

CHAPTER 2

Properties of Pure Substances

Simple System

A simple system is one in which the effects of motion, viscosity, fluid shear, capillarity, anisotropic stress, and external force fields are absent.

Homogeneous Substance

A substance that has uniform thermodynamic properties throughout is said to be homogeneous.

Pure Substance

A pure substance has a homogeneous and invariable chemical composition and may exist in more than one phase.

Examples:

1. Water (solid, liquid, and vapor phases)
2. Mixture of liquid water and water vapor
3. Carbon dioxide, CO_2
4. Nitrogen, N_2
5. Mixtures of gases, such as air, as long as there is no change of phase.²



FIGURE 3-1

Nitrogen and gaseous air are pure substances.

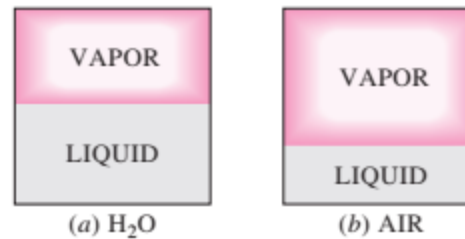


FIGURE 3-2

A mixture of liquid and gaseous water is a pure substance, but a mixture of liquid and gaseous air is not.

A pure substance is a system which is

- (i) *homogeneous in composition,*
- (ii) *homogeneous in chemical aggregation, and*
- (iii) *invariable in chemical aggregation.*

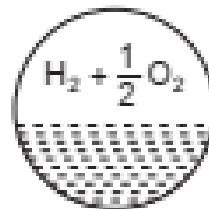
— “*Homogeneous in composition*” means that the composition of each part of the system is the *same* as the composition of every *other part*.

“*Composition* means the relative proportions of the chemical elements into which the sample can be analysed. It does not matter how these elements are combined.



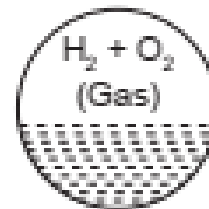
(a)

Satisfies condition (i)
Satisfies condition (ii)



(b)

Satisfies condition (i)
Does not satisfy
condition (ii)



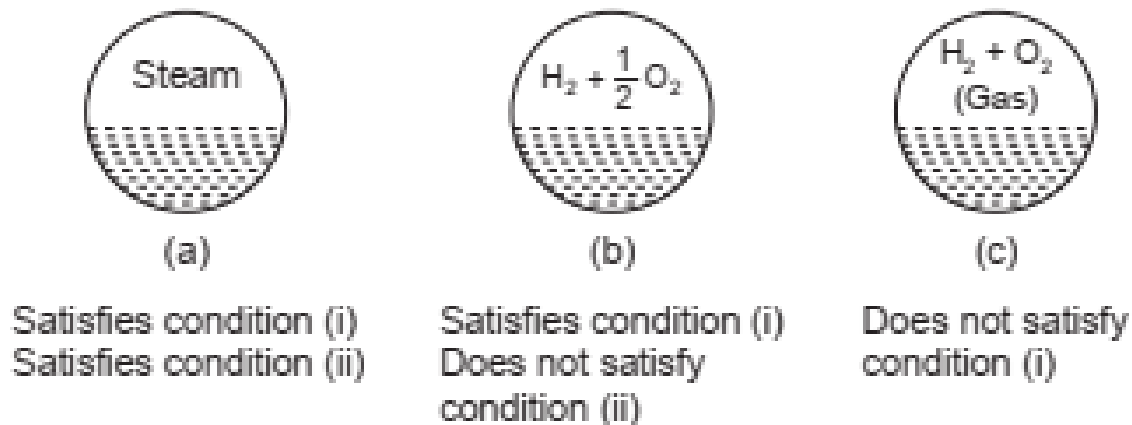
(c)

Does not satisfy
condition (i)

“Homogeneous in chemical aggregation” means that the chemical elements must be combined chemically in the same way in all parts of the system. Consideration of Fig. again shows that the system (a) satisfies this condition also ; for steam and water consist of identical molecules.

System (b) on the other hand is not homogeneous in chemical aggregation since in the upper part of the system the hydrogen and oxygen are not combined chemically (individual atoms of H and O are not uniquely associated), whereas in the lower part of the system the hydrogen and oxygen are combined to form water.

Note however that a uniform mixture of steam, hydrogen gas, and oxygen gas would be regarded as homogeneous in both composition and chemical aggregation whatever the relative proportions of the components.



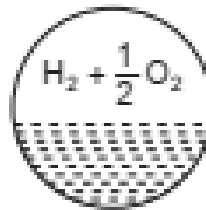
— “*Invariable in chemical aggregation*” means that the state of chemical combination of the system does not change with *time* (condition (i)) referred to variation with *position*).

Thus a mixture of hydrogen and oxygen, which changed into steam during the time that the system was under consideration, would not be a pure substance.



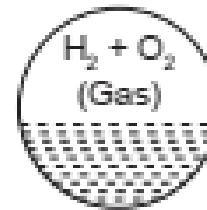
(a)

Satisfies condition (i)
Satisfies condition (ii)



(b)

Satisfies condition (i)
Does not satisfy
condition (ii)



(c)

Does not satisfy
condition (i)

Compressed Liquid and Saturated Liquid

Consider a piston–cylinder device containing liquid water at 20°C and 1 atm pressure (state 1). Under these conditions, water exists in the liquid phase, and it is called a **compressed liquid**, or a **subcooled liquid**, meaning that it is *not about to vaporize*.



At 1 atm and 20°C, water exists in the liquid phase (*compressed liquid*).

Heat is now transferred to the water until its temperature rises to, say, 40°C.

As the temperature rises, the liquid water expands slightly, and so its specific volume increases. To accommodate this expansion, the piston moves up slightly.

The pressure in the cylinder remains constant at 1 atm during this process since it depends on the outside barometric pressure and the weight of the piston, both of which are constant.

Water is still a compressed liquid at this state since it has not started to vaporize.

As more heat is transferred, the temperature keeps rising until it reaches 100°C (state 2, Fig).

At this point water is still a liquid, but any heat addition will cause some of the liquid to vaporize.

That is, a phase-change process from liquid to vapor is about to take place.

A liquid that is *about to vaporize* is called a **saturated liquid**. Therefore, state 2 is a saturated liquid state.

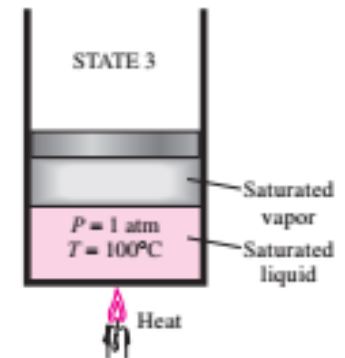


At 1 atm pressure and 100°C, water exists as a liquid that is ready to vaporize (*saturated liquid*).

Saturated Vapor and Superheated Vapor

Once boiling starts, the temperature stops rising until the liquid is completely vaporized. That is, the temperature will remain constant during the entire phase-change process if the pressure is held constant. This can easily be verified by placing a thermometer into boiling pure water on top of a stove. At sea level ($P = 1 \text{ atm}$), the thermometer will always read 100°C if the pan is uncovered or covered with a light lid.

During a boiling process, the only change we will observe is a large increase in the volume and a steady decline in the liquid level as a result of more liquid turning to vapor. Midway about the vaporization line (state 3, Fig.), the cylinder contains equal amounts of liquid and vapor.



As more heat is transferred, part of the saturated liquid vaporizes (*saturated liquid–vapor mixture*)

As we continue transferring heat, the vaporization process continues until the last drop of liquid is vaporized (state 4, Fig. 3–9). At this point, the entire cylinder is filled with vapor that is on the borderline of the liquid phase. Any heat loss from this vapor will cause some of the vapor to condense (phase change from vapor to liquid).

A vapor that is *about to condense* is called a **saturated vapor**. Therefore, state 4 is a saturated vapor state. A substance at states between 2 and 4 is referred to as a **saturated liquid–vapor mixture** since the *liquid and vapor phases coexist* in equilibrium at these states.

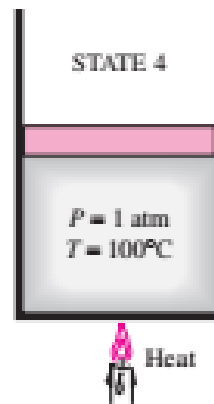


FIGURE 3–9

At 1 atm pressure, the temperature remains constant at 100°C until the last drop of liquid is vaporized (*saturated vapor*).

Once the phase-change process is completed, we are back to a single phase region again (this time vapor), and further transfer of heat results in an increase in both the temperature and the specific volume (Fig. 3–10).

At state 5, the temperature of the vapor is, let us say, 300°C ; and if we transfer some heat from the vapor, the temperature may drop somewhat but no condensation will take place as long as the temperature remains above 100°C (for $P=1\text{ atm}$). A vapor that is *not about to condense* (i.e., not a saturated vapor) is called a **superheated vapor**. Therefore, water at state 5 is a superheated vapor.

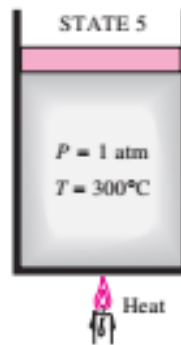


FIGURE 3–10

As more heat is transferred, the temperature of the vapor starts to rise (*superheated vapor*).

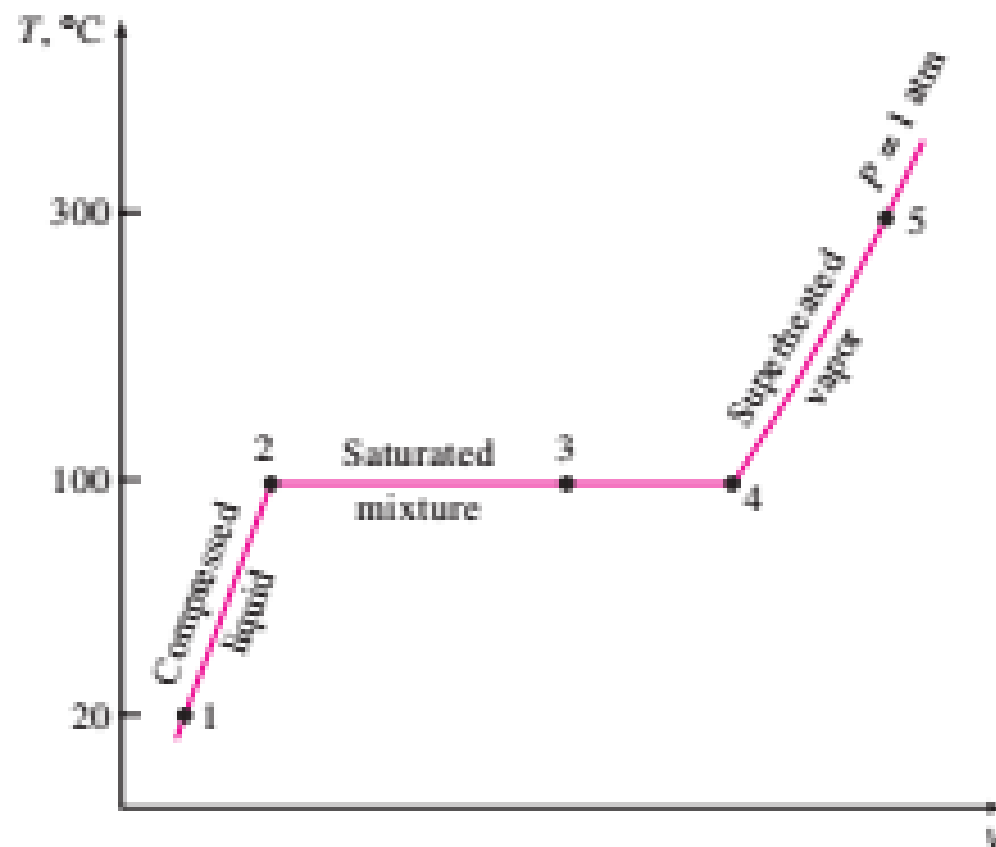
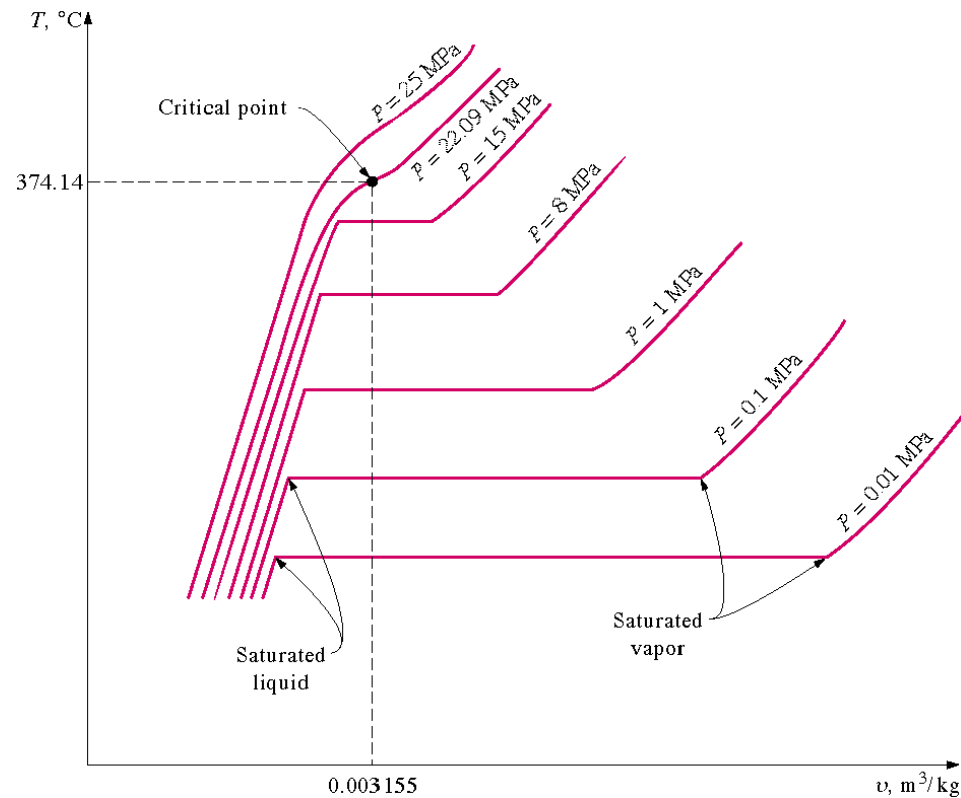
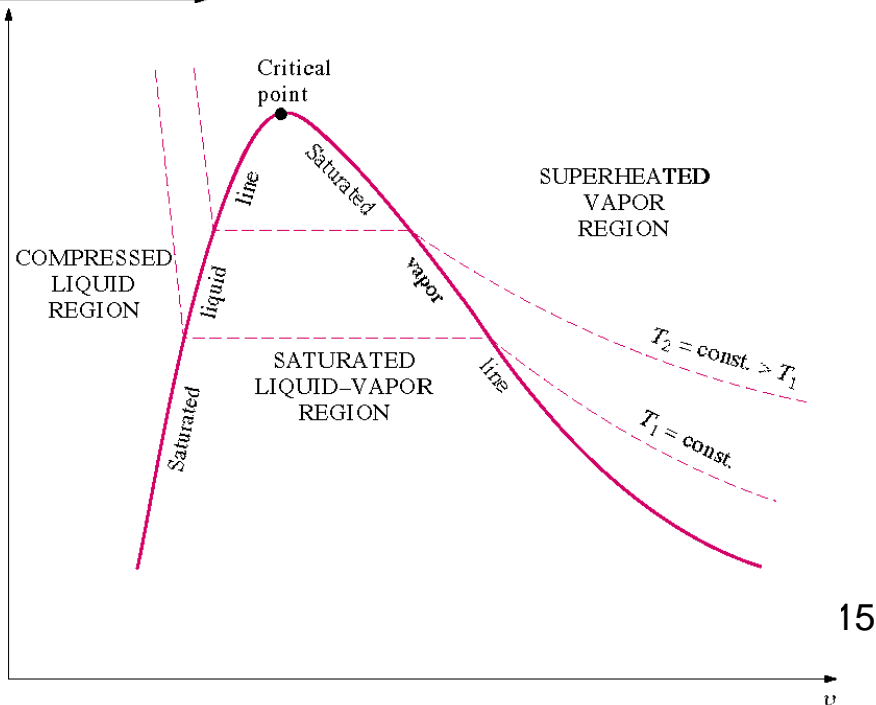
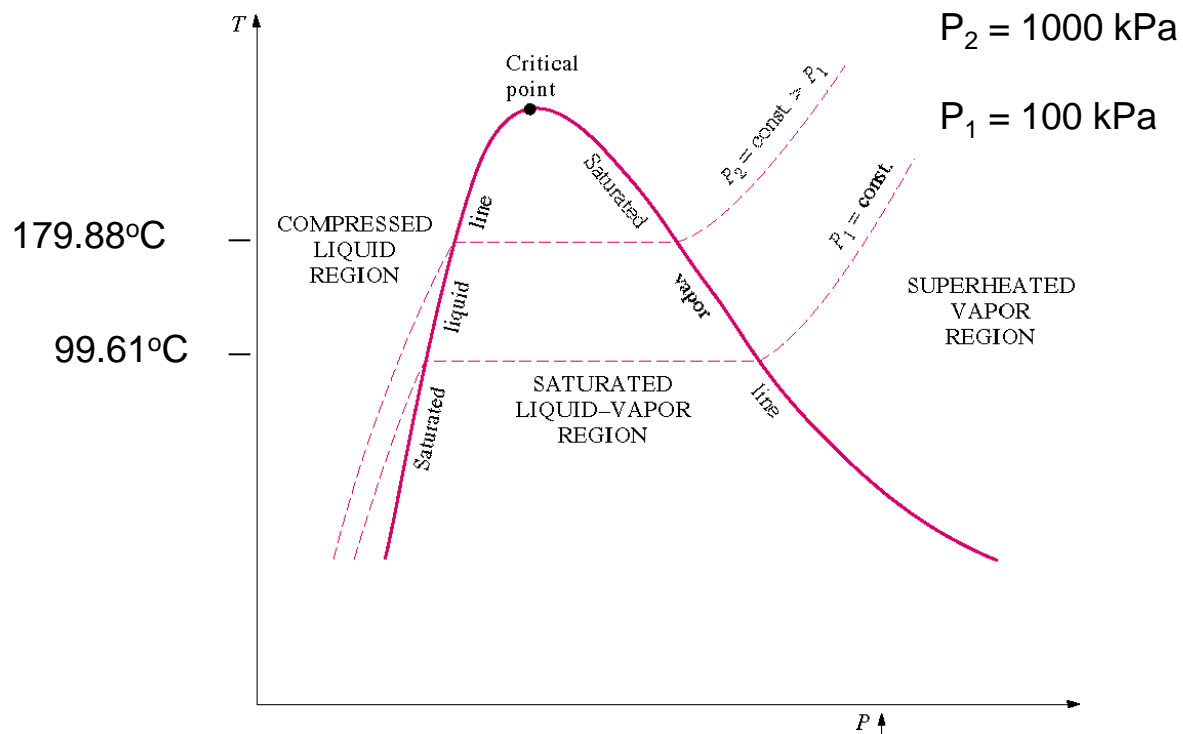


FIGURE 3-11

T - v diagram for the heating process of water at constant pressure.

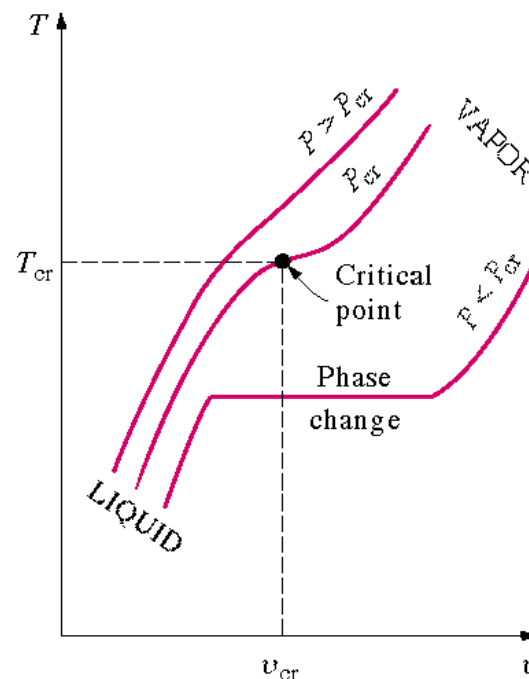


If all of the saturated liquid states are connected, the saturated liquid line is established. If all of the saturated vapor states are connected, the saturated vapor line is established. These two lines intersect at the critical point and form what is often called the “steam dome.” The region between the saturated liquid line and the saturated vapor line is called by these terms: saturated liquid-vapor mixture region, wet region (i.e., a mixture of saturated liquid and saturated vapor), two-phase region, and just the saturation region. Notice that the trend of the temperature following a constant pressure line is to increase with increasing volume and the trend of the pressure following a constant temperature line is to decrease with increasing volume.



The horizontal line that connects the saturated liquid and saturated vapor states is much shorter. As the pressure is increased further, this saturation line continues to shrink, as shown in Fig. and it becomes a point when the pressure reaches 22.06 MPa for the case of water. This point is called the **critical point**, and it is defined as *the point at which the saturated liquid and saturated vapor states are identical*.

The temperature, pressure, and specific volume of a substance at the critical point are called, respectively, the *critical temperature* T_{cr} , *critical pressure* P_{cr} , and *critical specific volume* v_{cr} . The critical-point properties of water are $P_{cr} = 22.06$ MPa, $T_{cr} = 373.95^\circ\text{C}$, and $v_{cr} = 0.003106$ m³/kg.

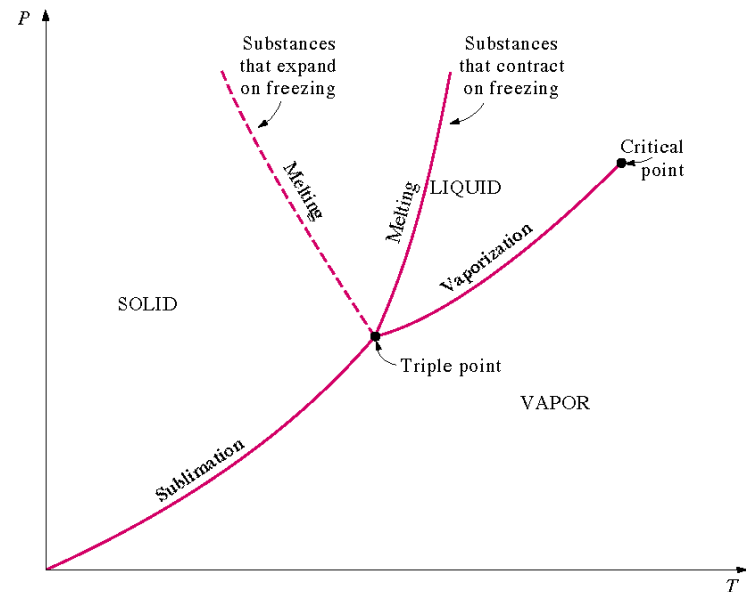


p-T (Pressure-Temperature) DIAGRAM FOR A PURE SUBSTANCE

The P - T Diagram

Figure shows the P - T diagram of a pure substance. This diagram is often called the **phase diagram** since all three phases are separated from each other by three lines. The sublimation line separates the solid and vapor regions, the vaporization line separates the liquid and vapor regions, and the melting (or fusion) line separates the solid and liquid regions.

These three lines meet at the triple point, where all three phases coexist in equilibrium. The vaporization line ends at the critical point because no distinction can be made between liquid and vapor phases above the critical point. Substances that expand and contract on freezing differ only in the melting line on the P - T diagram.



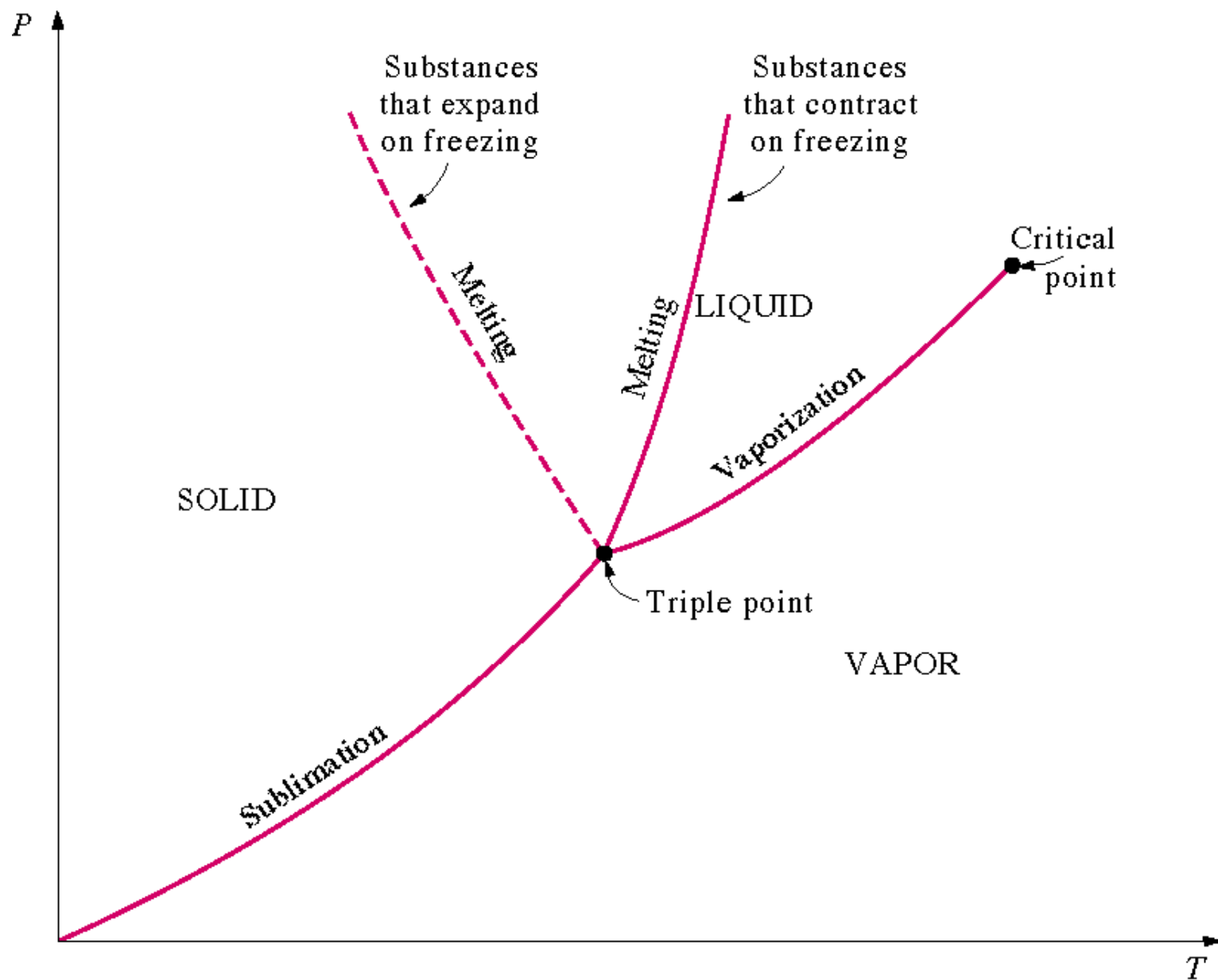
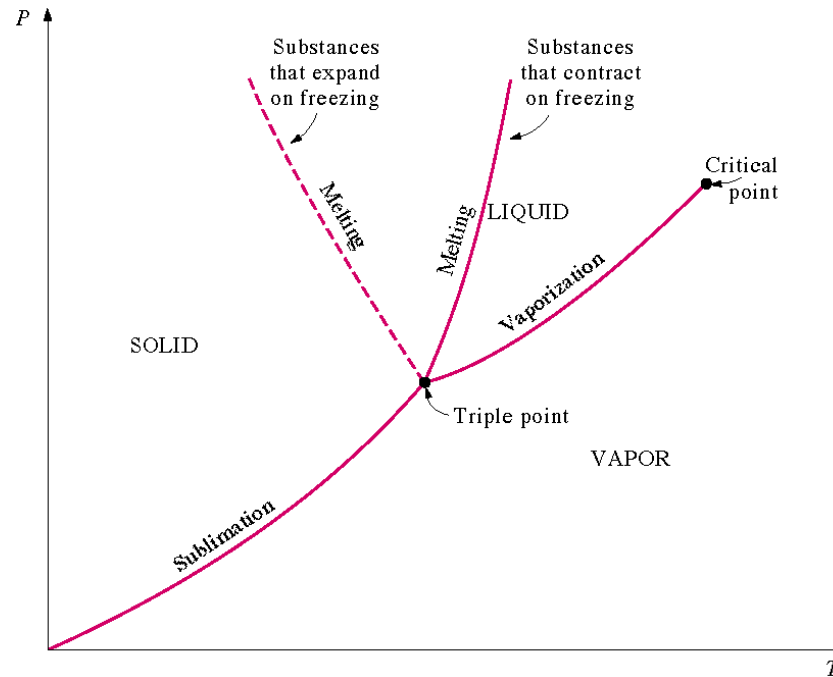


Figure 3-25 shows the P - T diagram, often called the phase diagram, for pure substances that contract and expand upon freezing.

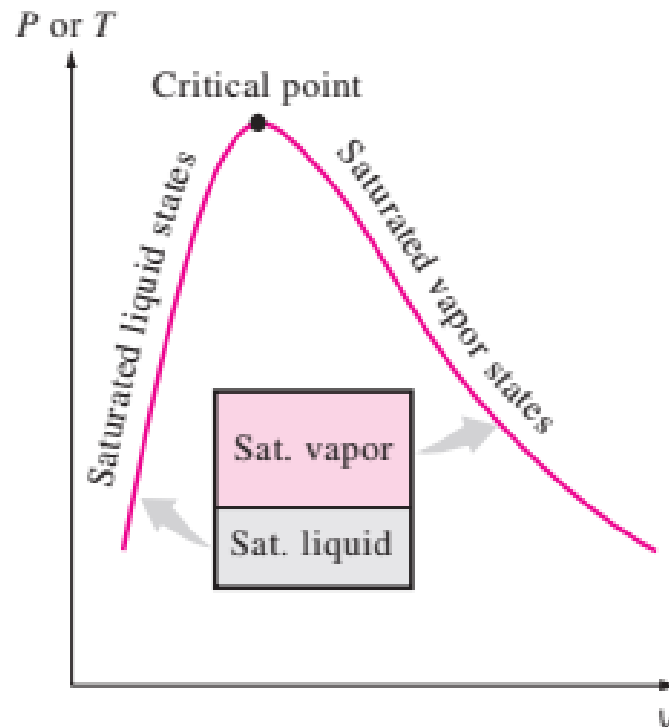


The triple point of water is 0.01°C , 0.6117 kPa (See Table 3-3).

The critical point of water is 373.95°C , 22.064 MPa (See Table A-1).

Saturated Liquid–Vapor Mixture

During a vaporization process, a substance exists as part liquid and part vapor. That is, it is a mixture of saturated liquid and saturated vapor (Fig). To analyze this mixture properly, we need to know the proportions of the liquid and vapor phases in the mixture. This is done by defining a new property called the **quality** x as the ratio of the mass of vapor to the total mass of the mixture.



Quality

- In a saturated liquid-vapor mixture, the mass fraction of the vapor phase is called the *quality* and is defined as

$$x = \frac{mass_{vapor}}{m_{total}}$$

The quality may have values between 0 (saturated liquid) and 1 (saturated vapor). It has no meaning in the compressed liquid or superheated vapor regions.

Quality has significance for *saturated mixtures* only. It has no meaning in the compressed liquid or superheated vapor regions. Its value is between 0 and 1. The quality of a system that consists of *saturated liquid* is 0 (or 0 percent), and the quality of a system consisting of *saturated vapor* is 1 (or 100 percent).

In saturated mixtures, quality can serve as one of the two independent intensive properties needed to describe a state. Note that *the properties of the saturated liquid are the same whether it exists alone or in a mixture with saturated vapor*.

Consider a tank that contains a saturated liquid–vapor mixture. The volume occupied by saturated liquid is V_f and the volume occupied by saturated vapor is V_g . The total volume V is the sum of the two:

$$V = V_f + V_g$$

$$V = mV \longrightarrow m_t V_{\text{avg}} = m_f V_f + m_g V_g$$

$$m_f = m_t - m_g \longrightarrow m_t V_{\text{avg}} = (m_t - m_g) V_f + m_g V_g$$

Dividing by m_t yields

$$v_{\text{avg}} = (1 - x) v_f + x v_g$$

since $x = m_g/m_t$. This relation can also be expressed as

$$v_{\text{avg}} = v_f + x v_{fg} \quad (\text{m}^3/\text{kg}) \quad (3-4)$$

where $v_{fg} = v_g - v_f$. Solving for quality, we obtain

$$x = \frac{v_{\text{avg}} - v_f}{v_{fg}} \quad (3-5)$$

Based on this equation, quality can be related to the horizontal distances on a P - v or T - v diagram (Fig. 3–36). At a given temperature or pressure, the numerator of Eq. 3–5 is the distance between the actual state and the saturated liquid state, and the denominator is the length of the entire horizontal line that connects the saturated liquid and saturated vapor states. A state of 50 percent quality lies in the middle of this horizontal line.

The analysis given above can be repeated for internal energy and enthalpy with the following results:

$$u_{\text{avg}} = u_f + xu_{fg} \quad (\text{kJ/kg}) \quad (3-6)$$

$$h_{\text{avg}} = h_f + xh_{fg} \quad (\text{kJ/kg}) \quad (3-7)$$

Tables of properties outside the dome

Compressed liquid or superheated vapor

Specify a state by values of PT

A partial listing of Table A–6.

$T, ^\circ\text{C}$	v m^3/kg	u kJ/kg	h kJ/kg
$P = 0.1 \text{ MPa} (99.61^\circ\text{C})$			
Sat.	1.6941	2505.6	2675.0
100	1.6959	2506.2	2675.8
150	1.9367	2582.9	2776.6
\vdots	\vdots	\vdots	\vdots
1300	7.2605	4687.2	5413.3
$P = 0.5 \text{ MPa} (151.83^\circ\text{C})$			
Sat.	0.37483	2560.7	2748.1
200	0.42503	2643.3	2855.8
250	0.47443	2723.8	2961.0

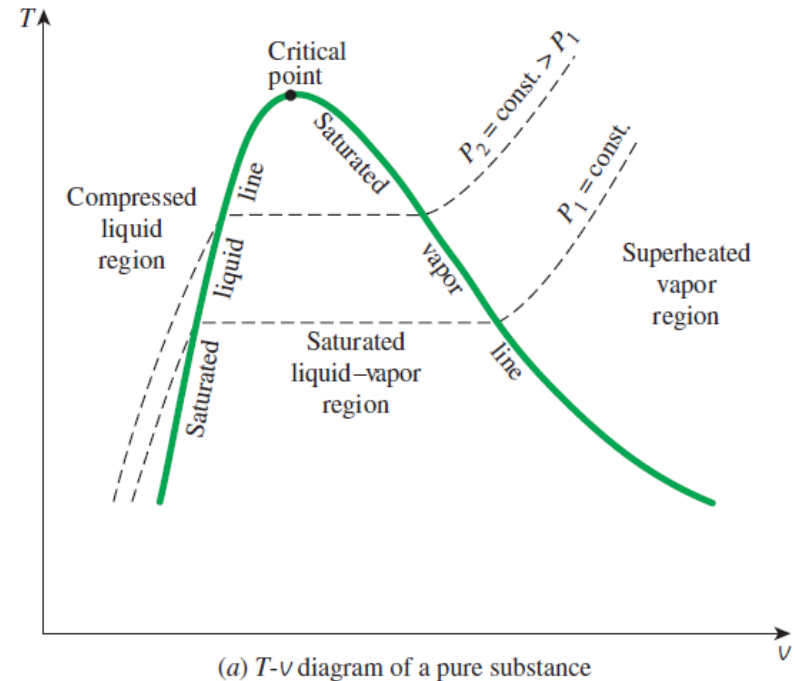


FIGURE 3–17

Property diagrams of a pure substance.

Tables of properties in the dome coexistent liquid and vapor

A partial list of Table A-4.

Temp. °C T	Sat. press. kPa P_{sat}	Specific volume m^3/kg	
		Sat. liquid ν_f	Sat. vapor ν_g
85	57.868	0.001032	2.8261
90	70.183	0.001036	2.3593
95	84.609	0.001040	1.9808

Specific
temperature

Corresponding
saturation
pressure

Specific
volume of
saturated
liquid

Specific
volume of
saturated
vapor

- **Table A-4:** Saturation properties of water under temperature.
- **Table A-5:** Saturation properties of water under pressure.

ν_f = specific volume of saturated liquid

ν_g = specific volume of saturated vapor

ν_{fg} = difference between ν_g and ν_f (that is $\nu_{fg} = \nu_g - \nu_f$)

Specify a state of coexistent phases

Specify a state by values of two variables: TV or PV, but not PT.

$$\text{quality} = \frac{\text{mass of vapor}}{\text{total mass}}$$

$$x = \frac{m_{\text{vapor}}}{m_{\text{total}}}$$

$0 < x < 1$: mixture of liquid and vapor

$x = 0$: saturated liquid

$x = 1$: saturated vapor

Rule of mixture

$$v_{\text{avg}} = v_f + x v_{fg} \quad (\text{m}^3/\text{kg})$$

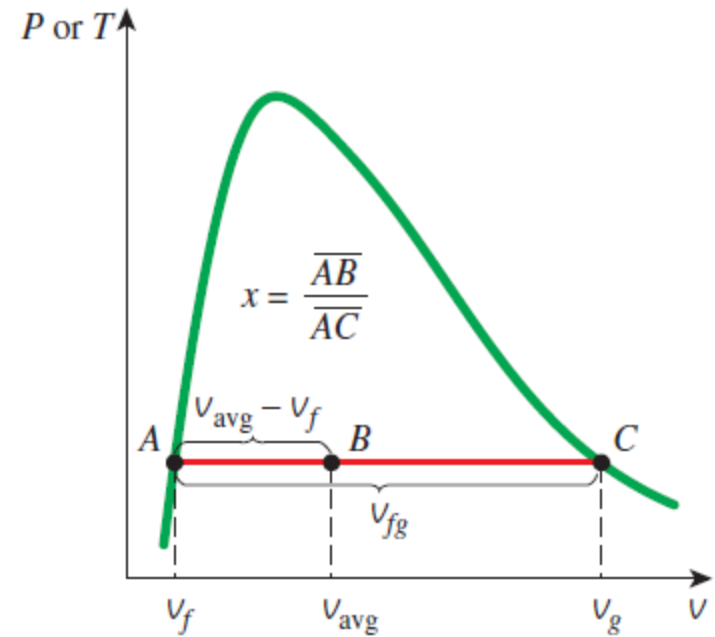


FIGURE 3–33

Quality is related to the horizontal distances on P - v and T - v diagrams.

Two more ways to specify a state of coexistent phases: Tx or Px .

The function $P(T,V)$

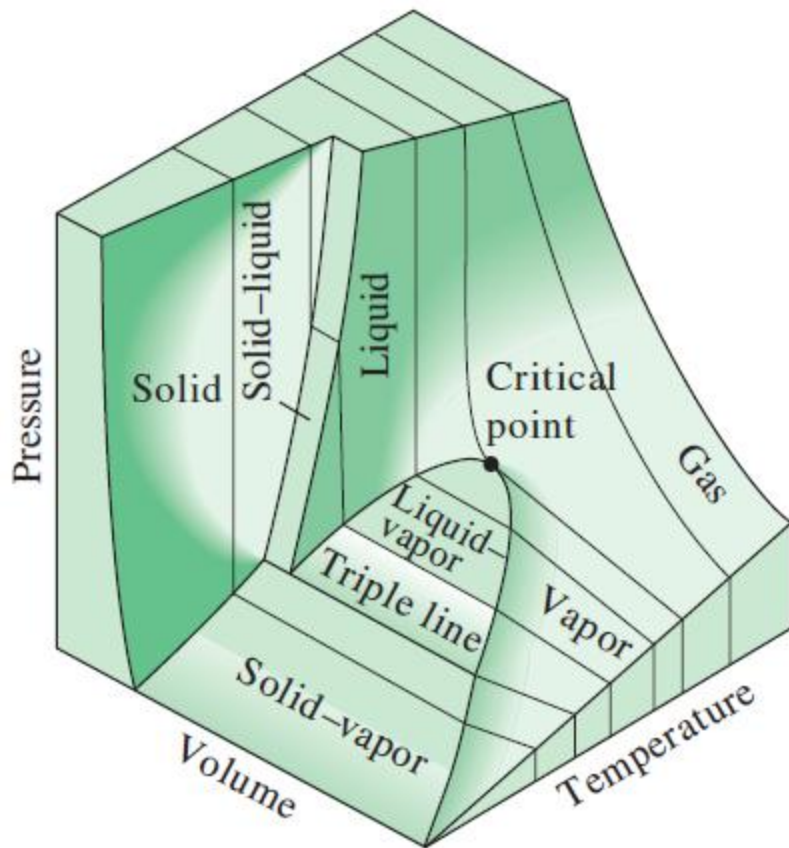


FIGURE 3-23

P - v - T surface of a substance that *contracts* on freezing.

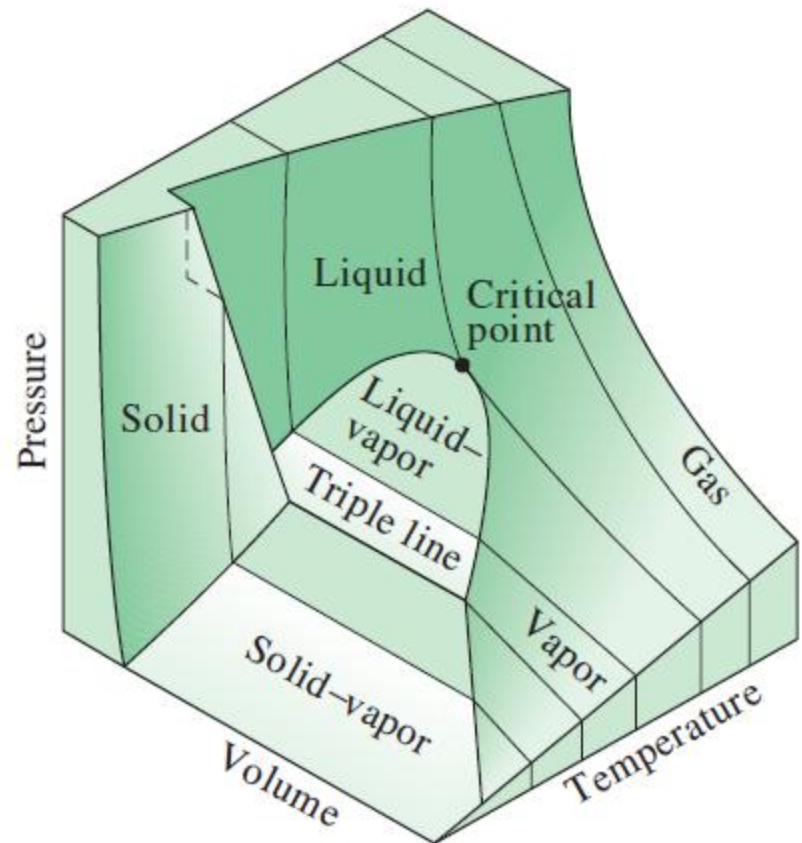


FIGURE 3-24

P - v - T surface of a substance that *expands* on freezing (like water).

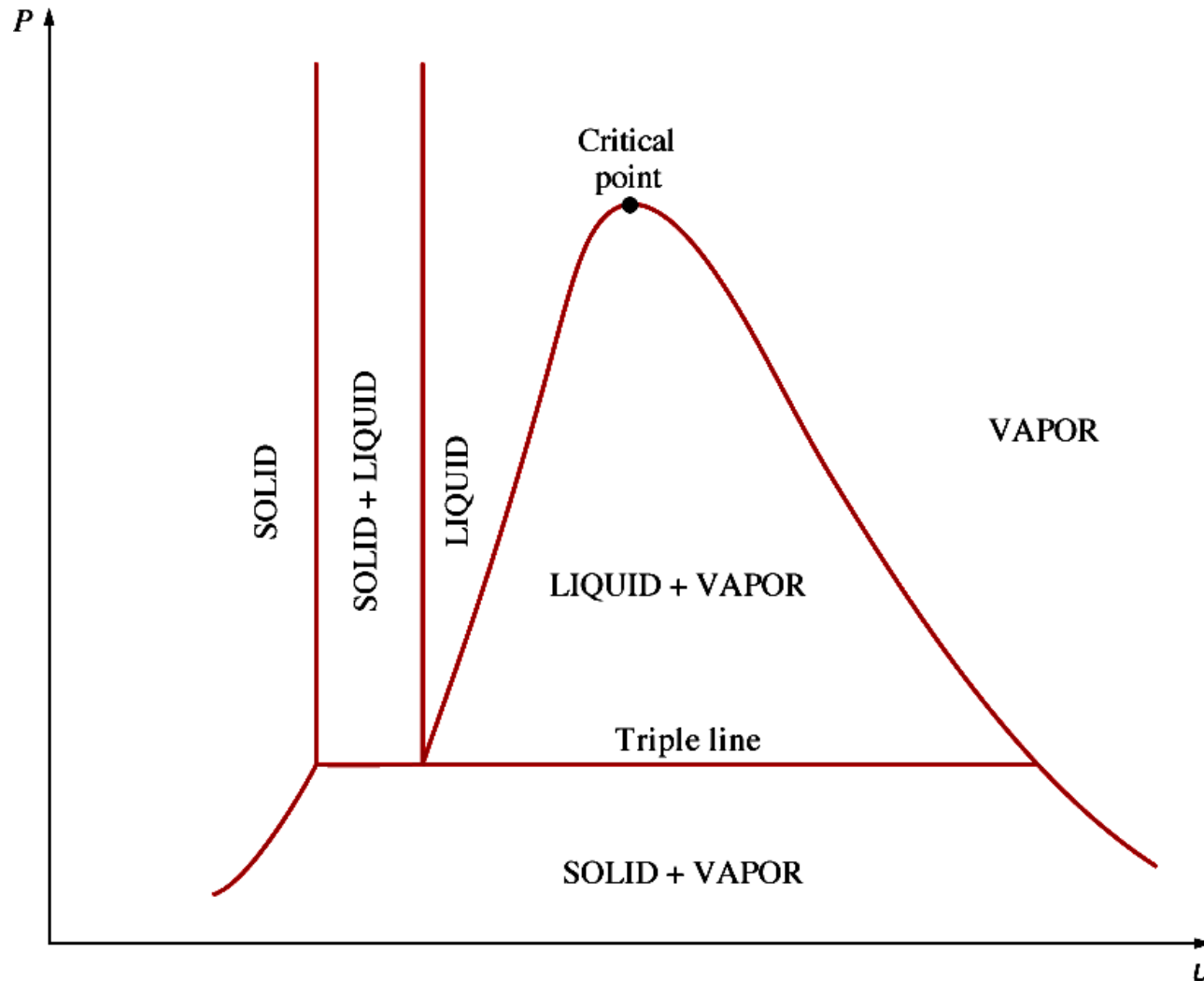
The two equilibrium diagrams developed so far represent the equilibrium states involving the liquid and the vapor phases only.

However, these diagrams can easily be extended to include the solid phase as well as the solid–liquid and the solid–vapor saturation regions. The basic principles discussed in conjunction with the liquid–vapor phase-change process apply equally to the solid–liquid and solid–vapor phase-change processes. Most substances contract during a solidification (i.e., freezing) process. Others, like water, expand as they freeze.

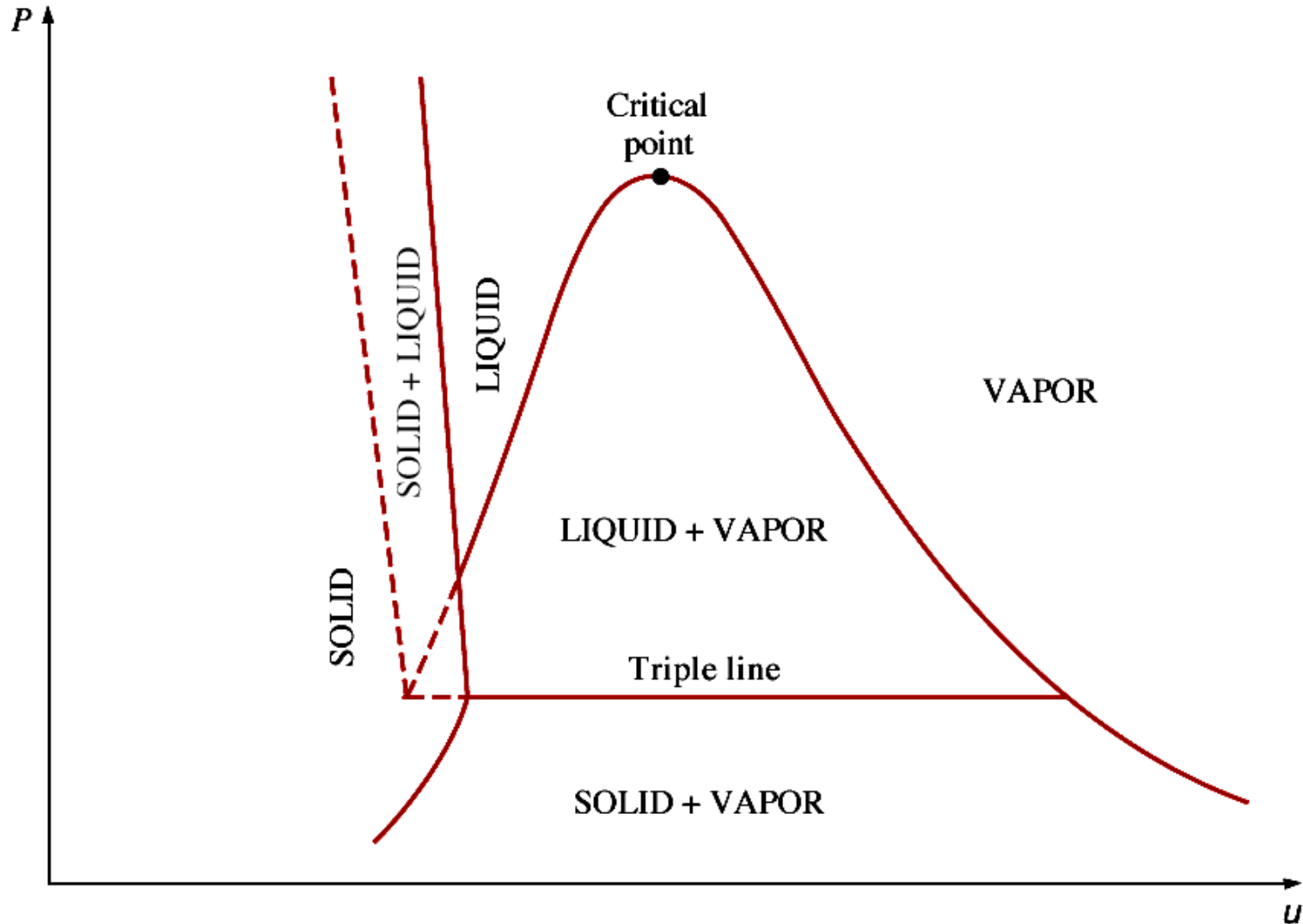
The P - v diagrams for both groups of substances are given in Figs. These two diagrams differ only in the solid–liquid saturation region. The T - v diagrams look very much like the P - v diagrams, especially for substances that contract on freezing.

The fact that water expands upon freezing has vital consequences in nature. If water contracted on freezing as most other substances do, the ice formed would be heavier than the liquid water, and it would settle to the bottom of rivers, lakes, and oceans instead of floating at the top. The sun's rays would never reach these ice layers, and the bottoms of many rivers, lakes, and oceans would be covered with ice at times, seriously disrupting marine life.

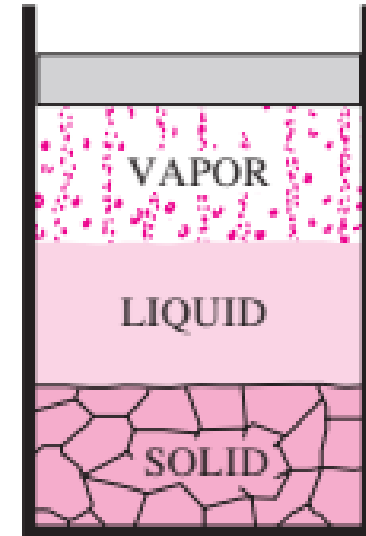
2-4 P - v Diagram of Substance that Contracts on Freezing



P - v Diagram of Substance that Expands on Freezing



We are all familiar with two phases being in equilibrium, but under some conditions all three phases of a pure substance coexist in equilibrium(Fig.). On P - v or T - v diagrams, these triple-phase states form a line called the **triple line**. The states on the triple line of a substance have the same pressure and temperature but different specific volumes. The triple line appears as a point on the P - T diagrams and, therefore, is often called the **triple point**.



At triple-point pressure and temperature, a substance exists in three phases in equilibrium.

For water, the triple-point temperature and pressure are 0.01°C and 0.6117 kPa , respectively

Triple-point temperatures and pressures of various substances

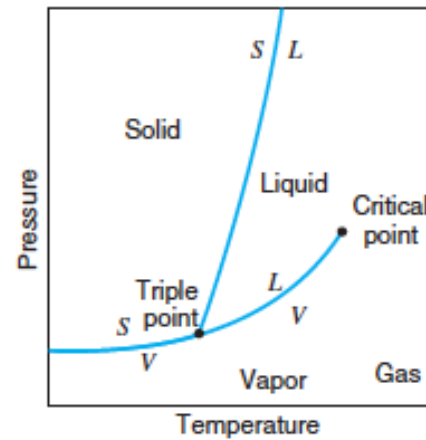
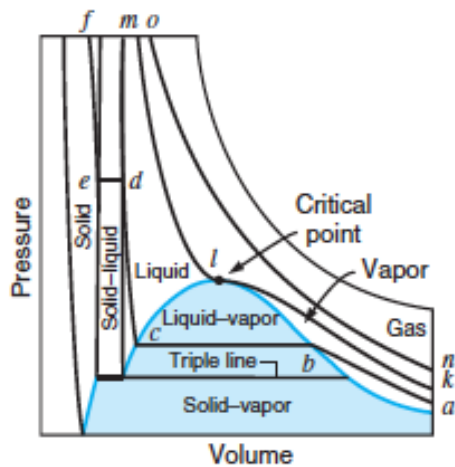
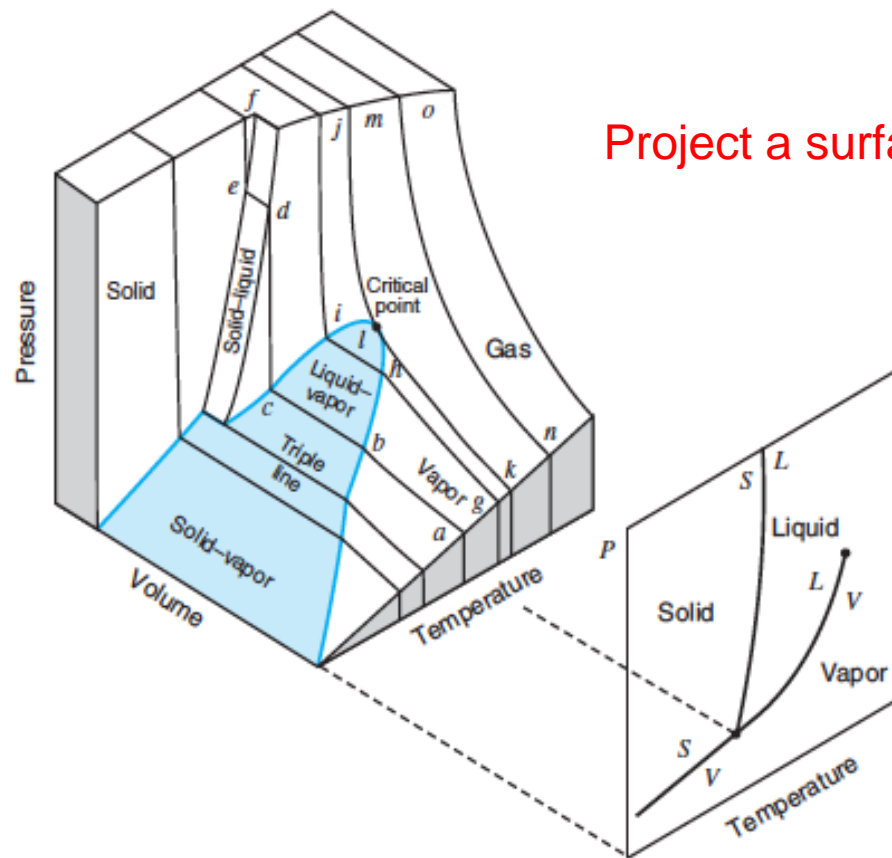
Substance	Formula	T_{tp} , K	P_{tp} , kPa
Acetylene	C_2H_2	192.4	120
Ammonia	NH_3	195.40	6.076
Argon	A	83.81	68.9
Carbon (graphite)	C	3900	10,100
Carbon dioxide	CO_2	216.55	517
Carbon monoxide	CO	68.10	15.37
Deuterium	D_2	18.63	17.1
Ethane	C_2H_6	89.89	8×10^{-4}
Ethylene	C_2H_4	104.0	0.12
Helium 4 (λ point)	He	2.19	5.1
Hydrogen	H_2	13.84	7.04
Hydrogen chloride	HCl	158.96	13.9
Mercury	Hg	234.2	1.65×10^{-7}
Methane	CH_4	90.68	11.7
Neon	Ne	24.57	43.2
Nitric oxide	NO	109.50	21.92
Nitrogen	N_2	63.18	12.6
Nitrous oxide	N_2O	182.34	87.85
Oxygen	O_2	54.36	0.152
Palladium	Pd	1825	3.5×10^{-3}
Platinum	Pt	2045	2.0×10^{-4}
Sulfur dioxide	SO_2	197.69	1.67
Titanium	Ti	1941	5.3×10^{-3}
Uranium hexafluoride	UF_6	337.17	151.7
Water	H_2O	273.16	0.61
Xenon	Xe	161.3	81.5
Zinc	Zn	692.65	0.065

The P - v - T Surface

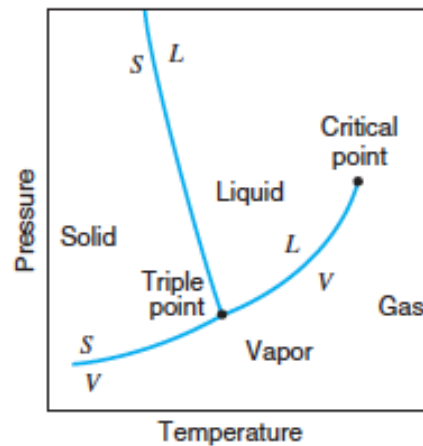
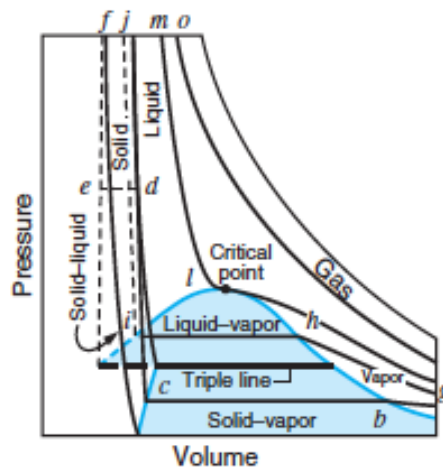
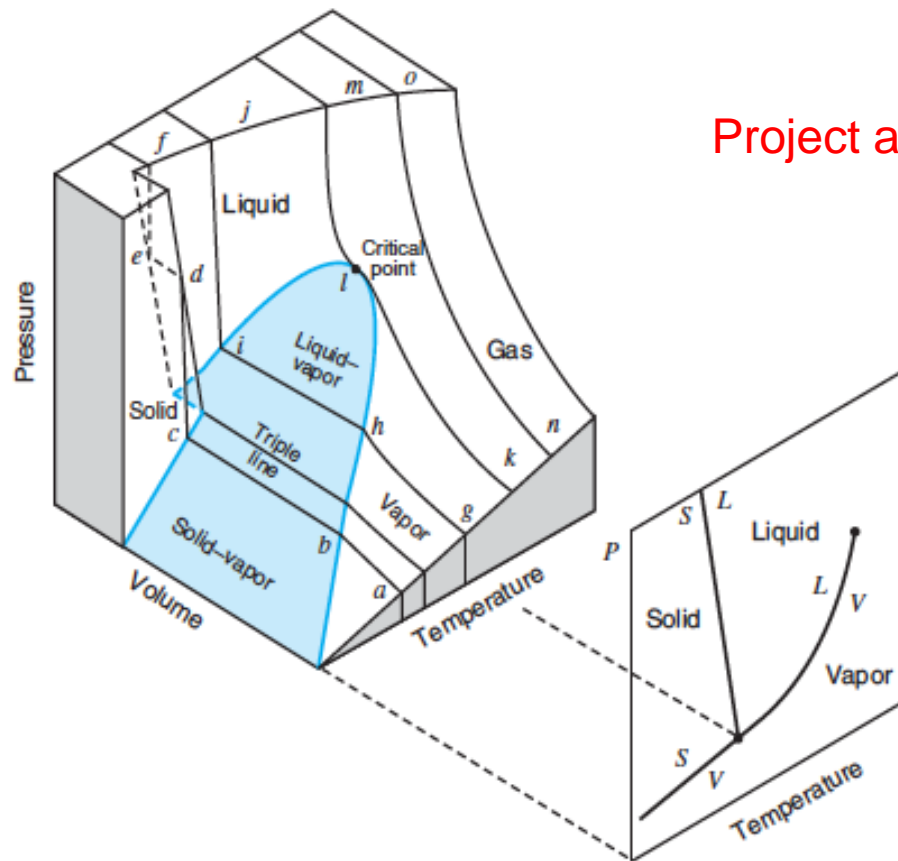
The state of a simple compressible substance is fixed by any two independent, intensive properties. Once the two appropriate properties are fixed, all the other properties become dependent properties. Remembering that any equation with two independent variables in the form $z = z(x, y)$ represents a surface in space, we can represent the P - v - T behavior of a substance as a surface in space, as shown in Figs.

All the two-dimensional diagrams we have discussed so far are merely projections of this three-dimensional surface onto the appropriate planes. A P - v diagram is just a projection of the P - v - T surface on the P - v plane, and a T - v diagram is nothing more than the bird's-eye view of this surface. The P - v - T surfaces present a great deal of information at once, but in a thermodynamic analysis it is more convenient to work with two-dimensional diagrams, such as the P - v and T - v diagrams.

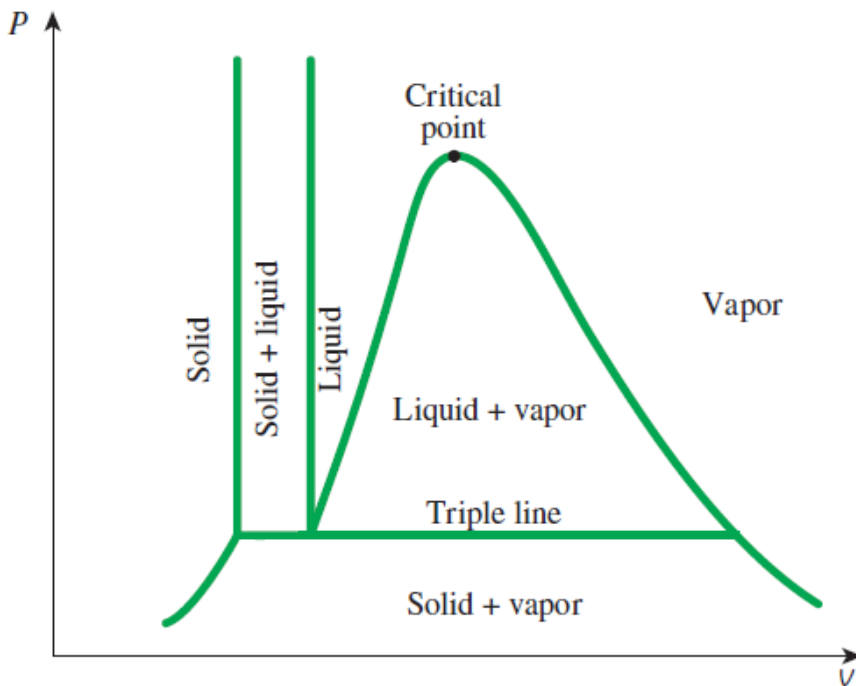
Project a surface in 3D to planes



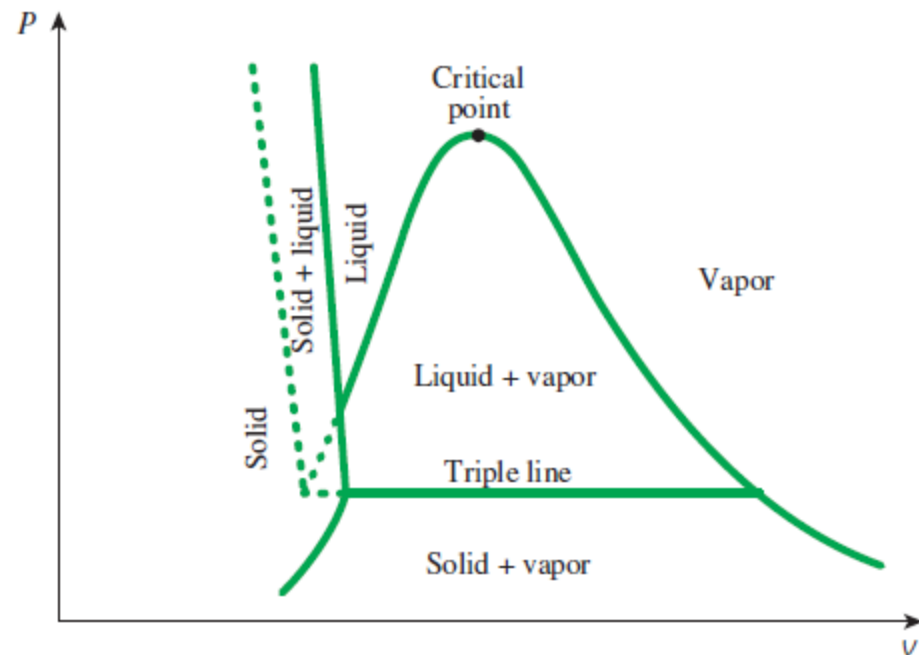
Project a surface in 3D to planes



Phase diagram on P-V plane



(a) P - v diagram of a substance that contracts on freezing



(b) P - v diagram of a substance that expands on freezing (such as water)

STEAM TABLES

Partial List of Table A-4

Sat. Temp. $^{\circ}\text{C}$ T	Sat. press kPa P_{sat}	Specific volume m^3/kg	
		Sat. liquid u_f	Sat. vapor u_g
85	57.83	0.001 033	2.828
90	70.14	0.001 036	2.361
95	84.55	0.001 040	1.982

Specific temperature

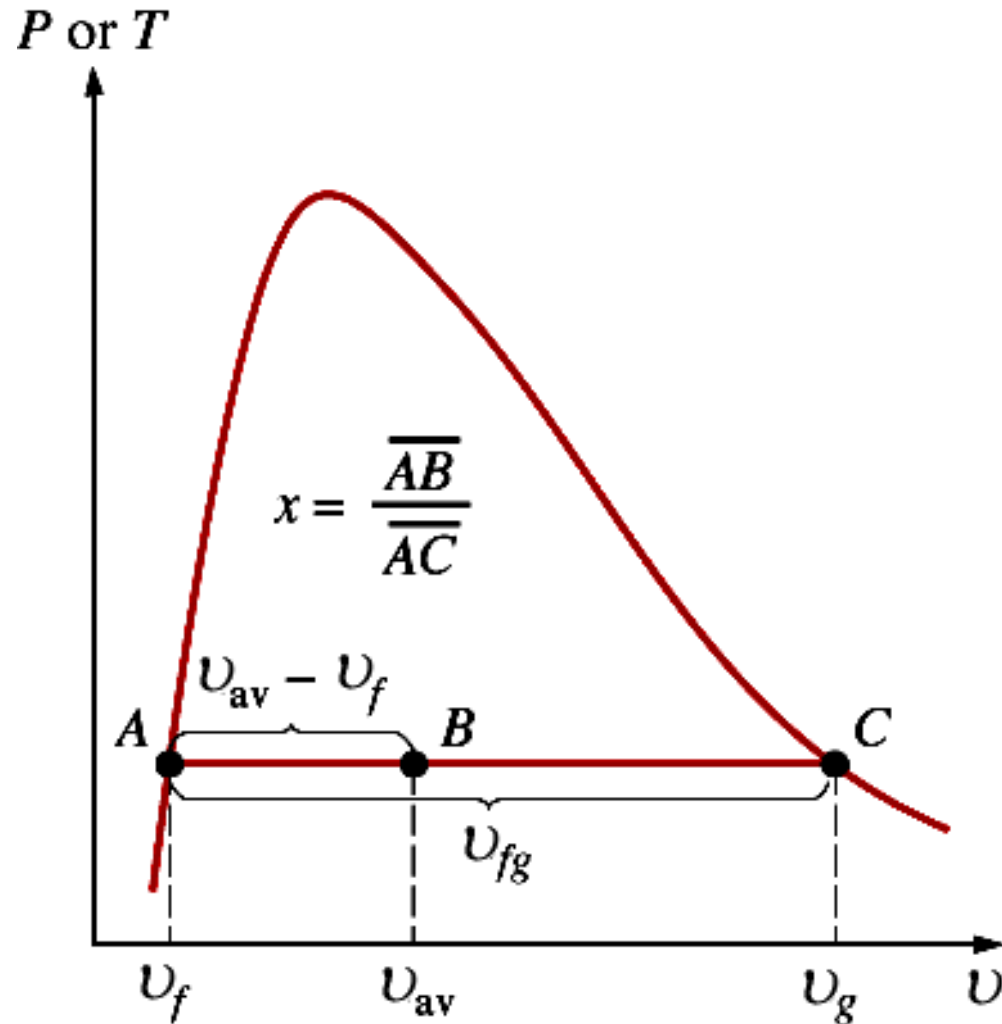
Corresponding saturation pressure

Specific volume of saturated liquid

Specific volume of saturated vapor

Quality Shown in P - v and T - v Diagrams

Quality is related to the horizontal differences of P - V and T - v diagrams



Partial List of Table A-6

$T, ^\circ\text{C}$	$v,$ m^3/kg	$u,$ kJ/kg	$h,$ kJ/kg
$P = 0.1 \text{ MPa } (99.63^\circ\text{C})$			
Sat.	1.6940	2506.1	2675.5
100	1.6958	2506.7	2676.2
150	1.9364	2582.8	2776.4
\vdots	\vdots	\vdots	\vdots
1300	7.260	4683.5	5409.5
$P = 0.5 \text{ MPa } (151.86^\circ\text{C})$			
Sat.	0.3749	2561.2	2748.7
200	0.4249	2642.9	2855.4
250	0.4744	2723.5	2960.7

Temp., T °C	Sat. Press., P_{sat} kPa	Specific volume, m^3/kg		Internal energy, kJ/kg			Enthalpy, kJ/kg			Entropy, $kJ/kg\cdot K$		
		Sat. liquid, v_f	Sat. vapor, v_g	Sat. liquid, u_f	Evap., u_{fg}	Sat. vapor, u_g	Sat. liquid, h_f	Evap., h_{fg}	Sat. vapor, h_g	Sat. liquid, s_f	Evap., s_{fg}	Sat. vapor, s_g
0.01	0.6117	0.001000	206.00	0.00	2374.9	2374.9	0.00	2500.9	2500.9	0.0000	9.1556	9.1556
5	0.8725	0.001000	147.03	21.02	2360.8	2381.8	21.02	2489.1	2510.1	0.0763	8.9487	9.0249
10	1.228	0.001000	106.32	42.02	2346.6	2388.7	42.02	2477.2	2519.2	0.1511	8.7488	8.8999
15	1.706	0.001001	77.885	62.98	2332.5	2395.5	62.98	2465.4	2528.3	0.2245	8.5559	8.7803
20	2.339	0.001002	57.762	83.91	2318.4	2402.3	83.91	2453.5	2537.4	0.2965	8.3696	8.6661
25	3.170	0.001003	43.340	104.83	2304.3	2409.1	104.83	2441.7	2546.5	0.3672	8.1895	8.5567
30	4.247	0.001004	32.879	125.73	2290.2	2415.9	125.74	2429.8	2555.6	0.4368	8.0152	8.4520
35	5.629	0.001006	25.205	146.63	2276.0	2422.7	146.64	2417.9	2564.6	0.5051	7.8466	8.3517
40	7.385	0.001008	19.515	167.53	2261.9	2429.4	167.53	2406.0	2573.5	0.5724	7.6832	8.2556
45	9.595	0.001010	15.251	188.43	2247.7	2436.1	188.44	2394.0	2582.4	0.6386	7.5247	8.1633
50	12.35	0.001012	12.026	209.33	2233.4	2442.7	209.34	2382.0	2591.3	0.7038	7.3710	8.0748
55	15.76	0.001015	9.5639	230.24	2219.1	2449.3	230.26	2369.8	2600.1	0.7680	7.2218	7.9898
60	19.95	0.001017	7.6670	251.16	2204.7	2455.9	251.18	2357.7	2608.8	0.8313	7.0769	7.9082
65	25.04	0.001020	6.1935	272.09	2190.3	2462.4	272.12	2345.4	2617.5	0.8937	6.9360	7.8296
70	31.20	0.001023	5.0396	293.04	2175.8	2468.9	293.07	2333.0	2626.1	0.9551	6.7989	7.7540
75	38.60	0.001026	4.1291	313.99	2161.3	2475.3	314.03	2320.6	2634.6	1.0158	6.6655	7.6812
80	47.42	0.001029	3.4053	334.97	2146.6	2481.6	335.02	2308.0	2643.0	1.0756	6.5355	7.6111
85	57.87	0.001032	2.8261	355.96	2131.9	2487.8	356.02	2295.3	2651.4	1.1346	6.4089	7.5435
90	70.18	0.001036	2.3593	376.97	2117.0	2494.0	377.04	2282.5	2659.6	1.1929	6.2853	7.4782
95	84.61	0.001040	1.9808	398.00	2102.0	2500.1	398.09	2269.6	2667.6	1.2504	6.1647	7.4151
100	101.42	0.001043	1.6720	419.06	2087.0	2506.0	419.17	2256.4	2675.6	1.3072	6.0470	7.3542
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360	18666	0.001895	0.006950	1726.16	625.7	2351.9	1761.53	720.1	2481.6	3.9165	1.1373	5.0537
365	19822	0.002015	0.006009	1777.22	526.4	2303.6	1817.16	605.5	2422.7	4.0004	0.9489	4.9493
370	21044	0.002217	0.004953	1844.53	385.6	2230.1	1891.19	443.1	2334.3	4.1119	0.6890	4.8009
373.95	22064	0.003106	0.003106	2015.8	0	2015.8	2084.3	0	2084.3	4.4070	0	4.4070

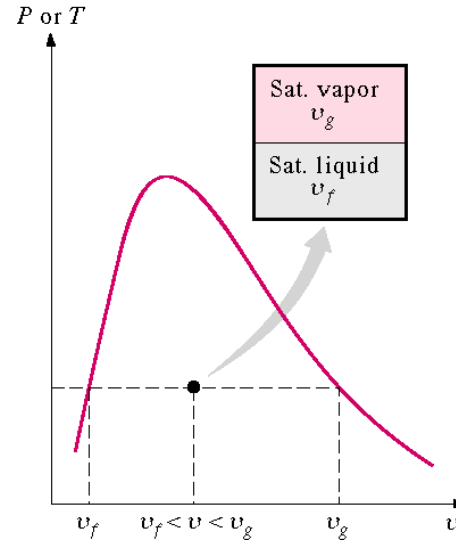
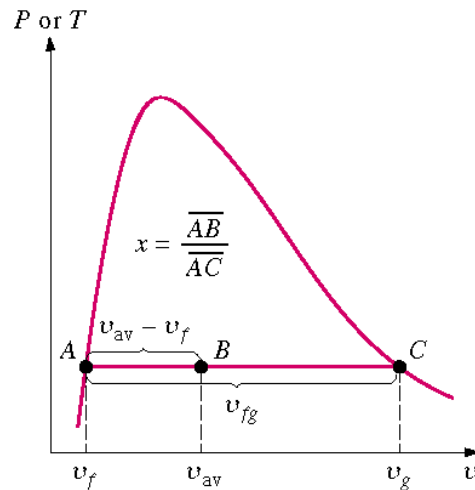
TABLE A-5

Saturated water-Pressure table

Press. <i>P</i> kPa	Sat. Temp., <i>T_{sat}</i> °C	Specific volume, m³/kg			Internal energy, kJ/kg		Enthalpy, kJ/kg			Entropy, kJ/kg·K		
		Sat. liquid, <i>v_f</i>	Sat. vapor, <i>v_g</i>	Sat. liquid, <i>u_f</i>	Evap., <i>u_{fg}</i>	Sat. vapor, <i>u_g</i>	Sat. liquid, <i>h_f</i>	Evap., <i>h_{fg}</i>	Sat. vapor, <i>h_g</i>	Sat. liquid, <i>s_f</i>	Evap., <i>s_{fg}</i>	Sat. vapor, <i>s_g</i>
0.6117	0.01	0.001000	206.00	0.00	2374.9	2374.9	0.00	2500.9	2500.9	0.0000	9.1556	9.1556
1.0	6.97	0.001000	129.19	29.30	2355.2	2384.5	29.30	2484.4	2513.7	0.1059	8.8690	8.9749
1.5	13.02	0.001001	87.964	54.69	2338.1	2392.8	54.69	2470.1	2524.7	0.1956	8.6314	8.8270
2.0	17.50	0.001001	66.990	73.43	2325.5	2398.9	73.43	2459.5	2532.9	0.2606	8.4621	8.7227
2.5	21.08	0.001002	54.242	88.42	2315.4	2403.8	88.42	2451.0	2539.4	0.3118	8.3302	8.6421
3.0	24.08	0.001003	45.654	100.98	2306.9	2407.9	100.98	2443.9	2544.8	0.3543	8.2222	8.5765
4.0	28.96	0.001004	34.791	121.39	2293.1	2414.5	121.39	2432.3	2553.7	0.4224	8.0510	8.4734
5.0	32.87	0.001005	28.185	137.75	2282.1	2419.8	137.75	2423.0	2560.7	0.4762	7.9176	8.3938
7.5	40.29	0.001008	19.233	168.74	2261.1	2429.8	168.75	2405.3	2574.0	0.5763	7.6738	8.2501
10	45.81	0.001010	14.670	191.79	2245.4	2437.2	191.81	2392.1	2583.9	0.6492	7.4996	8.1488
15	53.97	0.001014	10.020	225.93	2222.1	2448.0	225.94	2372.3	2598.3	0.7549	7.2522	8.0071
20	60.06	0.001017	7.6481	251.40	2204.6	2456.0	251.42	2357.5	2608.9	0.8320	7.0752	7.9073
25	64.96	0.001020	6.2034	271.93	2190.4	2462.4	271.96	2345.5	2617.5	0.8932	6.9370	7.8302
30	69.09	0.001022	5.2287	289.24	2178.5	2467.7	289.27	2335.3	2624.6	0.9441	6.8234	7.7675
40	75.86	0.001026	3.9933	317.58	2158.8	2476.3	317.62	2318.4	2636.1	1.0261	6.6430	7.6691
50	81.32	0.001030	3.2403	340.49	2142.7	2483.2	340.54	2304.7	2645.2	1.0912	6.5019	7.5931
75	91.76	0.001037	2.2172	384.36	2111.8	2496.1	384.44	2278.0	2662.4	1.2132	6.2426	7.4558
100	99.61	0.001043	1.6941	417.40	2088.2	2505.6	417.51	2257.5	2675.0	1.3028	6.0562	7.3589
125	105.97	0.001048	1.3750	444.23	2068.8	2513.0	444.36	2240.6	2684.9	1.3741	5.9100	7.2841
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20,000	365.75	0.002038	0.005862	1785.84	509.0	2294.8	1826.59	585.5	2412.1	4.0146	0.9164	4.9310
21,000	369.83	0.002207	0.004994	1841.62	391.9	2233.5	1887.97	450.4	2338.4	4.1071	0.7005	4.8076
22,000	373.71	0.002703	0.003644	1951.65	140.8	2092.4	2011.12	161.5	2172.6	4.2942	0.2496	4.5439
22,064	373.95	0.003106	0.003106	2015.8	0	2015.8	2084.3	0	2084.3	4.4070	0	4.4070

$$x = \frac{y - y_f}{y_{fg}}$$

The Lever Rule is illustrated in the following figures.



Superheated Water Table

A substance is said to be **superheated** if the given temperature is greater than the saturation temperature for the given pressure.

State 5 in Figure 3-11 is a superheated state.

In the superheated water Table A-6, T and P are the independent properties. The value of temperature to the right of the pressure is the saturation temperature for the pressure.

The first entry in the table is the saturated vapor state at the pressure.

TABLE A-6 Superheated water

T °C	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg·K
$P = 0.01 \text{ MPa (45.81°C)}$				
Sat.	14.670	2437.2	2583.9	8.1488
50	14.867	2443.3	2592.0	8.1741
100	17.196	2515.5	2687.5	8.4489
150	19.513	2587.9	2783.0	8.6893
200	21.826	2661.4	2879.6	8.9049
250	24.136	2736.1	2977.5	9.1015
300	26.446	2812.3	3076.7	9.2827
400	31.063	2969.3	3280.0	9.6094
500	35.680	3132.9	3489.7	9.8998
600	40.296	3303.3	3706.3	10.1631
700	44.911	3480.8	3929.9	10.4056
800	49.527	3665.4	4160.6	10.6312
900	54.143	3856.9	4398.3	10.8429
1000	58.758	4055.3	4642.8	11.0429
1100	63.373	4260.0	4893.8	11.2326
1200	67.989	4470.9	5150.8	11.4132
1300	72.604	4687.4	5413.4	11.5857

T °C	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg·K
$P = 0.05 \text{ MPa (81.32°C)}$				
Sat.	3.2403	2483.2	2645.2	7.5931
100	3.4187	2511.5	2682.4	7.6953
150	3.8897	2585.7	2780.2	7.9413
200	4.3562	2660.0	2877.8	8.1592
250	4.8206	2735.1	2976.2	8.3568
300	5.2841	2811.6	3075.8	8.5387
400	6.2094	2968.9	3279.3	8.8659
500	7.1338	3132.6	3489.3	9.1566
600	8.0577	3303.1	3706.0	9.4201
700	8.9813	3480.6	3929.7	9.6626
800	9.9047	3665.2	4160.4	9.8883
900	10.828	3856.8	4398.2	10.1000
1000	11.751	4055.2	4642.7	10.3000
1100	12.675	4259.9	4893.7	10.4897
1200	13.598	4470.8	5150.7	10.6704
1300	14.521	4687.3	5413.3	10.8429

Compressed Liquid Water Table

A substance is said to be a **compressed liquid** when the pressure is greater than the saturation pressure for the temperature.

It is now noted that state 1 in Figure 3-11 is called a compressed liquid state because the saturation pressure for the temperature T_1 is less than P_1 .

Data for water compressed liquid states are found in the compressed liquid tables, Table A-7. Table A-7 is arranged like Table A-6, except the saturation states are the saturated liquid states. Note that the data in Table A-7 begins at 5 MPa or 50 times atmospheric pressure.

TABLE A-7 Compressed liquid water

T °C	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg·K
$P = 5 \text{ MPa (263.94°C)}$				
Sat.	0.0012862	1148.1	1154.5	2.9207
0	0.0009977	0.04	5.03	0.0001
20	0.0009996	83.61	88.61	0.2954
40	0.0010057	166.92	171.95	0.5705
60	0.0010149	250.29	255.36	0.8287
80	0.0010267	333.82	338.96	1.0723
100	0.0010410	417.65	422.85	1.3034
120	0.0010576	501.91	507.19	1.5236
140	0.0010769	586.80	592.18	1.7344
160	0.0010988	672.55	678.04	1.9374
180	0.0011240	759.47	765.09	2.1338
200	0.0011531	847.92	853.68	2.3251
220	0.0011868	938.39	944.32	2.5127
240	0.0012268	1031.6	1037.7	2.6983
260	0.0012755	1128.5	1134.9	2.8841

T °C	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg·K
$P = 10 \text{ MPa (311.00°C)}$				
Sat.	0.0014522	1393.3	1407.9	3.3603
0	0.0009952	0.12	10.07	0.0003
20	0.0009973	83.31	93.28	0.2943
40	0.0010035	166.33	176.37	0.5685
60	0.0010127	249.43	259.55	0.8260
80	0.0010244	332.69	342.94	1.0691
100	0.0010385	416.23	426.62	1.2996
120	0.0010549	500.18	510.73	1.5191
140	0.0010738	584.72	595.45	1.7293
160	0.0010954	670.06	681.01	1.9316
180	0.0011200	756.48	767.68	2.1271
200	0.0011482	844.32	855.80	2.3174
220	0.0011809	934.01	945.82	2.5037
240	0.0012192	1026.2	1038.3	2.6876
260	0.0012653	1121.6	1134.3	2.8710
280	0.0013226	1221.8	1235.0	3.0565
300	0.0013980	1329.4	1343.3	3.2488

At pressures below 5 MPa for water, the data are approximately equal to the saturated liquid data at the given **temperature**. We approximate intensive parameter y , that is v , u , h , and s data as

$$y \cong y_f @ T$$

The enthalpy is more sensitive to variations in pressure; therefore, at high pressures the enthalpy can be approximated by

$$h \cong h_f @ T + v_f (P - P_{sat})$$

For our work, the compressed liquid enthalpy may be approximated by

$$h \cong h_f @ T$$

Saturated Ice-Water Vapor Table

When the temperature of a substance is below the triple point temperature, the saturated solid and liquid phases exist in equilibrium. Here we define the quality as the ratio of the mass that is vapor to the total mass of solid and vapor in the saturated solid-vapor mixture. The process of changing directly from the solid phase to the vapor phase is called sublimation. Data for saturated ice and water vapor are given in Table A-8. In Table A-8, the term **Subl.** refers to the difference between the saturated vapor value and the saturated solid value.

TABLE A-8
Saturated ice-water vapor

Temp., T °C	Sat. Press., P_{sat} kPa	Specific volume, m^3/kg		Internal energy, kJ/kg			Enthalpy, kJ/kg			Entropy, kJ/kg·K		
		Sat. ice, v_i	Sat. vapor, v_g	Sat. ice, u_i	Subl., u_{ig}	Sat. vapor, u_g	Sat. ice, h_i	Subl., h_{ig}	Sat. vapor, h_g	Sat. ice, s_i	Subl., s_{ig}	Sat. vapor, s_g
0.01	0.6117	0.0010909	206.0	-333.40		2374.5	-333.40		2500.5	-1.220		9.154
0	0.6112	0.0010909	206.2	-333.43	2707.9	2374.5	-333.43	2833.9	2500.5	-1.220	10.375	9.154
-2	0.5177	0.0010905	241.6	-337.63	2709.4	2371.8	-337.63	2834.5	2496.8	-1.236	10.453	9.218
-4	0.4375	0.0010902	283.8	-341.80	2710.8	2369.0	-341.80	2835.0	2493.2	-1.251	10.533	9.282
-6	0.3687	0.0010898	334.3	-345.94	2712.2	2366.2	-345.93	2835.4	2489.5	-1.267	10.613	9.347
-8	0.3100	0.0010895	394.7	-350.04	2713.5	2363.5	-350.04	2835.8	2485.8	-1.282	10.695	9.413
-10	0.2599	0.0010892	467.2	-354.12	2714.8	2360.7	-354.12	2836.2	2482.1	-1.298	10.778	9.480
·	·	·	·	·	·	·	·	·	·	·	·	·
·	·	·	·	·	·	·	·	·	·	·	·	·
-36	0.0200	0.0010850	5460.1	-404.40	2729.0	2324.6	-404.40	2838.4	2434.0	-1.499	11.969	10.470
-38	0.0161	0.0010847	6750.5	-408.07	2729.9	2321.8	-408.07	2838.4	2430.3	-1.514	12.071	10.557
-40	0.0128	0.0010844	8376.7	-411.70	2730.7	2319.0	-411.70	2838.3	2426.6	-1.530	12.174	10.644

The specific volume, internal energy, enthalpy, and entropy for a mixture of saturated ice and saturated vapor are calculated similarly to that of saturated liquid-vapor mixtures.

$$y_{ig} = y_g - y_i$$

$$y = y_i + x y_{ig}$$

where the quality x of a saturated ice-vapor state is

$$x = \frac{m_g}{m_i + m_g}$$

How to Choose the Right Table

The correct table to use to find the thermodynamic properties of a real substance can always be determined by comparing the known state properties to the properties in the saturation region. Given the temperature or pressure and one other property from the group v , u , h , and s , the following procedure is used. For example if the pressure and specific volume are specified, three questions are asked: For the given pressure,

Is $v < v_f$?

Is $v_f < v < v_g$?

Is $v_g < v$?

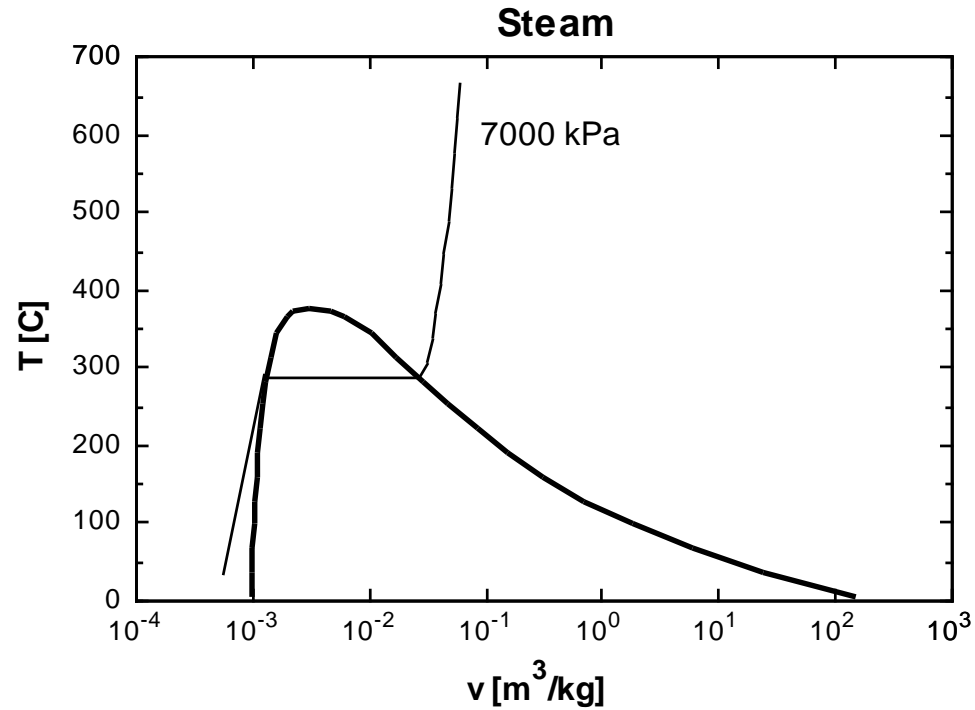
The answer to one of these questions must be yes. If the answer to the first question is yes, the state is in the compressed liquid region, and the compressed liquid tables are used to find the properties of the state. If the answer to the second question is yes, the state is in the saturation region, and either the saturation temperature table or the saturation pressure table is used to find the properties. Then the quality is calculated and is used to calculate the other properties, u , h , and s . If the answer to the third question is yes, the state is in the superheated region and the superheated tables are used to find the other properties.

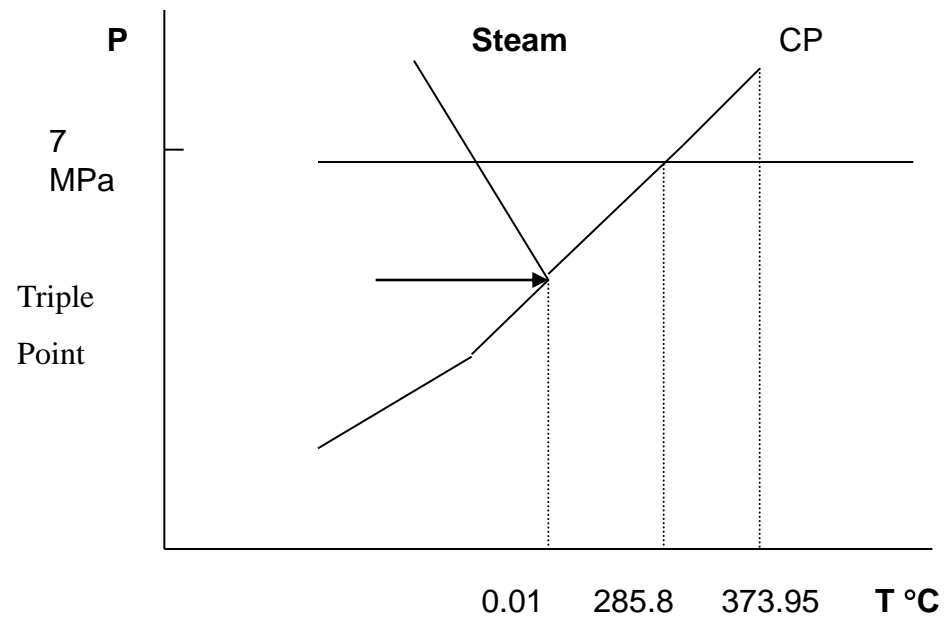
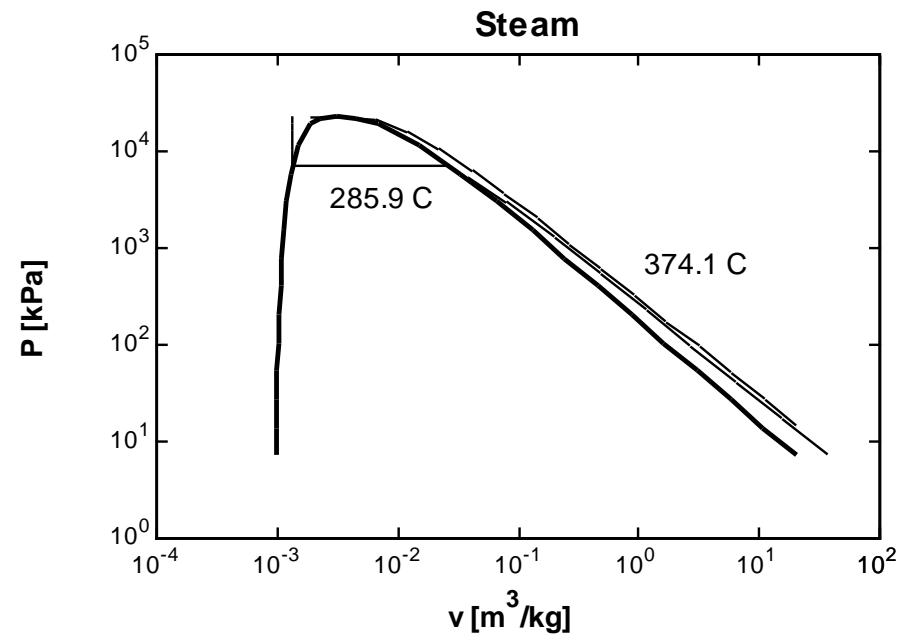
Some tables may not always give the internal energy. When it is not listed, the internal energy is calculated from the definition of the enthalpy as

$$u = h - Pv$$

Example 2-1

Find the internal energy of water at the given states for 7 MPa and plot the states on T - v , P - v , and P - T diagrams.





1. $P = 7$ MPa, dry saturated or saturated vapor

Using Table A-5,

$$u = u_g = 2581.0 \frac{\text{kJ}}{\text{kg}}$$

Locate state 1 on the T - v , P - v , and P - T diagrams.

2. $P = 7$ MPa, wet saturated or saturated liquid

Using Table A-5,

$$u = u_f = 1258.0 \frac{\text{kJ}}{\text{kg}}$$

Locate state 2 on the T - v , P - v , and P - T diagrams.

3. Moisture = 5%, $P = 7$ MPa

let moisture be y , defined as

$$y = \frac{m_f}{m} = 0.05$$

then, the quality is

$$x = 1 - y = 1 - 0.05 = 0.95$$

and using Table A-5,

$$\begin{aligned} u &= u_f + x(u_g - u_f) \\ &= 1258.0 + 0.95(2581.0 - 1257.6) \\ &= 2514.4 \frac{\text{kJ}}{\text{kg}} \end{aligned}$$

Notice that we could have used

$$u = u_f + x u_{fg}$$

Locate state 3 on the T - v , P - v , and P - T diagrams.

$$4. P = 7 \text{ MPa}, T = 600^\circ\text{C}$$

For $P = 7 \text{ MPa}$, Table A-5 gives $T_{\text{sat}} = 285.83^\circ\text{C}$. Since $600^\circ\text{C} > T_{\text{sat}}$ for this pressure, the state is superheated. Use Table A-6.

$$u = 3261.0 \frac{\text{kJ}}{\text{kg}}$$

Locate state 4 on the T - v , P - v , and P - T diagrams.

$$5. P = 7 \text{ MPa}, T = 100^\circ\text{C}$$

Using Table A-4, At $T = 100^\circ\text{C}$, $P_{\text{sat}} = 0.10142 \text{ MPa}$. Since $P > P_{\text{sat}}$, the state is compressed liquid.

Approximate solution:

$$u \cong u_{f @ T=100^\circ\text{C}} = 419.06 \frac{\text{kJ}}{\text{kg}}$$

Solution using Table A-7:

We do linear interpolation to get the value at 100°C . (We will demonstrate how to do linear interpolation with this problem even though one could accurately estimate the answer.)

$P \text{ MPa}$	$u \text{ kJ/kg}$
5	417.65
7	$u = ?$
10	416.23

The interpolation scheme is called “the ratio of corresponding differences.”

Using the above table, form the following ratios.

$$\frac{5-7}{5-10} = \frac{417.65-u}{417.65-416.23}$$

$$u = 417.08 \frac{\text{kJ}}{\text{kg}}$$

Locate state 5 on the T - v , P - v , and P - T diagrams.

$$6. P = 7 \text{ MPa}, T = 460^\circ\text{C}$$

Since $460^\circ\text{C} > T_{\text{sat}} = 385.83^\circ\text{C}$ at $P = 7 \text{ MPa}$, the state is superheated. Using Table A-6, we do a linear interpolation to calculate u .

T °C	u kJ/kg
450	2979.0
460	$u = ?$
500	3074.3

Using the above table, form the following ratios.

$$\frac{460 - 450}{500 - 450} = \frac{u - 2979.0}{3074.3 - 2979.0}$$

$$u = 2998.1 \frac{kJ}{kg}$$

Locate state 6 on the T - v , P - v , and P - T diagrams.

Example 2-2

Determine the enthalpy of 1.5 kg of water contained in a volume of 1.2 m³ at 200 kPa.

Recall we need two independent, intensive properties to specify the state of a simple substance. Pressure P is one intensive property and specific volume is another. Therefore, we calculate the specific volume.

$$v = \frac{\text{Volume}}{\text{mass}} = \frac{1.2 \text{ m}^3}{1.5 \text{ kg}} = 0.8 \frac{\text{m}^3}{\text{kg}}$$

Using Table A-5 at $P = 200$ kPa,

$$v_f = 0.001061 \text{ m}^3/\text{kg}, \quad v_g = 0.8858 \text{ m}^3/\text{kg}$$

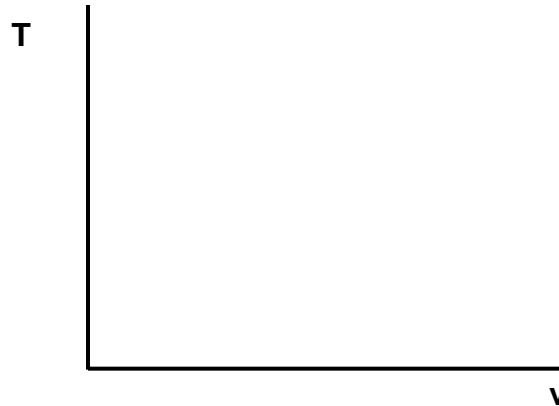
Now,

Is $v < v_f$? No

Is $v_f < v < v_g$? Yes

Is $v_g < v$? No

Locate this state on a T - v diagram.



We see that the state is in the two-phase or saturation region. So we must find the quality x first.

$$v = v_f + x(v_g - v_f)$$

$$\begin{aligned}
 x &= \frac{v - v_f}{v_g - v_f} \\
 &= \frac{0.8 - 0.001061}{0.8858 - 0.001061} \\
 &= 0.903 \quad (\text{What does this mean?})
 \end{aligned}$$

Then,

$$\begin{aligned}
 h &= h_f + x h_{fg} \\
 &= 504.7 + (0.903)(2201.6) \\
 &= 2492.7 \frac{\text{kJ}}{\text{kg}}
 \end{aligned}$$

Example 2-3

Determine the internal energy of refrigerant-134a at a temperature of 0°C and a quality of 60%.

Using Table A-11, for $T = 0^\circ\text{C}$,

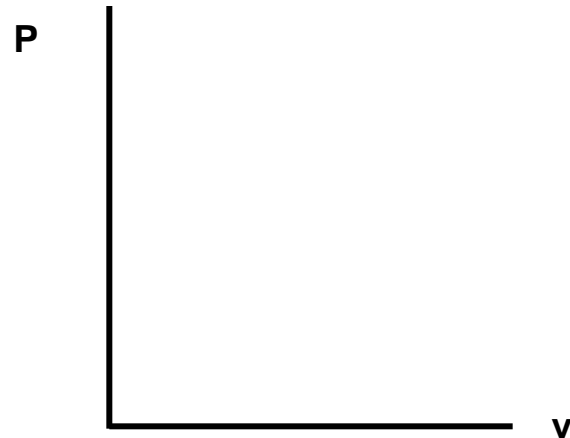
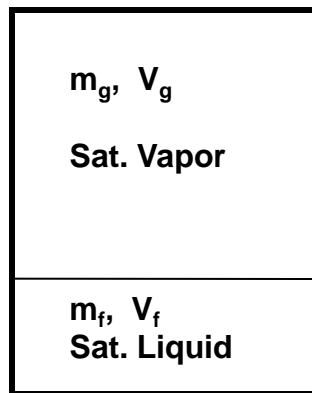
$$u_f = 51.63 \text{ kJ/kg} \qquad u_g = 230.16 \text{ kJ/kg}$$

then,

$$\begin{aligned}u &= u_f + x(u_g - u_f) \\&= 51.63 + (0.6)(230.16 - 51.63) \\&= 158.75 \frac{\text{kJ}}{\text{kg}}\end{aligned}$$

Example 2-4

Consider the closed, rigid container of water shown below. The pressure is 700 kPa, the mass of the saturated liquid is 1.78 kg, and the mass of the saturated vapor is 0.22 kg. Heat is added to the water until the pressure increases to 8 MPa. Find the final temperature, enthalpy, and internal energy of the water. Does the liquid level rise or fall? Plot this process on a P - v diagram with respect to the saturation lines and the critical point.



Let's introduce a solution procedure that we will follow throughout the course. A similar solution technique is discussed in detail in Chapter 1.

System: A closed system composed of the water enclosed in the tank

Property Relation: Steam Tables

Process: Volume is constant (rigid container)

For the closed system the total mass is constant and since the process is one in which the volume is constant, the average specific volume of the saturated mixture during the process is given by

$$v = \frac{V}{m} = \text{constant}$$

or

$$v_2 = v_1$$

Now to find v_1 recall that in the two-phase region at state 1

$$x_1 = \frac{m_{g1}}{m_{f1} + m_{g1}} = \frac{0.22 \text{ kg}}{(1.78 + 0.22) \text{ kg}} = 0.11$$

Then, at $P = 700 \text{ kPa}$

$$\begin{aligned} v_1 &= v_{f1} + x_1 (v_{g1} - v_{f1}) \\ &= 0.001108 + (0.11)(0.2728 - 0.001108) \\ &= 0.031 \frac{\text{m}^3}{\text{kg}} \end{aligned}$$

State 2 is specified by:

$$P_2 = 8 \text{ MPa}, \quad v_2 = 0.031 \text{ m}^3/\text{kg}$$

At $8 \text{ MPa} = 8000 \text{ kPa}$,

$$v_f = 0.001384 \text{ m}^3/\text{kg} \quad v_g = 0.02352 \text{ m}^3/\text{kg}$$

at 8 MPa , $v_2 = 0.031 \text{ m}^3/\text{kg}$.

Is $v_2 < v_f$? No

Is $v_f < v_2 < v_g$? No

Is $v_g < v_2$? Yes

Therefore, State 2 is superheated.

Interpolating in the superheated tables at 8 MPa, $v = 0.031 \text{ m}^3/\text{kg}$ gives,

$$T_2 = 361 \text{ }^\circ\text{C}$$

$$h_2 = 3024 \text{ kJ/kg}$$

$$u_2 = 2776 \text{ kJ/kg}$$

Since state 2 is superheated, the liquid level falls.

Extra Problem

What would happen to the liquid level in the last example if the specific volume had been $0.001 \text{ m}^3/\text{kg}$ and the pressure was 8 MPa?