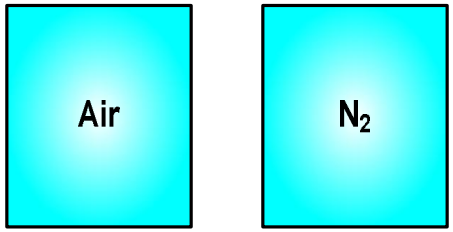
CHAPTER 2

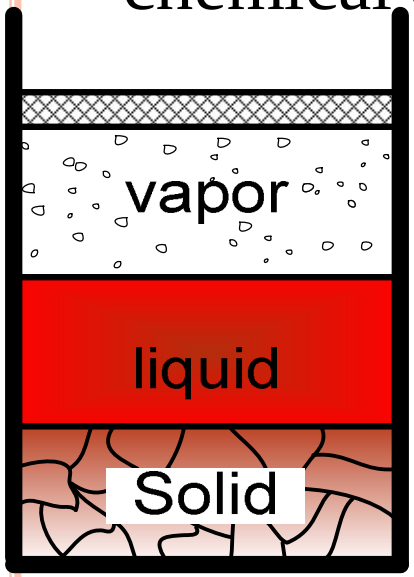
PROPERTIES OF PURE SUBSTANCE

PURE SUBSTANCE

- A substance that has a fixed chemical composition throughout is called a ***pure substance***.
  - Water
  - Nitrogen
  - Air
  - Helium
  - Carbon dioxide



- Pure substance may exist in different phases, but the chemical compositions is the same.



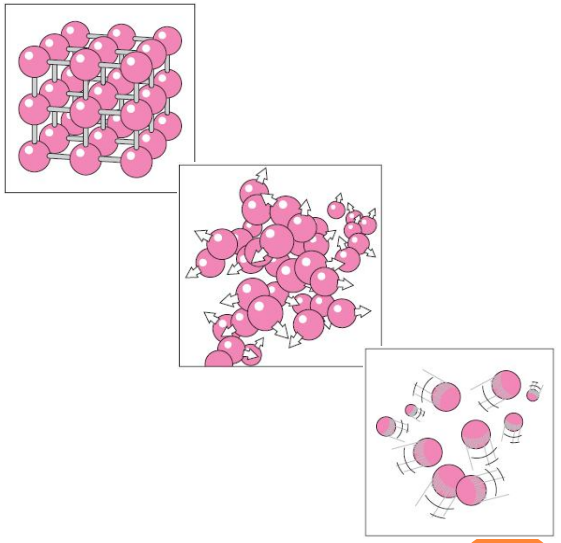
- water made up of two atoms of hydrogen and one atom oxygen. It will have the same composition when in ice, liquid and vapor forms.

State Principle

- An important concept in thermodynamics is the state principle:
- In dealing with a simple compressible substance, the thermodynamic state is completely defined by **specifying two independent intensive properties**.
- The concept of independent properties is particularly important in dealing with substances when more than one phase is present.
- For **example**, temperature and pressure are not independent properties when water (liquid) and steam (vapor) coexist.

CHANGE-PHASE PROCESSES OF PURE SUBSTANCE

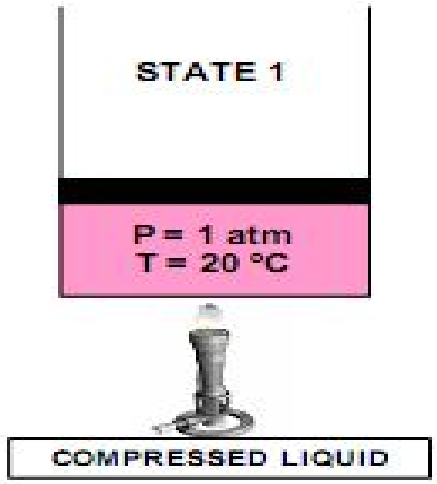
- Under different conditions a substance may appear in different phases. The three principal phases are solid, liquid and gas.
- Considering water, it can be exist as
  - Pure solid phase (ice)
  - Pure liquid phase
  - Pure vapor phase (steam)



- It can also exist as an equilibrium mixture of different

COMPRESSED LIQUID AND SATURATED LIQUID

- Consider the piston-cylinder device containing liquid water at 20^0c and 1 atm pressure.
- Under theses conditions, water exists in the liquid phase, and it is called a **compressed liquid** or **subcooled liquid**, meaning that it is **not about to vaporize**.
- As the temperature rises, the liquid water expands slightly, and so its specific volume increases.

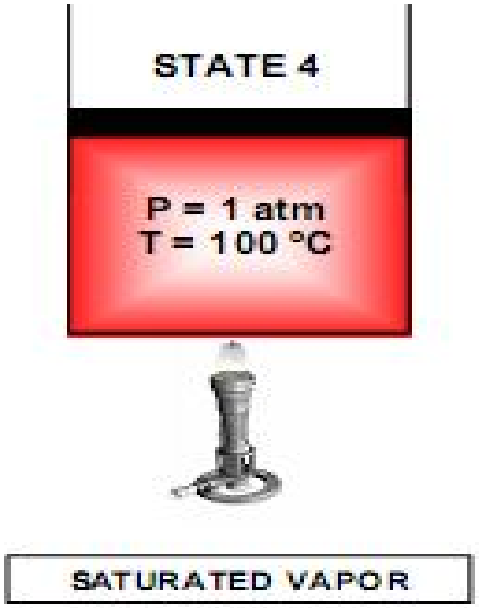


- As more heat is transferred, the temperature will keep rising until it reaches 100^0c.
- At the point, water is still a liquid, but any heat addition, will cause some of the liquid to vaporize.
- A liquid that is **about to vaporize** is called **saturated liquid**.

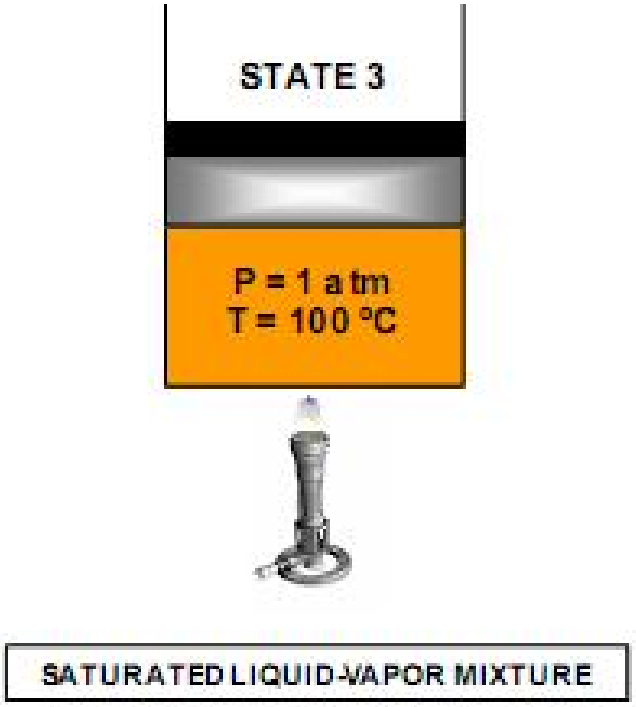


SATURATED VAPOR AND SUPERHEATED VAPOR

- Once boiling starts, the temperature will stop rising until the liquid is completely vaporized (100^0c and 1 atm).
- 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 **saturated vapor**.



- A substance at states between 2 and 4 is often referred to as a **saturated liquid-vapor mixture**,
- since the **liquid and vapor phases coexist in equilibrium** at these states.

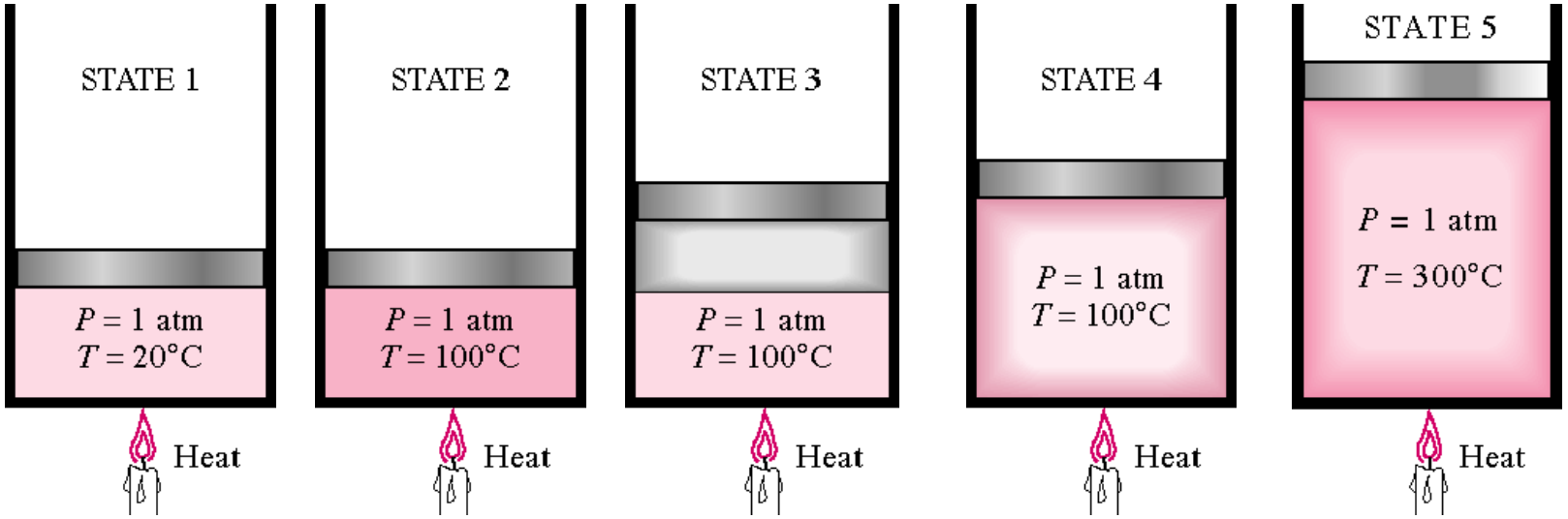


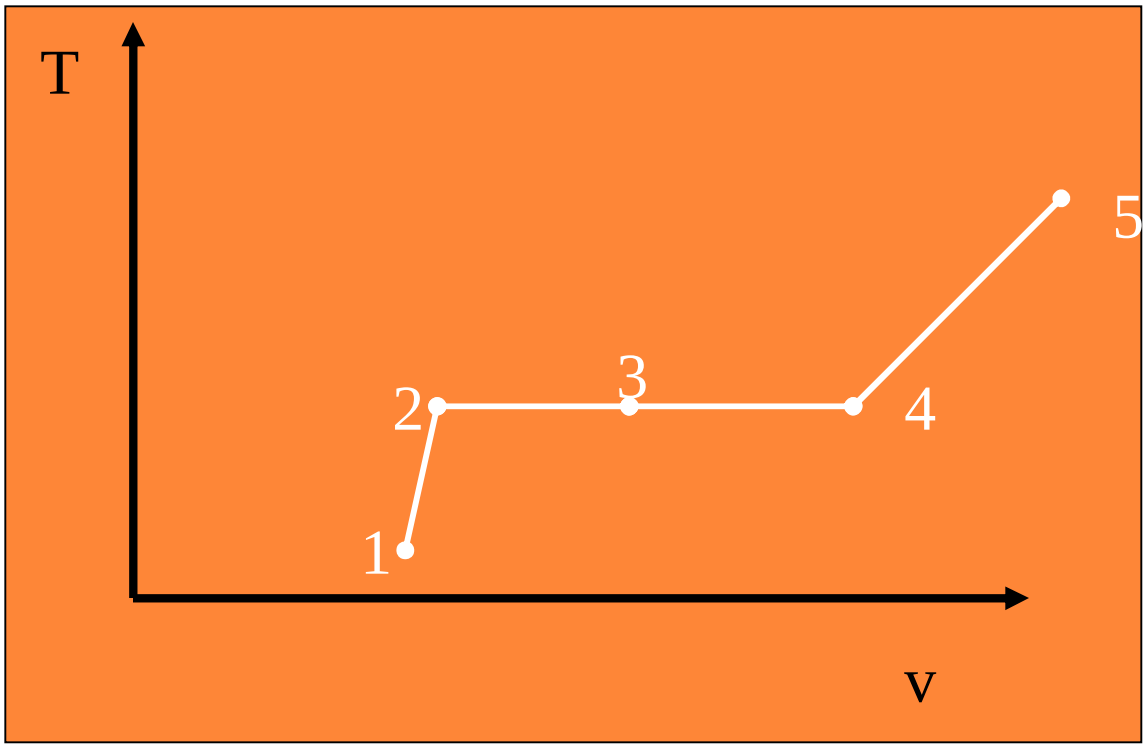
SATURATED LIQUID-VAPOR MIXTURE

- As more heat is added will result in an increase in both the temperature and the specific volume.

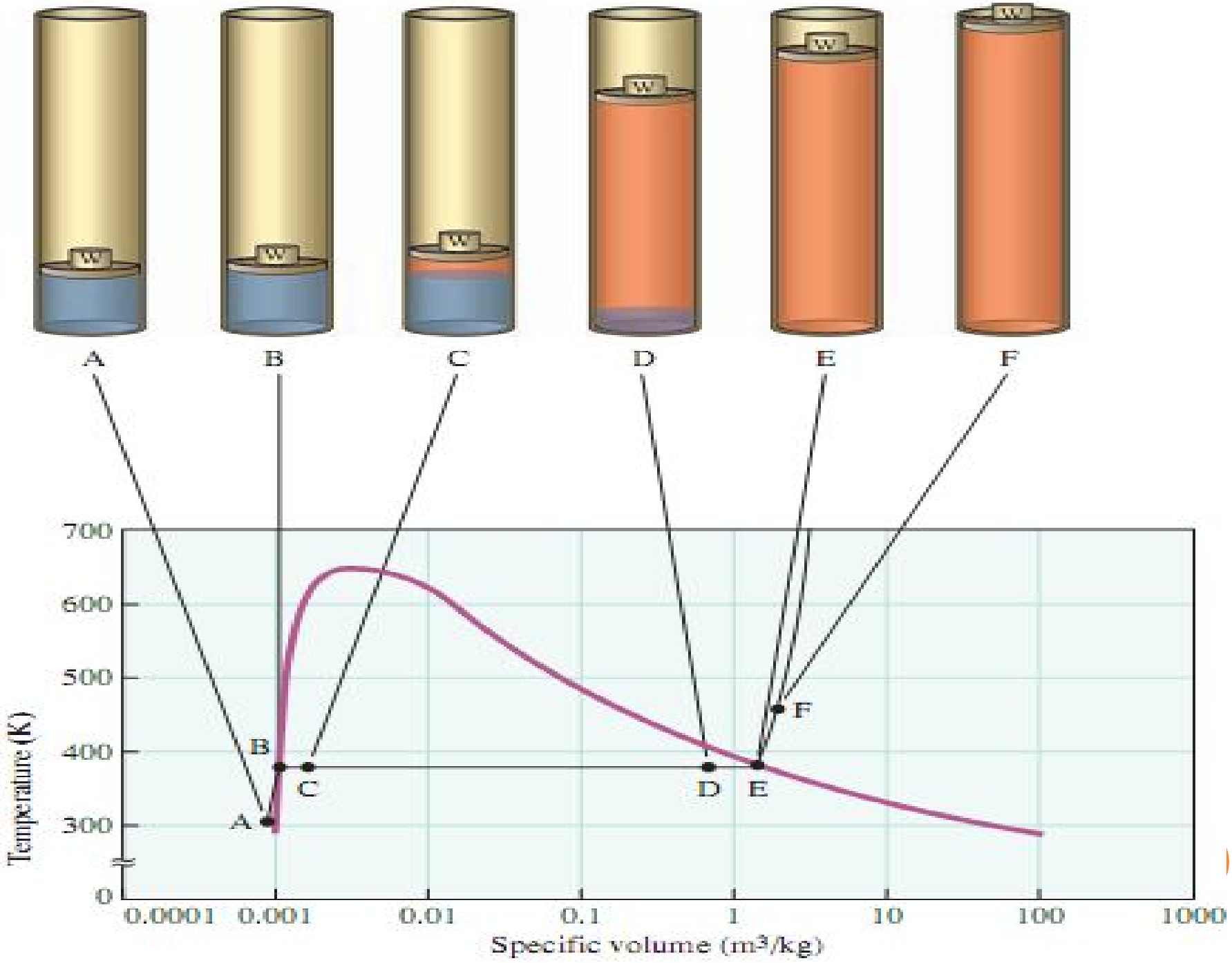
- At the state 5, the temperature of the vapor is, let us say, 300^0c; and if we transfer some heat from the vapor, the temperature may drop somewhat but no condensation will take place as long as the temperature remains above 100^0c (for p= 1 atm).
- A vapor that is **not about to condense** (i.e. not a saturated vapor) is called a **superheated vapor**.

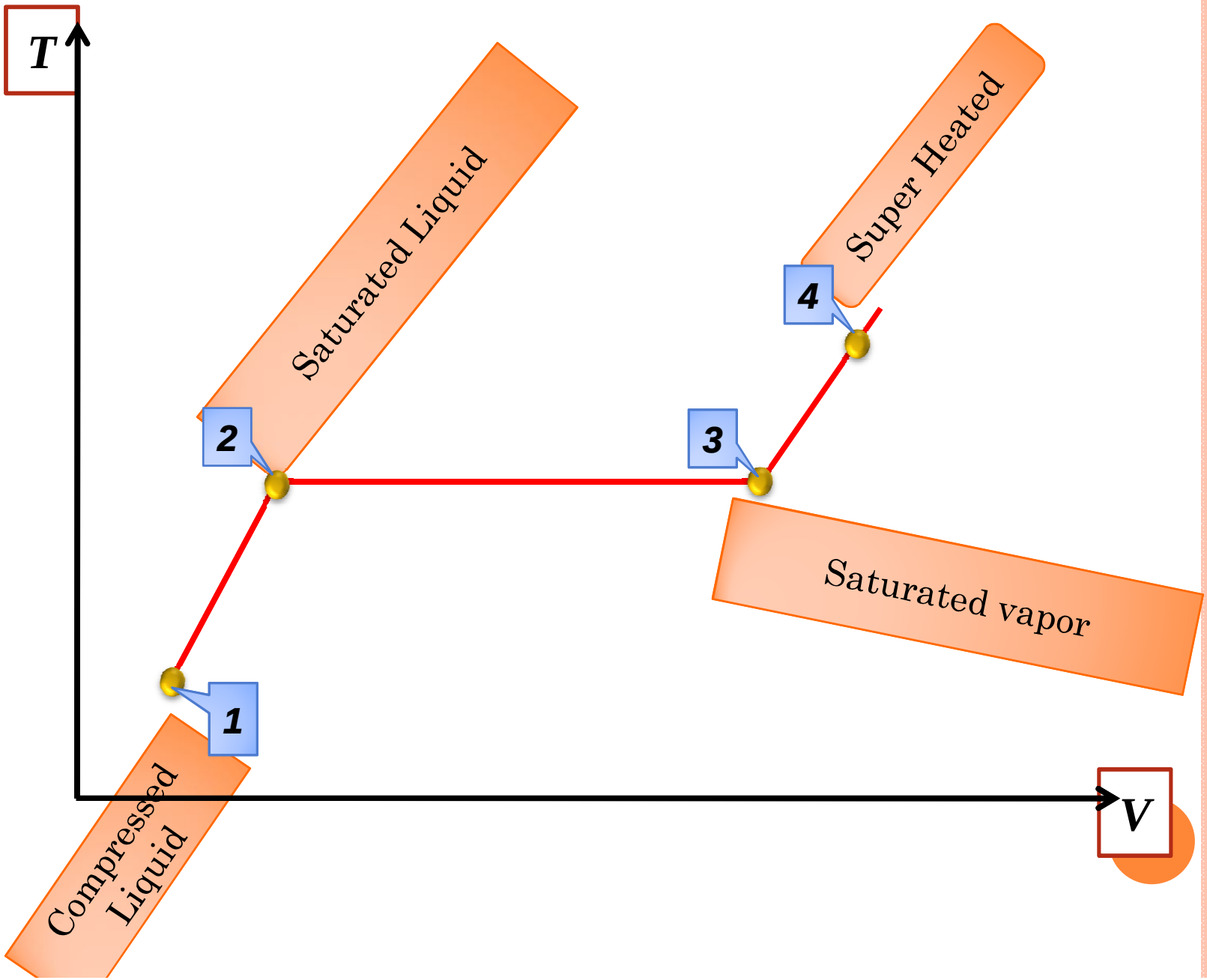


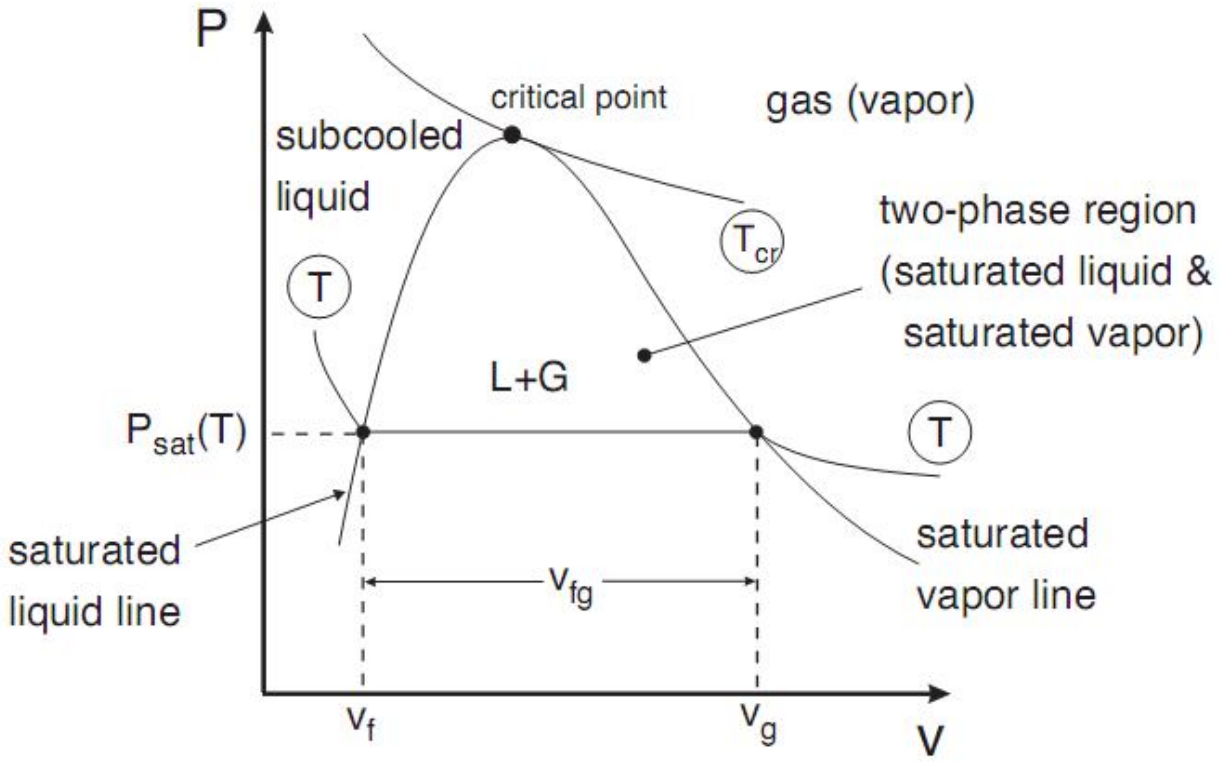




Phase Change Processes on a T-v diagram


W
A
B
C
D
E
F
700
600
500
400
300
0
Temperature (K)
0.0001
0.001
0.01
0.1
1
10
100
1000
Specific volume (m³/kg)


T
Saturated Liquid
Super Heated
4
2
3
Saturated vapor
1
Compressed Liquid
V



SATURATION TEMPERATURE AND SATURATION PRESSURE

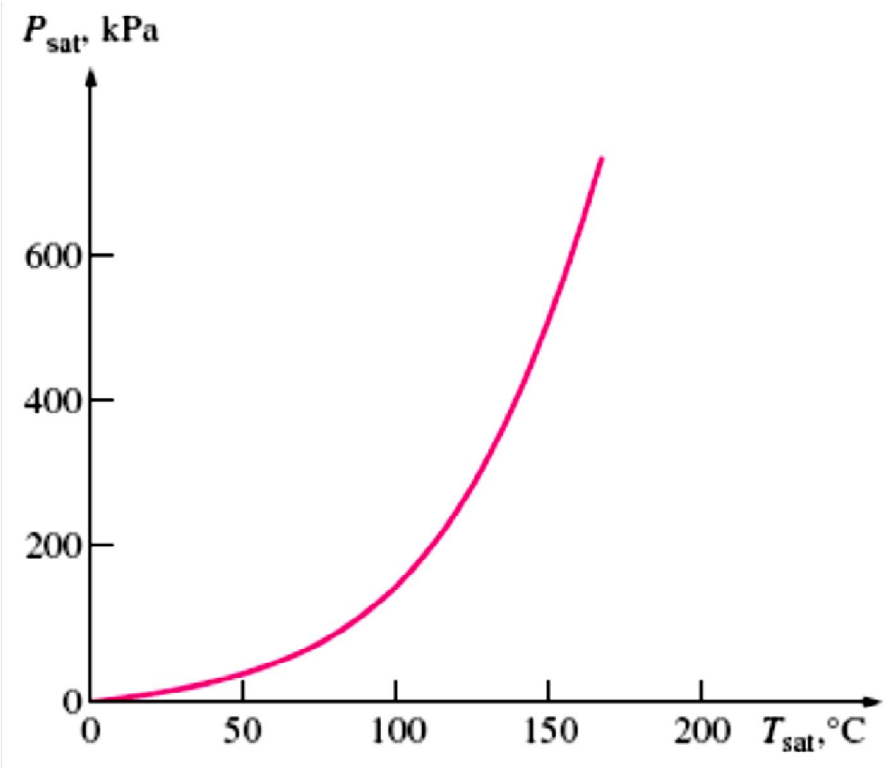
- Water boils at 100^0c is **incorrect.**
- Water boils at 100^0c at 1atm pressure is **correct.**

100^0c 1 atm (101.325kpa)

151.9^0c (50kpa)

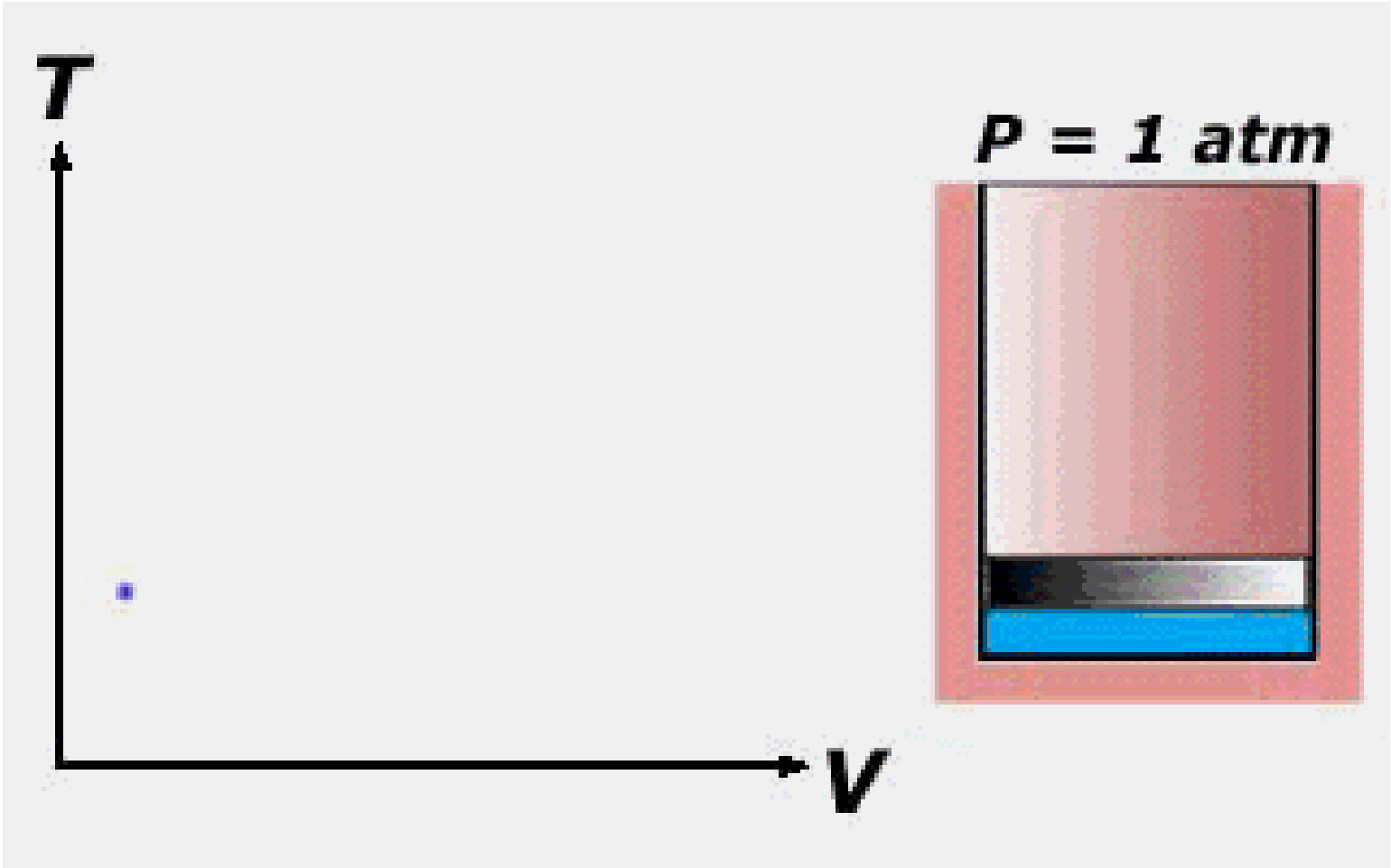
- The temperature at which water starts boiling depends on the pressure, therefore if the pressure is fixed, so is the boiling temperature.
- At a given pressure, the temperature at which a pure substance starts boiling is called the **saturation temperature** (T_{sat}).
- Likewise, at a given temperature, the pressure at which a pure substance starts boiling is called the **saturation pressure** (P_{sat}).

- During a phase change process, pressure and temperature are obviously **dependent** properties, and there is a definite relation between them, that is $T_{sat}=f(P_{sat})$.
- In single phase the two intensive properties (T and p) are independent properties.

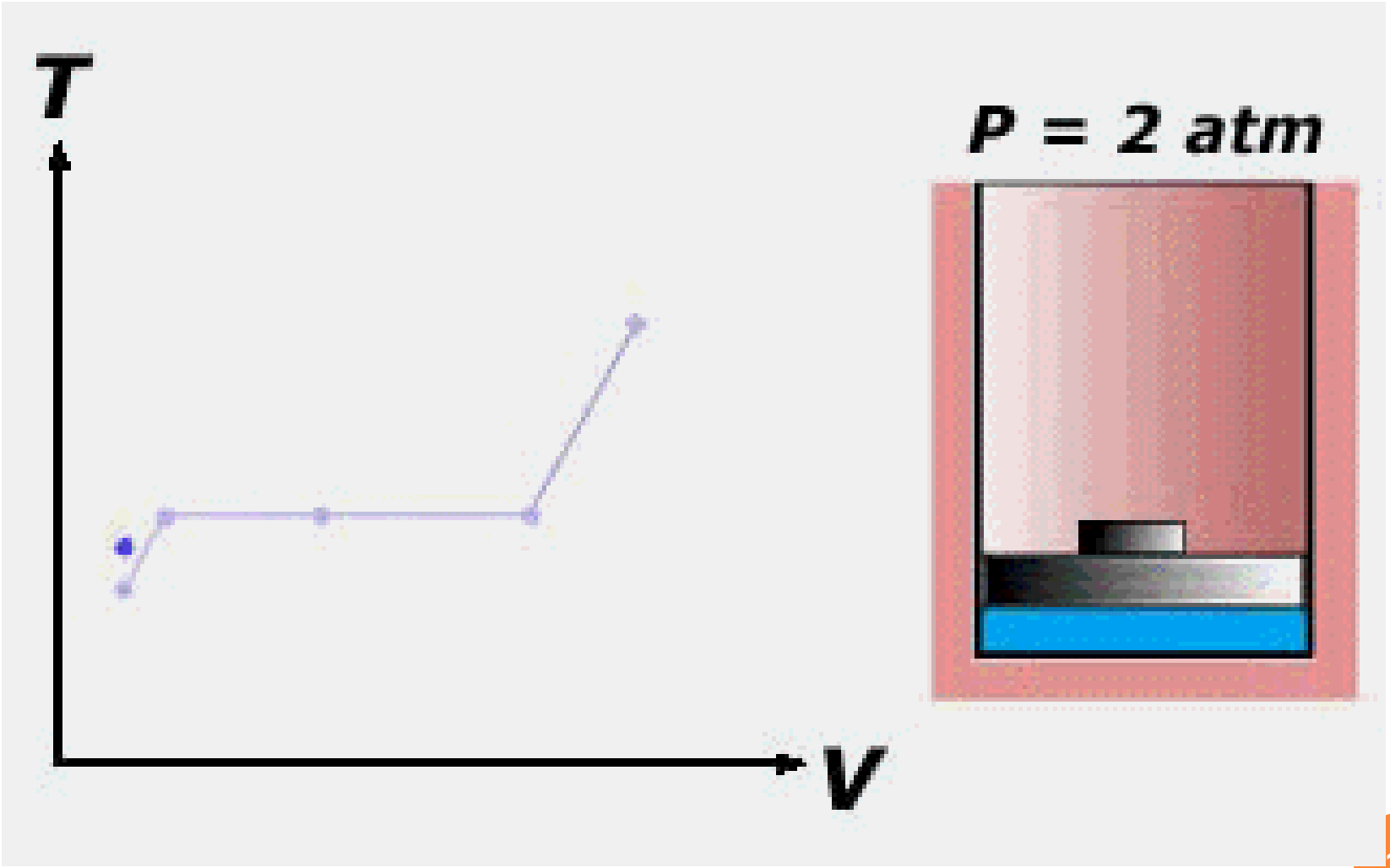


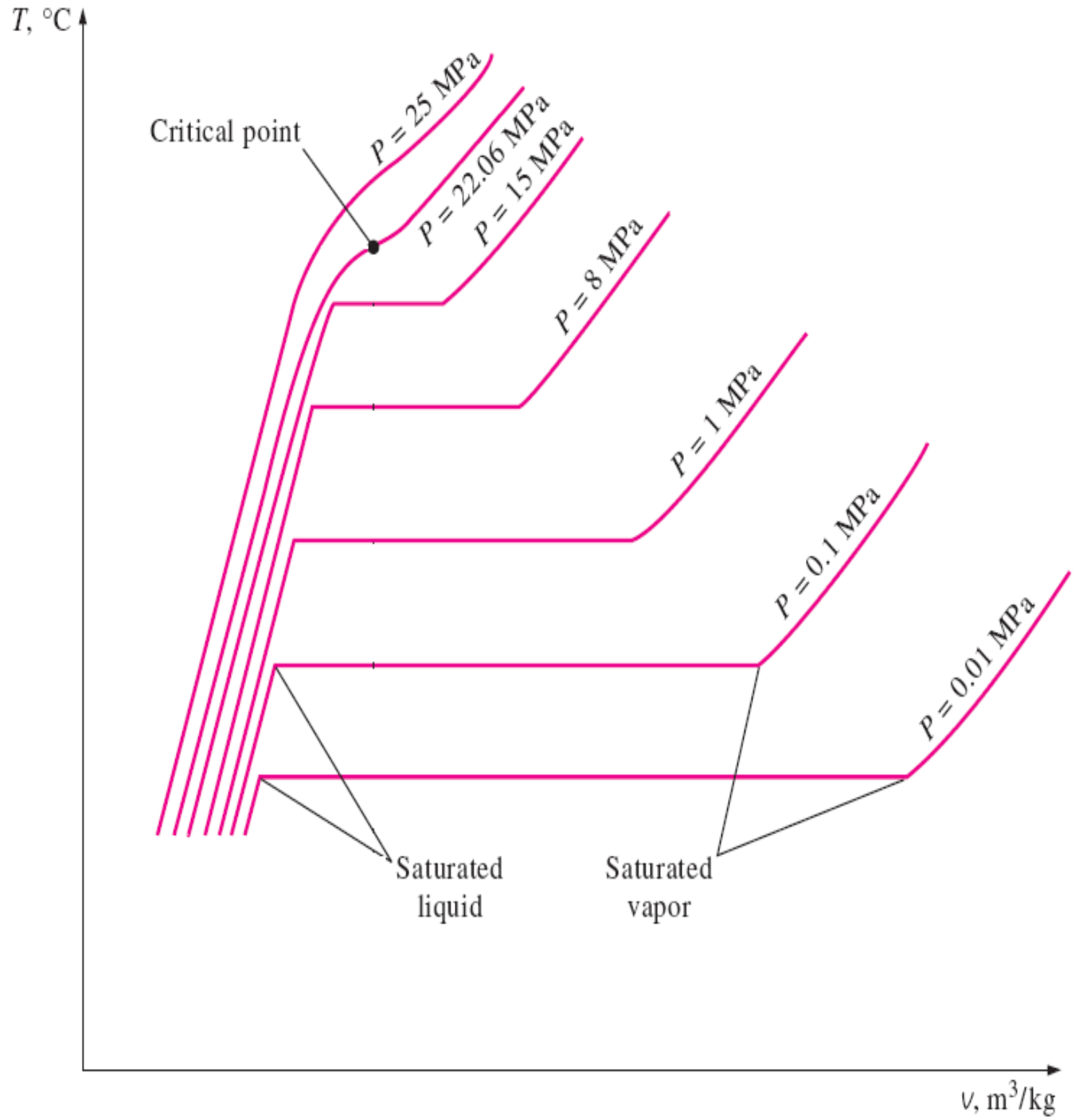
PROPERTY DIAGRAM FOR PHASE CHANGE PROCESSES

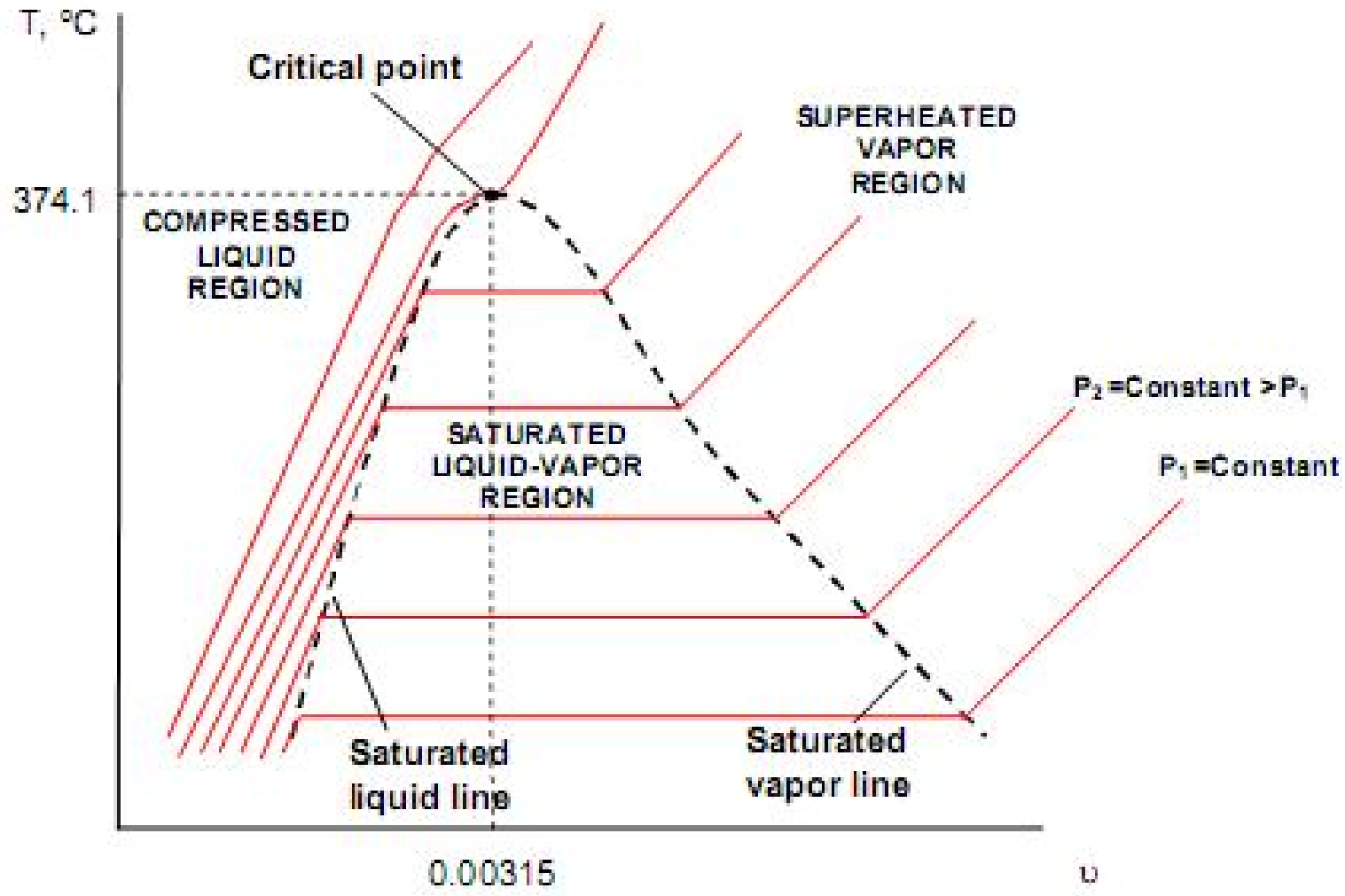
- Constant Pressure Heating in Piston-Cylinder at **P = 1 atm**.



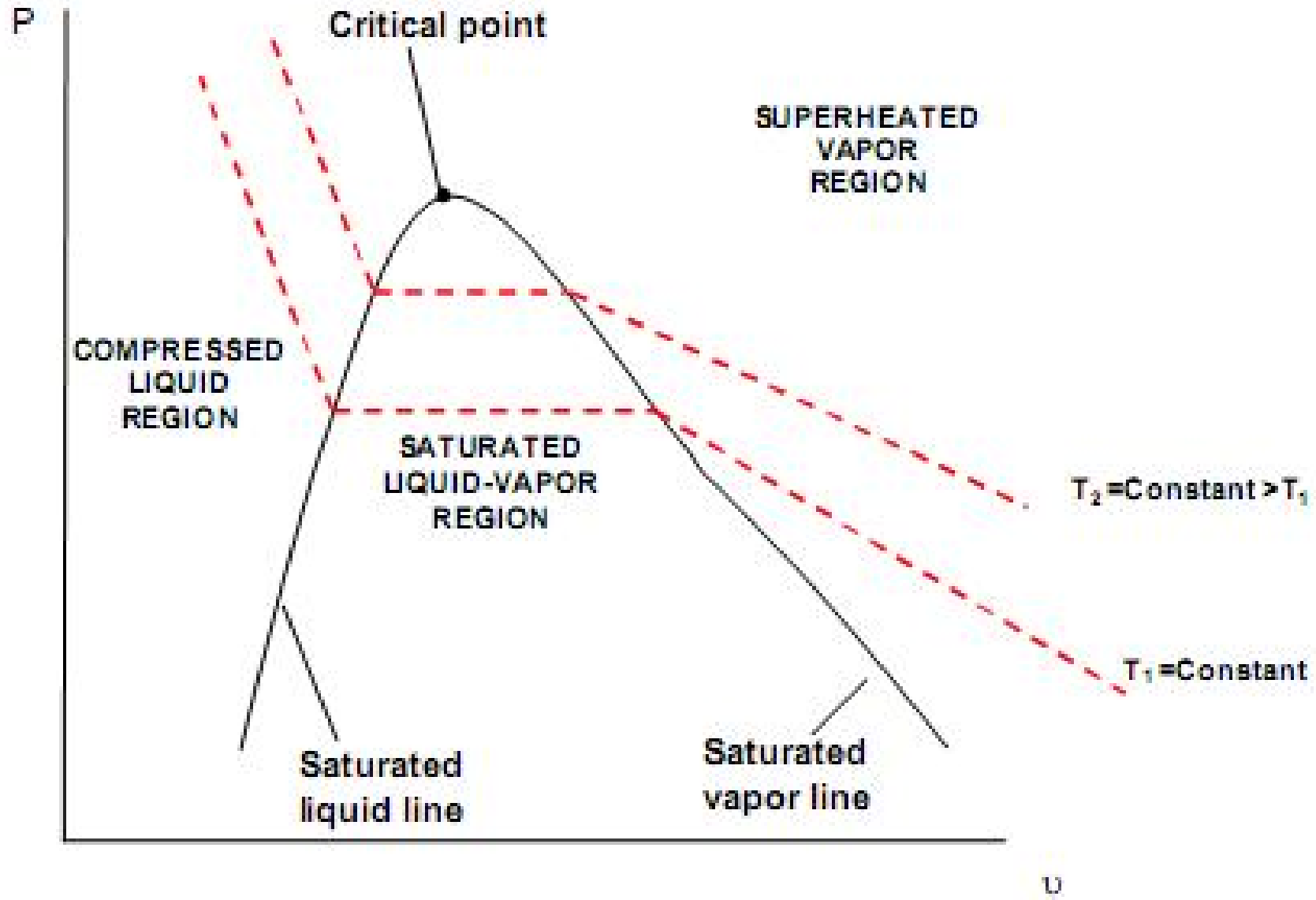
- Constant Pressure Heating in Piston-Cylinder at **P = 2 atm**.

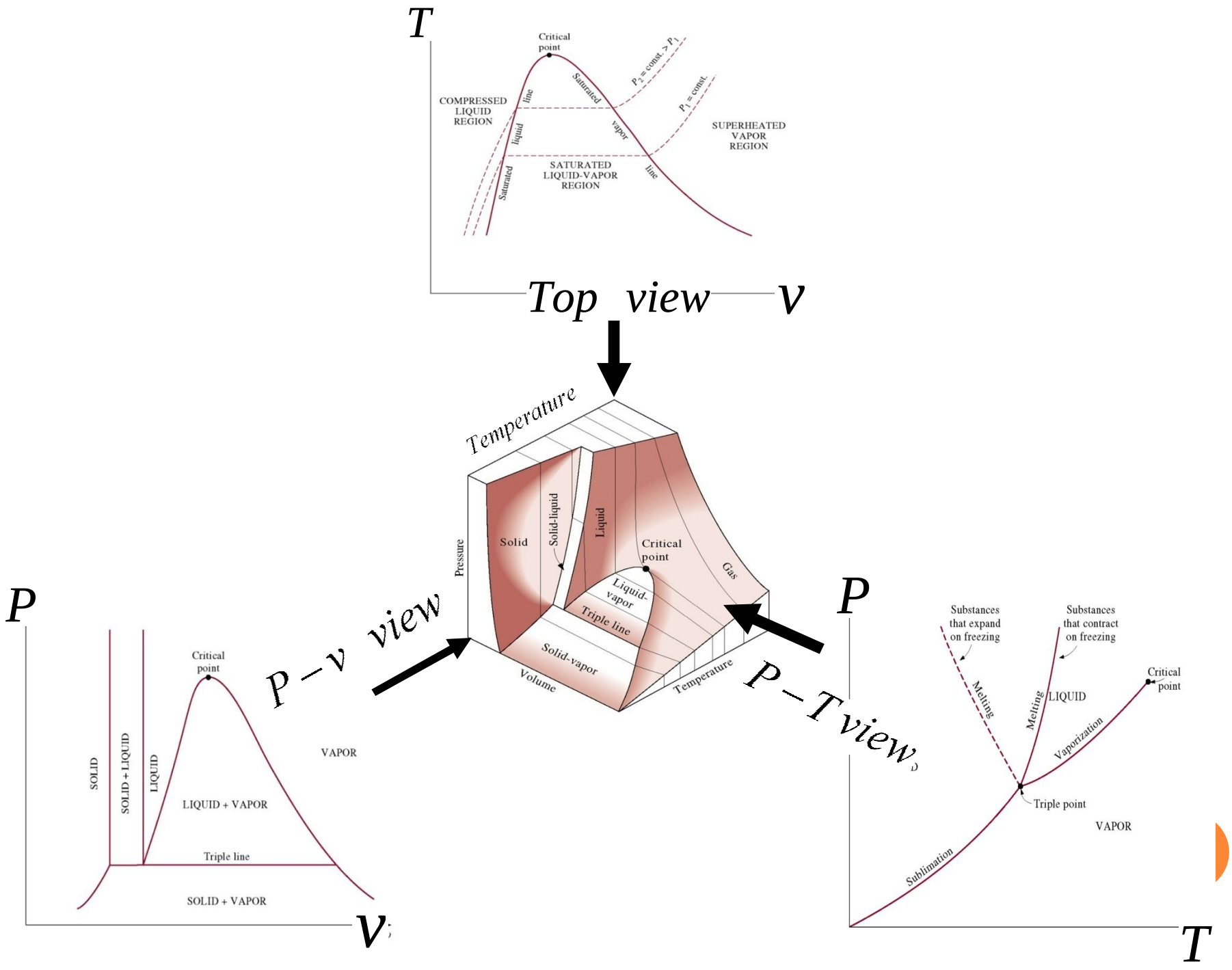



T, °C
Critical point
P = 25 MPa
P = 22.06 MPa
P = 15 MPa
P = 8 MPa
P = 1 MPa
P = 0.1 MPa
P = 0.01 MPa
Saturated liquid
Saturated vapor
v, m³/kg



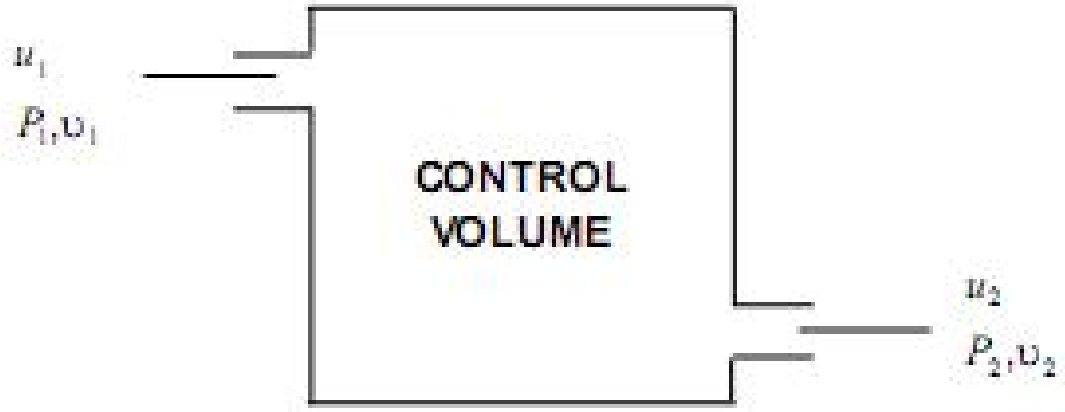
- **Critical point** may be defined as the point at which the saturated liquid and saturated vapor states are **identical**.


P
Critical point
SUPERHEATED
VAPOR
REGION
COMPRESSED
LIQUID
REGION
SATURATED
LIQUID-VAPOR
REGION
T2 =Constant > T1
T1 =Constant
Saturated
liquid line
Saturated
vapor line
υ


T
Critical point
Saturated liquid line
Saturated vapor line
P_2 = const. > P_1
P_1 = const.
COMPRESSED LIQUID REGION
SUPERHEATED VAPOR REGION
SATURATED LIQUID-VAPOR REGION
Top view
v
Temperature
Pressure
Solid
Solid-liquid
Liquid
Critical point
Gas
Liquid-vapor
Triple line
Solid-vapor
Volume
Temperature
P – v view
P – T view
P
Critical point
SOLID
SOLID + LIQUID
LIQUID
LIQUID + VAPOR
Triple line
SOLID + VAPOR
VAPOR
v
P
Substances that expand on freezing
Substances that contract on freezing
Melting
Melting
LIQUID
Critical point
Vaporization
Triple point
VAPOR
Sublimation
T

PROPERTY TABLES

- The properties are frequently presented in the form of tables.
- Enthalpy-A Combination property



- In the analysis of certain types of process, particularly in **power generation** and **refrigeration**, we frequently encounter the combination of properties U+PV.

- For the sake of simplicity and convenience, this combination is defined as a new property, **ENTHALPY**, and given the symbol H:

$$H = U + PV \quad (kJ)$$

$$h = u + P\upsilon \quad (kJ/kg)$$

SATURATED LIQUID AND SATURATED VAPOR STATES

- The properties of saturated liquid and saturated vapor for water are listed as below

Sat.		Specific volume m^3/Kg	
Temp. °C T	Press kPa P_{Sat}	Sat. Liquid υ_f	Sat. Vapor υ_g
85	57.83	0.001033	2.828
90	70.14	0.001036	2.361
95	84.55	0.001040	1.982

Specific temperature

Corresponding saturation pressure

Specific volume of saturated liquid

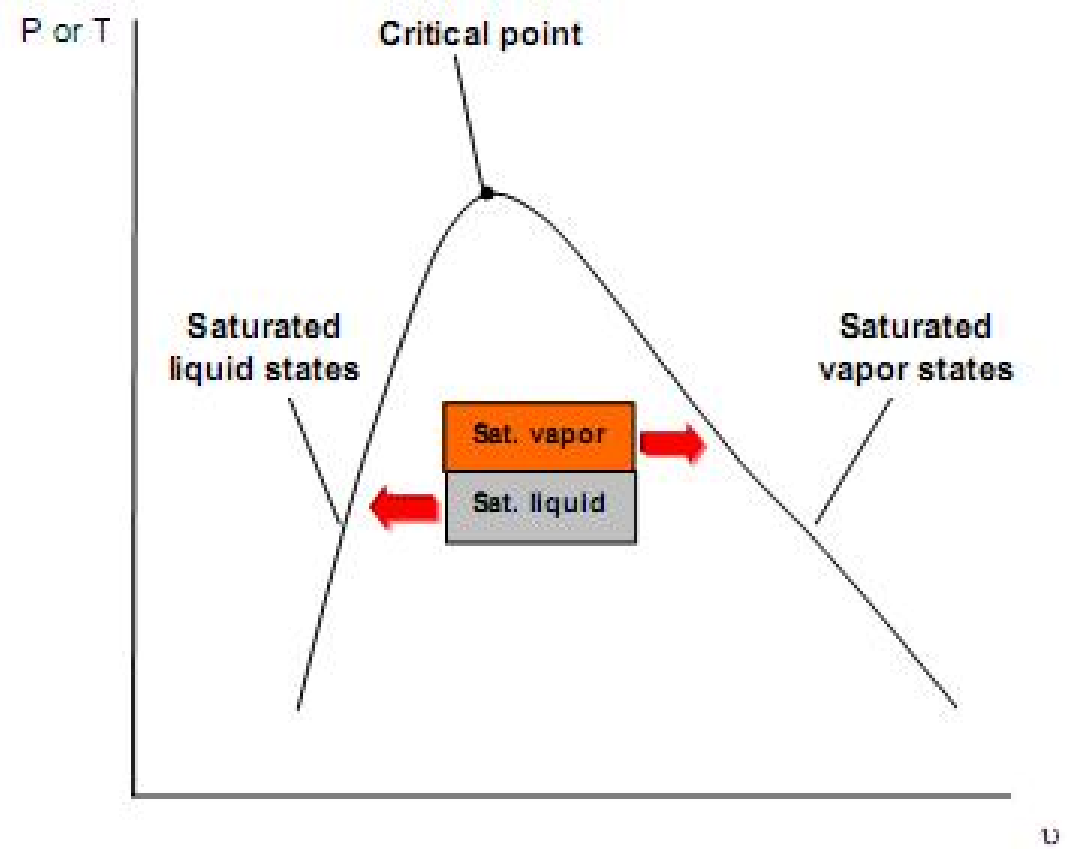
Specific volume of saturated vapor

- The amount of energy absorbed or released during a phase-change process is called the ***latent heat.***
- The quantity h_{fg} is called the **enthalpy of vaporization** (or latent heat of vaporization).
- It represents the amount of energy needed to vaporize a unit mass of saturated liquid at a given temperature or pressure and it is equivalent to the energy released during condensation.
- It decreases as the temperature or pressure increases, and it becomes zero at the critical point.
- The amount of energy absorbed during melting is called the ***latent heat of fusion*** and it is equivalent to the amount of energy released during freezing.

SATURATED LIQUID-VAPOR MIXTURE

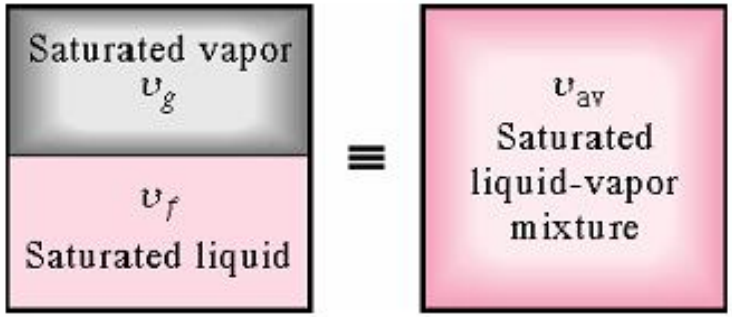
- During a **vaporization process**, a substance exists as part liquid and part vapor. That is, it is a mixture of saturated liquid and saturated vapor.
- To analyze this mixture property, we need to know the proportions of liquid and vapor phases in the mixture.
- This done by defining a new property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

$$x = \frac{m_{vapor}}{m_{total}}$$ Where: $$m_{total} = m_{liquid} + m_{vapor} = m_f + m_g$$



- The quality of a system that consist of **SATURATED LIQUID** is 0 (or 0 percent), and the quality of a system consisting of **SATURATED VAPOR** is 1 **(**100**%).**

- 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 v is the sum of these two:



$$V = V_f + V_g$$

$$V = mv \rightarrow m_t v_{av} = m_f v_f + m_g v_g$$

$$m_f = m_t - m_g \rightarrow m_t v_{av} = (m_t - m_g) v_f + m_g v_g$$

- Dividing by m_t yields

$$v_{av} = (1 - x)v_f + xv_g$$

$$x = m_g / m_t$$

$$v_{av} = v_f + xv_{fg} \ (m^3/kg)$$

$$v_{fg} = v_g - v_f$$

$$x = \frac{v_{av} - v_f}{v_{fg}}$$

Example

- A rigid tank contains 3 kg of (liquid and vapor) at a quality of 0.6. The specific volume of the liquid is and the specific volume of the vapor is Determine the :-
  - ✓ mass of the vapor,
  - ✓ mass of the liquid, and
  - ✓ specific volume of the mixture.

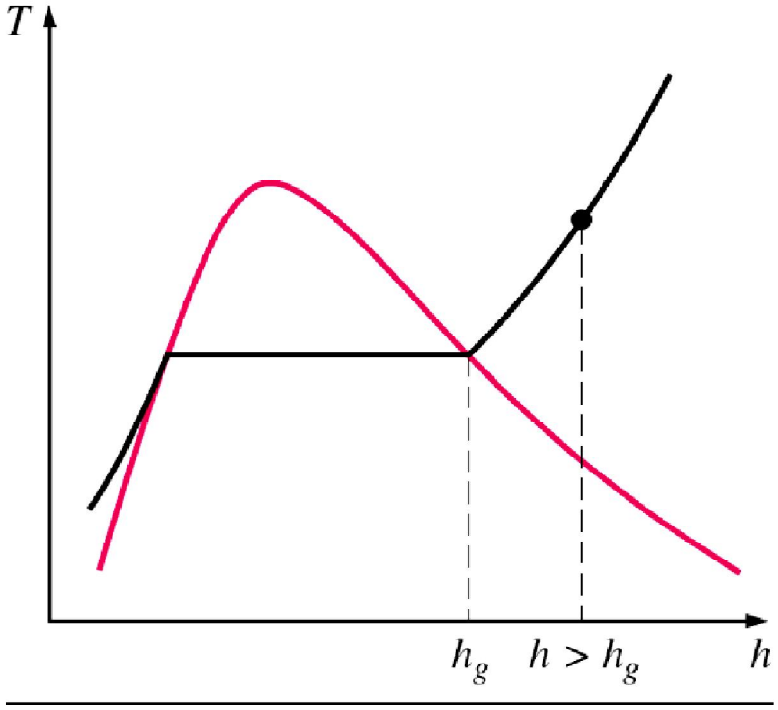
- This analysis given above can be repeated for internal energy and enthalpy with the following results:

$$u_{av} = u_f + xu_{fg} \quad \text{(kJ/kg)}$$

$$h_{av} = h_f + xh_{fg} \quad \text{(kJ/kg)}$$

SUPERHEATED VAPOR ($T>T_{sat}$)

- In the region to the right of the saturated vapor line, a substance exists as superheated vapor.
- the superheated region is a single phase region (vapor phases only).
- At pressures sufficiently below the critical pressure ($p<p_{cr}$) or temperatures sufficiently above the critical temperature ($T>T_{cr}$), a superheated vapor can be approximated as an **IDEAL GAS**.



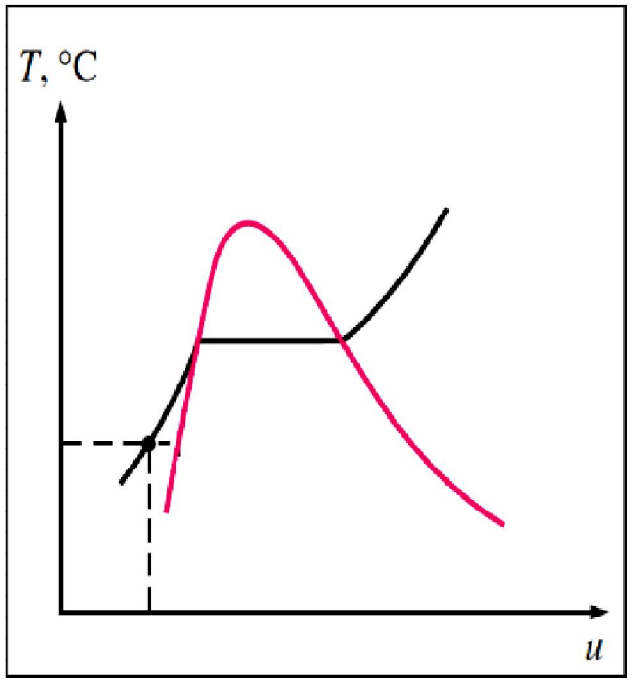
T °C	v m³/kg	u kJ/kg	h kJ/kg	s kJ/kg·K
	P = 0.05 MPa (81.32°C)			
Sat.	3.2403	2483.2	2645.2	7.5931
100	3.4187	2511.5	2682.4	7.6953
150	3.8897	2585.7	2780.2	7.9413
200	4.3562	2660.0	2877.8	8.1592
250	4.8206	2735.1	2976.2	8.3568
300	5.2841	2811.6	3075.8	8.5387
400	6.2094	2968.9	3279.3	8.8659
500	7.1338	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

SUPERHEATED VAPOR ($T>T_{sat}$)

- Compared to saturated vapor, superheated vapor is characterized by
  - Lower pressures ($P < P_{sat}$ at a given T)
  - Higher temperatures ($T > T_{sat}$ at a given P)
  - Higher specific volumes ($v > v_g$ at a given P or T)
  - Higher internal energies ($u > u_g$ at a given P or T)
  - Higher enthalpies ($h > h_g$ at a given P or T)

COMPRESSED LIQUID

- The properties of compressed liquid are relatively **independent of pressure**.
- Increasing the pressure of a compressed liquid 100 times often causes properties to change less than 1 percent.
- The property most affected by pressure is enthalpy.
- In the absence of compressed liquid data, a general approximation is to **treat compressed liquid as saturated liquid at the given temperature**.



COMPRESSED LIQUID

- In general, a compressed liquid is characterized by
  - higher pressure($P > P_{sat}$ at a given T)
  - Lower temperatures ($T < T_{sat}$ at a given P)
  - Lower specific volumes ($v < v_f$ at a given P or T)
  - Lower internal energies ($u < u_f$ at a given P or T)
  - Lower enthalpies ($h < h_f$ at a given P or T)
- This is because the compressed liquid properties depend on temperature more strongly that they do on pressure. Thus

$$y = y_{f@T}$$

How to Choose the Right Table

- 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,

$$\text{Is } v < v_f \text{ ?}$$

$$\text{Is } v_f < v < v_g \text{ ?}$$

$$\text{Is } v_g < v \text{?}$$

- If the answer to the first question is yes, the state is in the ***compressed liquid region.***
- If the answer to the second question is yes, the state is in the ***saturation mixture region.***
- If the answer to the third question is yes, the state is in the ***superheated region***

Example

Determine Phase(state) of water at each of the following points

a) $120^{o}C$, 100kPa — Super heated

b) 350kPa, $0.4992 m^3/kg$ — Saturated L.V Mixture

c) $150^{o}C$, $0.4992 m^3/kg$ — Super heated

d) 0.2MPa, $110^{o}C$ — Compressed liquid

Example

- Determine the internal energy of compressed liquid water at 80°C and 5 MPa, using
  a) data from the compressed liquid table and
  b) saturated liquid data.

What is the error involved in the second case?

Example

- Determine the missing properties and the phase descriptions in the following table for water

	T, °C	P, kPa	u, kJ/kg	x	Phase description
(*a*)		200		0.6	
(*b*)	125		1600		
(*c*)		1000	2950		
(*d*)	75	500			
(*e*)		850		0.0	

Example

- A closed, rigid container of volume $0.5m^3$ is placed on a hot plate. Initially the container holds a two-phase mixture of saturated liquid water and saturated vapor at p_1 = 1 bar with a quality of 0.5. after heating, the pressure in the container is p_2 = 1.5 bar . Indicate the initial and final states on a T-v diagram, and determine

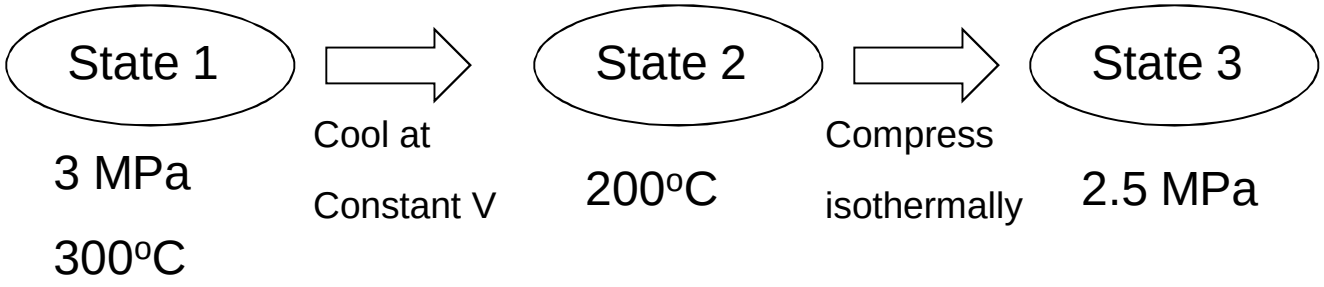
a) The temperature at each state

b) The mass of vapor present at each state

c) If heating continues, determine the pressure, in bar, when the container holds only saturated vapor.

Example:

- A cylinder-piston assembly initially contains water at 3 MPa and 300°C. The water is cooled at constant volume to 200 °C, then compressed isothermally to a final pressure of 2.5 MPa. Sketch the process on a T-v diagram and find the specific volume at the 3 states.



Example

- Heat is isothermally transferred into a piston-cylinder device containing water at 100^0C, 400 kPa until the pressure drops to 50 kPa. Draw a T - ν diagram with respect to the saturation lines for this process. Indicate the initial and final states and the direction of the process. Draw and label the temperature lines and insert values for T_1, T_2, T_{sat} , P_1, P_2, ν_1, ν_2, ν_f , and ν_g.

THE IDEAL-GAS EQUATION OF STATE

- Any equation that relates the **pressure**, **temperature** and **specific volume** of a substance is called **equation of state**.
- The simplest and the best known equation of state for substances in the gas phase is **the ideal-gas equation of state**.

$$P = R\left(\frac{T}{\upsilon}\right)$$

$$P\,\upsilon = RT$$

- Where the constant of proportionality R is called the **gas constant**.
- Equation above is called the **ideal-gas equation of state**, or simply the **ideal-gas relation**, and a gas that obeys this relation is called an **ideal gas**.
- In this equation, p is absolute pressure, T is the absolute temperature and v is the specific volume.
- The gas constant R is different for each gas and is determined from

$$R = \frac{R_u}{M} \quad \left[\text{kJ}/(\text{kg.K}) \text{ or } \text{kPa}.\text{m}^3/(\text{kg.K})\right]$$

- Where R_u is the **universal gas constant** and M is the **molar mass** (also called molecular weight) of the gas.
- The constant R_u is the same for all substance, and its value is

$$R_u = \begin{cases} 8.314\ \text{kJ/(kmol.K)} \\ 8.314\ \text{kPa.m}^3\text{/(kmol.K)} \\ 0.08314\ \text{bar.m}^3\text{/(kmol.K)} \\ 1.986\ \text{Btu/(lbmol.R)} \\ 10.73\ \text{psia.ft}^3\text{/(lbmol.R)} \\ 1545\ \text{ft.lbf/(lbmol.R)} \end{cases}$$

Values of the Gas Constant R of Selected Elements and Compounds

Substance	Chemical Formula	R (kJ/kg · K)	R (Btu/lb · °R)
Air	—	0.2870	0.06855
Ammonia	NH_3	0.4882	0.11662
Argon	Ar	0.2082	0.04972
Carbon dioxide	CO_2	0.1889	0.04513
Carbon monoxide	CO	0.2968	0.07090
Helium	He	2.0769	0.49613
Hydrogen	H_2	4.1240	0.98512
Methane	CH_4	0.5183	0.12382
Nitrogen	N_2	0.2968	0.07090
Oxygen	O_2	0.2598	0.06206
Water	H_2O	0.4614	0.11021

- The ideal gas equation of state can be written in several different forms:

$$V = m\upsilon \rightarrow PV = mRT$$

$$mR = (MN)R = NR_u \rightarrow PV = NR_uT$$

$$V = N\bar{\upsilon} \rightarrow P\bar{\upsilon} = R_uT$$

- Where $\bar{\upsilon}$ is the molar specific volume, i.e., the volume per unit mole(in m^3/kmol or ft^3/lbmol)

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

COMPRESSIBILITY FACTOR

-A measure of deviation from Ideal-gas behavior

- The deviation from ideal-gas behavior at a given temperature and pressure can accurately be accounted by introduction of a correction factor called **compressibility factor** Z. it is defined as:

$$Z = \frac{P\upsilon}{RT} \quad \text{or} \quad P\upsilon = ZRT$$

$$\upsilon_{ideal} = \frac{RT}{P}$$

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

- Obviously, Z = 1 for ideal gases, and for real gases

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

- Gases behave differently at a given temperature and pressure, but they behave very much the same at temperatures and pressures normalized with respect to their critical temperatures and pressure.
- The normalization is done as:

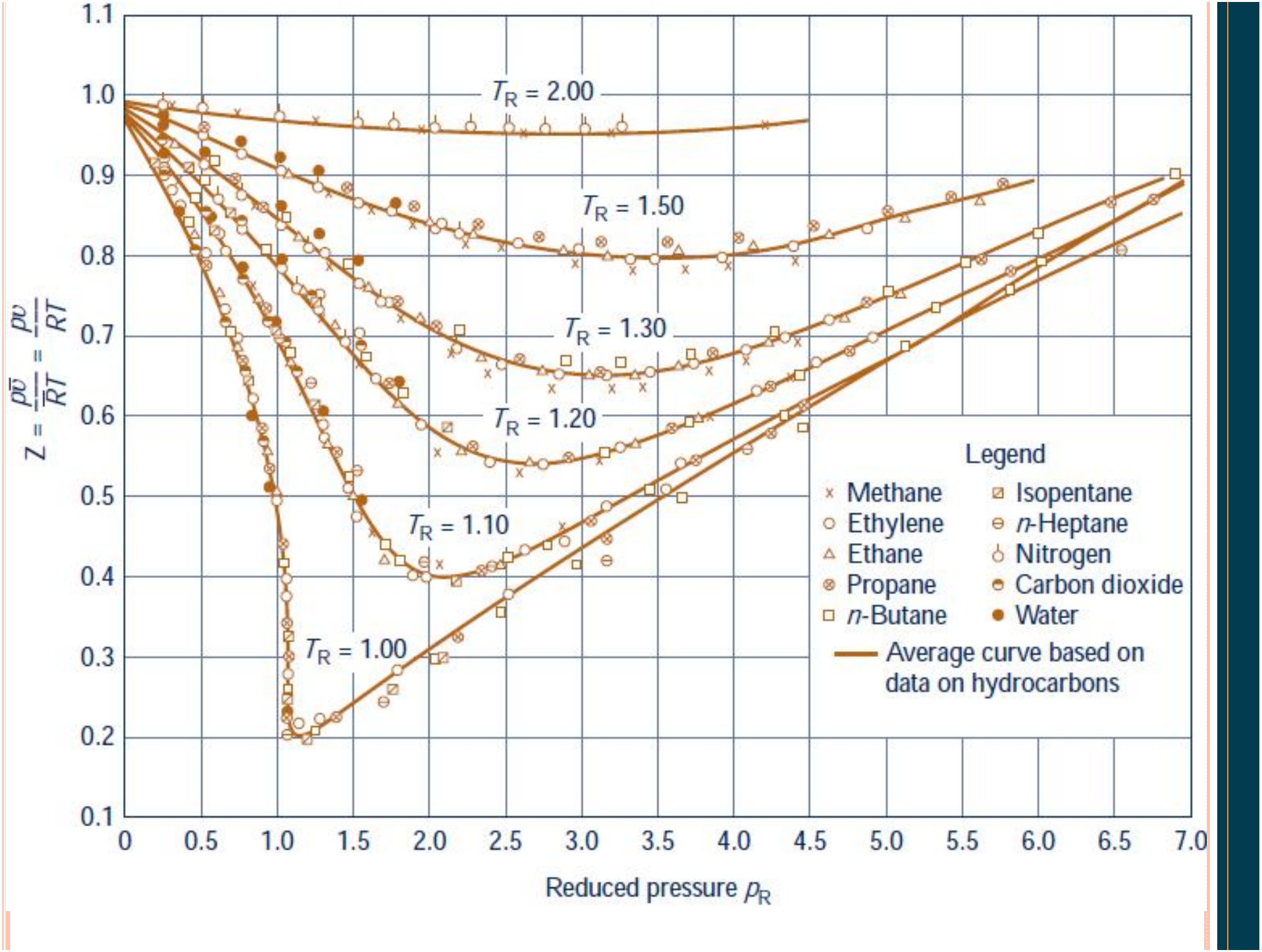
Where

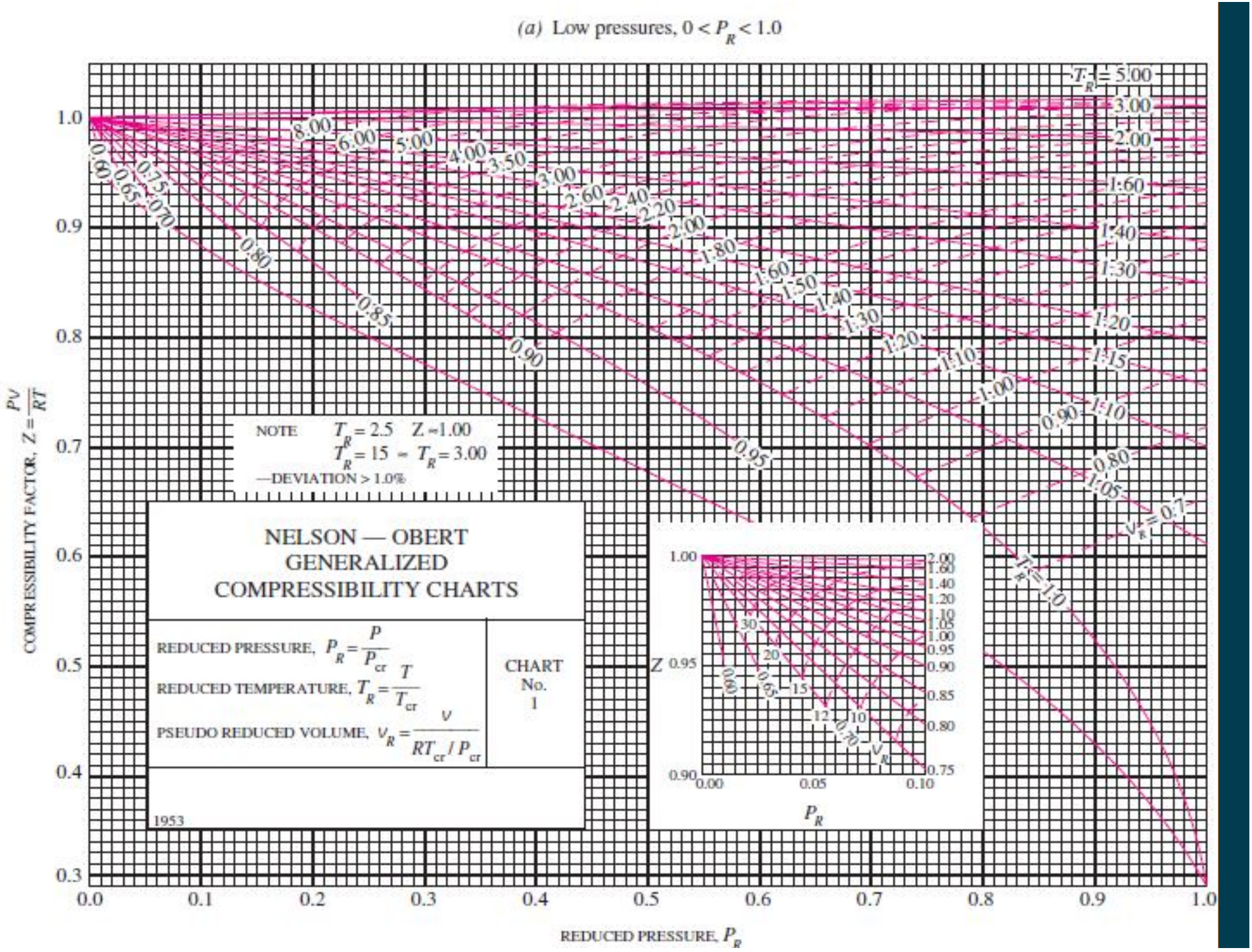
P_R=reduced pressure

P_{cr}=critical pressure

T=actual pressure

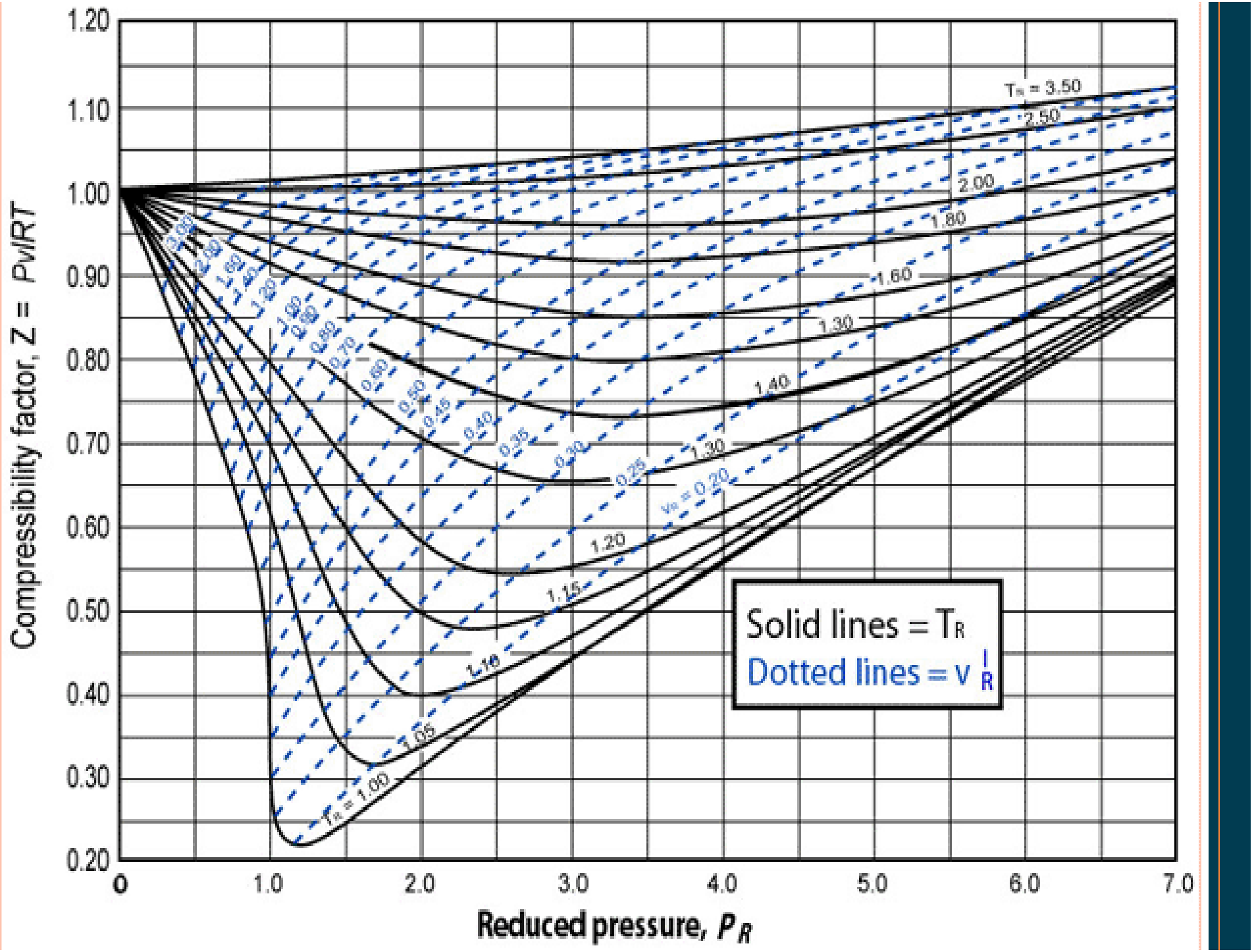
$$P_R = \frac{P}{P_{cr}} \quad \text{and} \quad T_R = \frac{T}{T_{cr}}$$


$Z = \frac{p\bar{v}}{\bar{R}T} = \frac{pv}{RT}$
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
Reduced pressure p_R
$T_R = 2.00$
$T_R = 1.50$
$T_R = 1.30$
$T_R = 1.20$
$T_R = 1.10$
$T_R = 1.00$
Legend
Methane
Ethylene
Ethane
Propane
n-Butane
Isopentane
n-Heptane
Nitrogen
Carbon dioxide
Water
Average curve based on data on hydrocarbons


(a) Low pressures, $0 < P_R < 1.0$
COMPRESSIBILITY FACTOR, $Z = \frac{PV}{RT}$
REDUCED PRESSURE, P_R
NOTE $T_R = 2.5$ $Z = 1.00$
$T_R = 1.5 - T_R = 3.00$
—DEVIATION > 1.0%
NELSON — OBERT
GENERALIZED
COMPRESSIBILITY CHARTS
REDUCED PRESSURE, $P_R = \frac{P}{P_{cr}}$
REDUCED TEMPERATURE, $T_R = \frac{T}{T_{cr}}$
PSEUDO REDUCED VOLUME, $V_R = \frac{V}{RT_{cr}/P_{cr}}$
CHART No. 1
1953
$T_R = 5.00$
3.00
2.00
1.60
1.40
1.30
1.20
1.15
1.10
1.05
1.00
0.95
0.90
0.85
0.80
$V_R = 0.7$
$T_R = 1.0$
8.00
6.00
5.00
4.00
3.50
3.00
2.60
2.40
2.20
2.00
1.80
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0.90
0.80
0.75
0.70
0.65
0.60
0.85
0.90
0.95
Z
P_R

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

Substance	Chemical Formula	M (kg/kmol)	T_c (K)	p_c (bar)	$Z_c = \frac{p_c v_c}{R T_c}$
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
Carbon	C	12.01	—	—	—
Carbon dioxide	CO_2	44.01	304	73.9	0.276
Carbon monoxide	CO	28.01	133	35.0	0.294
Copper	Cu	63.54	—	—	—
Ethane	C_2H_6	30.07	305	48.8	0.285
Ethanol	C_2H_5OH	46.07	516	63.8	0.249
Ethylene	C_2H_4	28.05	283	51.2	0.270
Helium	He	4.003	5.2	2.3	0.300
Hydrogen	H_2	2.016	33.2	13.0	0.304
Methane	CH_4	16.04	191	46.4	0.290
Methanol	CH_3OH	32.04	513	79.5	0.220
Nitrogen	N_2	28.01	126	33.9	0.291
Octane	C_8H_{18}	114.22	569	24.9	0.258
Oxygen	O_2	32.00	154	50.5	0.290
Propane	C_3H_8	44.09	370	42.7	0.276
Propylene	C_3H_6	42.08	365	46.2	0.276
Refrigerant 12	CCl_2F_2	120.92	385	41.2	0.278
Refrigerant 22	$CHClF_2$	86.48	369	49.8	0.267
Refrigerant 134a	CF_3CH_2F	102.03	374	40.7	0.260
Sulfur dioxide	SO_2	64.06	431	78.7	0.268
Water	H_2O	18.02	647.3	220.9	0.233


Compressibility factor, Z = PvIRT
Reduced pressure, P_R
Solid lines = T_R
Dotted lines = v'_R
T_R = 3.50
2.50
2.00
1.80
1.60
1.30
1.40
1.30
1.20
1.15
1.10
1.05
T_R = 1.00
v_R = 0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.60
0.70
0.80
0.90
1.00
1.20
1.40
1.60
1.80
2.00
2.50
3.00
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0

Example

- Determine the pressure of water vapor at 200^0C and $0.206 m^3/kg$, using the:
  A. steam table
  B. ideal gas equation
  C. generalized compressibility chart
- These charts show the conditions for which Z = 1 and the gas behaves as an ideal gas:
  1. $P_R < 10$ and $T_R > 2$ or $P < 10P_{cr}$ and $T > 2T_{cr}$
  2. $P_R << 1$ or $P << P_{cr}$