gases and fluids. States of one-phase liquid, vapor, gas, and fluid are distinguished from one another by their values of T and P relative to those at the critical point:

- (a) *Vapors* have $T < T_c$ and therefore they can be condensed by increasing the pressure while holding T constant.
- (b) *Gases* have $T > T_c$ but $P < P_c$, so they cannot be condensed without changing T ; e.g., they can be condensed by decreasing T at fixed P .
- (c) *Fluids* have $T > T_c$ and $P > P_c$, so like gases, they cannot be condensed without changing T , but when they are condensed by decreasing T at fixed P , no meniscus forms between fluid and liquid.

These formal distinctions are often ignored in everyday discourse, wherein we refer indiscriminately to a vapor as either vapor or gas and to liquids, vapors, and gases indiscriminately as fluids.

5.2 Pv Projections

If we project from the 3D surface in Figure 4.2 onto a plot of pressure vs volume, we obtain a Pv diagram as in Figure 5.2. One-phase states occupy areas, two-phase states occupy lines, and the SLV triple point projects as three points. Since Figure 4.2 is for a substance that expands on melting, one-phase solids have smaller molar volumes than one-phase liquids.

On the Pv diagram, the two-phase lines (melting, vapor-pressure, and sublimation) appear in pairs, for although the phases are in equilibrium at the same T and P , the two phases have different molar volumes. These two molar volumes can be connected by a straight horizontal line called a *tie line*; every tie line is at one temperature (an *isotherm*) and one pressure (an *isobar*). An infinite number of tie lines exist. Each melting line extends without limit to high pressures, but the two branches of the vapor-pressure curve coincide at a maximum pressure which identifies the critical point.

The diagram in Figure 5.2 is repeated in Figure 5.3, wherein we show three isotherms: a supercritical isotherm ($T > T_c$), the critical isotherm (T_c), and a subcritical isotherm ($T < T_c$). No isotherm has positive slope; that is, expanding a substance to larger volumes, while keeping T fixed, always decreases P . Note that the supercritical isotherm decreases monotonically with increasing volume, but the subcritical isotherm is piecewise continu-

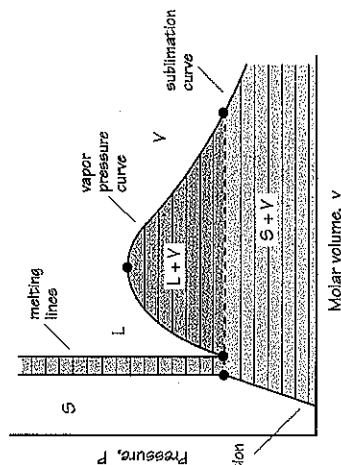


Figure 5.2 Schematic Pv diagram for a pure substance that expands on melting. Horizontal lines across two-phase regions are tie lines. Three filled circles on the dashed tie line mark the three volumes at the triple point. The solid and liquid portions of this diagram do not apply to water.

ous; part of the isotherm is a horizontal tie line that traverses the VLE region. Note also that the critical isotherm passes through a point of inflection at the critical point; this defines the critical point for a pure substance:

$$\left(\frac{\partial v}{\partial P}\right)_T \Big|_{cp} = 0 \quad (5.2)$$

$$\left(\frac{\partial^2 v}{\partial P^2}\right)_T \Big|_{cp} = 0 \quad (5.3)$$

So, if we have an equation of state, such as $P = P(T, v)$, for our pure material, then (5.2) and (5.3) give two algebraic equations that could be solved for two properties that would identify the critical point: either T_c and P_c or T_c and v_c .

5.3 States from Steam Tables

In Lecture 4 we pointed out that tables of thermodynamic properties are available for common substances. We now show how the PvT data in those tables are related to PT and Pv diagrams; to illustrate, we use excerpts from steam tables, such as that in Appendix I. Steam tables are usually presented in two parts: the *saturated* tables, which give property values along the

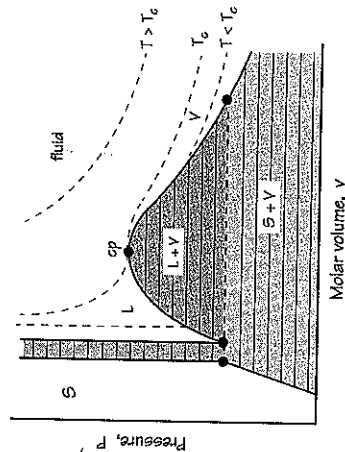


Figure 5.3 Same Pv diagram as in Figure 5.2, showing three isotherms across the fluid regions: one supercritical, one subcritical, and the critical isotherm.

vapor-liquid saturation curve, and the *superheated* tables, which pertain to one-phase vapor and gas states. Consider Figure 5.4, which contains an excerpt from a saturated table together with saturated states plotted on a PT diagram. That is, the plotted points in the figure are on the vapor-pressure curve, and they extend from the triple point to the critical point. Recall from the phase rule (4.6) that for a pure substance on a two-phase line, only one independent variable is required to set the state; typically, the temperature serves as the one variable. Nevertheless, saturated tables usually contain, not only the vapor pressures P^s at each T , but also specific or molar volumes for both the vapor and liquid. Moreover, some saturated steam tables contain the change in the volume on vaporization, Δv , which is merely the difference between the vapor and liquid volumes,

$$\Delta v = v_{\text{vap}} - v_{\text{liq}} \quad (5.4)$$

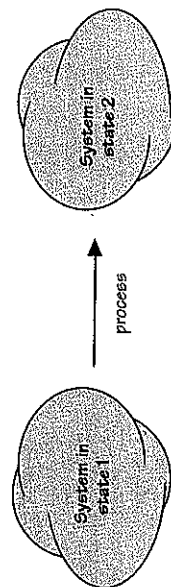
In the excerpt in Figure 5.4, Δv is labeled "evap".

Since saturated steam tables contain pressures, volumes, and temperatures, they can be used to construct the vapor-liquid envelope on Pv diagrams. This is illustrated in Figure 5.5. In a saturated table, at any one T and P^s the vapor and liquid are in equilibrium, and the two volumes can be connected by a tie line. Two such tie lines are shown in Figure 5.5.

When we move from a saturated table to a superheated table, we move from two-phase states to one-phase vapor states. Now the phase rule requires two property values to set the state; often T and P are used. Then, at selected values for T and P , superheated tables form an array of values for specific or molar volumes. Thus, we can use entries in superheated tables to plot isobars or isotherms; usually, isotherms are columns in the array, while isobars are rows. An excerpt from such a table is shown in Figure 5.6. The figure also contains representative isotherms on a Pv diagram.

5.4 What Phase is Your State?

In the standard thermodynamic problem, we need to determine the energy transfers associated with changing the state of a system,



Excerpt from Saturated Steam Table

P (bar)	T (°C)	v (L/mol)		
		liquid	evap	vapor
1	99.61	0.0168	30.436	30.517
20	212.4	0.0212	1.773	1.794
80	295.0	0.0249	0.399	0.424

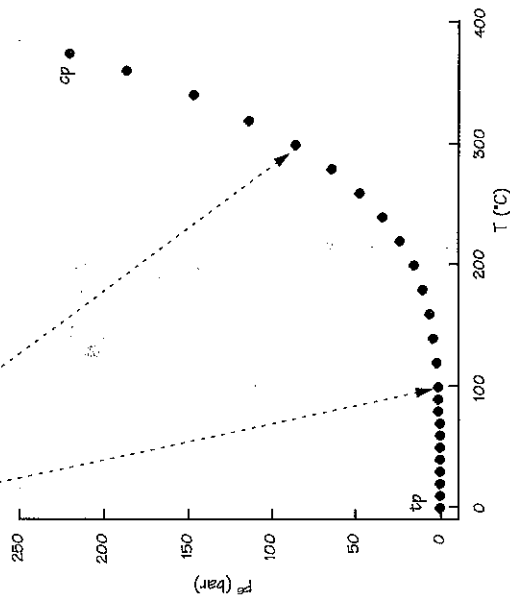


Figure 5.4 Saturated steam tables contain values of P , v , and T for states on the vapor-liquid saturation curve. Several such points (filled circles) are shown here, tracing out the vapor-pressure curve from the triple point (tp) to the critical point (cp).

Excerpt from Saturated Steam Table

P (bar)	T (°C)	v (L/mol)		
		liquid	evap	vapor
1	99.61	0.0168	30.436	30.517
20	212.4	0.0212	1.773	1.794
80	295.0	0.0249	0.399	0.424

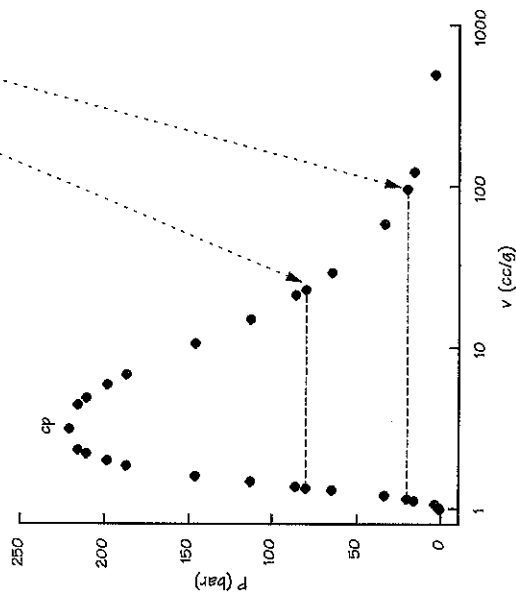


Figure 5.5 Saturated steam tables can also be used to construct the vapor-liquid envelope on a P - v diagram, as shown here. Selected points (filled circles) pass through a maximum at the critical point (cp). Saturated vapor and liquid phases in equilibrium have the same P and T , and can therefore be connected by tie lines across the two-phase region (broken horizontal lines). Two tie lines are shown here: one at 20 bar and 212.4°C, the other at 80 bar and 295.0°C. Note log scale on the abscissa.

Volumes (L/mol) from Superheated Steam Table

P (bar)	300°C	400°C
40	1.0606	1.3229
60	0.6520	0.8543
80	0.4374	0.6187

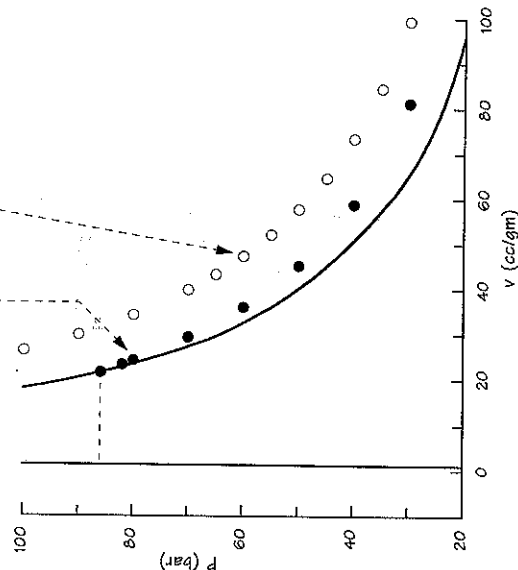


Figure 5.6 Superheated steam tables contain pressures and volumes for subcritical and supercritical isotherms of one-phase vapors and gases. The subcritical isotherm shown here is for 300°C (filled circles) and intersects the saturated vapor curve (solid line) at 85.93 bar. The supercritical isotherm is for 400°C (open circles) and does not intersect the saturation curve. Note the scale on the abscissa is linear on this plot.

To perform such calculations we must know the initial and final states; usually these states are specified by the temperature T , pressure P , composition (mole fractions x_i), and phase (solid, liquid, vapor, etc.). Here we focus on identifying the phase of a pure substance at a specified T and P . We must know the phase of each state before we can make legitimate approximations that enable us to carry out calculations (these will be discussed in Part III). Further, if the phases of states 1 and 2 differ, then the associated energy transfers are generally larger than if no phase change occurs. We now want to show that the phase can be determined without knowing the complete P - T diagram for our pure substance; in fact, we can often identify the phase from a rather modest amount of information.

Problem. Given T and P for a known pure substance, is the state solid, liquid, vapor, gas, fluid, or some combination of these? This situation is represented pictorially in Figure 5.7(a).

Solution Procedure.

- (1) Check whether or not the state is solid by comparing the known T with the normal melting temperature T_m . We assume

$$T > T_m \Rightarrow \text{not solid} \quad (5.5)$$

This is generally a good approximation because the melting lines of pure materials are nearly vertical on a PT diagram, as in Figure 5.7(b). Note that the assumption (5.5) does not preclude the possibility of fluid phases occurring at temperatures $T < T_m$; this can occur at low pressures, $P < 1$ atm. Be aware that T_m may not be low: strong attractive forces among molecules

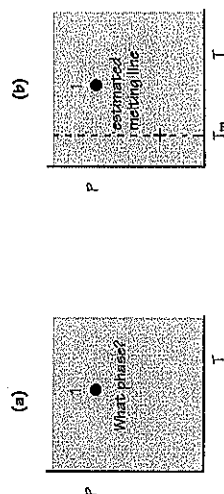


Figure 5.7 To analyze changes of state successfully, we must know where the initial and final states lie on a phase diagram. For example, consider a state (T_1, P_1) , as in (a). Then, (b) if we know the normal melting point (T_m) we can usually decide whether the substance is solid.

lead to high melting temperatures, such as in long-chain hydrocarbons (waxes) and substances with strong hydrogen bonding (like glacial acetic acid, for which $T_m \approx 60^\circ\text{F}$). Our interests are primarily with fluids, so we do not consider other solid-phase possibilities here.

(2) Check how the state lies relative to the critical point (T_c and P_c), as in Figure 5.8(a). If the state is supercritical, then the possibilities are these:

$$(a) \text{ If } T > T_c \text{ and } P > P_c \Rightarrow \text{dense fluid} \quad (5.6)$$

$$(b) \text{ If } T > T_c \text{ and } P < P_c \Rightarrow \text{gas} \quad (5.7)$$

(3) If the state has $T < T_c$ then the substance is either liquid or vapor or in two-phase VLE. To decide, we need another piece of information, preferably the vapor pressure P^s at the given T . Vapor pressures have been measured for most pure substances, and the data are usually correlated as a relatively simple function of T , as in Appendix D; in later lectures, we will discuss correlations for pure-component vapor pressures. With a value for $P^s(T)$, the possibilities are these (see Figure 5.8(b)):

$$(a) \text{ If } T < T_c \text{ and } P > P^s \Rightarrow \text{liquid} \quad (5.8)$$

$$(b) \text{ If } T < T_c \text{ and } P < P^s \Rightarrow \text{vapor} \quad (5.9)$$

(4) Note that if the state actually lies on the vapor-pressure curve, then the state could be one-phase saturated liquid, one-phase saturated vapor, or in two-phase vapor-liquid equilibrium (VLE).

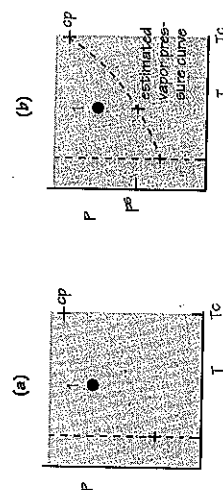


Figure 5.8 (a) If the phase is not solid and we know the critical point, then we can decide whether it is gas or fluid. (b) If it is neither solid, fluid, or gas and we know the vapor pressure P^s at T , then we can decide whether it is liquid or vapor. However, if $P_1 = P^s$, then we need still more information, as discussed in the text.

$$\text{If } T < T_c \text{ and } P = P^s \Rightarrow \text{liquid or vapor or VLE} \quad (5.10)$$

This means the state falls on a tie line, and therefore we must move from a PT diagram to a Pv diagram, because PT diagrams do not contain tie lines. To locate the state point on the tie line, we define the overall volume v^o as the total volume of the phase divided by the total number of moles present,

$$v^o = V/N \quad (5.11)$$

Then we can distinguish among the possibilities in (5.10) by comparing v^o with the molar volumes of the saturated liquid and vapor,

$$(a) \text{ If } v^o = v_f^s \Rightarrow \text{one-phase liquid} \quad (5.12)$$

$$(b) \text{ If } v^o = v_g^s \Rightarrow \text{one-phase vapor} \quad (5.13)$$

Otherwise, the state is a two-phase VLE situation. Values of pure-liquid molar volumes may be estimated from the correlation given in Appendix E; other methods will be described in Part III of these lectures. Melting points, boiling points, critical points, and vapor-pressure correlations are tabulated for a huge number of pure substances in standard reference books [1-3]; values for selected pure substances are tabulated in Appendices B and D.

The discussion in this section applies to stable equilibrium states; only stable states are reproducible and, in fact, these are the ones that usually occur. But it is possible, in a laboratory and in a processing facility, to create *metastable* one-phase states. These states can be hazardous, for in response to a small disturbance, they may suddenly and catastrophically relax to the stable equilibrium condition. If P and T are truly fixed, then the relaxation is accompanied by a large volume change that can amount to an implosion or an explosion. Metastable states will be discussed in later lectures.

Literature Cited

- [1] R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids*, 3rd ed., McGraw-Hill, New York, 1977.
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