Properties of Pure Substances

Pure Substance

A substance that has a fixed chemical composition throughout is called a *pure substance* such as water, air, and nitrogen.

A pure substance does not have to be of a single element or compound. 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.

Phases of a Pure Substance

A pure substance may exist in different phases. There are three principal phases *solid*, *liquid*, and *gas*.

A phase: is defined as having a distinct molecular arrangement that is homogenous throughout and separated from others (if any) by easily identifiable boundary surfaces.

A substance may have several phases within a principal phase, each with a different molecular structure. For example, carbon may exist as graphite or diamond in the solid phase, and ice may exist in seven different phases at high pressure.

Molecular bonds are the strongest in solids and the weakest in gases.

Solid: the molecules are arranged in a three-dimensional pattern (lattice) throughout the solid. The molecules cannot move relative to each other; however, they continually oscillate about their equilibrium position.

Liquid: the molecular spacing in liquid phase is not much different from that of the solid phase (generally slightly higher), except the molecules are no longer at fixed positions relative to each other.

Gas: the molecules are far apart from each other, and a molecular order does not exist. Gas molecules move randomly, and continually collide with each other and the walls of the container they are in.

Molecules in the gas phase are at a considerably higher energy level than they are in liquids or solid phases.

Phase-Change Processes of Pure Substances

Consider a process where a pure substance starts as a solid and is heated up at constant pressure until it all becomes gas. Depending on the prevailing pressure, the matter will pass through various phase transformations. At P_0:

1. Solid

2. Mixed phase of liquid and solid

3. Sub-cooled or compressed liquid (means it is not about to vaporize)

4. Wet vapor or saturated liquid-vapor mixture, the temperature will stop rising until the liquid is completely vaporized.

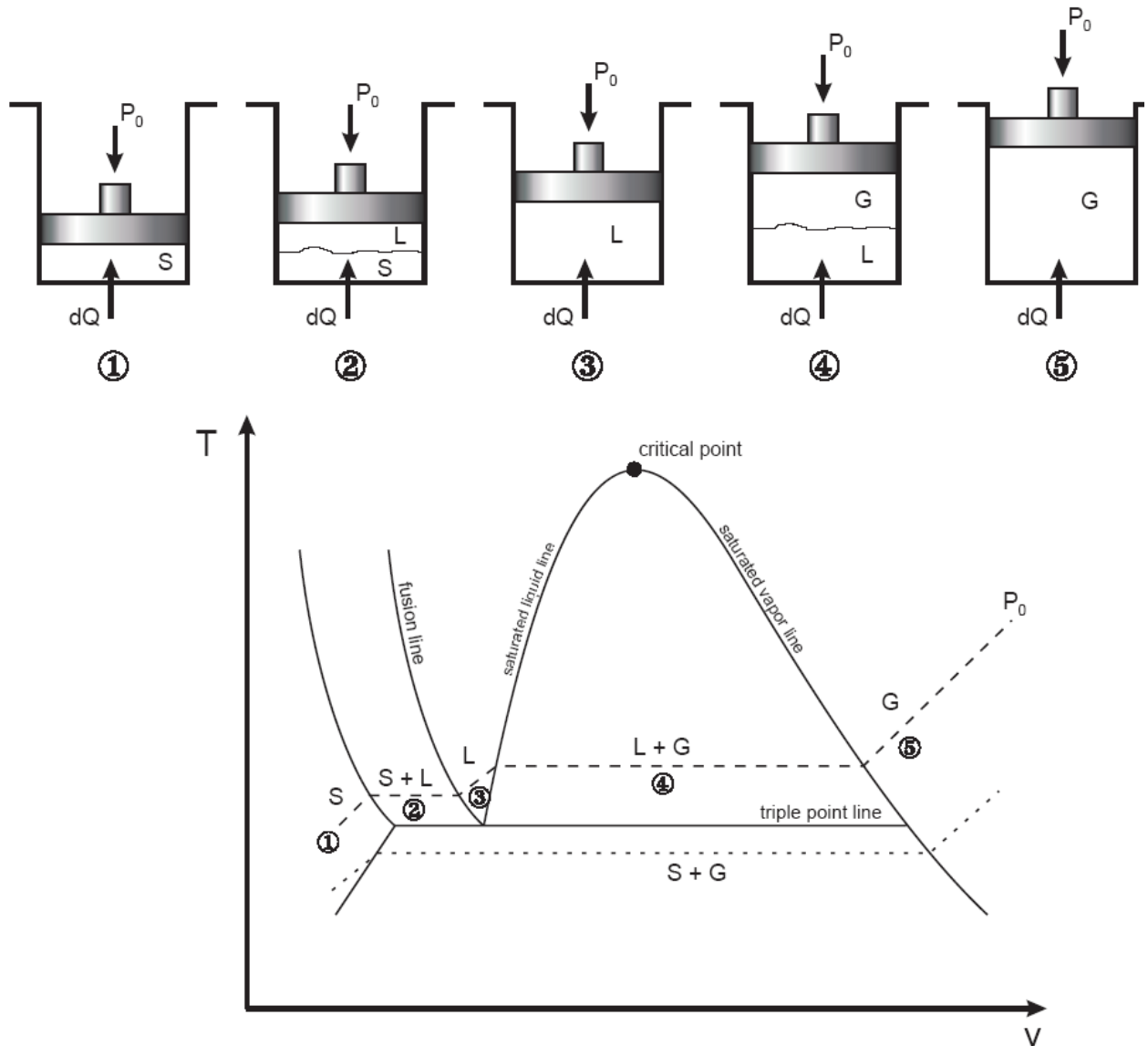5. Superheated vapor (a vapor that is not about to condense).

Fig. 1: T-v diagram for the heating process of a pure substance.

♦ 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 dependent properties, $T_{sat} = f(P_{sat})$.

- The *critical point* is the point at which the liquid and vapor phases are not distinguishable

- The "triple point" is the point at which the liquid, solid, and vapor phases can exist together. On P-v or T-v diagrams, these triple-phase states form a line called the *triple line*.

Table 1: Critical and triple point for water and oxygen.

	Critical Point		Triple Point	
	P (atm)	T (K /°C)	P (atm)	T (K /°C)
H_2O	218	647.30/(374.14)	0.006	273.17 (0.01)
O_2	50.136	154.80/(−118.36)	0.0015	54.16/(−219)

Vapor Dome

The general shape of a P-v diagram for a pure substance is very similar to that of a T-*v* diagram.
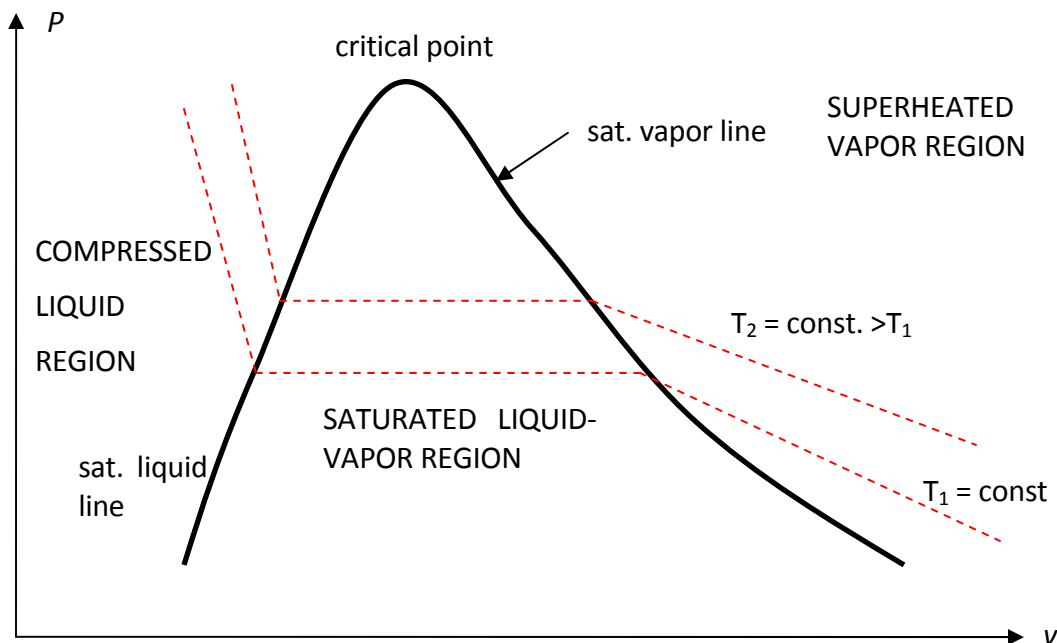

Fig. 2: P-v diagram of a pure substance.

The P-T or Phase Change Diagram

This is called phase diagram since all three phases are separated from each other by three lines. Most pure substances exhibit the same behavior.

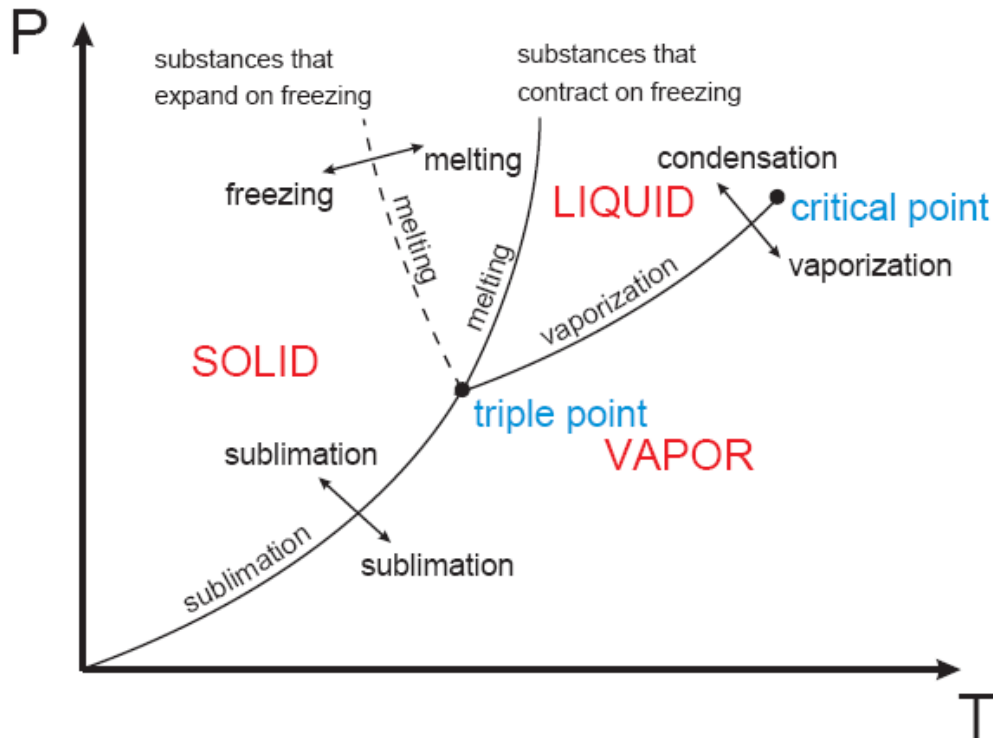♦ One exception is water. Water expands upon freezing.

Fig. 3: phase diagram of pure substances.

There are two ways that a substance can pass from solid phase to vapor phase i) it melts first into a liquid and subsequently evaporates, ii) it evaporates directly without melting (sublimation).

♦ the *sublimation line* separates the solid and the vapor.

♦ the *vaporization line* separates the liquid and vapor regions

♦ the *melting or fusion line* separates the solid and liquid.

♦ these three lines meet at the *triple point*.

▪ if $P<P_{TP}$, the solid phase can change directly to a vapor phase

▪ at $P<P_{TP}$ the pure substance cannot exist in the liquid phase. Normally ($P>P_{TP}$) the substance melts into a liquid and then evaporates.

▪ matter (like CO_2) which has a triple point above 1 atm sublimate under atmospheric conditions (dry ice)

- for water (as the most common working fluid) we are mainly interested in the liquid and vapor regions. Hence, we are mostly interested in boiling and condensation.

Property Tables

For most substances, the relationships among thermodynamic properties are too complex to be expressed by simple equations. Thus, properties are frequently presented in the form of tables, see Table A-4.

The subscript "*f*" is used to denote properties of a saturated liquid and "*g*" for saturated vapor. Another subscript, "*fg*", denotes the difference between the saturated vapor and saturated liquid values of the same property.

For example:

v_f = specific volume of saturated liquid

v_g = specific volume of saturated vapor

v_{fg} = difference between v_g and v_f ($v_{fg} = v_g - v_f$)

<u>Enthalpy</u>: is a property defined as *H = U + PV* (*kJ*) or *h = u + Pv (kJ/kg)* (per mass unit).

<u>Enthalpy of vaporization (or latent heat)</u>: represents the amount of energy needed to vaporize a unit mass of saturated liquid at a given temperature or pressure. It decreases as the temperature or pressure increase, and becomes zero at the critical point.

1- Saturated Liquid-Vapor Mixture

During vaporization, a mixture of part liquid part vapor exists. To analyze this mixture, we need to know the proportions of the liquid and vapor in the mixture. The ratio of the mass of vapor to the mass of the total mixture is called *quality, x*:

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

Saturated liquid-vapor mixture is treated as a combination of two sub-systems (two phases). The properties of the "mixture" are the *average* properties of the saturated liquid-vapor mixture.

$$V = V_f + V_g$$

$$m_t v_{ave} = m_f v_f + m_g v_g$$

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

dividing by m_t

$$v_{ave} = (1-x)v_f + xv_g \qquad \text{and} \qquad x = m_g / m_t$$

$$v_{ave} = v_f + xv_{fg} \qquad (m^3 / kg)$$
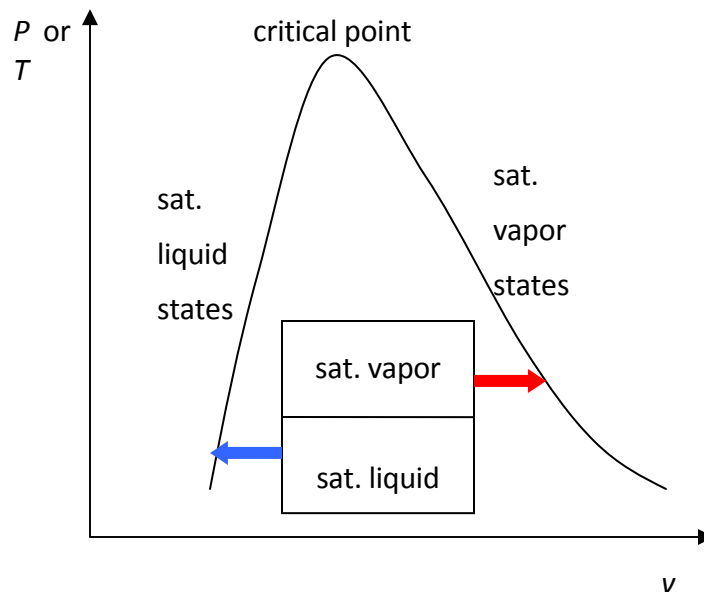
or,

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

Fig. 4: The relative amounts of liquid and vapor phases (*quality x*) are used to calculate the mixture properties.

Similarly,

$$u_{ave} = u_f + xu_{fg}$$

$$h_{ave} = h_f + xh_{fg}$$

Or in general, it can be summarized as $y_{ave} = y_f + x.y_{fg}$. Note that:

$$0 \leq x \leq 1$$

$$y_f \leq y_{ave} \leq y_g$$

Note: pressure and temperature are *dependent* in the *saturated mixture region*.
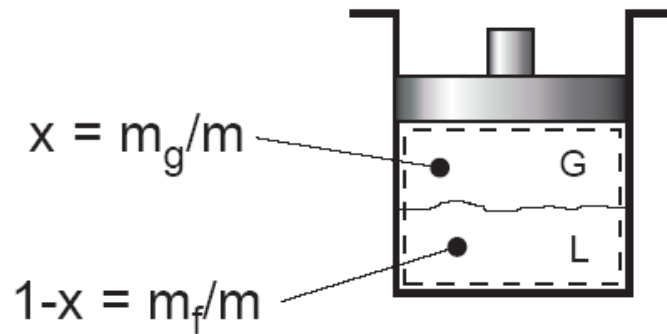
Fig. 5: Quality defined only for saturated liquid-vapor mixture.

Example 1: Saturated liquid-vapor mixture

A closed, rigid container of volume 0.5 m³ is placed on a hot plate. Initially the container holds a two-phase mixture of saturated liquid water and saturated water 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, in °C, at each state.

b) the mass of vapor present at each state, in kg.

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

Solution:

Assumptions:

1. Water in the container is a closed system.

2. States 1, 2, and 3 are equilibrium states.

3. The volume of container remains constant.

Two independent properties are required to fix state 1 and 2. At the initial state, the pressure and quality are known. Thus state 1 is known, as mentioned in the problem. The specific volume at state 1 is found using the given quality:

$$v_1 = v_{f1} + x_1 \left(v_{g1} - v_{f1} \right)$$
$$\text{From Table A - 5 at } P = 1 \, \text{bar} = 100 \, \text{kPa}$$
$$v_1 = 0.001043 + 0.5 \, (1.694 - 0.001043) = 0.8475 \quad m^3 / kg$$

At state 2, the pressure is known. Volume and mass remain constant during the heating process within the container, so $v_2=v_1$. For P_2= 0.15 MPa, Table A-5 gives v_{f2}= 0.001053 and v_{g2}=1.1593 m³/kg. Since
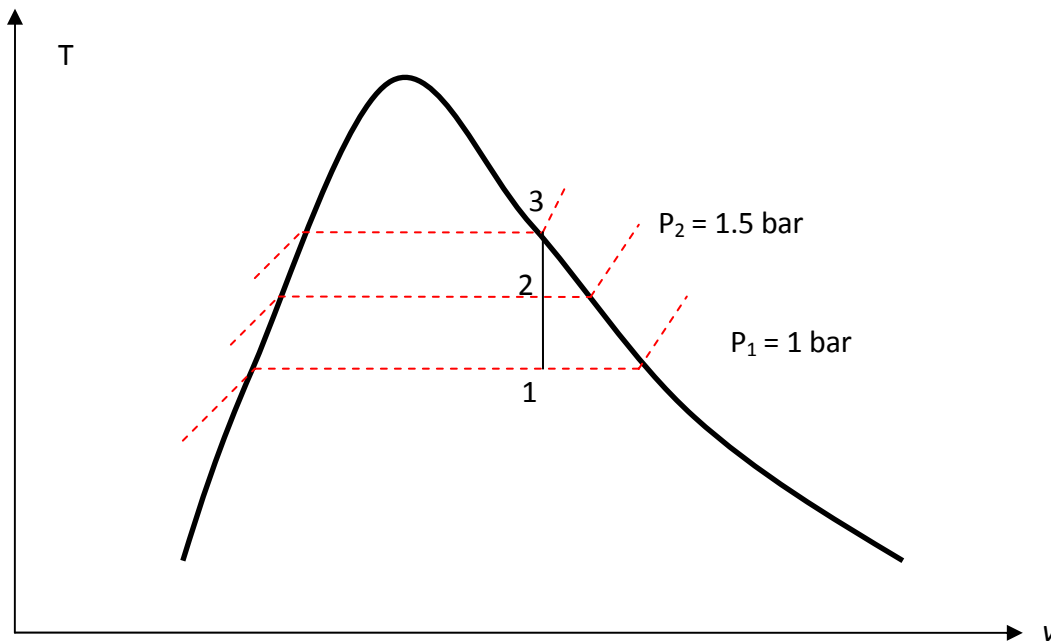
$$v_{f2} < v_2 < v_{g2}$$

State 2 must be in the two-phase region as well. Since state 1 and 2 are in the two-phase liquid-vapor region, the temperatures correspond to the saturation temperatures for the given. Table A-5:

$$T_1 = 99.63 \text{ °C and } T_2 = 111.4 \text{ °C}$$

To find the mass of water vapor present, we first find the total mass, m.

$$m = \frac{V}{v} = \frac{0.5m^3}{0.8475m^3/kg} = 0.59kg$$

$$m_{g1} = x_1 m = 0.5(0.59kg) = 0.295kg$$

The mass of vapor at state 2 is found similarly using quality x_2. From Table A-5, for $P_2 = 1.5$ bar, we have:

$$x_2 = \frac{v - v_{f2}}{v_{g2} - v_{f2}}$$

$$x_2 = \frac{0.8475 - 0.001053}{1.159 - 0.001053} = 0.731$$

$$m_{g2} = 0.731(0.59kg) = 0.431 \quad kg$$

If heating continued, state 3 would be on the saturated vapor line, as shown in on the *T-v* diagram above. Thus, the pressure would be the corresponding saturation pressure. Interpolating in Table A-5 at $v_g = 0.8475$ m³/kg, we get $P_3 = 2.11$ bar.

2- Superheated Vapor

Superheated region is a single phase region (vapor only), temperature and pressure are no longer dependent. See Table A-6 for superheated vapor properties.

If T>> $T_{critical}$ or P<<$P_{critical}$, then the vapor can be approximated as an "ideal gas".

3- Compressed (or Sub-cooled) Liquid

The properties of a liquid are relatively independent of pressure (incompressible).

A general approximation is to treat compressed liquid as saturated liquid at the given saturation temperature.

$$y \approx y_{f@T}$$

The property most affected by pressure is enthalpy. For enthalpy use the following approximation:

$$h \approx h_{f@T} + v_f\left(P - P_{sat}\right)$$

The Ideal-Gas Equation of State

Any equation that relates the pressure, temperature, and specific volume of a substance is called an *equation of state*.

The simplest and best known equation of state for substances in the gas phase is the *ideal-gas* equation of state.

Gas and *vapor* are often used as synonymous words. The vapor phase of a substance is called a *gas* when it is above the critical temperature. *Vapor* usually implies a gas that is not far from a state of condensation.

It is experimentally observed that at a low pressure the volume of a gas is proportional to its temperature:

$$Pv = RT$$

Where R is the gas constant. The above equation is called the ideal-gas equation of state (ideal gas relation). Since R is a constant for a gas, one can write:

$$R = \frac{P_1 v_1}{T_1} = \frac{P_2 v_2}{T_2}$$

where 1 and 2 denote two states of an ideal gas. The constant R is different for each gas; see Table 2-3 in Cengel book.

R_u = 8.314 kJ / (kmol. K) is the universal gas constant, R = R_u /M.

The molar mass, M (*kg/kmol*): is defined as the mass of one mole of a substance. The mass of a system is equal to the product of its molar mass M and the mole number N:

$$m = MN \quad (kg)$$

See Table A-1 for R and M for several substances. An ideal gas is an *imaginary* substance that obeys the relation *Pv = RT*. It is experimentally observed that the ideal gas closely approximate the P-v-T behavior of real gases at low densities.

- ➢ In the range of practical interest, many familiar gases such as air, nitrogen, oxygen, hydrogen, helium, argon, neon, and CO_2 can be treated as ideal gases with negligible error.

- ➢ Water vapor (in general see Fig. 4-49 Cengel book), refrigerant vapor in refrigerators **should not be** treated as ideal gases.

- ➢ Water vapor at pressures below 10 kPa can be treated as an ideal gas, regardless of temperature.

Compressibility Factor

The assumption of ideal gas relation implies that:

➢ the gas particles take up negligible volume

➢ the intermolecular potential energy between particles is small

➢ particles act independent of one another

However, real gases deviate from ideal gas behavior. This deviation at given temperature and pressure can be accurately accounted for by introduction of a correction factor called the *compressibility factor* Z.

$$Z = \frac{Pv}{RT} \qquad or \qquad Pv = ZRT$$

or $Z = v_{actual} / v_{ideal}$. Obviously, $Z=1$ for ideal gases.

Gases behave very much the same at temperatures and pressures normalized with respect to their critical temperatures and pressures.

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

Here P_R and T_R are called the *reduced pressure* and *temperature*, respectively.

By curve-fitting all the data, the general compressibility chart is obtained which can be used for all gases.
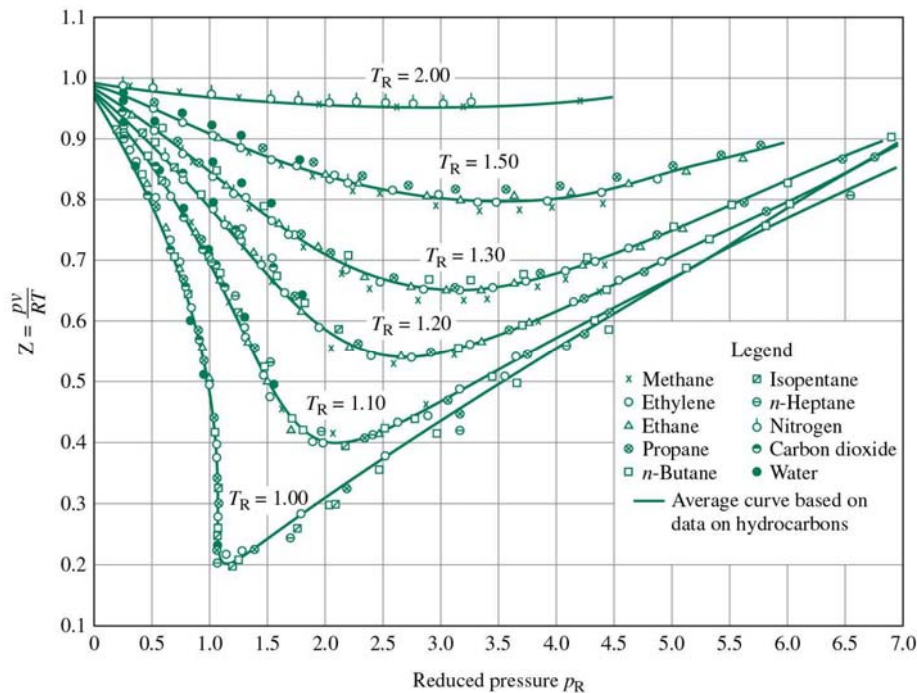

Fig. 6: Z factor, general compressibility chart.

From the Z chart, one can conclude:

- ➢ at very low pressure ($P_R \ll 1$), the gases behave as an ideal gas regardless of temperature
- ➢ at high temperatures ($T_R > 2$), ideal gas behavior can be assumed.
- ➢ the deviation is highest in the vicinity of the critical point.

Example 2: Ideal Gas

Determine the specific volume of R-134a at 1 MPa and 50°C, using (a) ideal gas equation (b) the generalized compressibility chart. Compare the values obtained with the actual value of 0.02171 m³/kg.

Solution:

From Table A-1, for R-134a, R = 0.0815 kPa.m³/(kg.K), P_{cr} = 4.067 MPa, and T_{cr} = 374.3 K

(a) Ideal gas equation of state

$$v = \frac{RT}{P} = \frac{\left[0.0815\ kPa.m^3 /(kg.K)\right](323\ K)}{(1000\ kPa)} = 0.02632\ m^3 / kg$$

Comparing with the tabulated value, using ideal gas equation one would get an error of (0.02632-0.02171)/0.02171=0.212 or 21.2%.

(b) To determine the correction factor Z,

$$P_R = \frac{P}{P_{cr}} = \frac{1 MPa}{4.067 MPa} = 0.246$$

$$T_R = \frac{T}{T_{cr}} = \frac{323 K}{374.3 K} = 0.863$$

From Fig. A-28, Z= 0.84. Thus,

v = Z v$_{ideal}$ = 0.84 (0.02632 m³/kg) =0.02211 m³/kg

The error is less than 2%.

Therefore, in the absence of exact tabulated data, the generalized compressibility chart can be used with confidence.