Chapter # 3
# PROPERTIES OF PURE SUBSTANCES

Objectives

➢ Demonstrate understanding of key concepts including phase and pure substance, state principle for simple compressible systems, p-v-T surface, saturation temperature and saturation pressure, two-phase liquid-vapor mixture, quality, enthalpy, and specific heats.

➢ Sketch T-v, p-v, and phase diagrams, and locate states on these diagrams.

➢ Retrieve property data from Tables A-1 through A-23.

➢ Learn and apply the ideal and non-ideal gas model for thermodynamic analysis.

➢ Examine the moving boundary work or *PdV* work commonly encountered in reciprocating devices such as automotive engines and compressors.

Pure Substance

- A substance that has <u>a fixed chemical composition throughout</u>.
- It may exist in more than one phase e.g. H_2O
- Some mixture of gases behave like pure substance <u>if no phase change occurs</u> e.g. air.
- Examples:
  - A mixture of liquid and gaseous air is not a pure substance due to different chemical composition of the two phases of air.
  - A mixture of non-soluble oil with water is not a pure substance.

N_2 gas

Vapor
Liquid

H_2O

Air

Vapor
Liquid
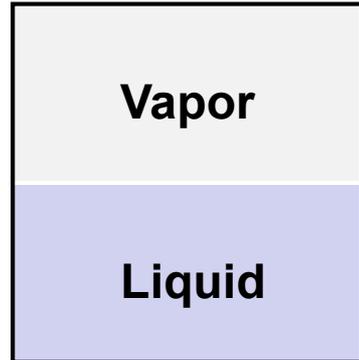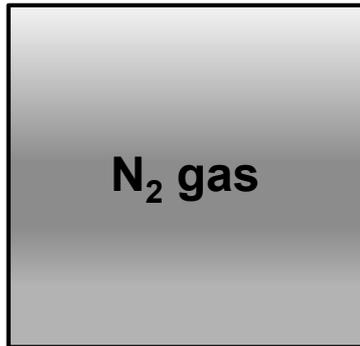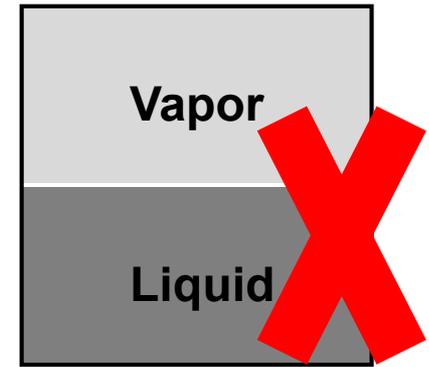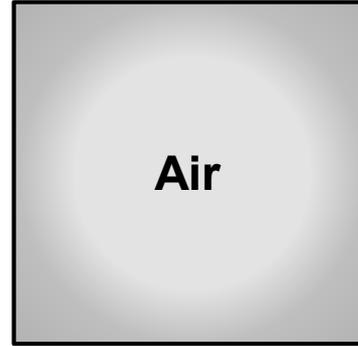
Air

STATE POSTULATE / PRINCIPLE

Simple compressible system: If a system involves no electrical, magnetic, gravitational and surface tension effects.

- The number of properties required to fix the state of a (simple compressible) system is given by the **state postulate**:
  - *The state of a simple compressible system is completely specified by two independent, intensive properties.*

The example of such properties are temperature (**T**), pressure (**P**), specific volume (**v**), density (**ρ**), specific internal energy (**u**) and specific enthalpy (**h**).
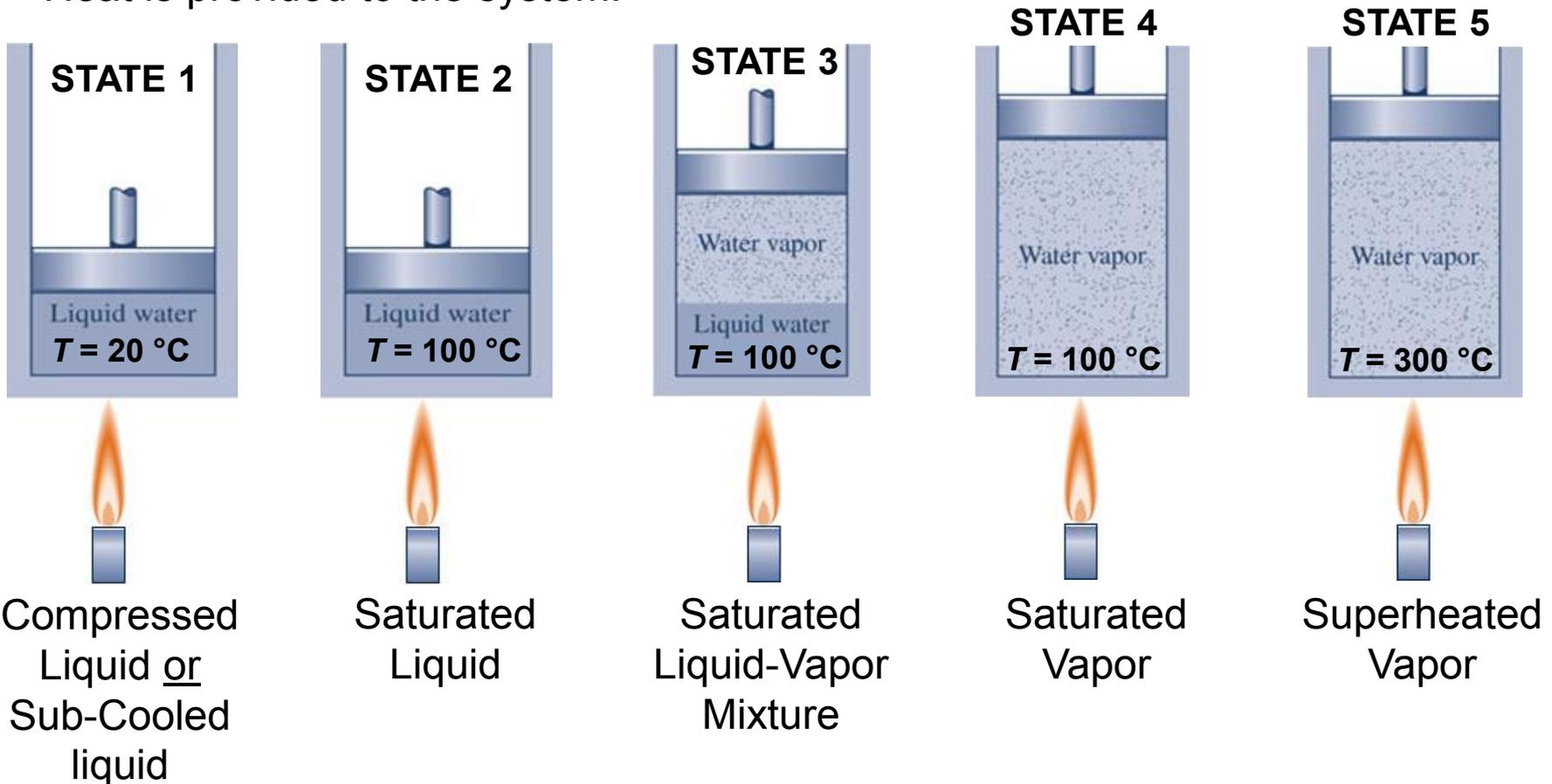
Among alternative sets of two independent intensive properties, **(T, v)** and **(p, v)** are frequently convenient.

Note: Not all of the relevant intensive properties are independent.

Phase change of a pure substance

Phase changes of a pure substance

- Water in piston cylinder arrangement (free moving piston).
- Initial water temperature is 20 ºC.
- The external pressure is **constant** (i.e. atmospheric pressure).
- The pressure due to weight of the piston is neglected.
- Heat is provided to the system.

STATE 1 — Liquid water $T = 20\ °C$ — Compressed Liquid <u>or</u> Sub-Cooled liquid

STATE 2 — Liquid water $T = 100\ °C$ — Saturated Liquid

STATE 3 — Water vapor / Liquid water $T = 100\ °C$ — Saturated Liquid-Vapor Mixture

STATE 4 — Water vapor $T = 100\ °C$ — Saturated Vapor

STATE 5 — Water vapor $T = 300\ °C$ — Superheated Vapor

Phase change of a pure substance

Saturation temperature T_{sat}

The temperature at which a pure substance changes phase at a given pressure.

Saturation pressure P_{sat}

The pressure at which a pure substance changes phase at a given temperature.

Compressed liquid (sub-cooled liquid):

A substance that it is *not about to vaporize.* Temperature is below the saturation temperature.

Saturated liquid:

A liquid that is *about to vaporize.*

Saturated liquid–vapor mixture:

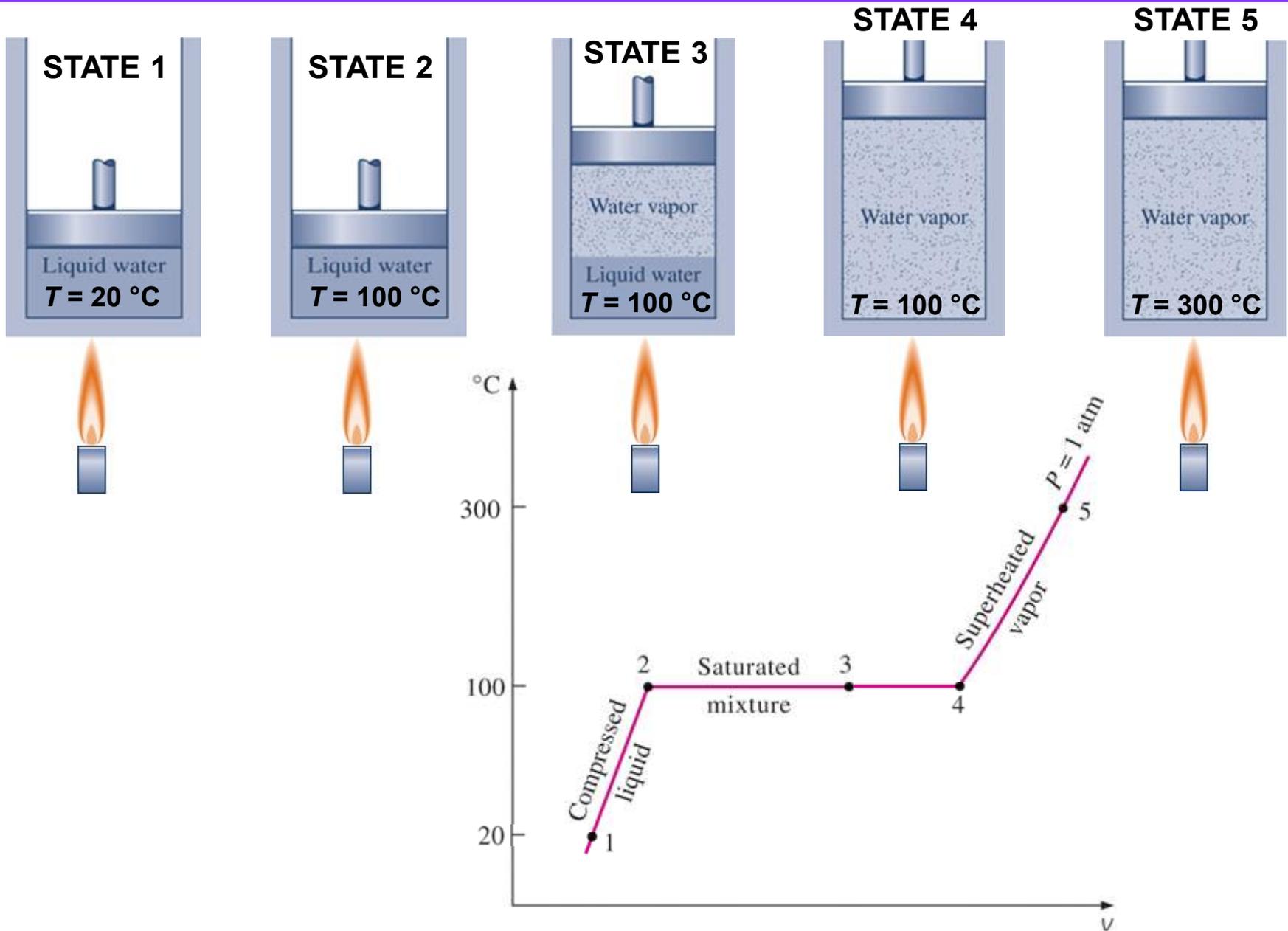The state at which the *liquid and vapor phases co-exist* in equilibrium.

Saturated vapor:

A vapor that is *about to condense.*

Superheated vapor:

A vapor that is *not about to condense* (i.e., not a saturated vapor). Temperature is above the saturation temperature.

Process Diagram (T-v Diagram)

Latent Heat

Latent heat:

The amount of energy absorbed or released during a phase-change process.

**Latent heat of vaporization:**

The amount of energy absorbed during vaporization and it is equivalent to the energy released during condensation.

Latent heat of fusion:

The amount of energy absorbed during melting. It is equivalent to the amount of energy released during freezing.

The magnitudes of the latent heats depend on the temperature OR pressure at which the phase change occurs (*Temperature and Pressure cannot be independently changed during a phase-change process*).

At 1 atm pressure, the latent heat of fusion of water is 333.7 kJ/kg and the latent heat of vaporization is 2256.5 kJ/kg.
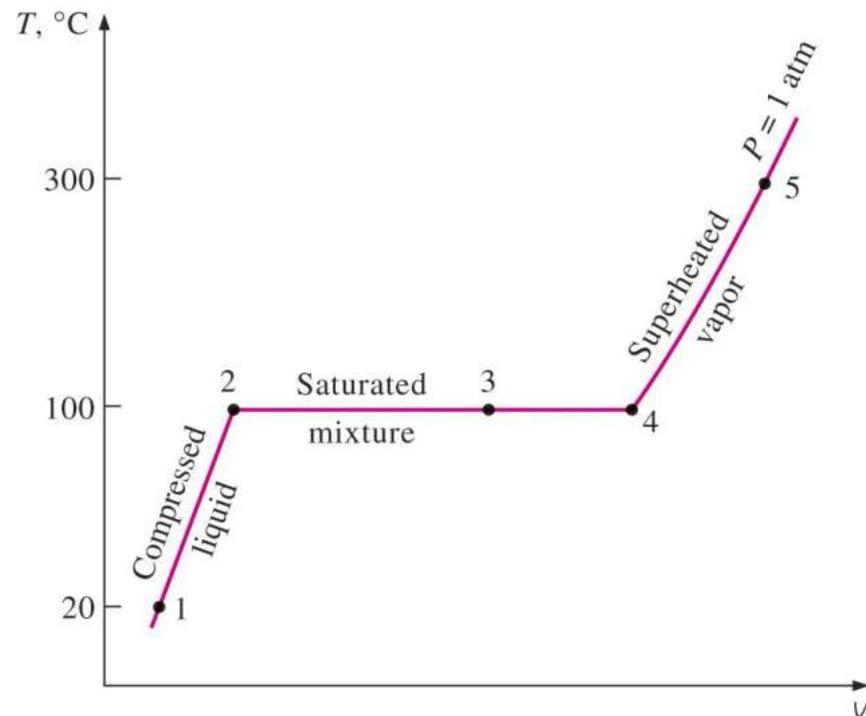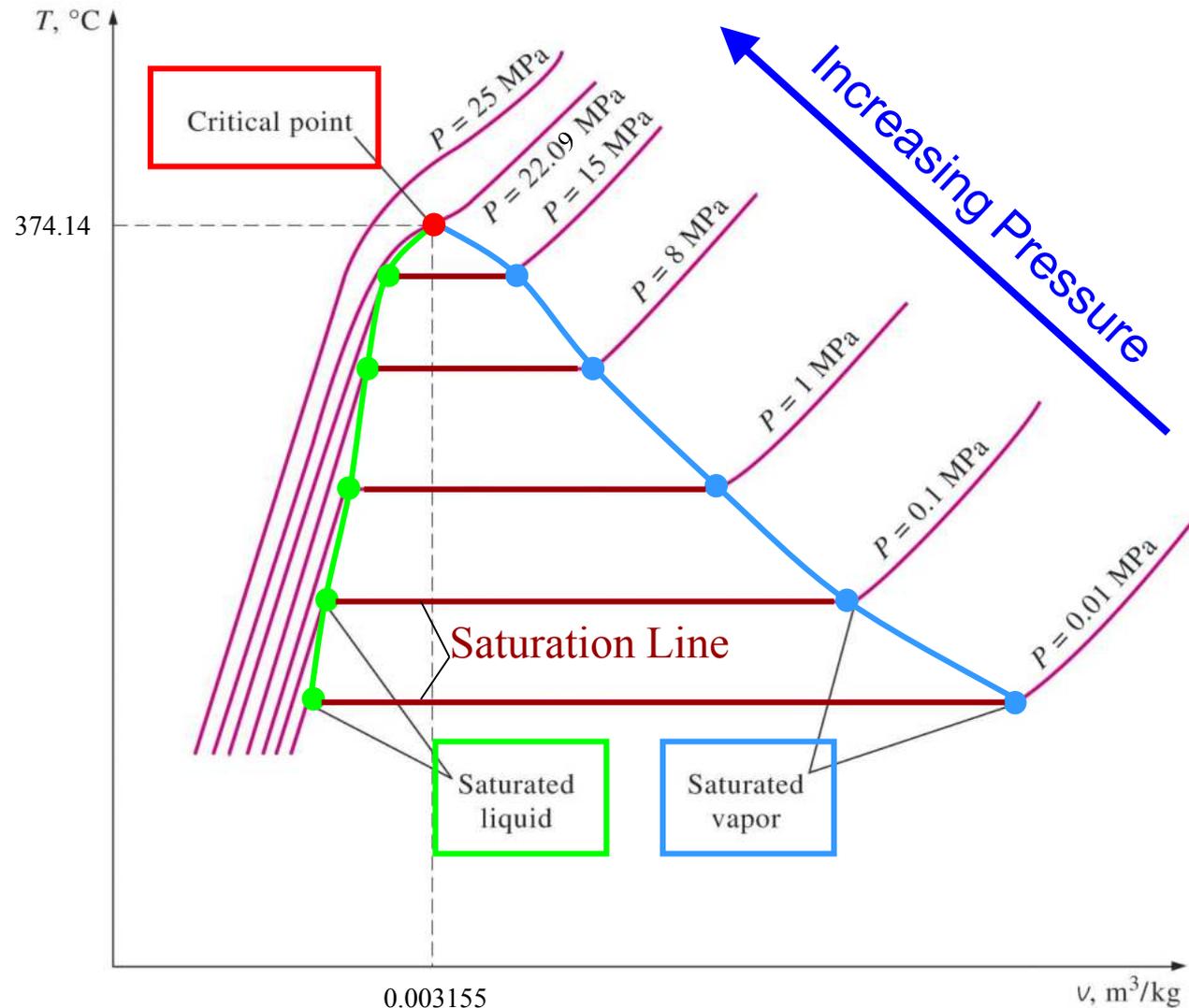
Process Diagram (T-v Diagram)
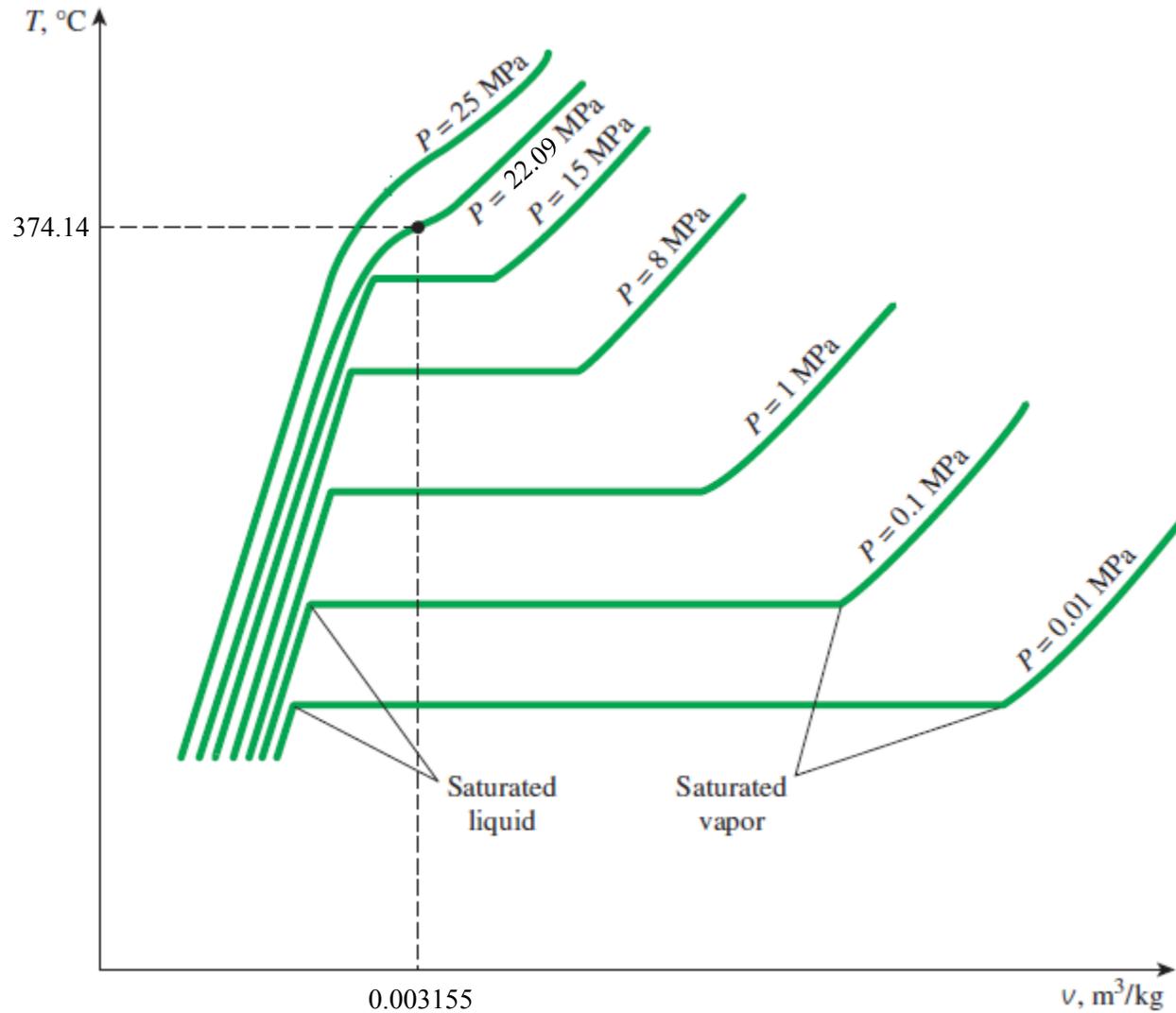
Process Diagram (T-v Diagram)

With increasing pressure

- Specific volume of saturated liquid increases

- Specific volume of saturated vapor decreases

- Length of the saturation line decreases

- Finally the saturation line becomes a point called "critical point"

- A saturated liquid line can be drawn by joining the saturated liquid points.

- A saturated vapor line can be drawn by joining the saturated vapor points.

- The two lines meet each other at critical point

Process Diagram (T-v Diagram)

- saturated liquid line
- saturated vapor line
- compressed liquid region
- superheated vapor region
- saturated liquid–vapor mixture region (wet region)

Critical point:

•The point at which the saturated liquid and saturated vapor states are identical.

•Associated properties are called *Critical Temperature (T_c), Critical Pressure (P_c) and Critical Specific Volume (v_c)*

•*Table A-1* contains critical properties of various substances
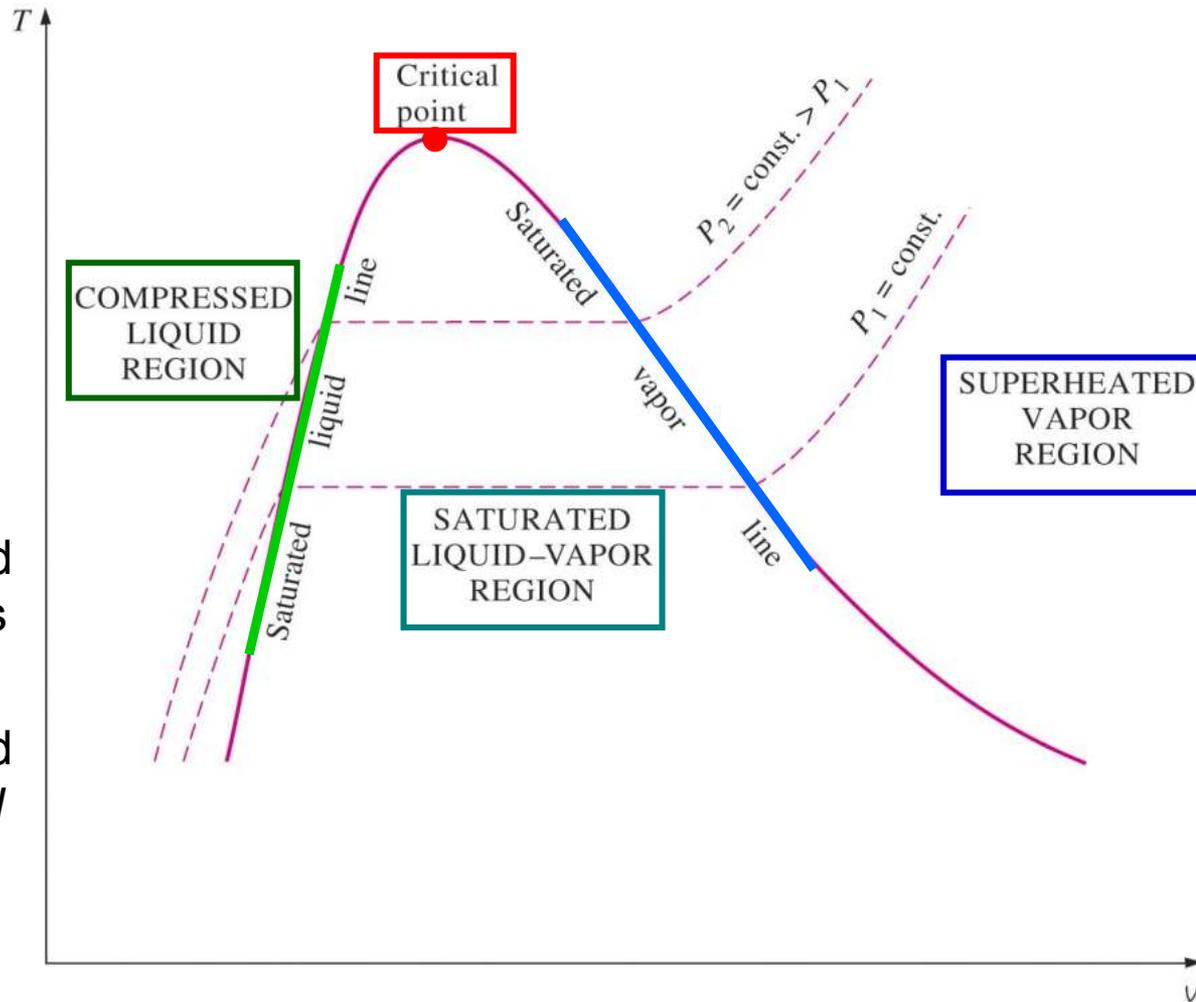
Process Diagram (T-v Diagram)

Atomic or Molecular Weights and Critical Properties of Selected Elements and Compounds

Substance	Chemical Formula	M (kg/kmol)	T_c (K)	p_c (bar)	$Z_c = \dfrac{p_c v_c}{RT_c}$
Acetylene	C_2H_2	26.04	309	62.8	0.274
Air (equivalent)	—	28.97	133	37.7	0.284
Ammonia	NH_3	17.03	406	112.8	0.242
Argon	Ar	39.94	151	48.6	0.290
Benzene	C_6H_6	78.11	563	49.3	0.274
Butane	C_4H_{10}	58.12	425	38.0	0.274

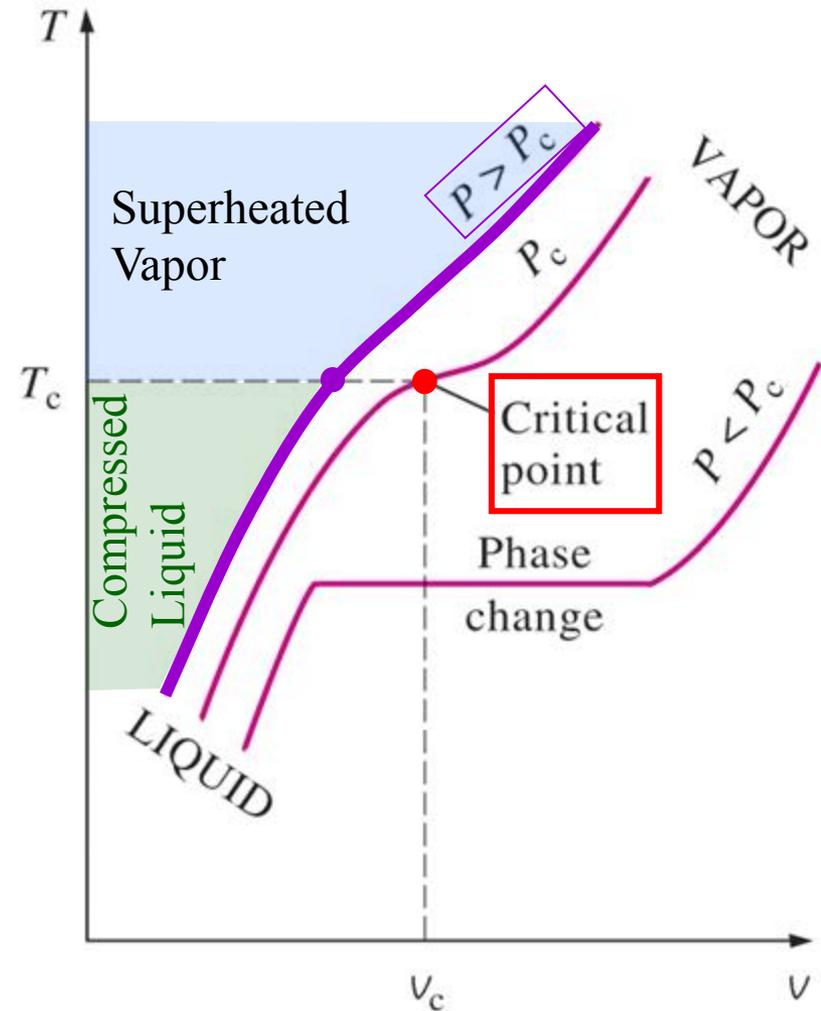# Process Diagram (T-v Diagram)

Super Critical Region (P > P_c)

At supercritical pressures ($P > P_c$), there is no distinct phase-change (boiling) process.

For $P > P_c$

If $T < T_c$ → Compressed Liquid

If $T > T_c$ → Superheated Vapor

Process Diagram (P-v Diagram)

Consider H$_2$O at initial state as shown:

➤ In what state the substance is?
➤ How can it be converted into saturated liquid <u>at constant temperature</u>?
➤ How can it be converted into saturated vapor?
  ❓ Can we add heat?
  ❓ If yes then would not temperature increase?
  ❓ Specific volume decreases or increases?
➤ How can it be converted into superheated vapor <u>at constant temperature?</u>

$P = 1$ MPa
$T = 150$ °C
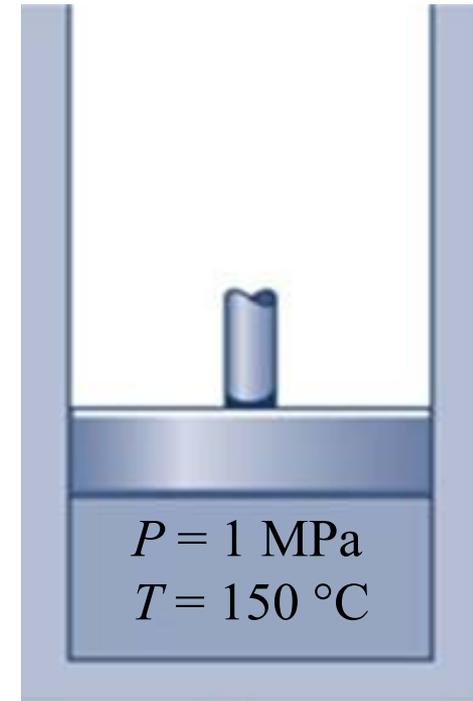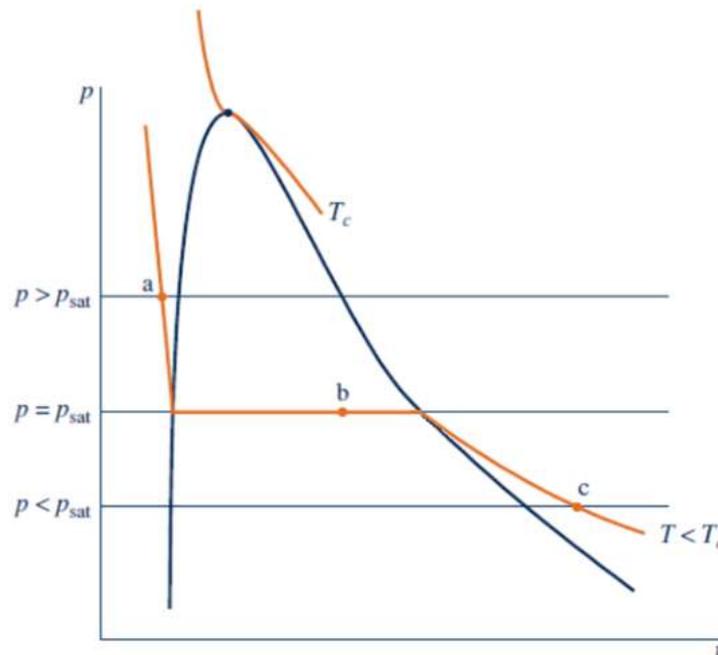
Process Diagram (P-v Diagram)

On a P-v diagram, for $P > P_c$
region to the right of $T = T_c$ line → Superheated Vapor
region to the left of $T = T_c$ line → Compressed Liquid

Include the Solid Phase (P-v Diagram)

p–v diagram for a substance that contracts on freezing.

p–v diagram for a substance that expands on freezing.

Three phases can exist in equilibrium along the line labeled **triple line**.
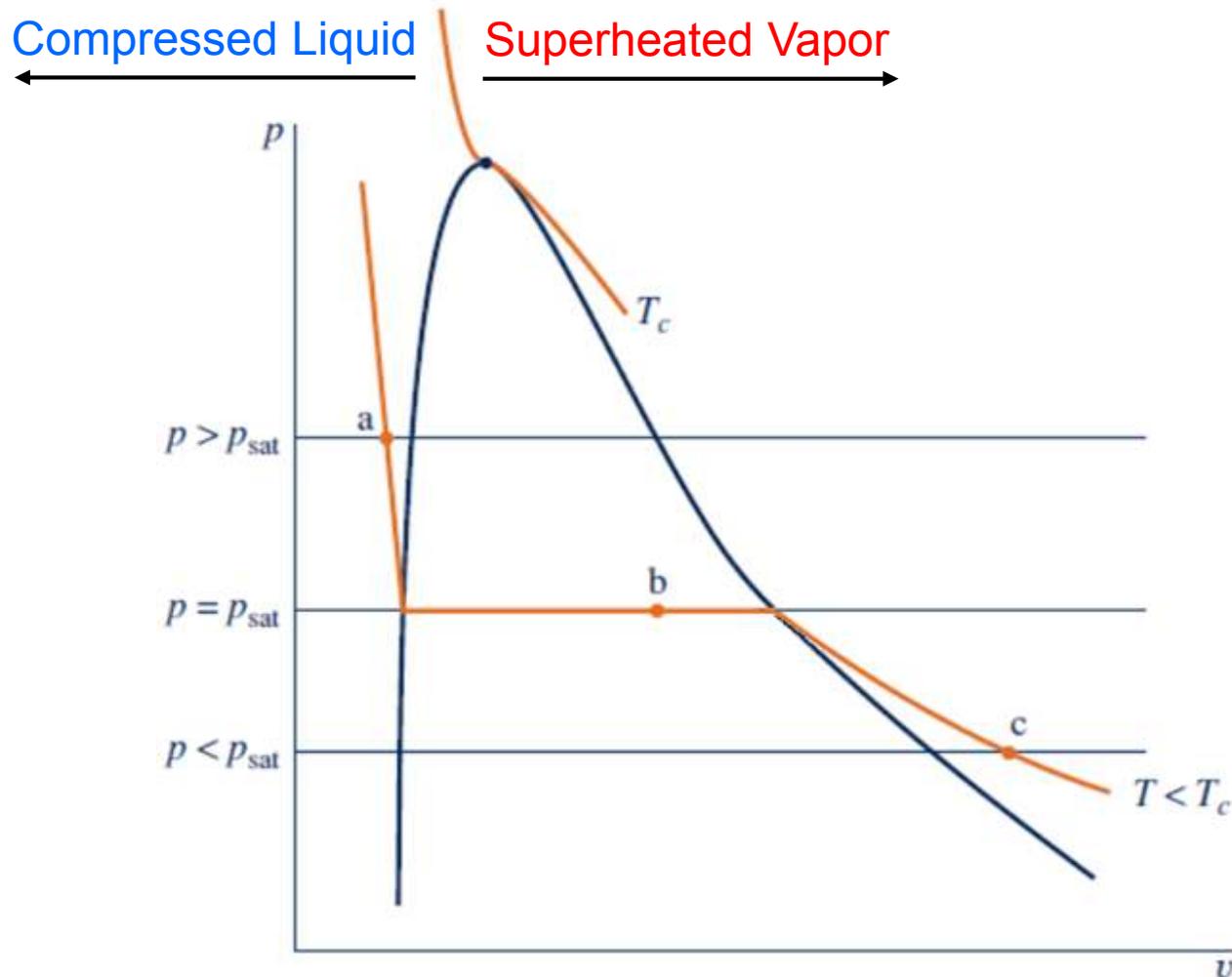
P-T Diagram (Phase Diagram)

Melting Line: Solid and Liquid are in equilibrium

Vaporization Line: Liquid and vapor are in equilibrium

Sublimation Line: Solid and vapor are in equilibrium

Triple Point: All three phases exist in equilibrium

For water,
$T_{tp} = 0.01°C$
$P_{tp} = 0.6117$ kPa
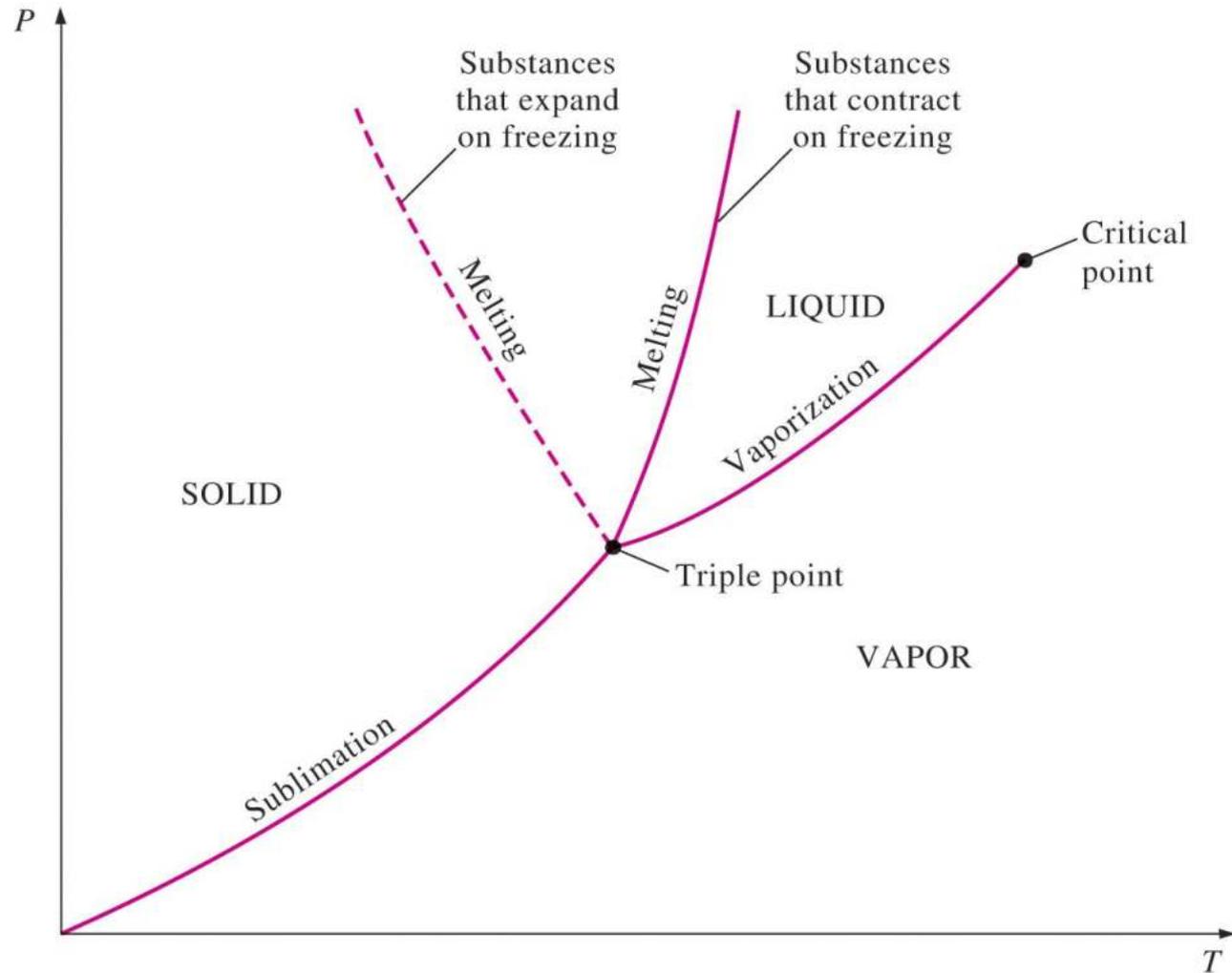
In a phase diagram,
the two-phase *regions* reduce to *lines*

The P-v-T 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.
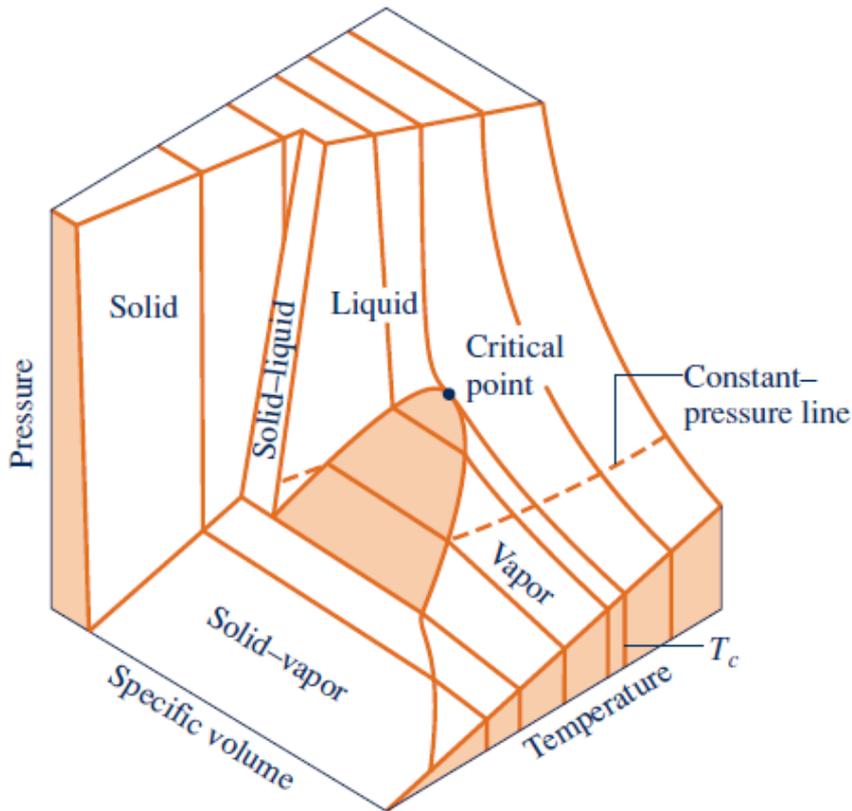
p–v–T surface for a substance that contracts on freezing.
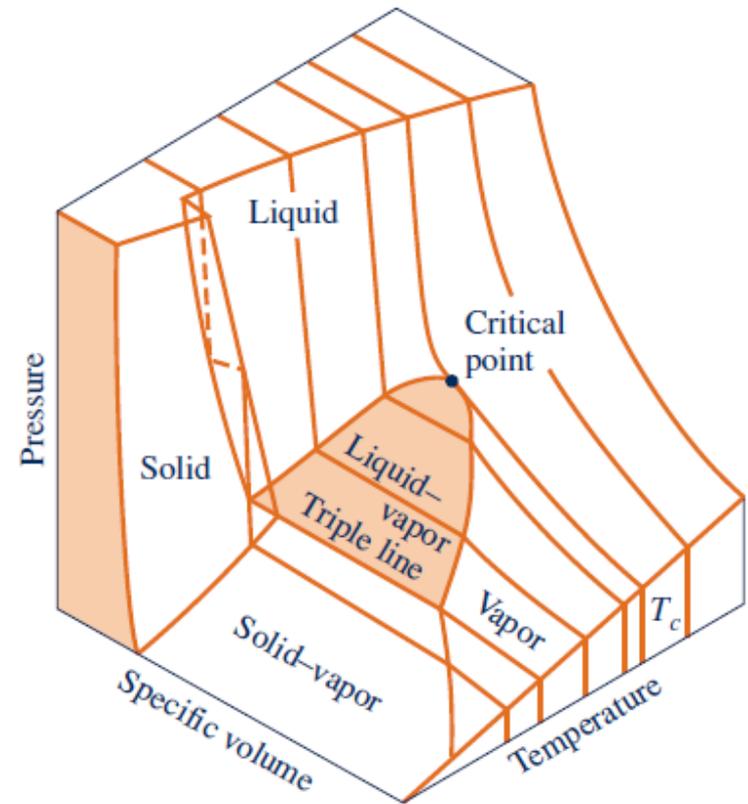
p–v–T surface for a substance that expands on freezing.

Property Tables for Phase Change Materials

State postulate:

Any 2 independent properties can completely define the state of a simple compressible substance

For most substances, the relationships among thermodynamic properties are too complex to be expressed by simple equations.

Therefore, properties are frequently presented in the form of tables.

Given any **2 independent properties**, all others can be found from table.
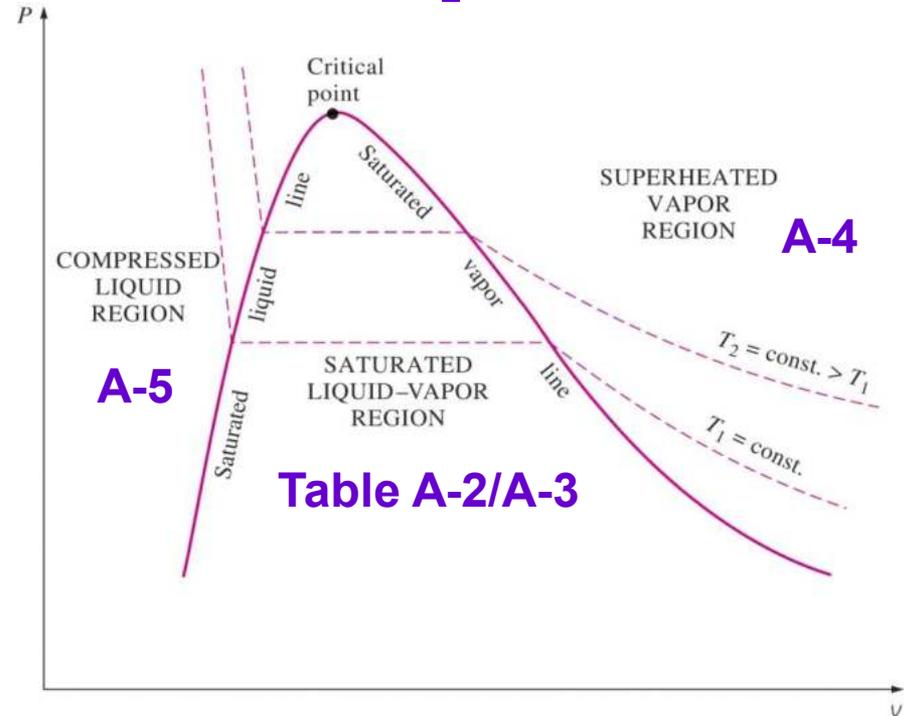
For water (H_2O)

Each region has a corresponding table

REGION	For water (H_2O)	For R-134a
Saturated liquid-vapor region	Table A-2/A-3	Tables A-10/A-11
Superheated region	Table A-4	Table A-12
Compressed liquid region	Table A-5	
Saturated solid-vapor	Table A-6	

INTERNAL ENERGY, ENTHALPY

Internal energy: The sum of all the microscopic forms of energy. Includes thermal, chemical, nuclear etc. We only consider thermal energy here.

Sensible energy: The portion of the internal energy of a system associated with the kinetic energies of the molecules.

Latent energy: The internal energy associated with the phase change of a system.

Enthalpy: A Combination Property

The combination $h = u + Pv$ is needed for open systems (Control Volumes) and is called *"enthalpy"*

Dashed line defines
the control volume
boundary

Inlet *i*

Exit *e*

$$\left. \begin{array}{ll} \text{thus} & H = U + PV \\ \text{or, specific enthalpy} & h = u + Pv \end{array} \right\} \text{units} \left\{ \begin{array}{l} kJ \\ kJ/kg \end{array} \right.$$
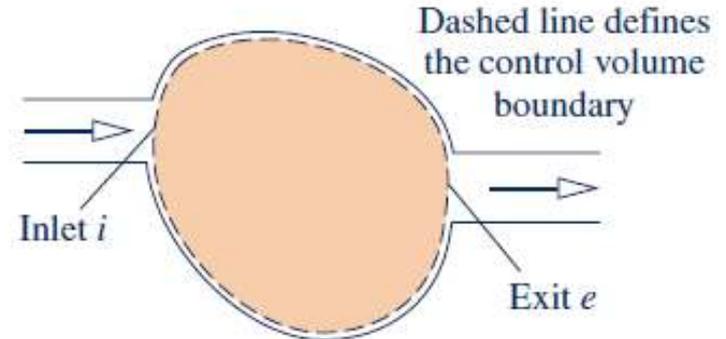
Another property **specific entropy (*s*)** related to 2nd law of thermodynamics is also listed in the tables which will be defined in Chapter 6.

Tables: Saturated Liquid / Vapor / Mixture

TABLE A-2

Properties of Saturated Water (Liquid–Vapor): Temperature Table

Pressure Conversions:
1 bar = 0.1 MPa
= 10^2 kPa

Temp. °C	Press. bar	Specific Volume m^3/kg Sat. Liquid $v_f \times 10^3$	Sat. Vapor v_g	Internal Energy kJ/kg Sat. Liquid u_f	Sat. Vapor u_g	Enthalpy kJ/kg Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Entropy kJ/kg·K Sat. Liquid s_f	Sat. Vapor s_g
.01	0.00611	1.0002	206.136	0.00	2375.3	0.01	2501.3	2501.4	0.0000	9.1562
4	0.00813	1.0001	157.232	16.77	2380.9	16.78	2491.9	2508.7	0.0610	9.0514
5	0.00872	1.0001	147.120	20.97	2382.3	20.98	2489.6	2510.6	0.0761	9.0257
6	0.00935	1.0001	137.734	25.19	2383.6	25.20	2487.2	2512.4	0.0912	9.0003
8	0.01072	1.0002	120.917	33.59	2386.4	33.60	2482.5	2516.1	0.1212	8.9501

TABLE A-3

Properties of Saturated Water (Liquid–Vapor): Pressure Table

Pressure Conversions:
1 bar = 0.1 MPa
= 10^2 kPa

Press. bar	Temp. °C	Specific Volume m^3/kg Sat. Liquid $v_f \times 10^3$	Sat. Vapor v_g	Internal Energy kJ/kg Sat. Liquid u_f	Sat. Vapor u_g	Enthalpy kJ/kg Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Entropy kJ/kg·K Sat. Liquid s_f	Sat. Vapor s_g
0.04	28.96	1.0040	34.800	121.45	2415.2	121.46	2432.9	2554.4	0.4226	8.4746
0.06	36.16	1.0064	23.739	151.53	2425.0	151.53	2415.9	2567.4	0.5210	8.3304
0.08	41.51	1.0084	18.103	173.87	2432.2	173.88	2403.1	2577.0	0.5926	8.2287
0.10	45.81	1.0102	14.674	191.82	2437.9	191.83	2392.8	2584.7	0.6493	8.1502
0.20	60.06	1.0172	7.649	251.38	2456.7	251.40	2358.3	2609.7	0.8320	7.9085

Tables: Saturated Liquid / Vapor / Mixture

Table A–2: Saturation properties of water under temperature.

Table A–3: Saturation properties of water under pressure.

} Both are the same tables.

A partial list of Table A–2.

Temp. °C	Press. bar	Specific Volume m³/kg	
		Sat. Liquid $v_f \times 10^3$	Sat. Vapor v_g
.01	0.00611	1.0002	206.136
4	0.00813	1.0001	157.232
5	0.00872	1.0001	147.120
6	0.00935	1.0001	137.734
8	0.01072	1.0002	120.917

Saturation temperature

Corresponding saturation pressure

Specific volume of saturated liquid

Specific volume of saturated vapor

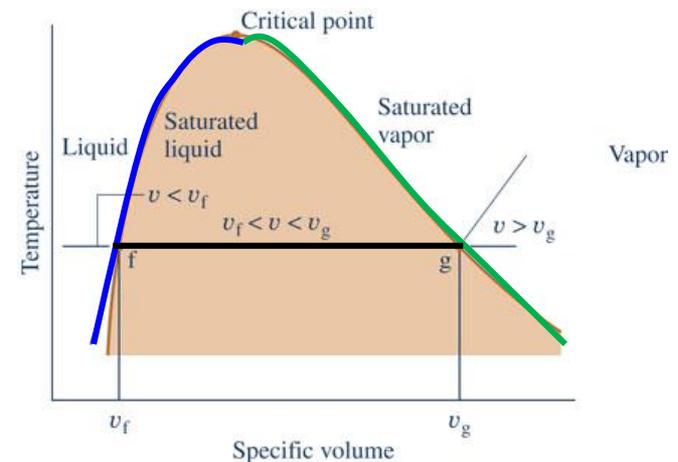Subscript **_f_** used for **_Saturated liquid_**
e.g. v_f, u_f, h_f, s_f

Subscript **_g_** used for **_Saturated vapor_**
e.g. v_g, u_g, h_g, s_g

Subscript **_fg_** used for **difference**
e.g. $v_{fg} = v_g - v_f$, $h_{fg} = h_g - h_f$

Saturated Liquid-Vapor Mixture Region

Quality (x) :

The ratio of the mass of vapor to the total mass of the mixture.

$$x = \frac{m_{vapor}}{m_{liquid} + m_{vapor}}$$
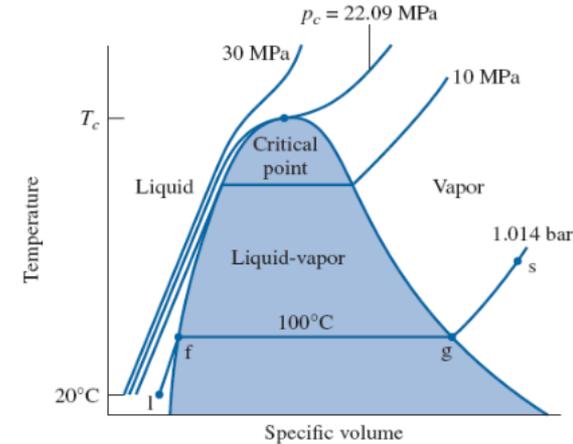
Quality is between **0** and **1** $\longrightarrow$ **0: sat. liquid**, **1: sat. vapor**.

Quality is defined at T_{sat} and P_{sat} _only_
It is *not defined* for *Compressed liquid* or *Superheat vapor*

e.g.
- for *Sat.* liquid $x = 0$ no vapor
- for *Sat.* vapor $x = 1$ all vapor
- for *Sat.* mixture $0 < x < 1$ some liquid some vapor
- for compressed liquid   ✗   not defined
- for superheated vapor   ✗   not defined

Saturated Liquid-Vapor Mixture Region

▶ The specific volume of a two-phase liquid-vapor mixture can be determined by using the saturation tables and quality, x.

▶ The total volume of the mixture is the sum of the volumes of the liquid and vapor phases:

$$V = V_{\text{liq}} + V_{\text{vap}}$$

▶ Dividing by the total mass of the mixture, **m**, *an average specific volume for the mixture* is:

$$v = \frac{V}{m} = \frac{V_{\text{liq}}}{m} + \frac{V_{\text{vap}}}{m}$$

▶ With $V_{\text{liq}} = m_{\text{liq}} v_{\text{f}}$, $V_{\text{vap}} = m_{\text{vap}} v_{\text{g}}$, $m_{\text{vap}}/m = x$, and $m_{\text{liq}}/m = 1 - x$:

$$v = (1 - x)v_{\text{f}} + x v_{\text{g}} = v_{\text{f}} + x(v_{\text{g}} - v_{\text{f}}) \quad \textbf{(Eq. 3.2)}$$
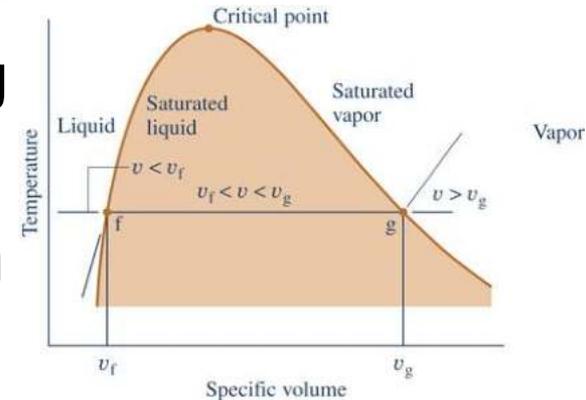
Saturated Liquid-Vapor Mixture Region

▶ Since pressure and temperature are NOT independent properties in the two-phase liquid-vapor region, they cannot be used to fix the state in this region.

▶ The property, quality (x), defined only in the two-phase liquid-vapor region, and either temperature or pressure can be used to fix the state in this region.

$$v = (1 - x)v_f + xv_g = v_f + x(v_g - v_f) \quad \text{(Eq. 3.2)}$$
$$u = (1 - x)u_f + xu_g = u_f + x(u_g - u_f) \quad \text{(Eq. 3.6)}$$
$$h = (1 - x)h_f + xh_g = h_f + x(h_g - h_f) \quad \text{(Eq. 3.7)}$$

Saturated Liquid-Vapor Mixture Region

► **Example**: A system consists of a two-phase liquid-vapor mixture of water at 5 °C and a quality of 0.4. *Determine the specific volume, in m³/kg, of the mixture.*

► **Solution**: Apply **Eq. 3.2**, $v = v_f + x(v_g - v_f)$

Substituting values from **Table A-2**: $v_f = 0.0010001$ m³/kg and $v_g = 147.12$ m³/kg:

$$v = 0.0010001 \text{ m}^3/\text{kg} + 0.4(147.12 - 0.0010001) \text{ m}^3/\text{kg}$$
$$v = \mathbf{58.849 \text{ m}^3/\text{kg}}$$

TABLE A-2

Pressure Conversions:
1 bar = 0.1 MPa
= 10² kPa

Properties of Saturated Water (Liquid–Vapor): Temperature Table

Temp. °C	Press. bar	Specific Volume m³/kg		Internal Energy kJ/kg		Enthalpy kJ/kg			Entropy kJ/kg · K	
		Sat. Liquid $v_f \times 10^3$	Sat. Vapor v_g	Sat. Liquid u_f	Sat. Vapor u_g	Sat. Liquid h_f	Evap. h_{fg}	Sat. Vapor h_g	Sat. Liquid s_f	Sat. Vapor s_g
.01	0.00611	1.0002	206.136	0.00	2375.3	0.01	2501.3	2501.4	0.0000	9.1562
4	0.00813	1.0001	157.232	16.77	2380.9	16.78	2491.9	2508.7	0.0610	9.0514
5	0.00872	1.0001	147.120	20.97	2382.3	20.98	2489.6	2510.6	0.0761	9.0257
6	0.00935	1.0001	137.734	25.19	2383.6	25.20	2487.2	2512.4	0.0912	9.0003

Superheated Vapor Region

►**Example**: *Determine v, u, h and s at* 6 MPa *and* 440°C.

- ►v = 0.05122 m³/kg
- ►u = 2970 kJ/kg
- ►h = 3277.3 kJ/kg
- ►s = 6.6853 kJ/kg·K

T °C	v m³/kg	u kJ/kg	h kJ/kg	s kJ/kg·K	v m³/kg	u kJ/kg	h kJ/kg	s kJ/kg·K
	p = 40 bar = 4.0 MPa (T_{sat} = 250.4°C)				p = 60 bar = 6.0 MPa (T_{sat} = 275.64°C)			
Sat.	0.04978	2602.3	2801.4	6.0701	0.03244	2589.7	2784.3	5.8892
280	0.05546	2680.0	2901.8	6.2568	0.03317	2605.2	2804.2	5.9252
320	0.06199	2767.4	3015.4	6.4553	0.03876	2720.0	2952.6	6.1846
360	0.06788	2845.7	3117.2	6.6215	0.04331	2811.2	3071.1	6.3782
400	0.07341	2919.9	3213.6	6.7690	0.04739	2892.9	3177.2	6.5408
440	0.07872	2992.2	3307.1	6.9041	0.05122	2970.0	3277.3	6.6853
500	0.08643	3099.5	3445.3	7.0901	0.05665	3082.2	3422.2	6.8803
540	0.09145	3171.1	3536.9	7.2056	0.06015	3156.1	3517.0	6.9999
600	0.09885	3279.1	3674.4	7.3688	0.06525	3266.9	3658.4	7.1677
640	0.1037	3351.8	3766.6	7.4720	0.06859	3341.0	3752.6	7.2731
700	0.1110	3462.1	3905.9	7.6198	0.07352	3453.1	3894.1	7.4234
740	0.1157	3536.6	3999.6	7.7141	0.07677	3528.3	3989.2	7.5190

Superheated Vapor Region

► When a state does not fall exactly on the grid of values provided by property tables, linear interpolation between adjacent entries is used.

► **Example**: *Determine the specific volume of water* at 1 MPa and 215°C.

$$slope = \frac{(0.2275 - 0.2060)}{(240 - 200)} = \frac{(v - 0.2060)}{(215 - 200)} \rightarrow v = 0.2140 \text{ m}^3/\text{kg}$$

$$slope = \frac{\Delta v}{\Delta T}$$

P = 1.00 MPa	
T (°C)	**v (m³/kg)**
200	0.2060
215	v =?
240	0.2275

p = 10.0 bar = 1.0 MPa (T_{sat} = 179.91°C)			
Sat.	0.1944	2583.6	2778.1	6.5865
200	0.2060	2621.9	2827.9	6.6940
240	0.2275	2692.9	2920.4	6.8817
280	0.2480	2760.2	3008.2	7.0465
320	0.2678	2826.1	3093.9	7.1962
360	0.2873	2891.6	3178.9	7.3349

Tables for Compressed Liquid

▶ *Determine the specific volume of water* at 2.5 MPa and 40 ºC.

▶ **Solution**: $v = 0.0010067 \text{ m}^3/\text{kg}$

Let us investigate the effect of pressure:

From saturated tables

At T = 40 ºC,
P_{sat} = 7.384 kPa and v_f = 0.0010078 m^3/kg

Increase in pressure:
(2500-7.384)/7.384
≈ 338 Times
Decrease in volume:
(0.0010078-0.0010067)/0.0010078
≈ 0.11%

Volume of a liquid changes appreciably with change in temperature BUT negligibly with change in pressure

TABLE A-5

Properties of Compressed Liquid Water

T °C	$v \times 10^3$ m^3/kg	u kJ/kg	h kJ/kg	s kJ/kg · K
	$p = 25$ bar = 2.5 MPa (T_{sat} = 223.99ºC)			
20	1.0006	83.80	86.30	.2961
40	1.0067	167.25	169.77	.5715
80	1.0280	334.29	336.86	1.0737
100	1.0423	418.24	420.85	1.3050
140	1.0784	587.82	590.52	1.7369
180	1.1261	761.16	763.97	2.1375
200	1.1555	849.9	852.8	2.3294
220	1.1898	940.7	943.7	2.5174
Sat.	1.1973	959.1	962.1	2.5546

Tables for Compressed Liquid

Thus, if compressed liquid data/table is not given, we may assume

$$v(T, p) \approx v_f(T) \quad \text{(Eq. 3.11)}$$
$$u(T, p) \approx u_f(T) \quad \text{(Eq. 3.12)}$$

h is comparatively more sensitive to pressure.

▶ An approximate value for *h* at liquid states can be obtained using **Eqs. 3.11** and **3.12** in the definition $h = u + pv$: $h(T, p) \approx u_f(T) + pv_f(T)$ or alternatively

$$h(T, p) \approx h_f(T) + v_f(T)[p - p_{sat}(T)] \quad \text{(Eq. 3.13)}$$

@40 ºC, 2.5 MPa

$$h(T, p) \approx 167.57 + 0.0010078[2500 - 7.384] = 170.08 \text{ kJ/kg}$$

▶ When the underlined term in **Eq. 3.13** is small

$$h(T, p) \approx h_f(T) \quad \text{(Eq. 3.14)}$$

Tables for Solid-Vapor

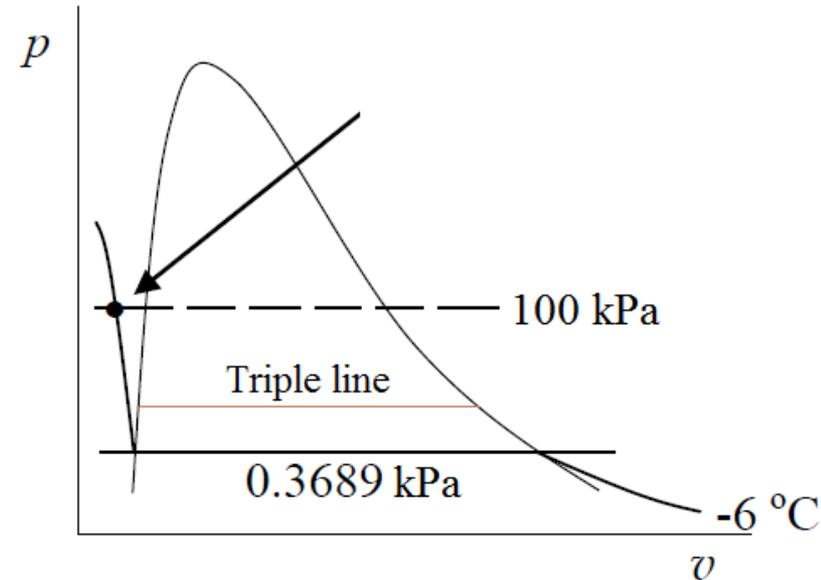If temperature is less than the triple point temperature (0.01 °C for water),

$$P > P_{sat@T} \rightarrow SOLID$$
$$P < P_{sat@T} \rightarrow VAPOR$$

▶ **Example:** *Determine phase and specific volume of water* at -6 °C and 100 kPa.

This is called "Compressed solid". It is approximated as a saturated solid at given temperature using **Table A-6.**

▶ $v = 0.0010898$ m³/kg

TABLE A-6

Properties of Saturated Water

Pressure Conversions:
1 bar = 0.1 MPa
= 10² kPa

Temp. °C	Pressure kPa	Sat. Solid $v_i \times 10^3$	Sat. Vapor v_g
.01	.6113	1.0908	206.1
0	.6108	1.0908	206.3
−2	.5176	1.0904	241.7
−4	.4375	1.0901	283.8
−6	.3689	1.0898	334.2
−8	.3102	1.0894	394.4

Tables for Solid-Vapor

In the two-phase solid-vapor (sublimation) region, *quality* is again understood as mass fraction of vapor with the difference that it is a **solid/vapor mixture** and not a liquid/vapor mixture.

$$x = \frac{m_{vapor}}{m_{solid} + m_{vapor}}$$

▶ **Example:** *If water is cooled isochorically from 500 kPa, 25% quality, what is the mass fraction of solid at -10 °C? Show P-v sketch also.*

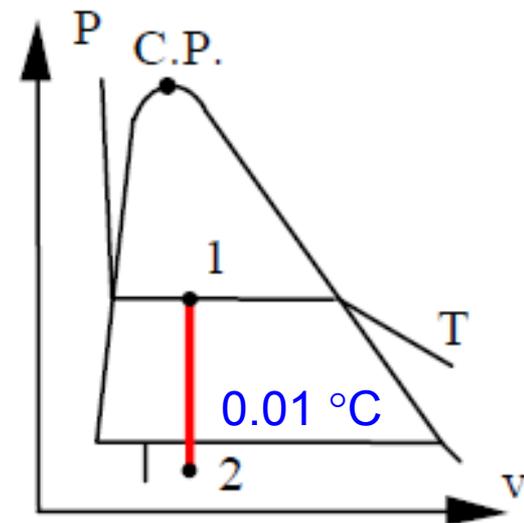Constant volume and mass $\Rightarrow v_1 = v_2 = V/m$

From Table A-3,

$v_1 = v_f + x_1(v_g - v_f) = 1.0926 \times 10^{-3} + 0.25(0.3749 - 1.0926 \times 10^{-3})$
$v_1 = 0.094544 \text{ m}^3/\text{kg} = v_2$

$v_2 = v_i + x_2(v_g - v_i)$
$0.094544 = 1.0891 \times 10^{-3} + x_2(466.7 - 1.0891 \times 10^{-3})$
$x_2 = 0.0002 \Rightarrow x_{solid} = 1 - 0.0002 = 0.9998$

Note: Use ideal gas law for vapor region, $v_g = R_w T/P$

Reference states and reference values

We need to fix the states and assign values to them so that all other values are given with respect to (w.r.t) these states

- ➤ The values of u, h, and s cannot be measured directly, and they are calculated from measurable properties using the relations between properties.
- ➤ However, those relations give the *changes* in properties, not the values of properties at specified states.
- ➤ Therefore, we need to choose a convenient *reference state* and assign a value of *zero* for a convenient property or properties at that state.

	Reference state	
Water	Sat. liquid at 0.01°C	$u = 0$ & $s = 0$
R-134a	Sat. liquid at -40°C	$h = 0$ & $s = 0$

Because of reference states some properties may have –ve values e.g. all u's and h's for sat. solid H_2O are –ve **(See A-6)**

Note:
$$\Delta u = (u_2 - u_1) = (u_2 - u_{ref}) - (u_1 - u_{ref})$$

Complete the Table for H$_2$O

T, °C	P, kPa	h, kJ/kg	x	Phase description
120.2	200	**2046.03**	0.7	**Saturated Liquid-Vapour Mixture**
140	**361.3**	1800	**0.5646**	**Sat. Liq-Vap Mixture**
177.65	950	**752.82**	0.0	**Saturated Liquid**
80	500	**334.91**	**UNDEFINED**	**Compressed Liquid**
200	700	**2844.8**	**UNDEFINED**	**Superheated Vapour**

$$h = h_f + x(h_g - h_f)$$

Problem

10-kg of **R-134a** fill a 1.348-m³ rigid container at an initial temperature of -40 °C. The container is then heated until the pressure is 200 kPa. *Determine the final temperature and the initial pressure. Also, draw the process on a P-v diagram.*

System: Closed, R-134a, P_1=?, T_2=?

State 1
T_1 = -40 °C
m_1 = 10 kg
V_1 = 1.348 m³

isochoric

State 2
P_2 = 200 kPa
$m_1 = m_2$
$V_1 = V_2$

$v_1 = v_2$

R-134a
-40°C
10 kg
1.348 m³

$$v_1 = v_2 = \frac{V}{m} = \frac{1.348\,\text{m}^3}{10\,\text{kg}} = 0.1348\,\text{m}^3/\text{kg}$$

$$\Rightarrow @\,T_1, v_f < v_1 < v_g : \quad P_1 = P_{\text{sat}\,@\,-40°C} = \boxed{51.64\ \text{kPa}}\ \text{(Table A-11)}$$

The final state is superheated vapor and the temperature is determined by interpolation to be

| **P = 200 kPa**	
T (°C)	**v (m³/kg)**
60	0.13201
?	0.1348
70	0.13639

$\boxed{T_2 = 66.37\ °C}$
(Table A-12)
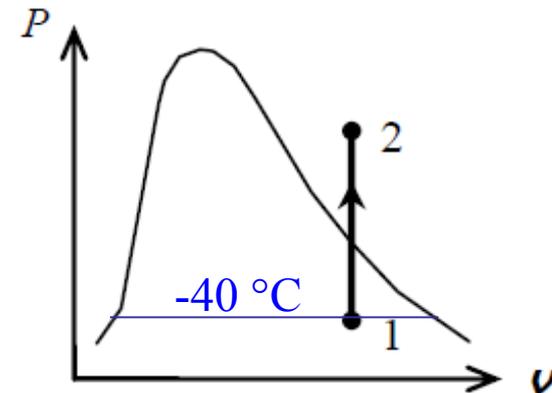
Problem

100-kg of **R-134a** at 200 kPa are contained in a piston cylinder device whose volume is 12.311 m³. The piston is now moved until the volume is one-half its original size. This is done such that the pressure does not change. *Determine the final temperature and the change in the (specific) internal energy. Also, draw the process on a P-v diagram.*

System: Closed, R-134a, T_2=?, Δu=?

State 1		State 2
P_1 = 200 kPa	isobaric	P_2 = P_1
m_1 = 100 kg		m_1 = m_2
V_1 = 12.311 m³		V_2 = V_1/2

R-134a
200 kPa
100 kg
12.322 m³
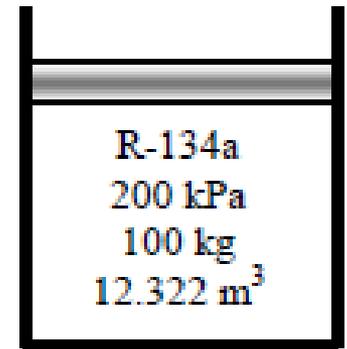
$$v_1 = \frac{V}{m} = \frac{12.311}{100} = 0.12311 \, m^3/kg \Rightarrow @ P_1, v_1 > v_g : u_1 = 261.26 \, kJ/kg \text{ (Table A-12)}$$
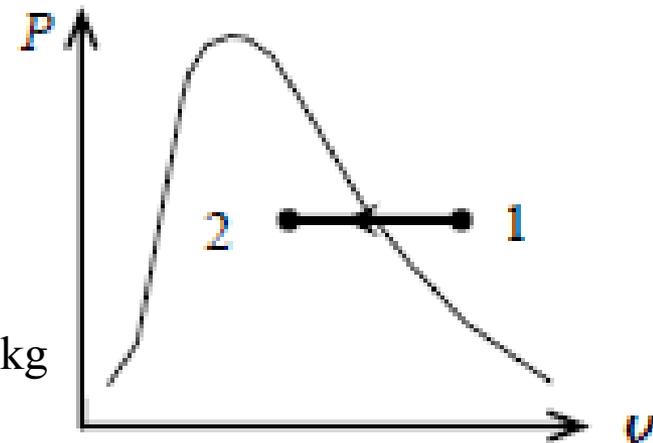
$$v_2 = \frac{v_1}{2} = \frac{0.12311}{2} = 0.061555 \, m^3/kg$$

$$\Rightarrow @ P_2, v_f < v_2 < v_g : T_2 = T_{sat} = -10.09 \, °C \text{ (Table A-11)}$$

$$x_2 = \frac{v_2 - v_f}{v_{fg}} = \frac{0.061555 - 0.0007532}{0.0993 - 0.0007532} = 0.6170$$

$$u_2 = u_f + x_2 u_{fg} = 36.69 + 0.617(221.43 - 36.69) = 150.67 \, kJ/kg$$

$$\Rightarrow \Delta u = u_2 - u_1 = -110.59 \, kJ/kg$$

Problem

Water initially at 200 kPa, 300 °C is contained in a piston-cylinder device fitted with stops. It is allowed to cool at constant pressure until it exists as a saturated vapor and the piston rests on the stops. Then the water continues to cool until the pressure is 100 kPa. *On the T-v diagram, sketch with respect to the saturation lines, the process curves passing through the initial, intermediate and final states of the water.*
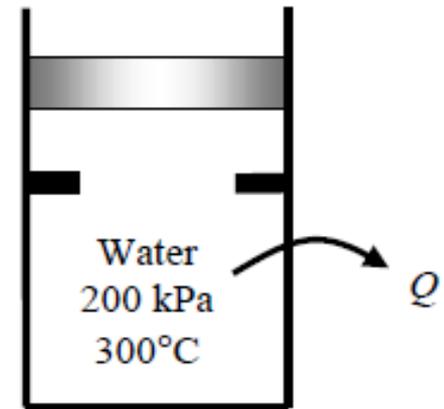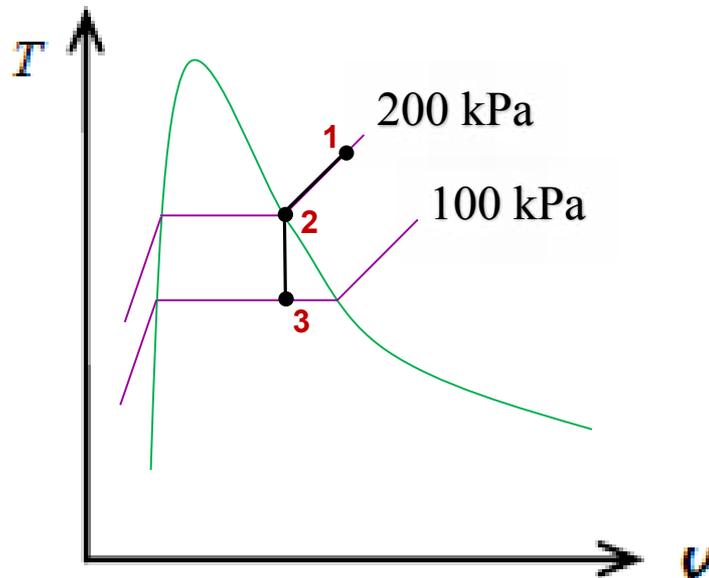
The Ideal Gas Equation of State

Equation of state: Any equation that relates the pressure, temperature, and specific volume of a substance.

Ideal gas equation of state

This equation predicts the *P-v-T* behavior of a gas quite accurately within some properly selected region.

$$Pv = RT \qquad \text{with} \quad R = \frac{R_u}{M}$$

v : Specific volume (m^3/kg)

R: Gas constant (kJ/kg-K)

R_u: Universal gas constant (8.3145 kJ/kmol-K)

M: Molar mass or Molecular weight (kg/kmol), **Table A-1**

Molar mass: *M* can simply be defined as *the mass of one mole* (also called a *gram-mole*, abbreviated gmol) *of a substance in grams*, or *the mass of one kmol* (also called a *kilogram-mole*, abbreviated kgmol) *in kilograms*.
Simply it's value is equal to the molecular weight of the substance

The Ideal Gas Equation of State

Ideal gas equation of state: **(Other Forms)**

$$PV = NR_uT$$

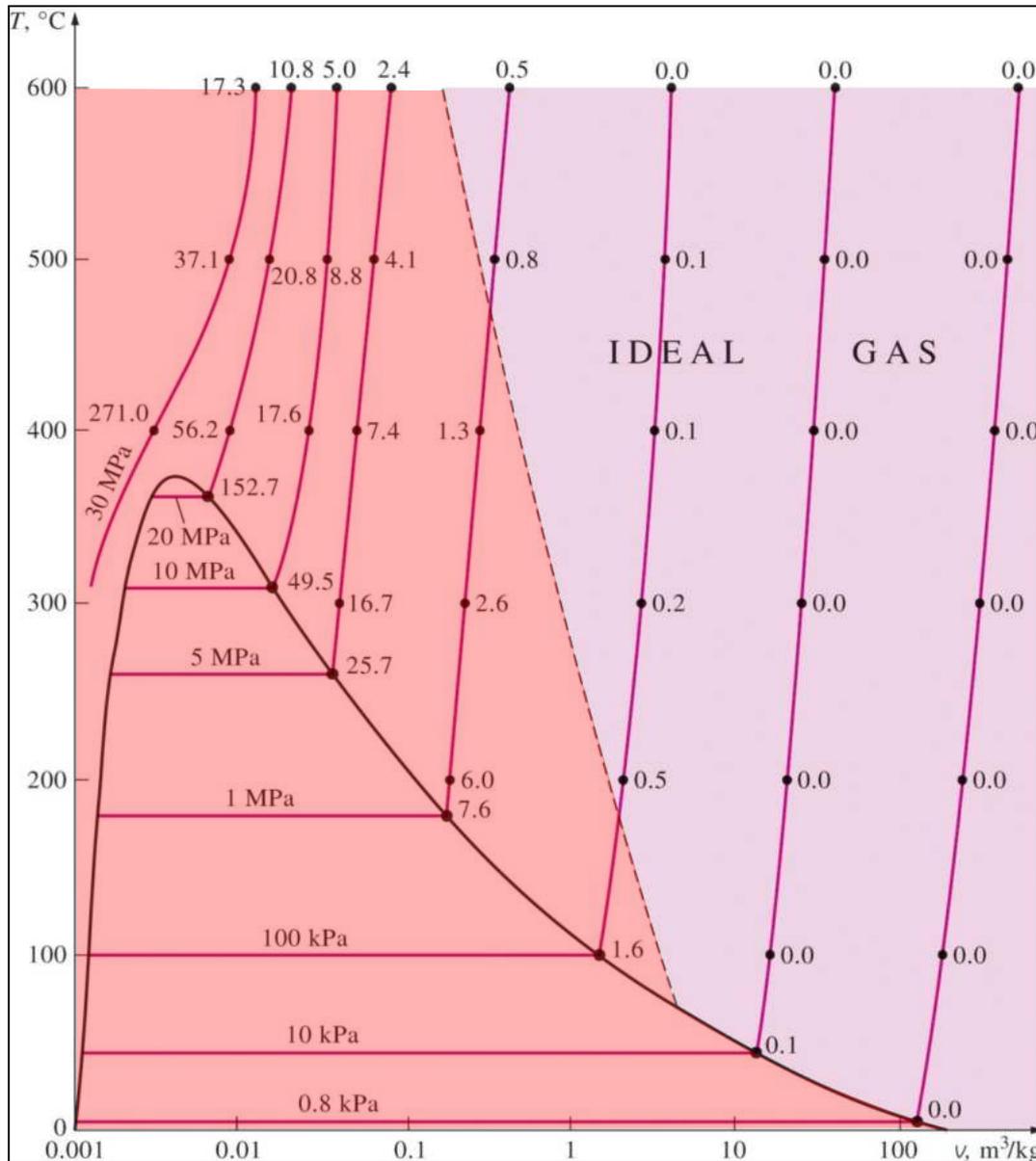Since $m = M \times N$

$$PV = mRT$$

Using $v = V / m$

$$Pv = RT$$ or $$P = \rho RT$$

On writing for two states (with a fixed mass)

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Validity of Ideal Gas Equation for Water Vapor

Percentage of error ($[|v_{table} - v_{ideal}|/v_{table}] \times 100$) involved in assuming steam to be an ideal gas

At pressures below 10 kPa, water vapor can be treated as an ideal gas, *regardless of its temperature*, with negligible error (less than 0.1 percent).

At higher pressures, however, the ideal gas assumption yields unacceptable errors, particularly in the vicinity of the critical point and the saturated vapor line.

Applicability Factors:
Low density i.e.:
Low P @ any T
High P @ high T
(Far from Critical Point)

Validity of Ideal Gas Equation

Ideal gas equation of state:

The ideal-gas relation often is not applicable to real gases; thus, care should be exercised when using it.

Real gases behave as an ideal gas at low densities (i.e., low pressure, high temperature because *molecules are far away*).

Question: What is the criteria for low pressure and high temperature?
Answer: The pressure or temperature of a gas is high or low relative to its critical temperature or pressure.

Gases deviate from the ideal-gas behavior the most in the neighborhood of the critical point.
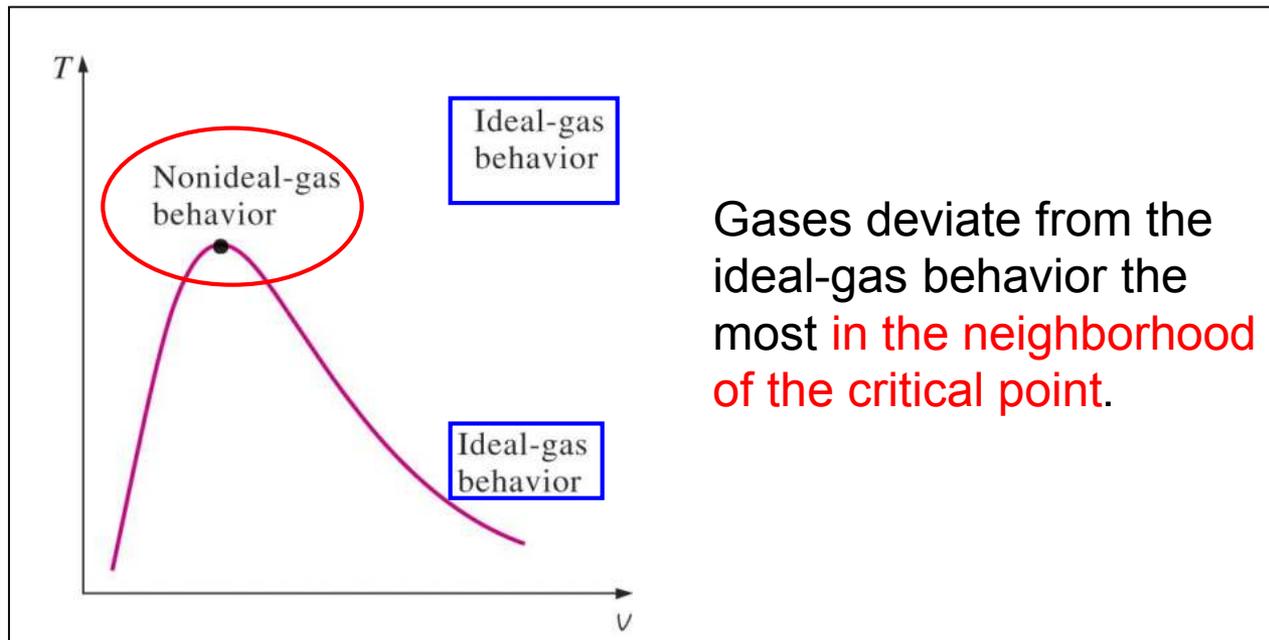
Compressibility Factor

Compressibility factor Z:

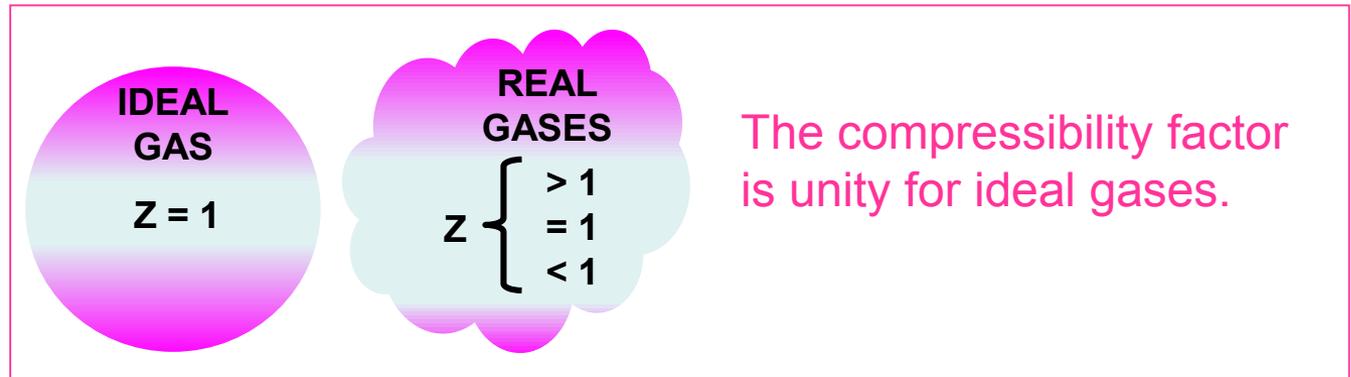A factor that accounts for the deviation of real gases from ideal-gas behavior at a given temperature and pressure.

$$Pv = RT \Rightarrow \frac{Pv}{RT} = 1 \begin{cases} & \text{This is an approximation.} \\ & \text{Experimentally this ratio may not be equal to 1} \end{cases}$$

We define:

$$Z = \frac{Pv}{RT}$$

Also:

$$Z = \frac{v_{actual}}{v_{ideal}}$$

IDEAL GAS
Z = 1

REAL GASES

$$Z \begin{cases} > 1 \\ = 1 \\ < 1 \end{cases}$$

The compressibility factor is unity for ideal gases.

The farther away Z is from unity, the more the gas deviates from ideal-gas behavior.
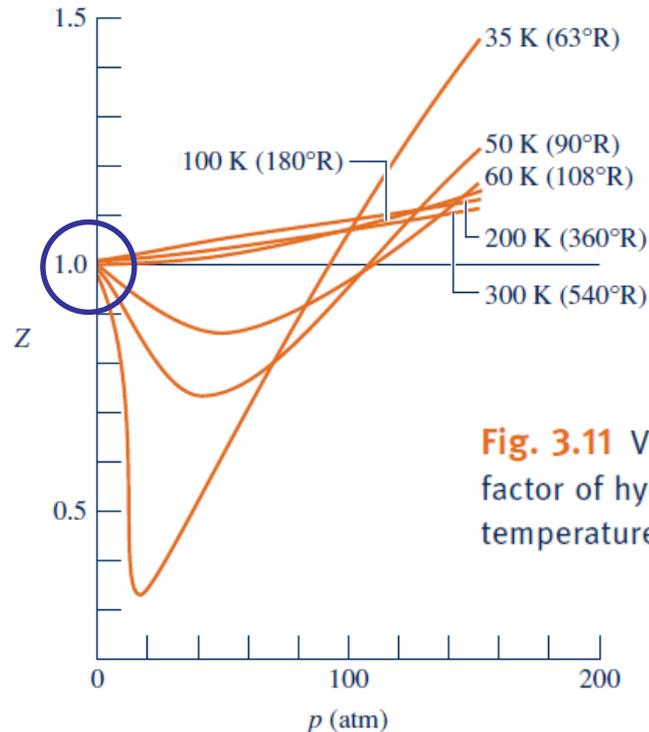
Compressibility Chart

Compressibility factor Z:

How to find Compressibility Factor ?

• *Experimentally v at a given temperature T for various P,*

• Record in a table

@ given temperature T

P_{exp}	v_{exp}	$z = \dfrac{P_{exp} v_{exp}}{R T_{exp}}$

Repeat for various T

Fig. 3.11 Variation of the compressibility factor of hydrogen with pressure at constant temperature.

If P → 0 then Z→ 1 @ all T because at low pressure molecules are far away

Problem: Different compressibility chart for Different Gases

Generalized Compressibility Chart

Compressibility factor _Z_:

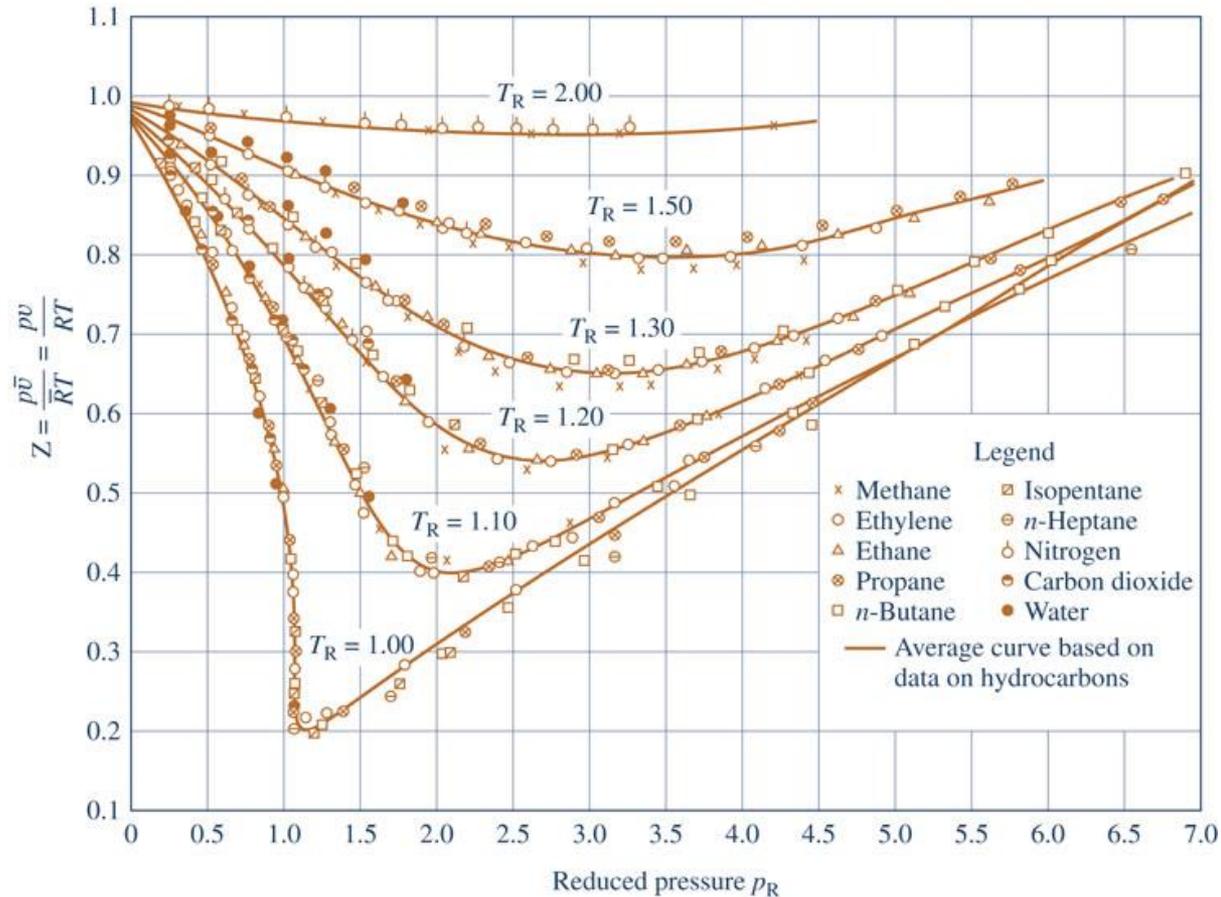Compressibility Chart developed with _Reduced Temperature and Reduced Pressure_

Table A-1:
T_c and P_c

$$T_R = \frac{T}{T_c} \;\; ; \;\; P_R = \frac{P}{P_c}$$

The _Z_ factor for various gases is approximately the same at the same reduced pressure and temperature.

At T_R = 1.0, the compressibility factor varies between 0.2 and 1.0. Less variation is observed as T_R takes higher values.


Chart axes: $Z = \frac{p\bar{v}}{\bar{R}T} = \frac{pv}{RT}$ (vertical), Reduced pressure p_R (horizontal)

Curves labeled: $T_R = 2.00$, $T_R = 1.50$, $T_R = 1.30$, $T_R = 1.20$, $T_R = 1.10$, $T_R = 1.00$

Legend:
× Methane   ⊠ Isopentane
○ Ethylene   ⊖ n-Heptane
△ Ethane   ◌ Nitrogen
⊗ Propane   ⊖ Carbon dioxide
□ n-Butane   ● Water
— Average curve based on data on hydrocarbons

Generalized Compressibility Chart

Determine the specific volume of **air** at 13.2 MPa and 199 K based on (*a*) the ideal-gas equation, (*b*) the generalized compressibility chart.
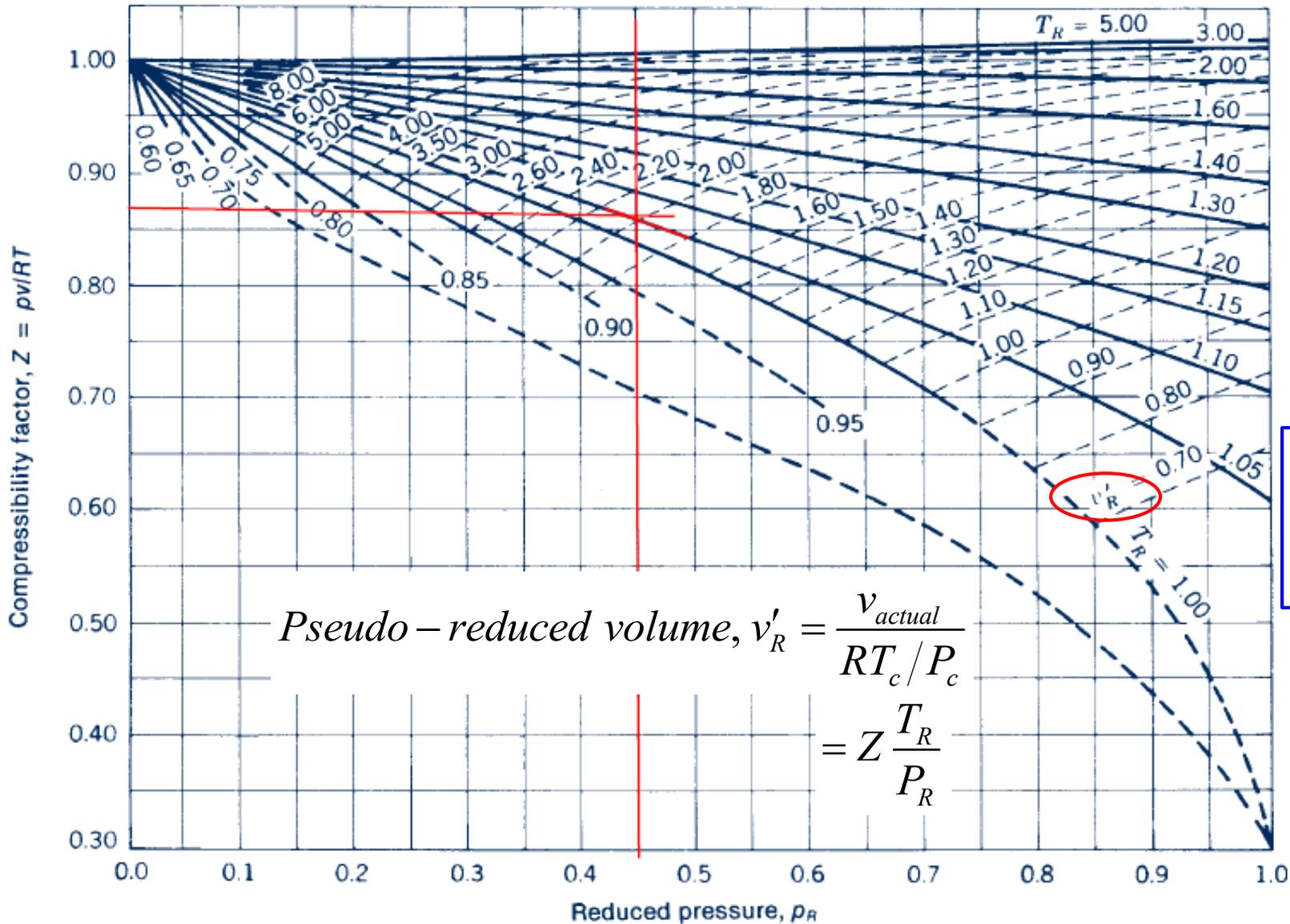
T_R = 199 K/132.5 K = **1.5**, p_R = 13.2 MPa/3.77 MPa = **3.5** where T_c and p_c for air are from **Table A-1**.

$$Z = 0.8$$
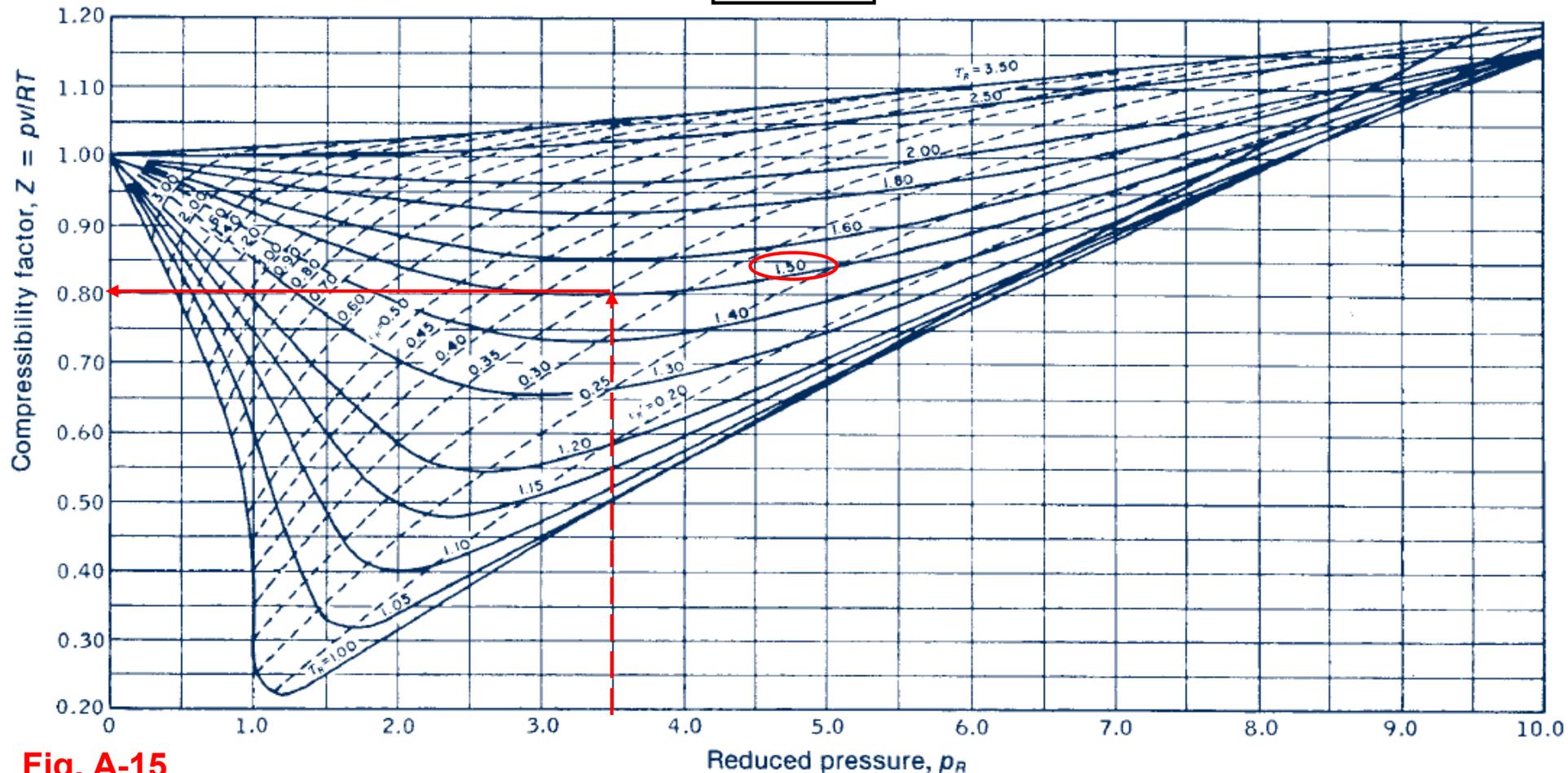
Fig. A-15

Generalized Compressibility Chart

Calculate v'_R in previous problem

$$Pseudo-reduced\ volume,\ v'_R = \frac{v_{actual}}{RT_c/P_c}$$

$$= Z\frac{T_R}{P_R}$$

Figure A-1 Generalized compressibility chart, $p_R \leq 1.0$. *Source*: E. F. Obert, *Concepts of Thermodynamics*, McGraw-Hill, New York, 1960.