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B-KUL-Z55337
Applied Thermodynamics

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Adapted from: Y.A. Cengel, M. A. Boles, Thermodynamics – An Engineering Approach (5th Edition)

Chapter 3

Properties of Pure Substances

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Pure Substances

- A pure substance is a substance that has a fixed chemical composition (H_20, N_2, H_2, etc.).
- A pure substance does not have to be of a single chemical element or compound. A mixture of various chemical elements or compounds also qualifies as a pure substance as long as the mixture is **homogeneous**..
  - Example: air contains N_2 and O_2, but it is considered as a pure substance
  - Counter-example: oil + water
- A mixture of two or more phases of a pure substance is still a pure substance as long as the chemical composition of all phases is the same
  - Example: mixture of ice and liquid water
  - Counter-example: mixture of liquid air and gazeous air (at a given pressure, all the air compounds do not condense at the same temperature, the composition is thus different in the liquid and vapor phases)

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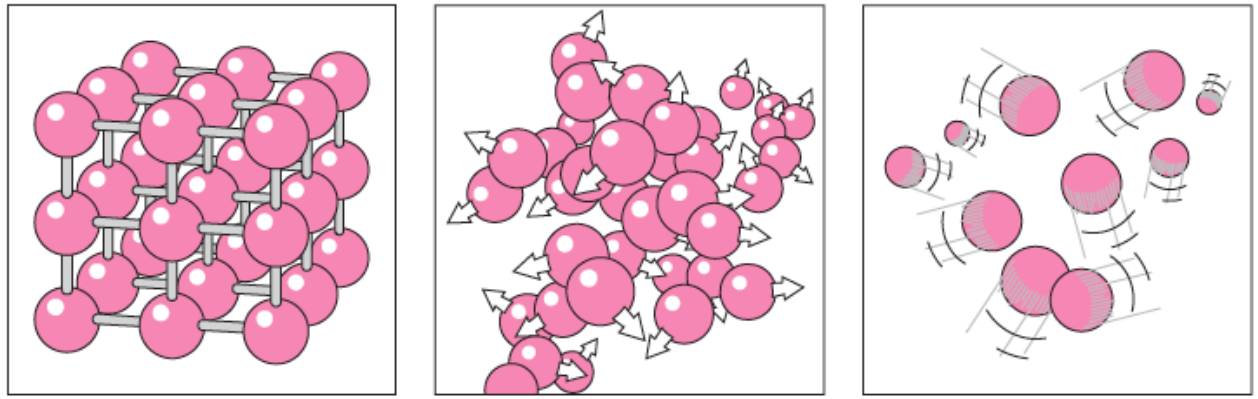
Phases of a pure substance

- 3 principal phases: solid, liquid, gas
- « sub-phases » can exist within a principal phase: for example carbon has two solid structures (graphite or diamond)
- Intermolecular forces decrease when going from solids (a) to liquids (b) and gazes (c).
- In a liquid, the molecules are no longer at fixed positions
- In a gas, they are far apart from each other



(a) (b) (c)

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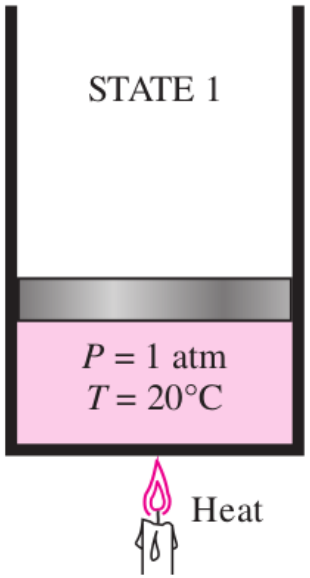
Phase-change of pure substances

- two phases of a pure substance can coexist in equilibrium (for example liquid water and steam in the boiler of a power plant) => two-phase mixture
- In this section we will mainly focus on the liquid/gas mixture
- Example of a piston-cylinder containing liquid water:

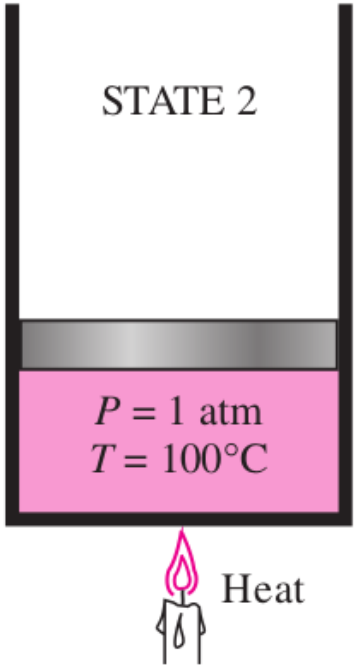
STATE 1: Sub-cooled liquid



Phase-change of pure substances

STATE 2: saturated liquid:

- ✓ Water is still in liquid state
- ✓ Any heat input would cause the water to start boiling. The liquid is *about to vaporize*



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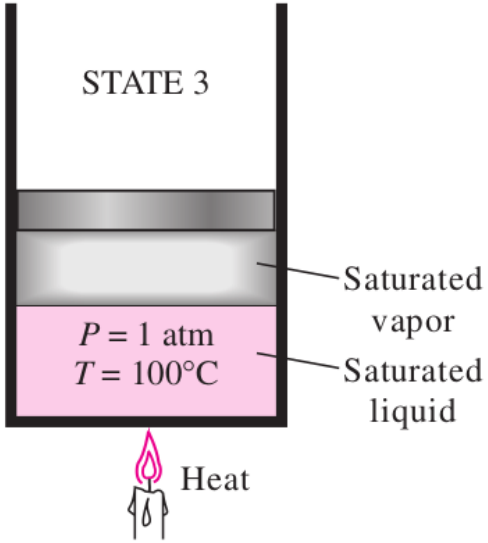
Phase-change of pure substances

STATE 3: mixture between saturated liquid and saturated vapor

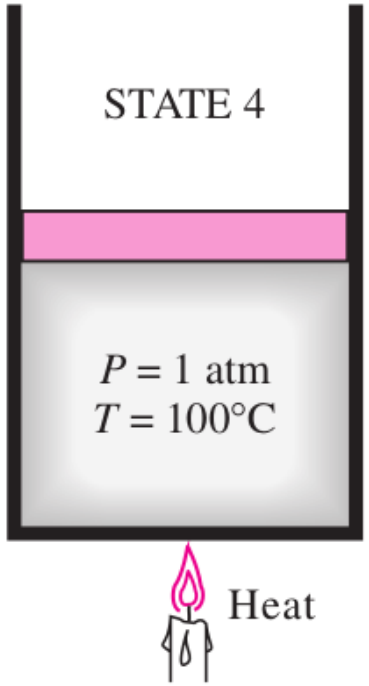
- ✓ During this phase transition, temperature remains constant
- ✓ Volume (total and specific) increases
- ✓ The saturated liquid level decreases, as it is evaporated



Phase-change of pure substances

STATE 4: saturated vapor

- ✓ One single phase
- ✓ Any heat loss would create liquid droplets. The vapor is *about the condense*.



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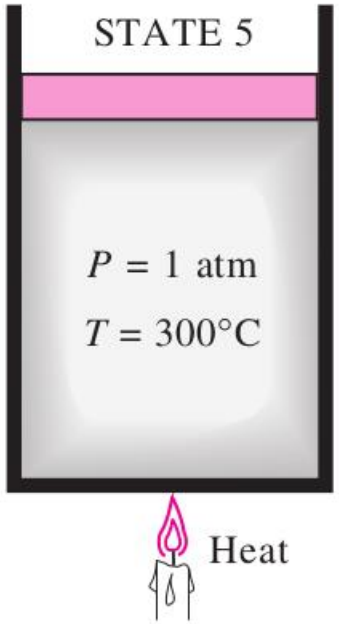
Phase-change of pure substances

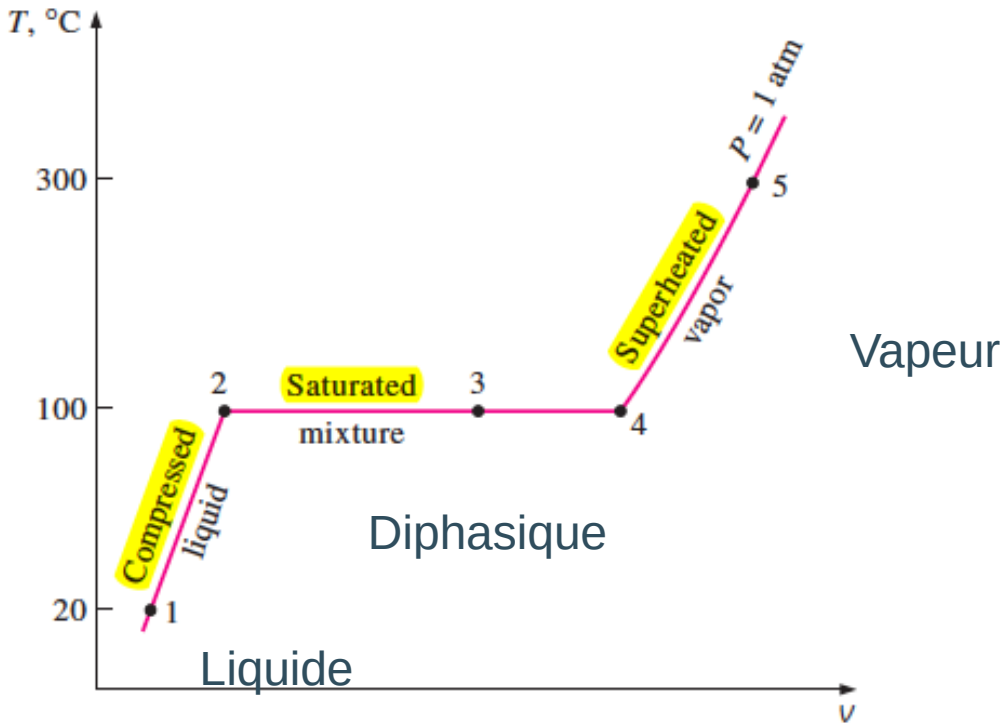
STATE 5: superheated vapor

- ✓ One single phase
- ✓ Adding/removing heat entails an increase/decrease of the temperature



Saturation pressure and temperature

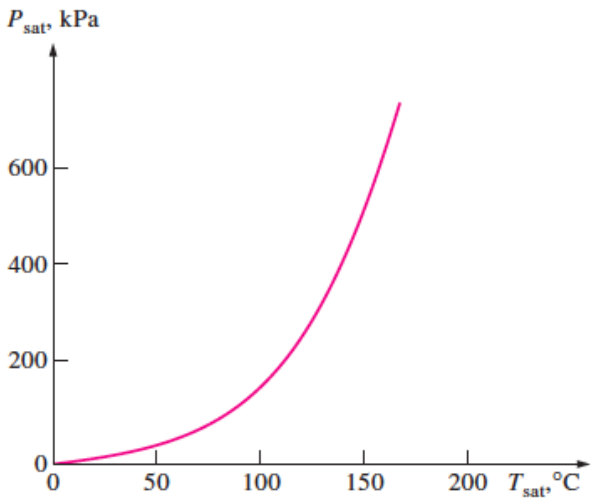
- At 1 atm, water boils as soon as its temperature reaches 100°C (= saturation temperature)
- The saturation temperature depends on the pressure
- At 100°C, water boils as soon as its pressures is decreased down to 1 atm (= saturation pressure)



Saturation pressure and temperature

- The amount of energy absorbed or released during a phase-change process is called the **latent heat.**
  - ✓ Latent heat of vaporization: energy absorbed during vaporization (water at 1 atm: 2256.5 kJ/kg
  - ✓ Later heat of fusion: energy released during condensation (water at 1 atm: 333.7 kJ/kg
- During a phase change, p and T are no longer independent (for a pure substance):

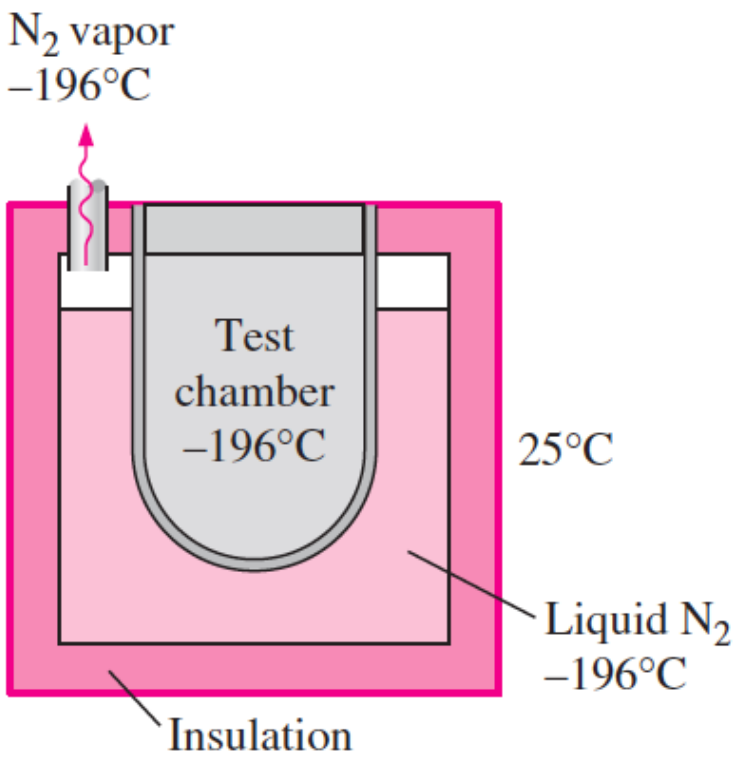
$$T_{sat} = f(P_{sat})$$



- *The boiling temperature decreases with the altitude*
- *Example: at 2000 m the standard pressure is 79.50 kPa (=0.79 atm), which corresponds to a boiling temperature of 93.3°C*

Saturation pressure and temperature

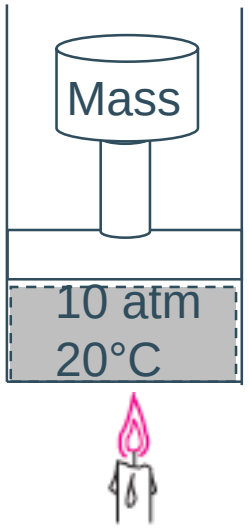
- Example of a liquid nitrogen cryogenic test bench:
  - ✓ Saturation temperature of N_2 at1 atm: -196°C
  - ✓ Test vessel surrounded by N_2 in two-phase state
  - ✓ Communication with the atmosphere (P=1 atm)
  - ✓ Any heat addition causes an evaporation of nitrogen
  - ✓ The temperature remains constant at -196°C as long as there is liquid.

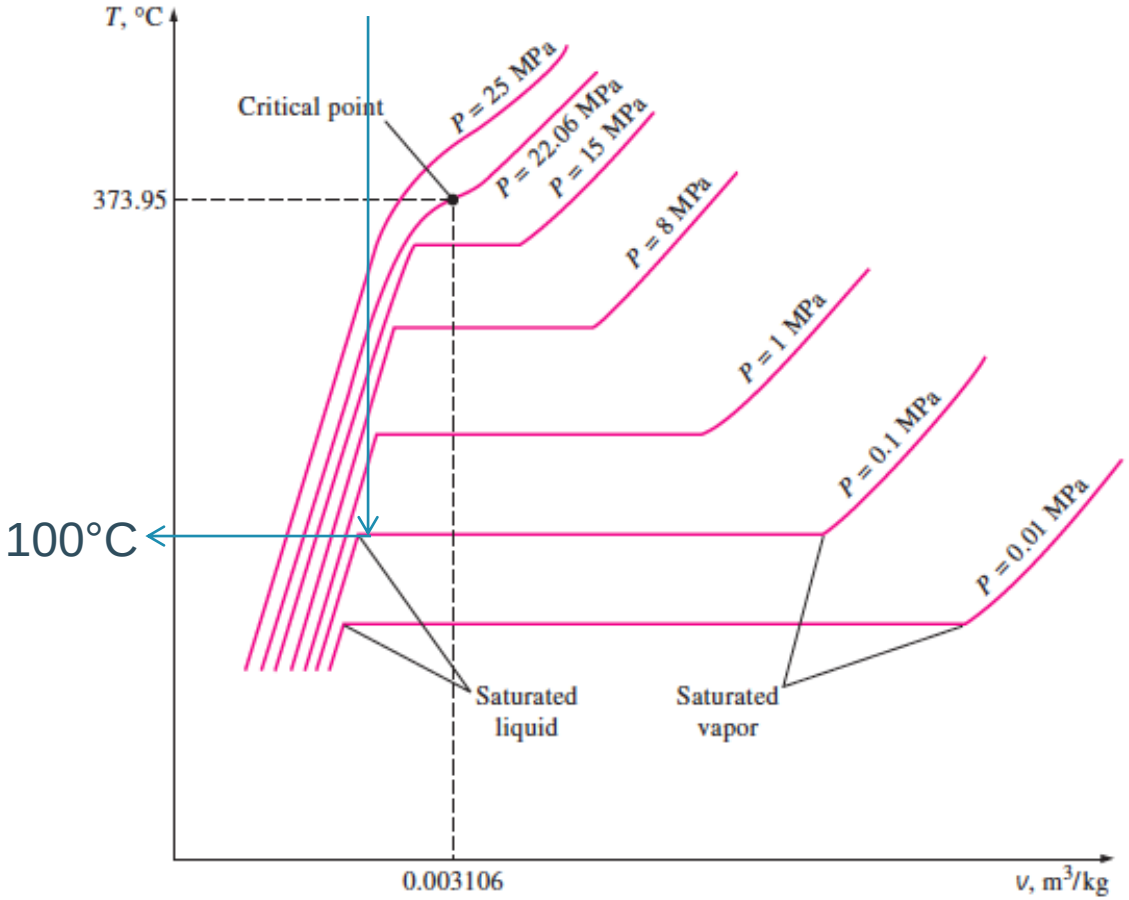


Property diagrams for phase-change processes

T-v Diagram

- The piston-cylinder experience is repeated with different masses above the cylinder => the water pressure is changed

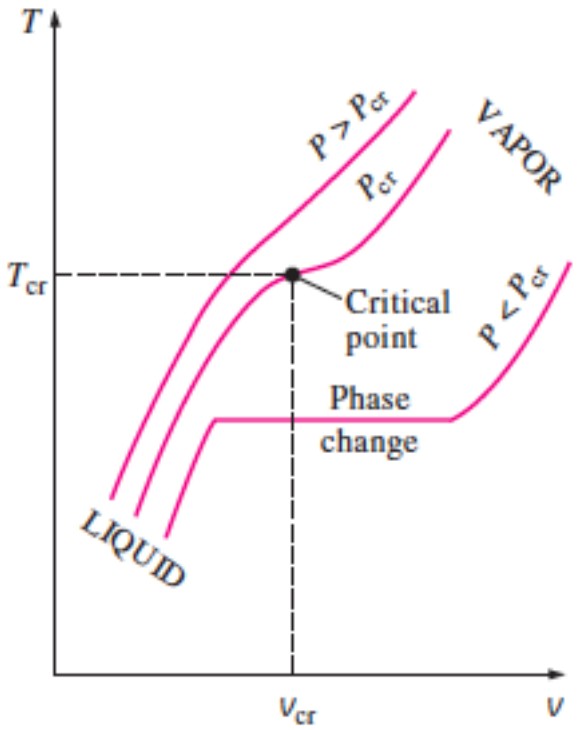




Property diagrams for phase-change processes

T-v Diagram

- When the pressure increases the length of the « horizontal saturation line » decreases.
- At the **critical pressure**, the line disappears: the saturated liquid state and the saturated vapor state are identical.
- **The critical point** is defined by P_{cr}, T_{cr} et v_{cr}:
- For water: P_{cr} = 22.06 Mpa, T_{cr} = 373.95°C et v_{cr} = 0.003106 m^3/kg
- When $P>P_{cr}$:
  - ✓ No apparent phase transition
  - ✓ One signel phase that resembles a vapor
  - ✓ Specific volume increases continually



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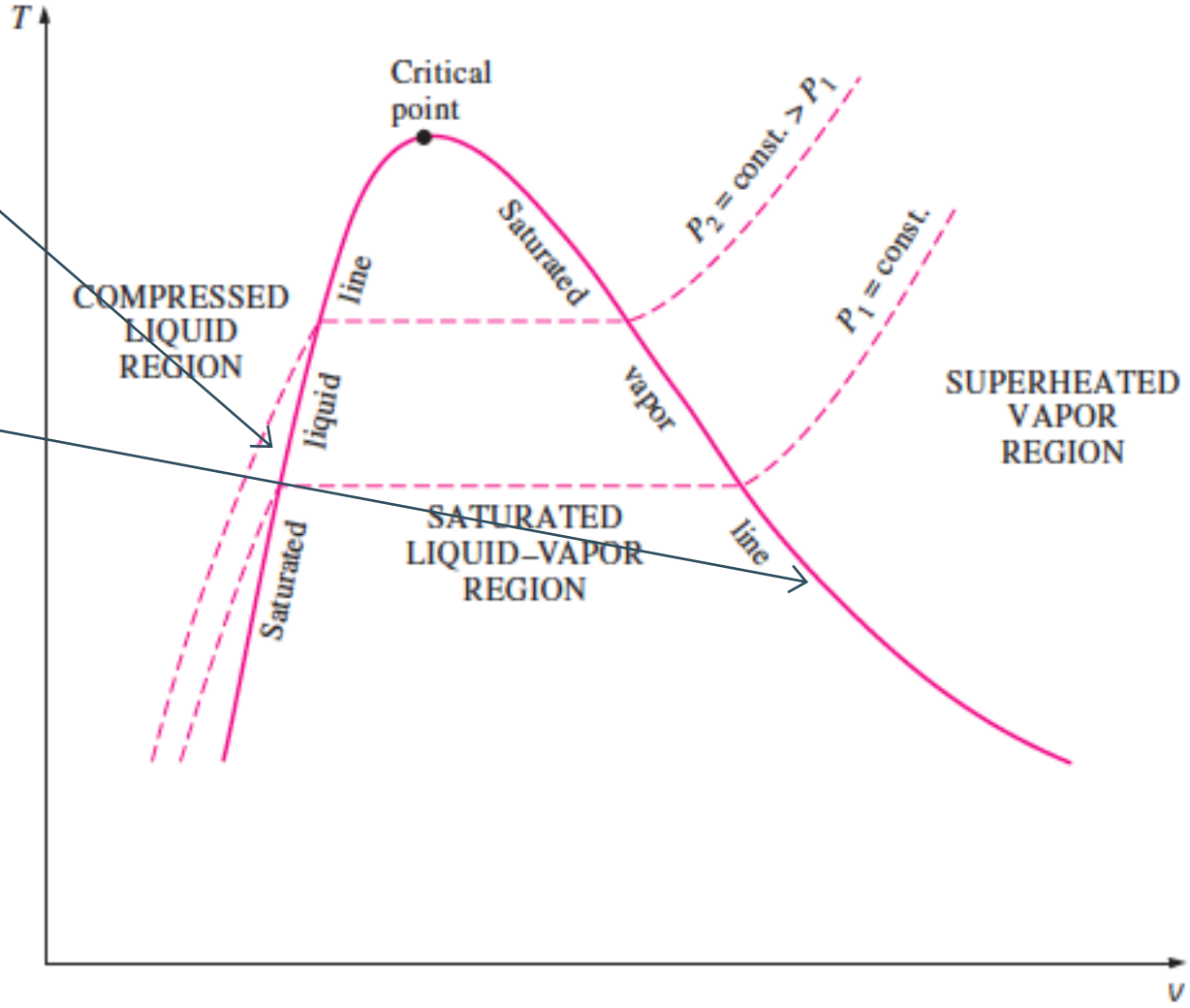
Property diagrams for phase-change processes

T-v Diagram

- By connecting all the saturated liquid states, we obtain the **saturated liquid line**
- By connecting all the saturated vapora states, we obtain the **saturated vapor line**



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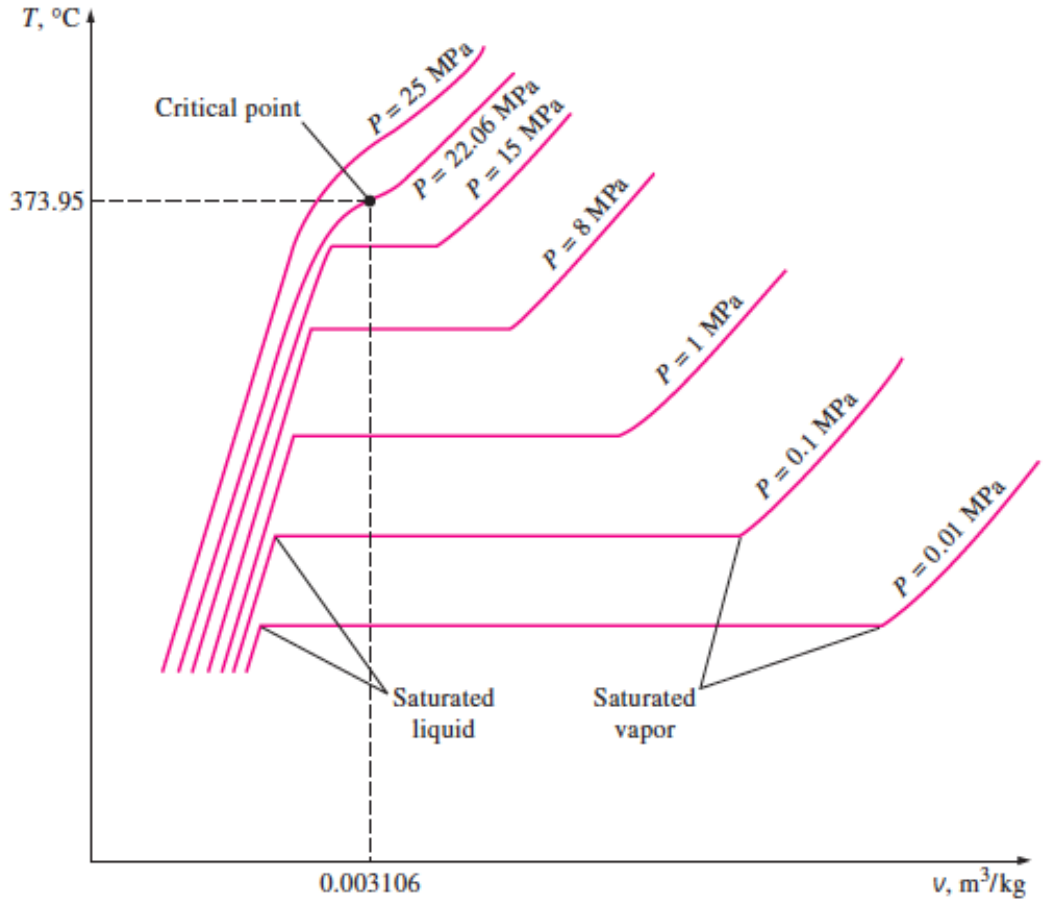
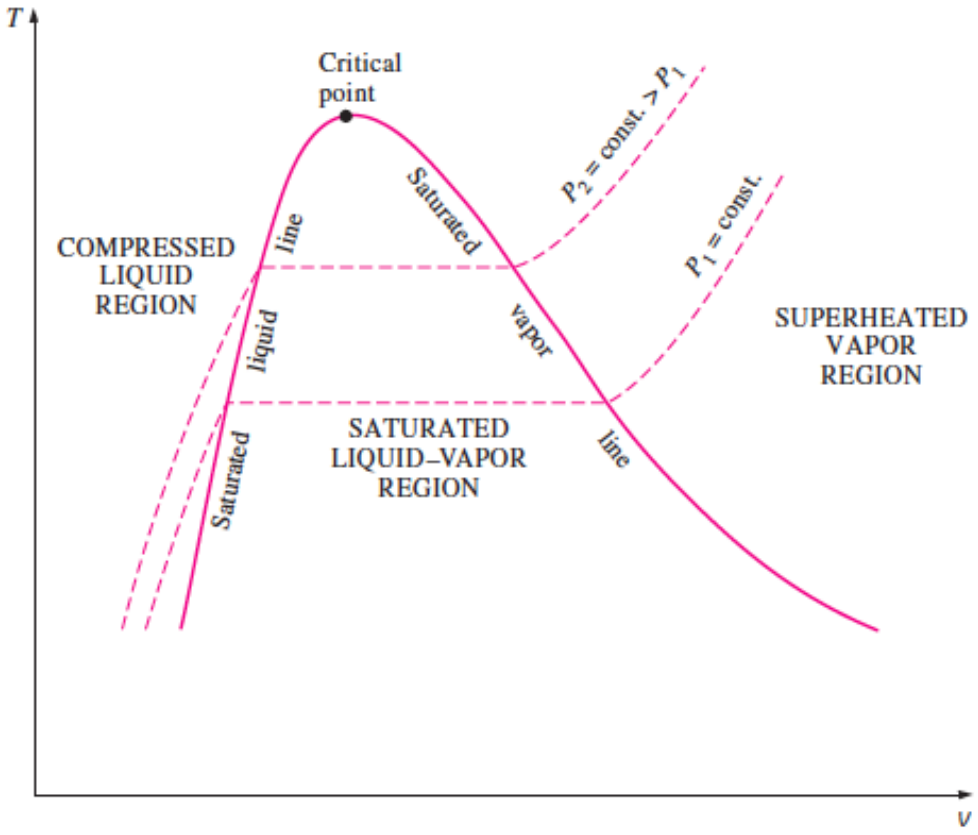
Property diagrams for phase-change processes

T-v Diagram





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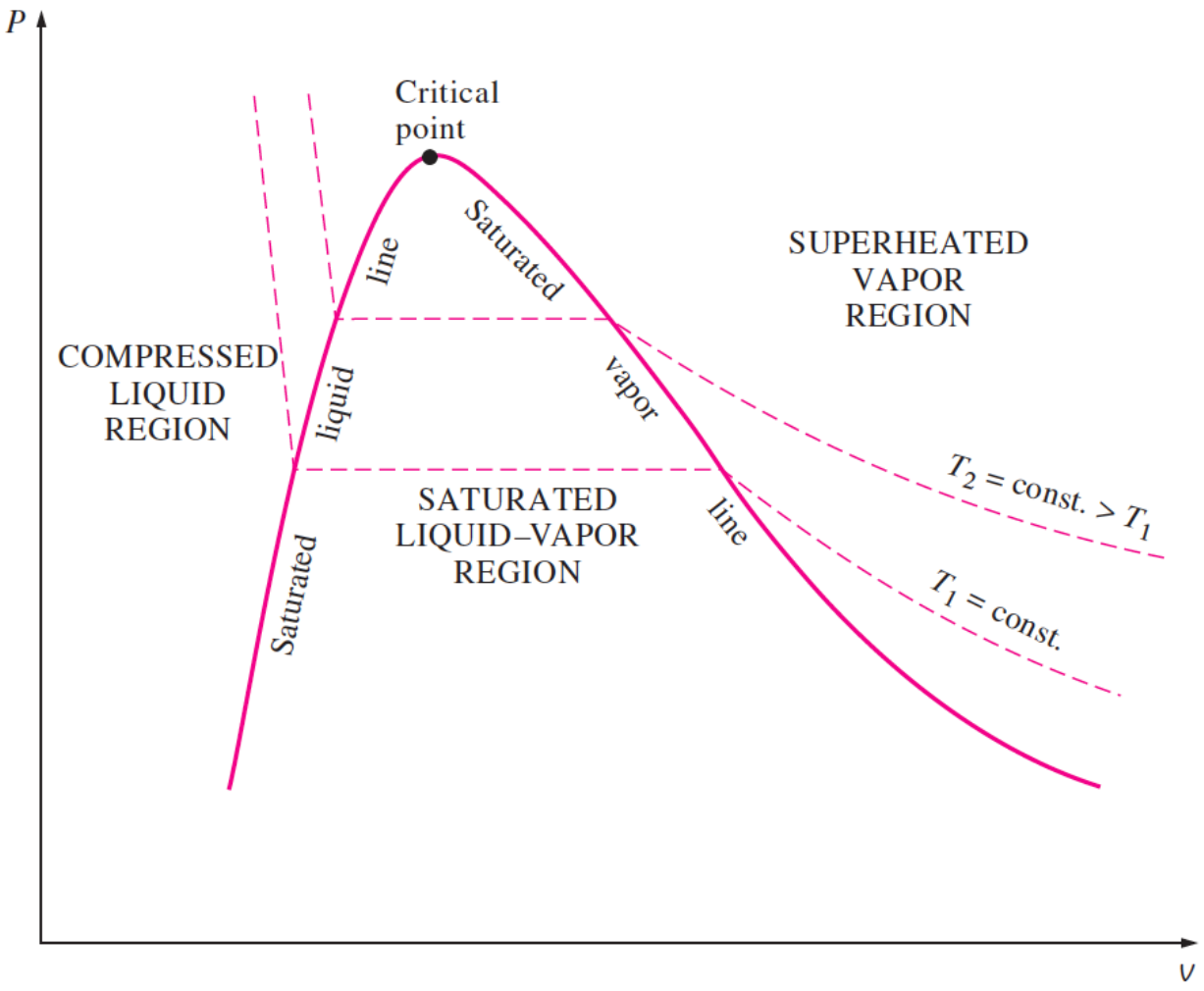
Property diagrams for phase-change processes

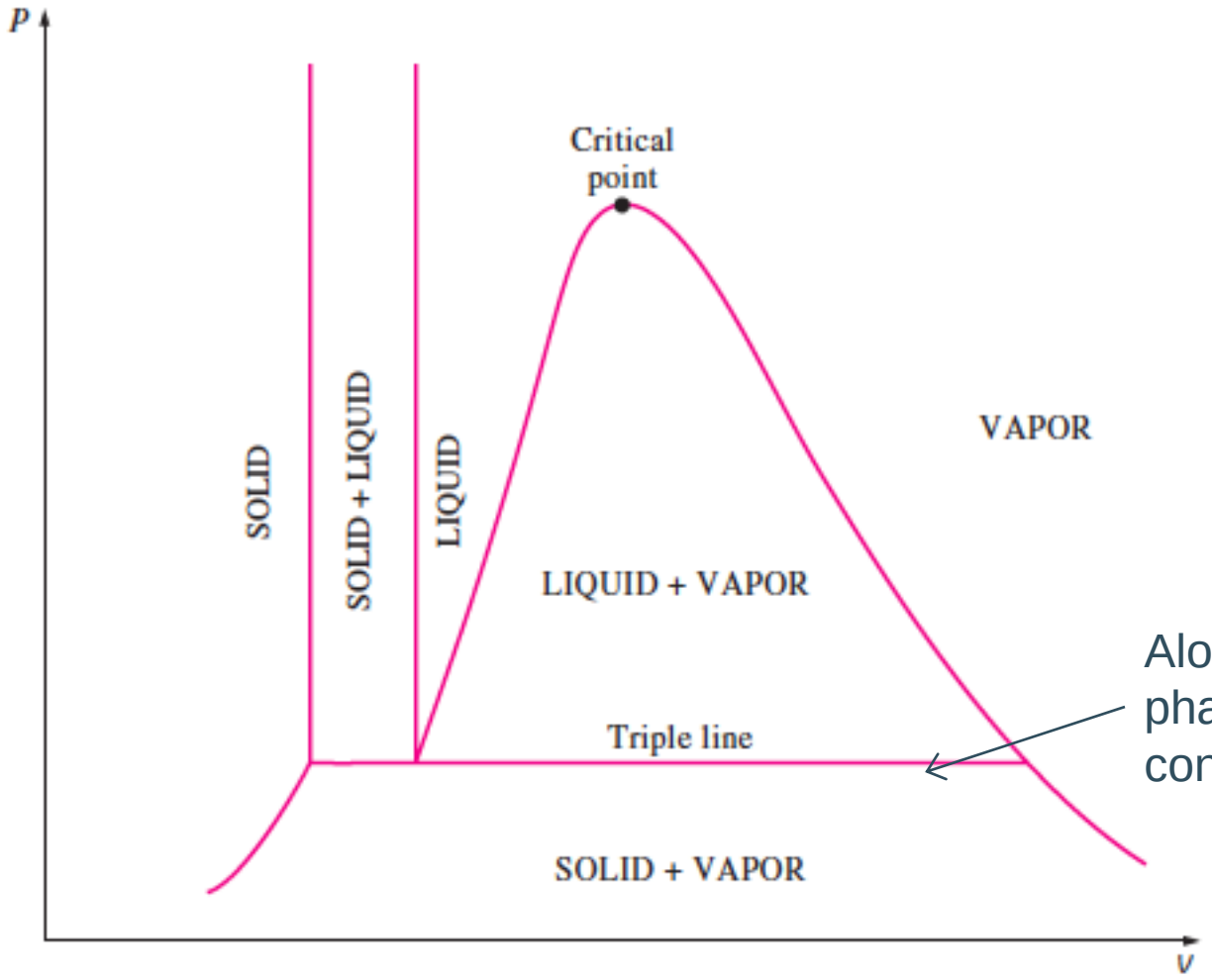
P-v Diagram

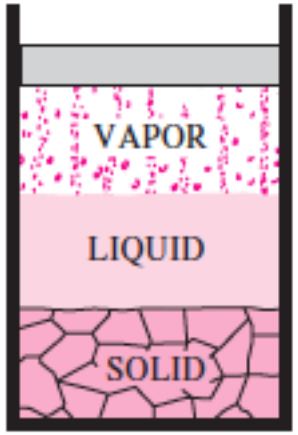
- By maintaining the temperature constant in the piston-cylinder system and exchanging heat we can draw the pressure-volume diagram
- On an isothermal line, pressure decreases if the specific volume increases, except in the two-phase region



Property diagrams for phase-change processes

Adding the solid phase





Along the triple line, three phases are present. P and T are constant, only v varies.

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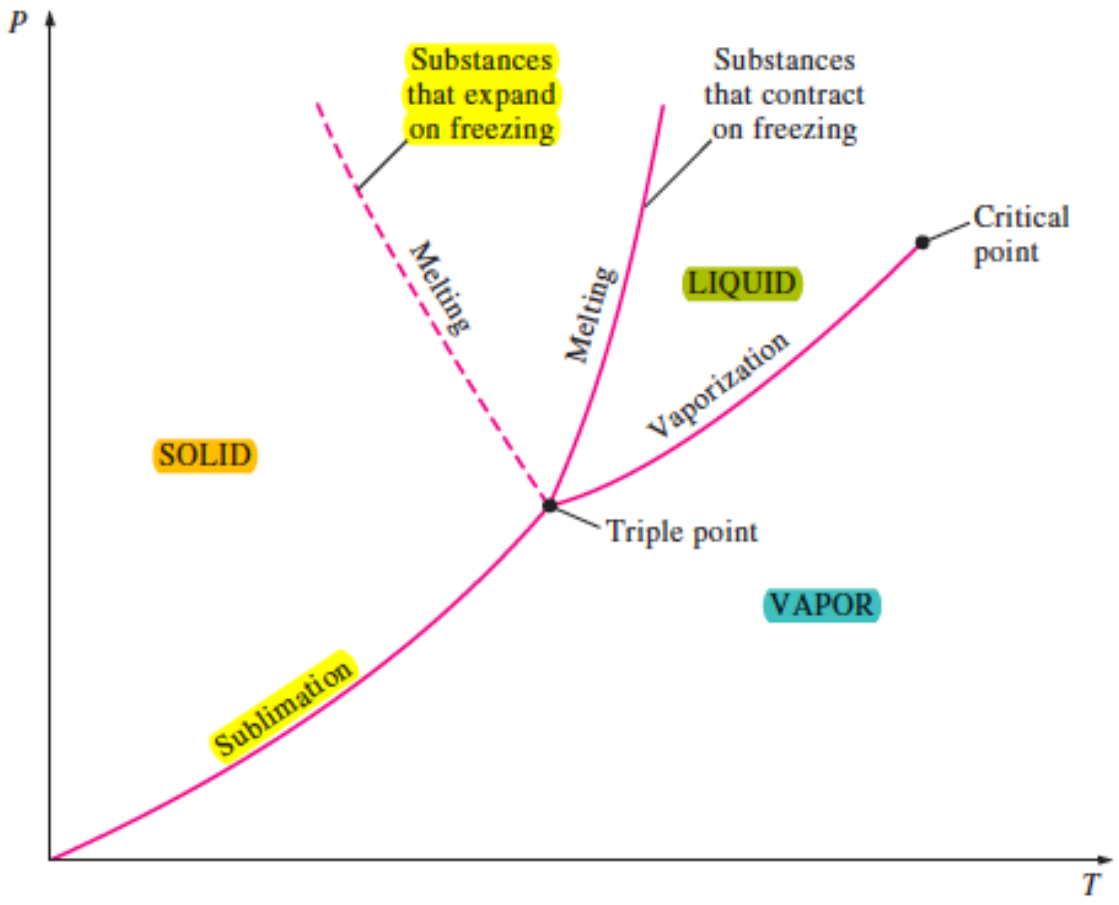
Property diagrams for phase-change processes

Adding the solid phase



- The triple line appears a triple point in the P-T diagram.
- For water: 0.01°C and 0.6117 kPa
- No more liquid phase below the triple point pressure
- The triple point is the only point where the 3 phases coexist.

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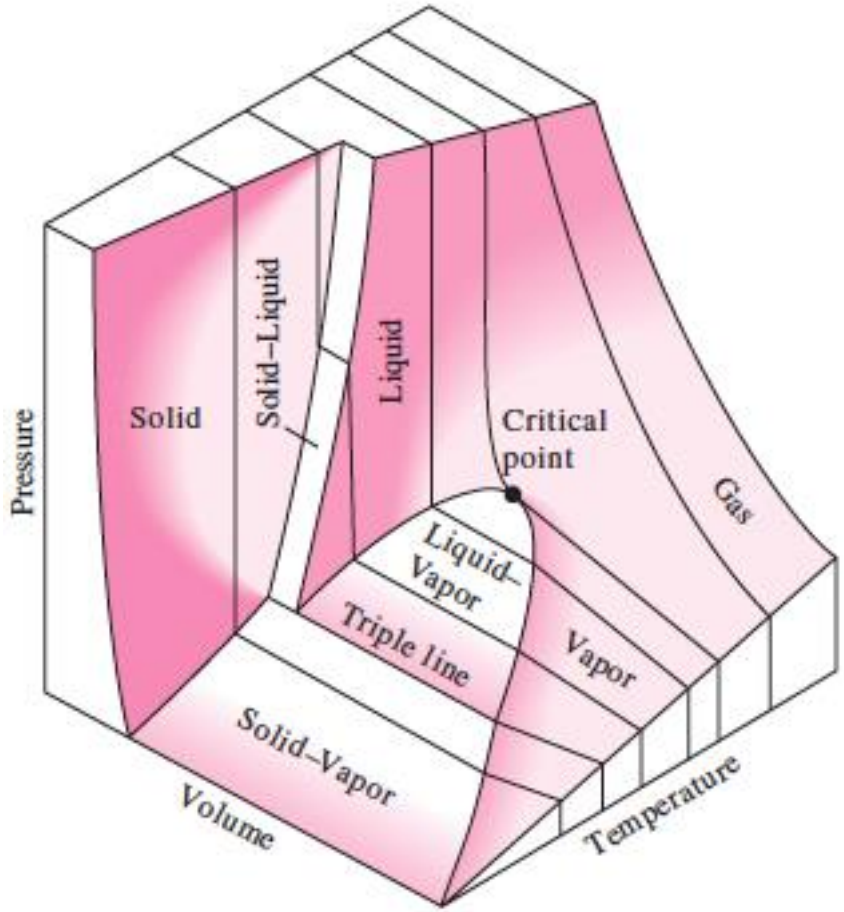
Property diagrams for phase-change processes

P-v-T diagram



- Single-phase regions: curved surfaces.
- Two-phase regions: perpendicular to the p-T plane

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Property tables

- For most substances, the relations between the thermodynamic variables are too complex to be expressed with simple equations.
- The variables are usually expressed in separate measurement tables:
  - ✓ Subcooled liquid
  - ✓ Superheated vapor
  - ✓ Saturated regions
- The tables provide the internal energy *u*, the enthalpy *h*, the entropy *s* as a function of the temperature *T* and the specific volume *v*.

$$h = u + Pv$$

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Property tables

Saturated states

v_f	specific volume of the saturated liquid
v_g	specific volume of the saturated vapor
$v_{fg} = v_g - v_f$	difference between v_g and v_f
h_{fg}	vaporization enthalpy (= latent heat of vaporization)
	Energy required to vaporize of mass of liquid at constant T and P

Temp. °C T	Sat. press. kPa P_{sat}	Specific volume m³/kg Sat. liquid v_f	Sat. vapor v_g
85	57.868	0.001032	2.8261
90	70.183	0.001036	2.3593
95	84.609	0.001040	1.9808

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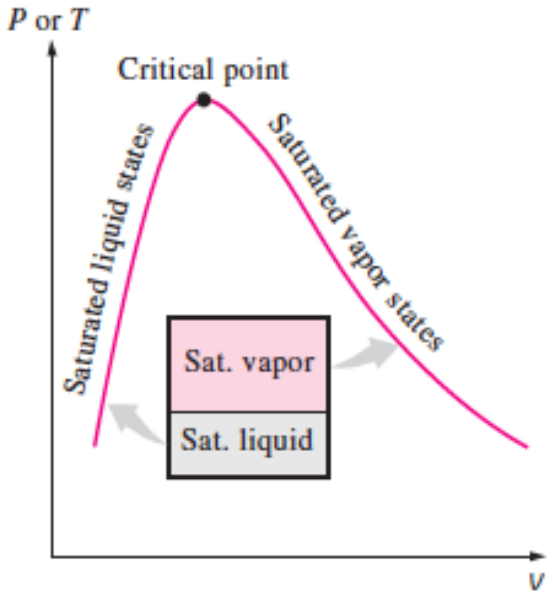
Property tables

Saturated states

- Mixture of saturated liquid and saturated vapor
- We can define the properties of this mixture only if we know the proportion of liquid and vapor
- This is defined by the **quality** (a.k.a vapor quality):

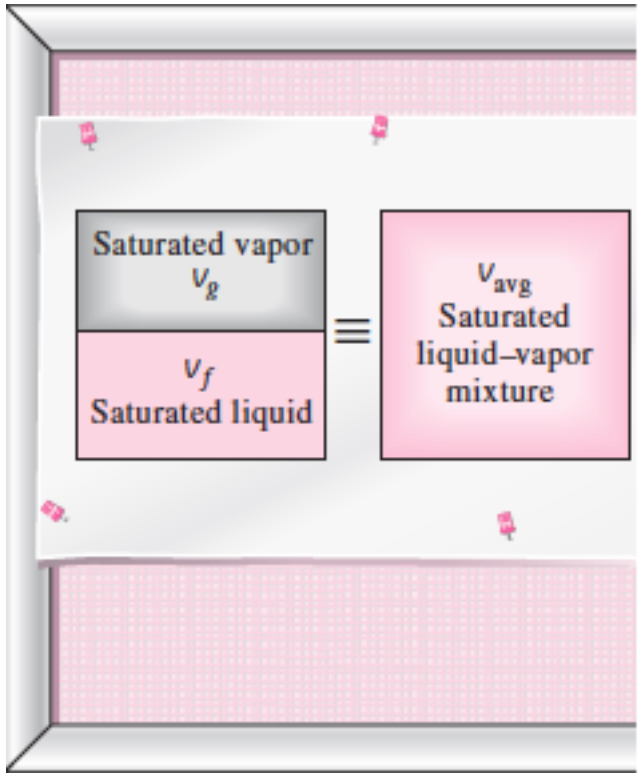
$$x = \frac{m_g}{m_f + m_g}$$



- Quality has significance for saturated mixtures only
- Quality can be used as one of the two variables to determine the state of a substance (cfr state postulate)
- During the vaporization process, only the amount of saturated liquid (or vapor) changes, not its properties

Property tables

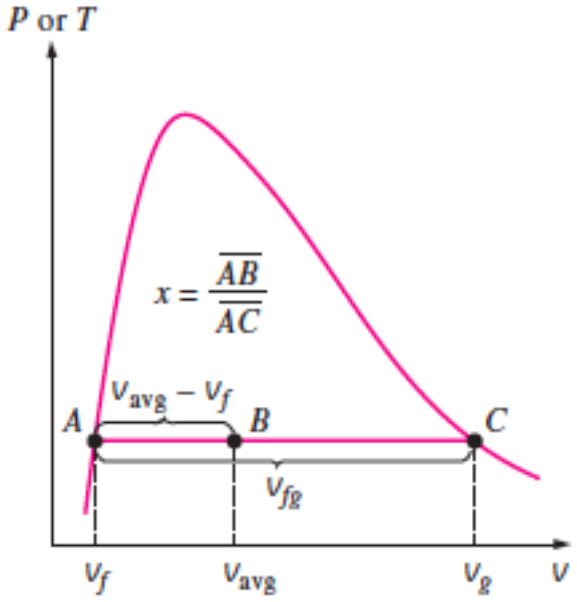
Saturated states



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

$$u_{avg} = (1 - x).u_f + x.u_g$$

$$h_{avg} = (1 - x).h_f + x.h_g$$



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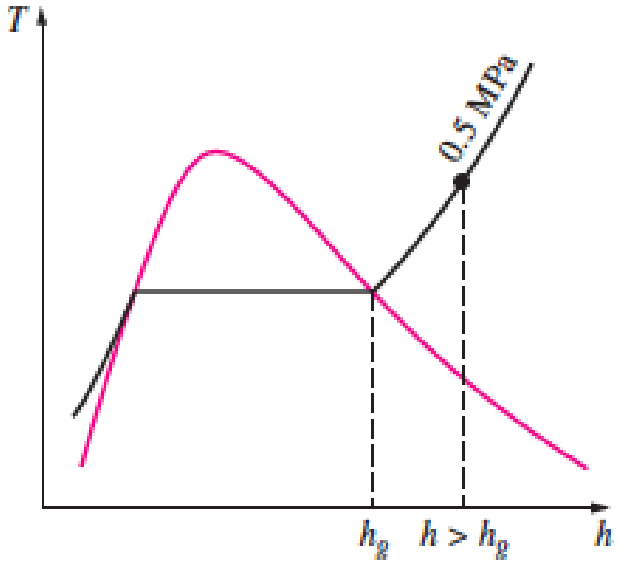
Property tables

Superheated vapor

- Region on the right of the saturated vapor line
- Only the vapor phase exists (single-phase zone)
- T and P are independent

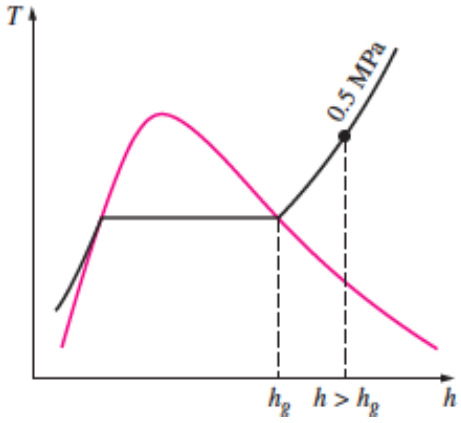


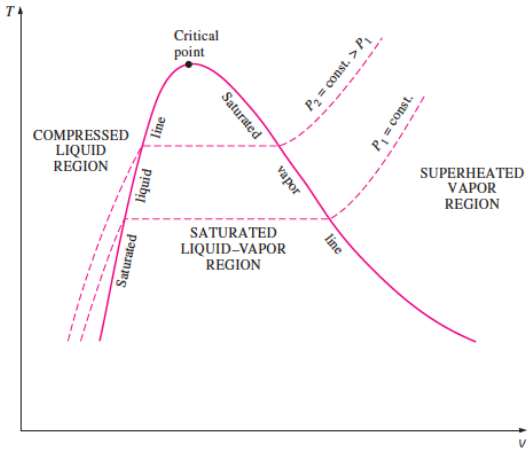
T,°C	v m³/kg	u kJ/kg	h kJ/kg
	$P = 0.1$ MPa (99.61°C)		
Sat.	1.6941	2505.6	2675.0
100	1.6959	2506.2	2675.8
150	1.9367	2582.9	2776.6
⋮	⋮	⋮	⋮
1300	7.2605	4687.2	5413.3
	$P = 0.5$ MPa (151.83°C)		
Sat.	0.37483	2560.7	2748.1
200	0.42503	2643.3	2855.8
250	0.47443	2723.8	2961.0

Property tables

Superheated vapor

- Superheated vapor differs from saturated vapor:
  - ✓ Lower pressure ($P<P_{sat}$) at the same temperature T
  - ✓ Higher temperature ($T>T_{sat}$) at the same pressure P
  - ✓ Higher specific volume $v>v_g$ at the same P or T
  - ✓ Higher internal energy $u>u_g$ at the same P or T
  - ✓ Higher enthalpy $h>h_g$ at the same P or T





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Property tables

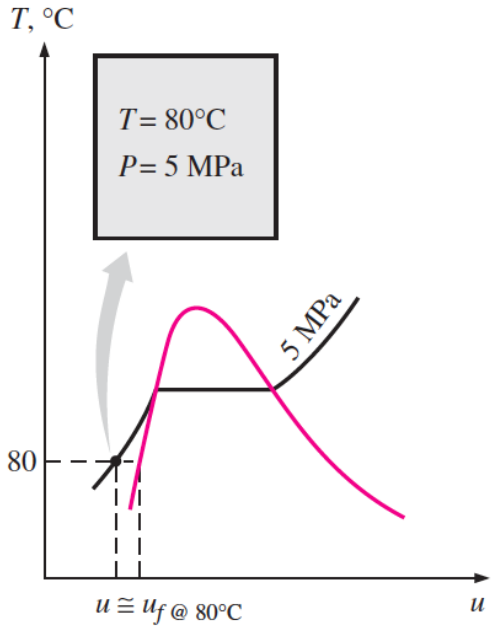
Compressed liquid (= subcooled liquid)

- The properties of compressed liquid are almost independent from the pressure (increasing P by a factor 100 only cause a change in the other properties of ~1%)
- As a consequence, complex tables are not required
- **For u and v**: As a good approximation, we consider that the properties of the subcooled liquid are the same as that of the saturated liquid at the same temperature (the properties of compressd liquid are not sensitive to P, but are sensitive to T!)

$$u \cong u_{f@T}$$
$$v \cong v_{f@T}$$

- **For h**: Enthalpy of the subcooled liquid depends on the pressure since h=u+pv. Use the following equation:

$$h \cong h_{f@T} + v_{f@T}.\left(P - P_{sat,T}\right)$$



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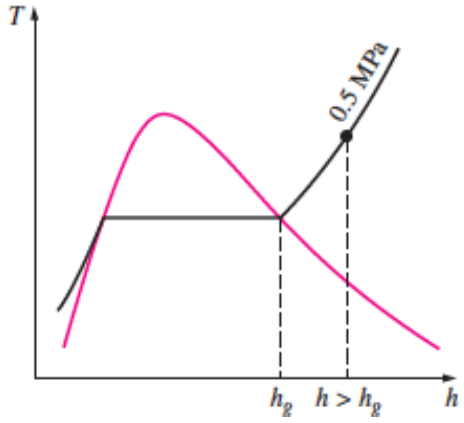
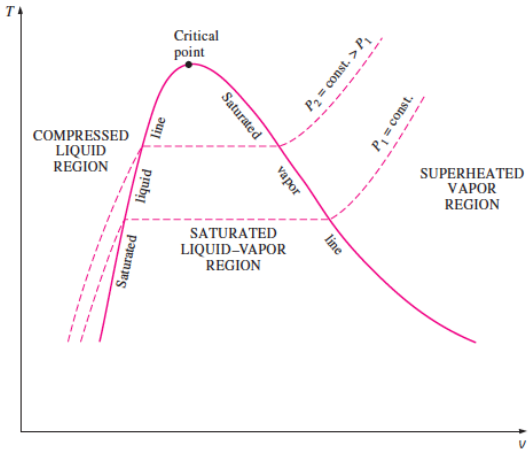
Property tables

Compressed liquid (= subcooled liquid)

- Compressed liquid differs from saturated liquid:
  - ✓ Pressure is higher $P>P_{sat}$ for a given temperature T
  - ✓ Temperature is low $T<T_{sat}$ for a given pressure P
  - ✓ Specific volume is lower $v<v_l$ for a given T or P
  - ✓ Internal energy is lower $u<u_l$ for a given T or P
  - ✓ Enthalpy is lower $h<h_l$ for a given T or P





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Property tables

Reference state

- The properties u, h and s cannot be measured directly
- They are calculated from other measurable thermodynamic properties (e.g. T, p, rho), and relations expressing their *variations* (detailed in the following classes).
- Since these relations provide variations and not an absolute value, we must define a reference state, where the properties are equal to zero.

- Example of water:
  - ✓ The reference state is the saturated liquid at 0.01°C.
  - ✓ Internal energy and entropy are equal to zero in the reference state.
- Example of R134a (refrigerant)
  - ✓ The reference state is the saturated liquid at 40°C
  - ✓ Enthalpy and entropy are equal to zero in the reference state

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The ideal gas equation of state

- The thermodynamic tables are not convenient to use
- As alternative we can try to find simple analytical relations between the thermodynamic properties.
- Any equation that relates *T*, *P* and *v* is called an **equation of state**
- An example equation of state is the ideal gas law:

$$P.v = \frac{R_u}{MM}.T$$

$$R_u = \begin{cases} 8.31447\ \mathrm{kJ/kmol \cdot K} \\ 8.31447\ \mathrm{kPa \cdot m^3/kmol \cdot K} \\ 0.0831447\ \mathrm{bar \cdot m^3/kmol \cdot K} \\ 1.98588\ \mathrm{Btu/lbmol \cdot R} \\ 10.7316\ \mathrm{psia \cdot ft^3/lbmol \cdot R} \\ 1545.37\ \mathrm{ft \cdot lbf/lbmol \cdot R} \end{cases}$$

- This relation « works » well for gases with low densities (H_2, N_2, O_2, CO_2, water vapor in the air)
- But it does not work for dense gases (steam in a steam turbine, refrigerant in a fridge)

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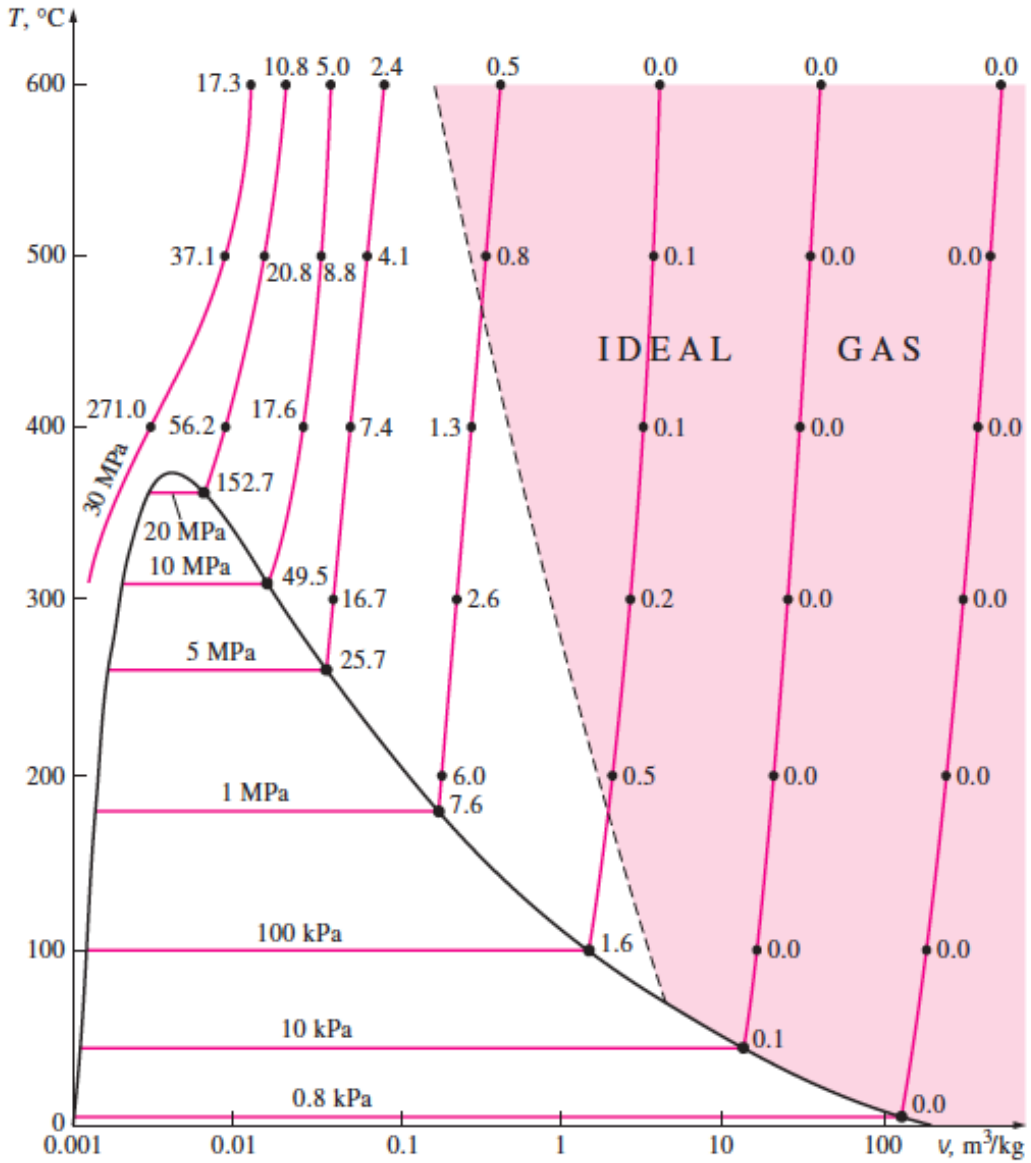
Ideal gas equation of state

- Is water vapor an ideal gas?

⇒ Below 10 kPa, yes, regardless of the temperature

⇒ Humidity in the air can be modeled as an ideal gas

⇒ At high pressure, the error between the real properties and the ideal gas law become significant, especially close to the critical point and to the saturated vapor line



Percentage of error ($[|v_{table} - v_{ideal}|/v_{table}] \times 100$) involved in assuming steam to be an ideal gas, and the region where steam can be treated as an ideal gas with less than 1 percent error.

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Ideal gas equation of state

EXAMPLE 3–10 Mass of Air in a Room

Determine the mass of the air in a room whose dimensions are 4 m × 5 m × 6 m at 100 kPa and 25°C.

Solution The mass of air in a room is to be determined.

Analysis A sketch of the room is given in Fig. 3–48. Air at specified conditions can be treated as an ideal gas. From Table A–1, the gas constant of air is $R = 0.287$ kPa · m³/kg · K, and the absolute temperature is $T = 25°C + 273 = 298$ K. The volume of the room is

$$V = (4\text{ m})(5\text{ m})(6\text{ m}) = 120\text{ m}^3$$

The mass of air in the room is determined from the ideal-gas relation to be

$$m = \frac{PV}{RT} = \frac{(100\text{ kPa})(120\text{ m}^3)}{(0.287\text{ kPa}\cdot\text{m}^3/\text{kg}\cdot\text{K})(298\text{ K})} = \mathbf{140.3\text{ kg}}$$

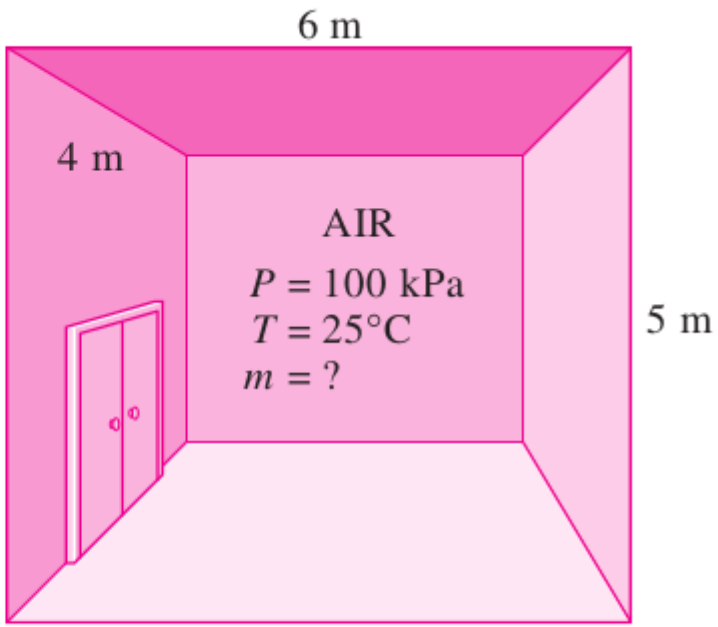

FIGURE 3–48

Schematic for Example 3–10.

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Exercises in EES

3–31 Complete this table for refrigerant-134a:

T, °C	P, kPa	v, m^3/kg	Phase description
−8	320		
30		0.015	
	180		Saturated vapor
80	600		

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Exercises in EES

3–48 A cooking pan whose inner diameter is 20 cm is filled with water and covered with a 4-kg lid. If the local atmospheric pressure is 101 kPa, determine the temperature at which the water starts boiling when it is heated.

Answer: 100.2°C

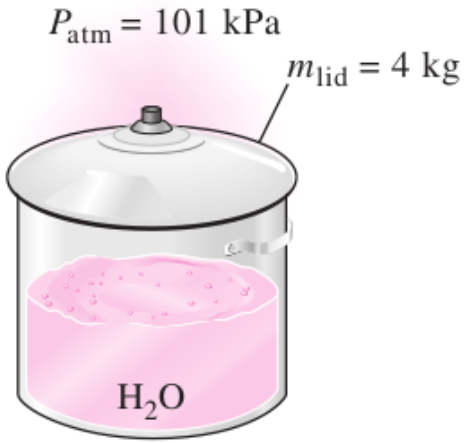

FIGURE P3–48

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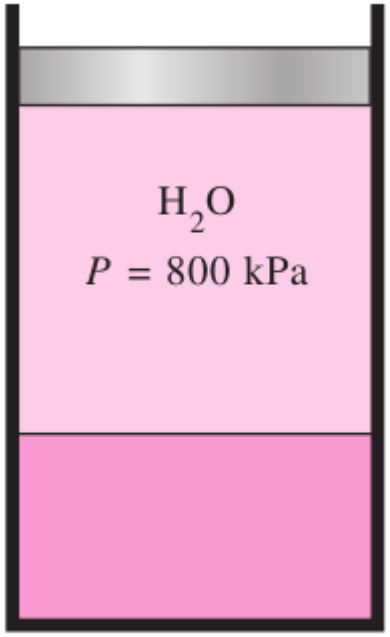
Exercises in EES

3–55 A piston–cylinder device contains 0.1 m^3 of liquid water and 0.9 m^3 of water vapor in equilibrium at 800 kPa. Heat is transferred at constant pressure until the temperature reaches 350°C.

(*a*) What is the initial temperature of the water?
(*b*) Determine the total mass of the water.
(*c*) Calculate the final volume.
(*d*) Show the process on a *P*-*v* diagram with respect to saturation lines.



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Exercises in EES

3–75 The pressure in an automobile tire depends on the temperature of the air in the tire. When the air temperature is 25°C, the pressure gage reads 210 kPa. If the volume of the tire is 0.025 m^3, determine the pressure rise in the tire when the air temperature in the tire rises to 50°C. Also, determine the amount of air that must be bled off to restore pressure to its original value at this temperature. Assume the atmospheric pressure is 100 kPa.

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