

Chapter 2

Properties of pure substance

2-1. Pure substance

A pure substance has a fixed chemical composition throughout is called a **pure substance**. Water, nitrogen, helium, and carbon dioxide, for example, are all pure substances.

A pure substance does not have to be of a single chemical element or compound, however. A mixture of various chemical elements or compounds also qualifies as a pure substance as long as the mixture is homogeneous. Air, for example, is a mixture of several gases, but it is often considered to be a pure substance because it has uniform chemical composition (**Fig. 2-1**).

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 (**Fig. 2-2**). A mixture of liquid and gaseous water is a pure substance because both phases have the same chemical composition, but a mixture of liquid and gaseous air is not since the composition of liquid air is different from the composition of gaseous air, and thus the mixture is no longer chemically homogeneous.

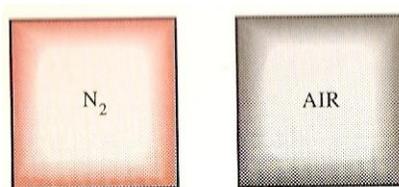


Figure 2-1. Nitrogen and gaseous air are pure substances.

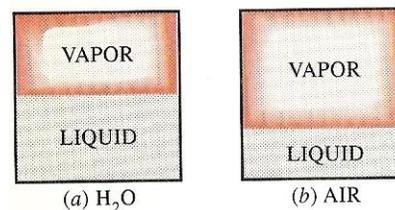


Figure 2-2. A mixture of liquid and gaseous water is a pure substance, but a mixture of liquid and gaseous air is not.

2-2. Phases of a pure substance

We all know from experience that **substances exist in different phases**. At room temperature and pressure, copper is a solid, mercury is a liquid, and nitrogen is a gas.

When studying phases or phase changes in thermodynamics, one does not need to be concerned with the molecular structure and behavior of different phases.

The molecules in **solid** are arranged in a three-dimensional pattern (lattice) which is repeated throughout the solid (**Fig. 2-3**). Because of the small distances between molecules in a solid, the attractive forces of molecules on each other are large and keep the molecule at fixed positions within the solid.

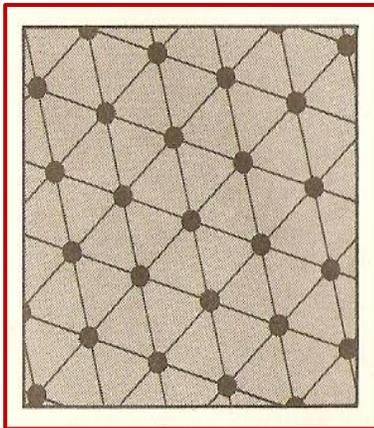


Figure 2-3. The molecules in a solid are kept at fixed positions by large intermolecular forces.

The molecule spacing in **liquid** phase is not much different from that of the solid phase, except the molecules are no longer at positions relative to each other. In a liquid, chunks of molecules float about each other (**Fig. 2-6**).

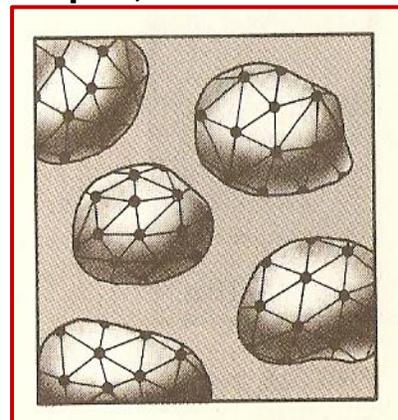


Figure 2-6. In the liquid phase, chunks of molecules float about each other.

In the **gas phase**, the molecules are far apart from each other, and a molecular order is nonexistent. Gas molecules move about at random, continually colliding with each other and the walls of the container they are in (**Fig. 2-7**).

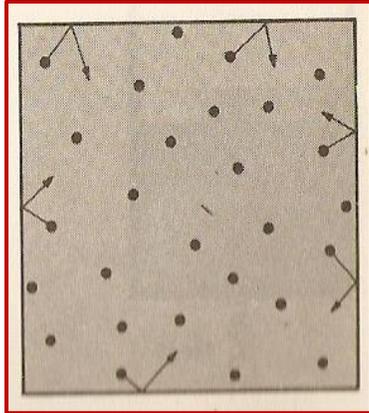


Figure 2-7. In the gas phase, the molecules are at the highest energy level and move about at random.

2-3. Phase-change processes of pure substances

There are many practical situations where two phases of a pure substance coexist in equilibrium. Water exists as a mixture of liquid and vapor in the boiler and the condenser of a steam power plant.

Compressed liquid and saturated liquid

Consider a piston-cylinder device containing liquid water at 20°C and 1 atm pressure (**state 1, Fig. 2-8**). Under these 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*. Heat is now added to the water until temperature rises to 40°C. As the temperature rises the liquid water will expand slightly, and so its specific volume will increase. As more heat is added, the temperature will keep rising until it reaches 100°C (**state 2, Fig.2-9**). At this point water is still a liquid, but any heat addition, will cause some of the liquid to vaporize. At liquid is *about to vaporize* is called a **saturated liquid**. Therefore, state 2 is a saturated liquid state.

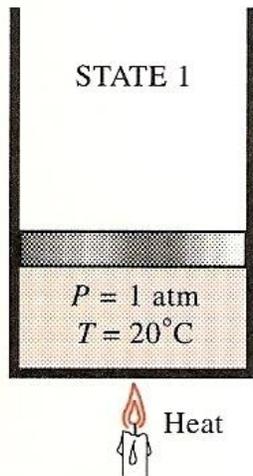


Figure 2-8. At 1 atm and 20°C water exists in the liquid phase (*compressed liquid*).

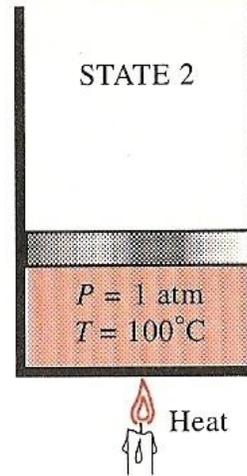


Figure 2-9. At 1 atm and 100°C water exists as a liquid which ready to vaporize (*saturated liquid*).

Saturated vapor and superheated vapor

Once boiling starts, the temperature will stop rising until the completely vaporized. That is the temperature will remain constant during the entire phase-change process if the pressure is held constant.

Midway about the vaporization line (**state 3, Fig. 2-10**), the cylinder contain equal amounts of liquid and vapor. Vaporization process will continue until the last drop of liquid is vaporized (**state 4, Fig. 2-11**). At this point, the entire cylinder is filled with vapor which is on the borderline of liquid phase. Any heat loss from this vapor which will cause some of the vapor to condense. A vapor which is about to condense is called a **saturated vapor**. Further transfer of heat will result in an increase in both temperature and specific volume (**state 5, Fig. 2-12**). A vapor which is not about to condense is called a **superheated vapor**.

The constant pressure phase-change is given on $T-v$ diagram (Fig.2-13).

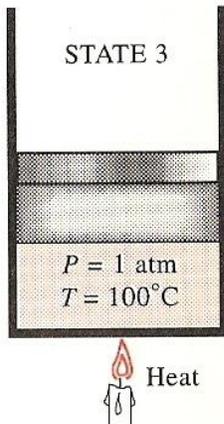


Figure 2-10. As more heat is added, part of saturated liquid vaporizes (*saturated liquid-vapor mixture*).

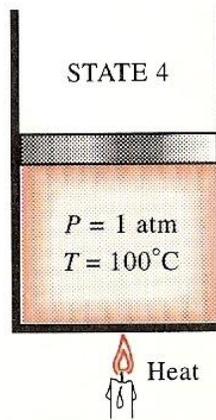


Figure 2-11. At 1-atm pressure, the temperature remains constant at 100°C until the last drop of liquid is vaporized (*saturated vapor*).

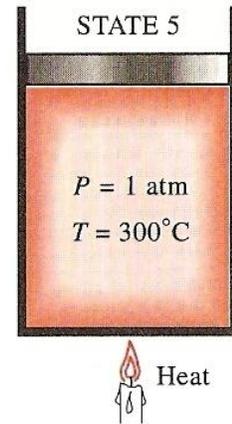


Figure 2-12. As more heat is added, the temperature of the vapor starts to rise (*superheated vapor*).

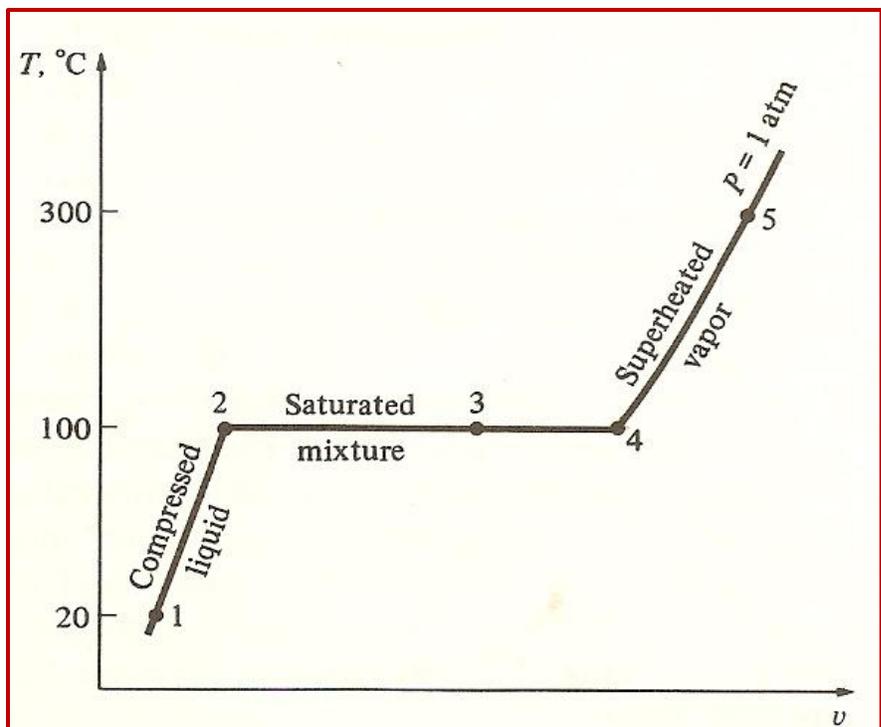


Figure 2-13. $T-v$ diagram for the heating process of water at constant pressure.

Saturated temperature and saturated pressure

Water boils at **100°C** at **1-atm** pressure. 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, $T_{sat} = f(P_{sat})$. A plot of T_{sat} vs P_{sat} , such as the one given for water in (Fig. 2-15), is called a **liquid-vapor saturation curve**. A curve of this kind is characteristic of all pure substances.

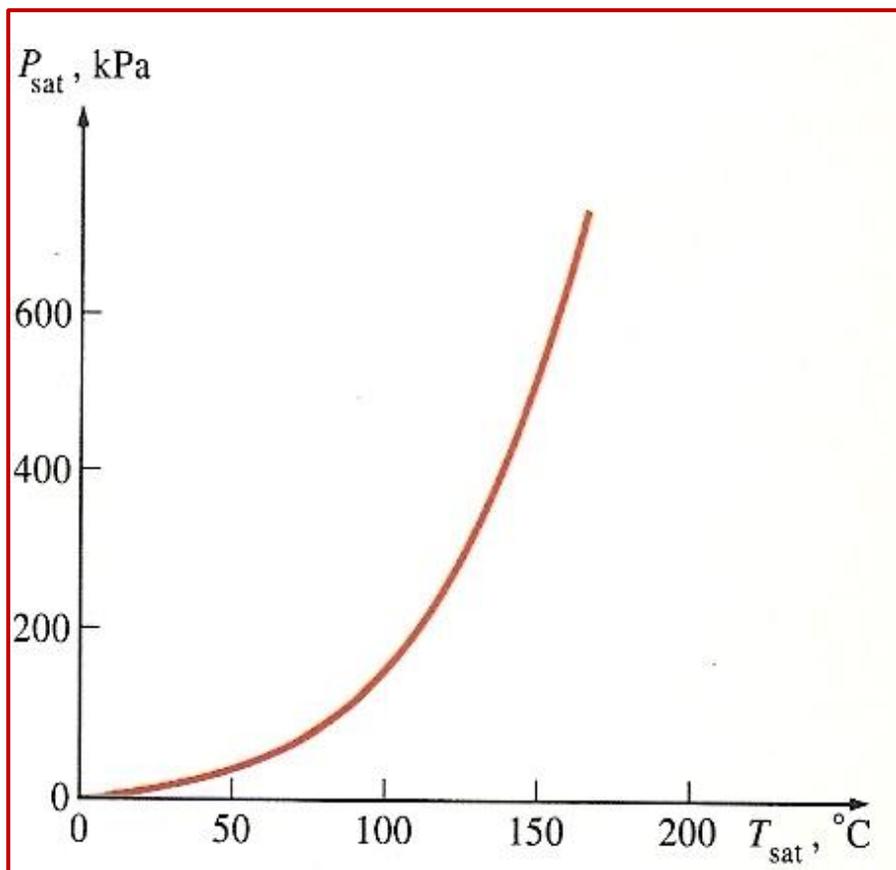


Figure 2-15. The liquid-vapor saturation curve of a pure substance (numerical values are for water).

2-4. Property diagrams for phase-change processes

The variations of properties during phase-change processes are best studied and understood with the help of property diagrams.

1. The T - v diagram

The phase –change process of water at 1-atm pressure was described in detail in the last section and plotted on a T - v diagram in (Fig. 2-13). Now we repeat this process at different pressures to develop the T - v diagram for water. As heat is added to the water at this new higher pressure, the process will follow a path which looks very much like the process path at 1-atm pressure as shown in (Fig.2-17), but there are some noticeable differences:

- Water will start boiling at much higher temperature at this new higher pressure.
- Specific volume of the saturated liquid is larger.
- Specific volume of the saturated vapor is smaller.
- The horizontal line that connects the saturated liquid and saturated vapor is much shorter.

As pressure is increased further, this saturation line will continue to get shorter, and it will become a point when the **pressure reaches 22.09 MPa** for the case of water. This point is called the **critical point**, at which **the saturated liquid and saturated vapor states are identical**.

The temperature, pressure and, specific volume of a substance at the critical point are called, respectively, the **critical temperature T_{cr}** , **critical pressure P_{cr}** , and **critical specific volume v_{cr}** . The critical-point properties of water are $P_{cr} = 22.09$ MPa, $T_{cr} = 374.14^\circ\text{C}$, and $v_{cr} = 0.003155$ m³/kg.

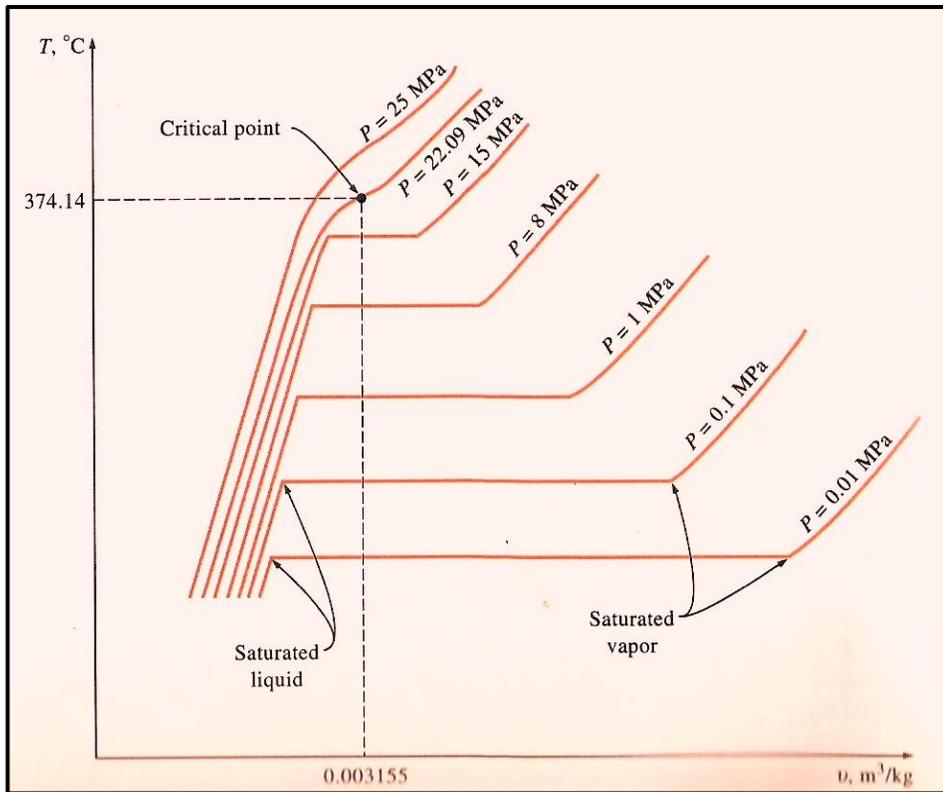


Figure 2-17. T - v diagram of constant-pressure phase-change processes of a pure substance at various pressures (numerical values are for water).

At pressures above the critical pressure, there will not be distinct phase-change process (**Fig. 2-18**).

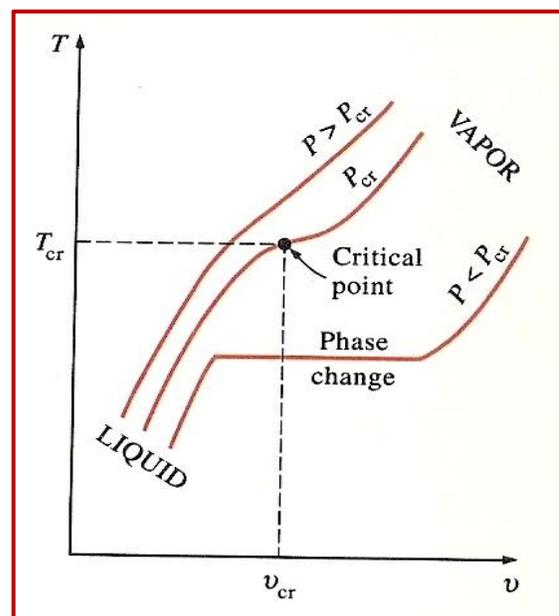


Figure 2-18. At supercritical pressures ($P > P_{cr}$), there is no distinct phase-change (boiling) process.

Above the critical state there is no line that separates the **compressed liquid region** and the **superheated vapor region**. However, it is customary to refer to the substance as **superheated vapor** at temperatures above the critical temperature (**Fig. 2-19**).

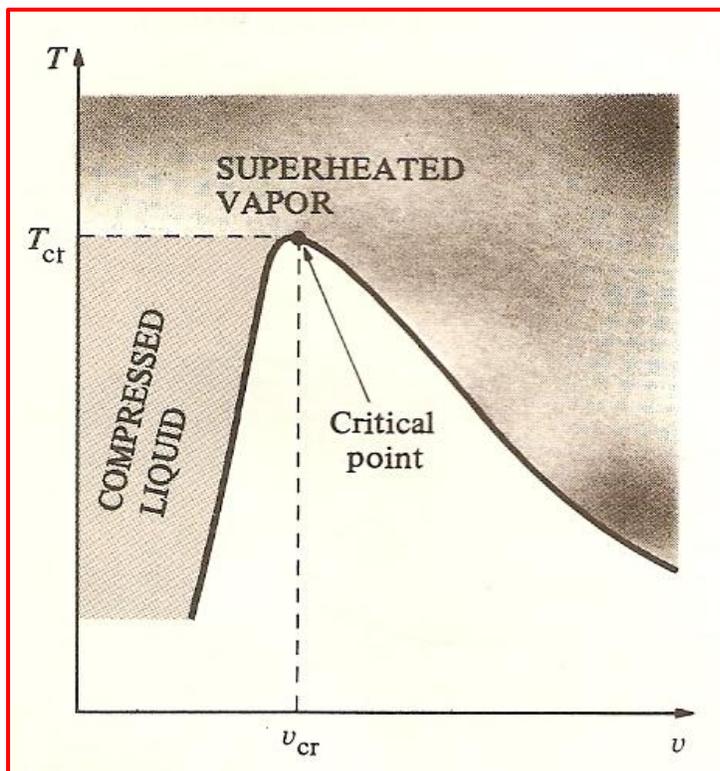


Figure 2-19. Above the critical temperature, a substance is considered to be a superheated vapor.

The saturated liquid states in (**Fig.2-17**) can be connected by a line which is called the **saturated liquid line**, and **saturated vapor states** in the same figure can be connected by another line which is called the **saturated vapor line**. These two lines meet each other at the critical point, forming a dome as shown in (**Fig. 2-20**). All the compressed liquid states are located in the region to the left of the saturated liquid line, and it is called the **compressed liquid region**. All the superheated vapor states are

located to the right of the saturated vapor line which is called the **superheated vapor region**.

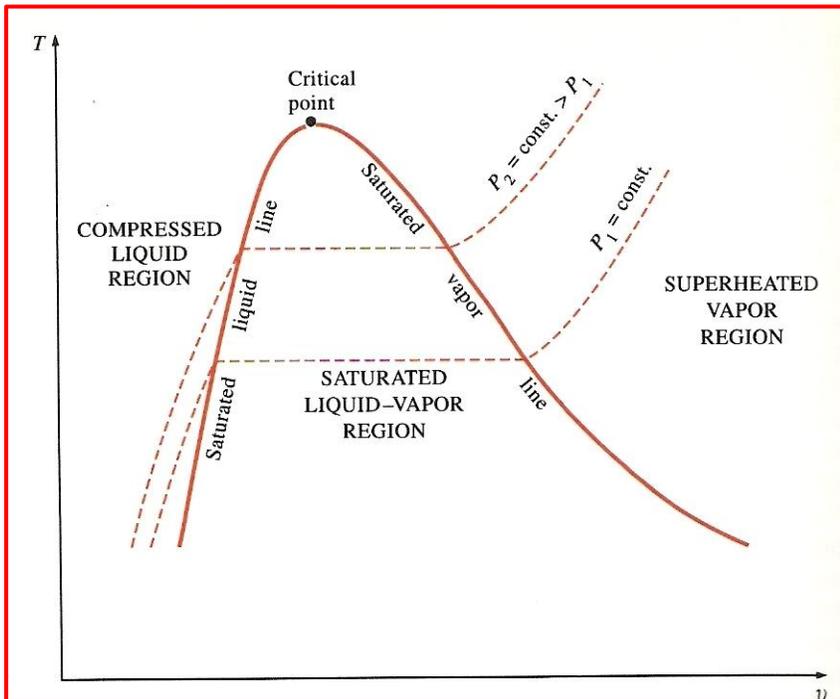


Figure 2-20. T - v diagram of a pure substance.

2. The P - v diagram

The general shape of the P - v diagram of a pure substance is very much like the T - v diagram, but the $T = \text{constant}$ lines on this diagram have a downward trend, as shown in (Fig. 2-21).

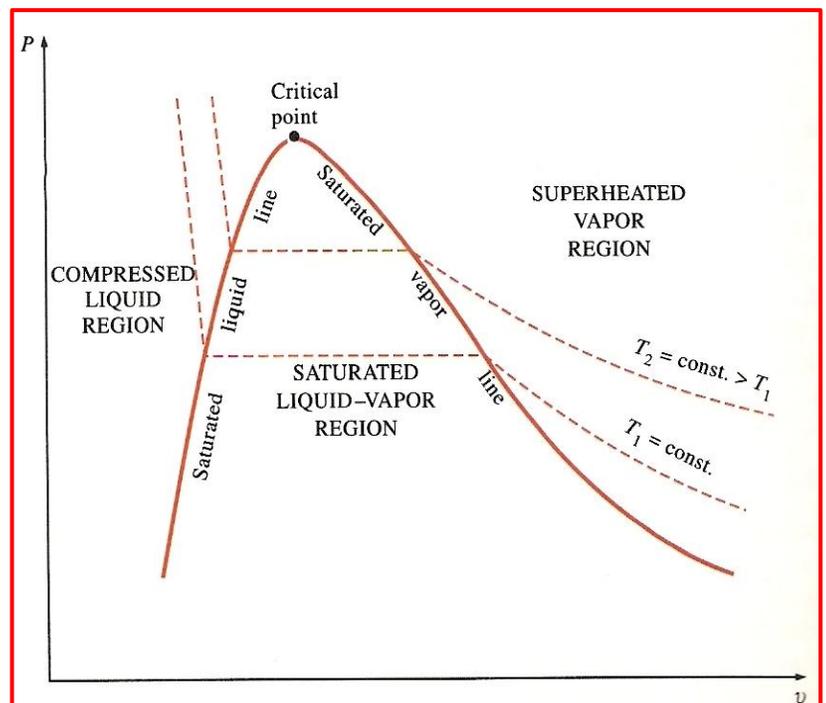


Figure 2-21. P - v diagram of a pure substance.

2-6. Property tables

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.

Enthalpy-a combination property

In the analysis of certain types of processes, particularly in power generation and refrigeration (Fig. 2-31), 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 :

$$H = U + PV \quad (\text{kJ}) \quad (2-1)$$

or, per unit mass,

$$h = u + Pv \quad (\text{kJ/kg}) \quad (2-2)$$

where, H = total enthalpy, and u = specific total enthalpy

P = pressure, V = volume, and v = specific volume

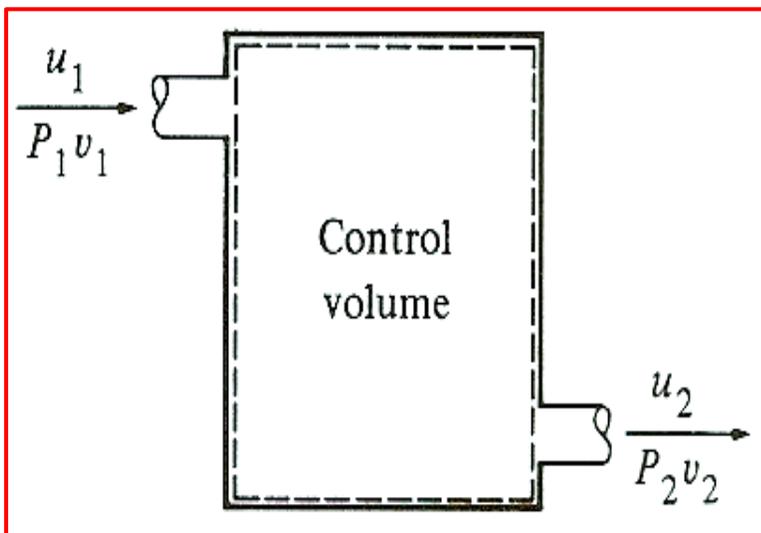


Figure 2-31. The combination $u + Pv$ is frequently encountered in the analysis of control volumes.

The product **pressure** x **volume** has energy units (Fig.2-32).

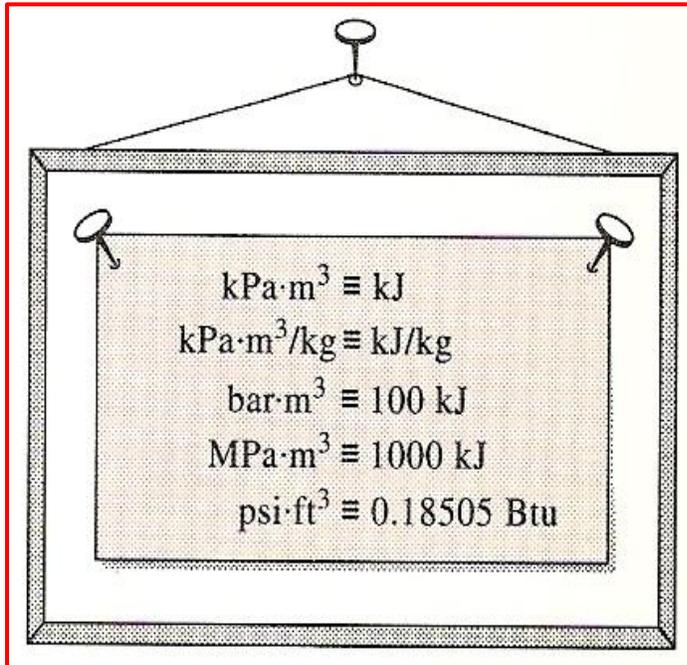


Figure 2-32. The product **pressure** x **volume** has energy units.

1a Saturated liquid and saturated vapor states

The properties of saturated liquid and saturated vapor for water are listed in **Tables A-4** and **A-5**. It is more convenient to use **Table A-4** when temperature is given and **Table A-5** when pressure is given.

The use of **Table A-4** is illustrated in **Fig. 2-33**.

Sat. Temp. °C T	Sat. press kPa P_{sat}	Specific volume m^3/kg	
		Sat. liquid v_f	Sat. vapor v_g
85	57.83	0.001 033	2.828
90	70.14	0.001 036	2.361
95	84.55	0.001 040	1.982

Labels with arrows pointing to the table:

- Specific temperature (points to 85, 90, 95)
- Corresponding saturation pressure (points to 57.83, 70.14, 84.55)
- Specific volume of saturated liquid (points to 0.001 033, 0.001 036, 0.001 040)
- Specific volume of saturated vapor (points to 2.828, 2.361, 1.982)

Figure 2-33. A partial list of **Table A-4**.

The subscript f is used to denote properties of a saturated liquid, the subscript g to denote the properties of saturated vapor, and the subscript fg is used to denote the difference between the saturated vapor and liquid values of the same property (Fig. 2-34). 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 (that is, $v_{fg} = v_g - v_f$)

h_{fg} = enthalpy of vaporization (or latent heat of vaporization)

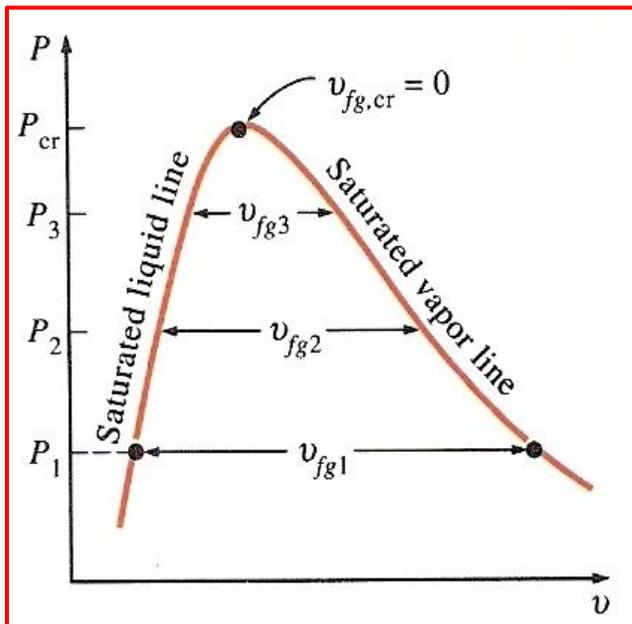


Figure 2-34. v_{fg} decreases as P or T increases, and becomes zero at the critical point.

Example 2-1.

A rigid tank contains **50 kg** of **saturated liquid water** at **90°C**. Determine **pressure** in the tank and the **volume** of the tank.

Solution.

The state of the saturated liquid water is shown on a T - v diagram in Fig. 2-35. Since saturation conditions exist in the tank, the pressure must be the saturation pressure at 90°C .

$$P = P_{\text{sat}} @ 90^\circ\text{C} = 70.14 \text{ kPa} \quad (\text{Table A-4})$$

The specific volume of saturated liquid at 90°C is:

$$v = v_f @ 90^\circ\text{C} = 0.001036 \text{ m}^3/\text{kg} \quad (\text{Table A-4})$$

The total volume of the tank is determine from:

$$V = mv = (50 \text{ kg})(0.001036 \text{ m}^3/\text{kg}) = 0.0518 \text{ m}^3$$

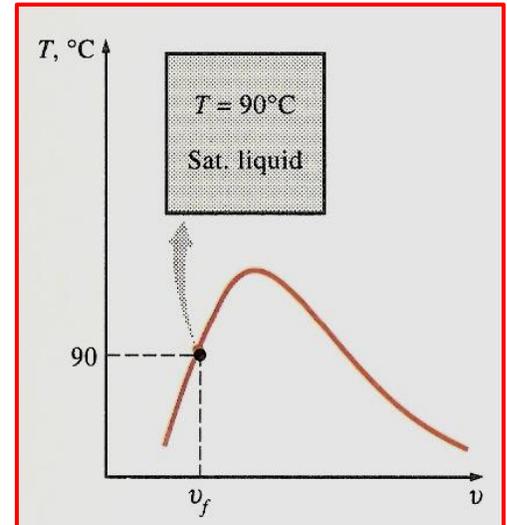


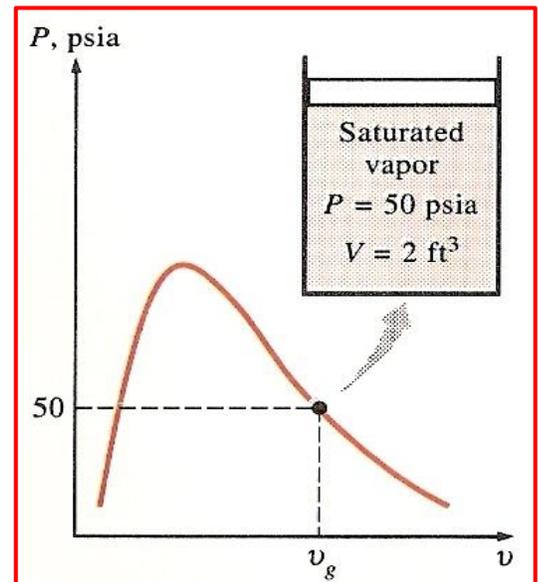
Figure 2-35. Schematic and T - v diagram for Example 2-1.

Example 2-2.

A piston –cylinder device contains 2 ft^3 of saturated water vapor at 50-psia pressure. Determine the **temperature** of the vapor and the **mass** of the vapor inside the cylinder.

Solution. The state of the saturated water vapor is shown on a P - v diagram in Fig.2-36. Since the cylinder contains saturated vapor at 50 psia , the temperature inside must be the saturation temperature at this pressure.

Figure 2-36. Schematic and P - v diagram for Example 2-2.



$$T = T_{\text{sat}} @ 50 \text{ psia} = 281.03^\circ\text{F} \quad (\text{Table A-5E})$$

The **specific volume** of the saturated vapor at **50 psia** is:

$$v = v_g @ 50 \text{ psia} = 8.518 \text{ ft}^3/\text{lbm} \quad (\text{Table A-5E})$$

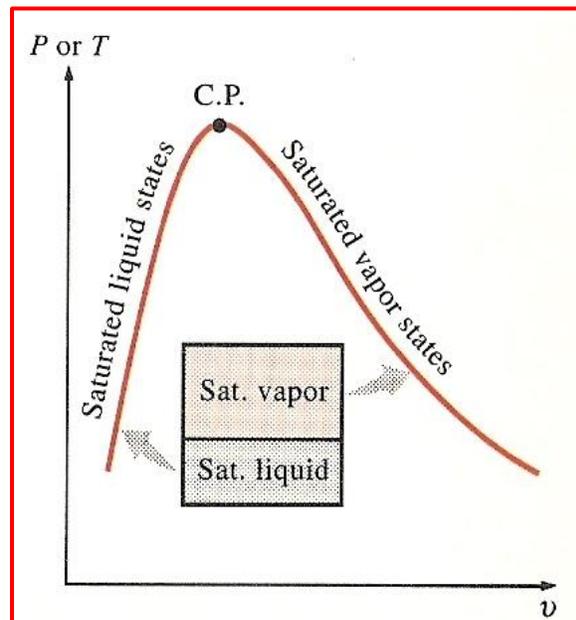
Then the **mass** of water vapor inside the cylinder becomes:

$$m = \frac{V}{v} = \frac{2 \text{ ft}^3}{8.518 \text{ ft}^3/\text{lbm}} = 0.235 \text{ lbm}$$

1b Saturated liquid-vapor mixture

During a vaporization process, a substance exists as part liquid and part vapor. That is, it is a mixture of saturated liquid and saturated vapor (**Fig. 2-38**).

Figure 2-38. The relative amounts of liquid and vapor phases in a saturated mixture are specified by quality x .



Quality x is the ratio of the **mass of vapor** to the **total mass of the mixture**:

$$x = \frac{m_{\text{vapor}}}{m_{\text{total}}} \quad (2-3)$$

where, $m_{\text{total}} = m_{\text{liquid}} + m_{\text{vapor}} = m_f + m_g$

Quality has significance for saturated mixture only. Its value is always between **0** and **1** (Fig. 2-39). The quality of a system that consists of saturated liquid is **0** (or **0 percent**), and the **quality** of a system consists of saturated vapor is **1** (or **100 percent**).

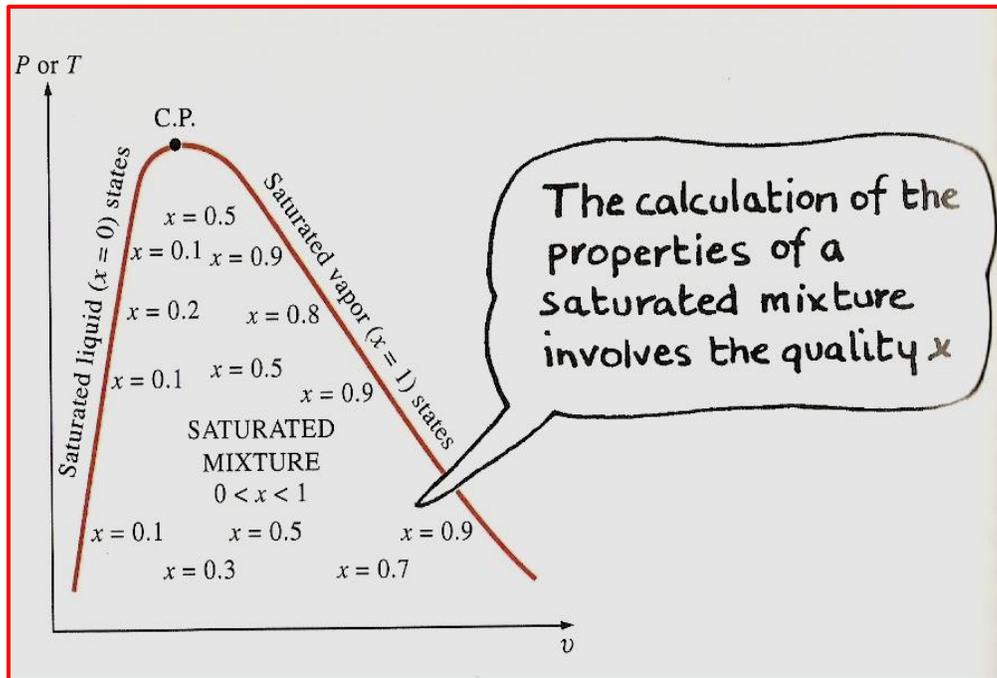


Figure 2-39. Quality can have values between 0 and 1, and it has significance only at states under the saturation curve.

Consider a tank (Fig. 2-40) that contains a saturated liquid-vapor mixture.

The volume occupied by saturated liquid is V_f and the volume occupied by saturated vapor is V_g . The total volume V is the sum of these two:

$$V = V_f + V_g$$

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

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

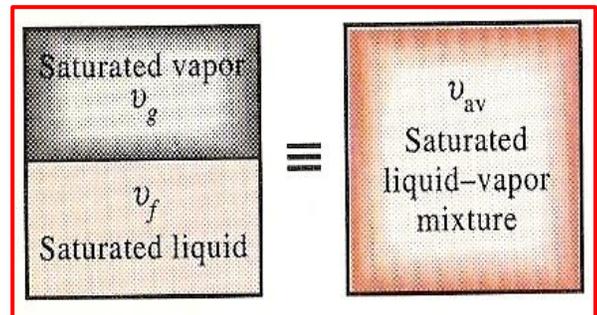


Figure 2-40. A two-phase system can be treated as a homogeneous mixture for computational purposes.

Dividing by m_t yields:

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

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

$$v_{av} = v_f + x v_{fg} \quad (\text{m}^3/\text{kg}) \quad (2-4)$$

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

$$x = \frac{v_{av} - v_f}{v_{fg}} \quad (2-5)$$

Based on this equation, quality can be related to the horizontal distances on a P - v or T - v diagram (Fig.2-41).

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

$$u_{av} = u_f + x u_{fg} \quad (\text{kJ/kg}) \quad (2-6)$$

$$h_{av} = h_f + x h_{fg} \quad (\text{kJ/kg}) \quad (2-7)$$

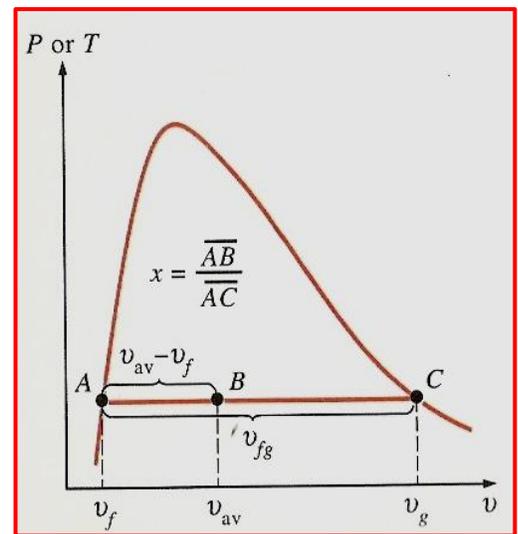


Figure 2-41. Quality is related to the horizontal distances on P - v and T - v diagrams.

In general form:

$$y_{av} = y_f + x y_{fg} \quad (2-8)$$

where y is v , u , or h . The subscript “av” (for “average”) is usually dropped or simplicity. The values of the average properties of the mixtures are always between the values of the saturated liquid and the saturated vapor properties (Fig. 2-42). That is:

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

Finally, all the saturated-mixture states are located under the saturation curve, and to analyze saturated mixtures, all we need are saturated liquid and saturated vapor data (Tables A-4 and A-5 in the case of water).

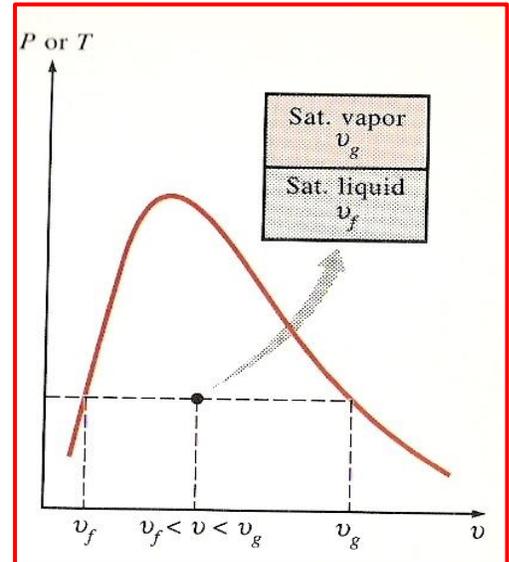


Figure 2-42. The v value of a saturated liquid-vapor mixture lies between the v_f and v_g values at the specified T or P .

Example 2-4.

A rigid tank contains **10 kg** of water at **90°C**. If **8 kg** of the water is in the liquid form and the rest is in vapor form, determine **(a)** the **pressure** in the tank **(b)** the **volume** of the tank?

Solution.

(a) The state of the **saturated liquid-vapor mixture** is shown in (Fig. 2-43). Since the two phases coexist in equilibrium, we have a saturated mixture and the pressure must be the saturation pressure at the given temperature.

$$P = P_{sat @ 90^\circ\text{C}} = 70.14 \text{ kPa} \quad (\text{Table A-4})$$

(b) At **90°C**, v_f and v_g values are $v_f = 0.001036 \text{ m}^3/\text{kg}$ and

$$v_g = 2.361 \text{ m}^3/\text{kg} \quad (\text{Table A-4}).$$

$$\begin{aligned}
 V &= V_f + V_g = m_f v_f + m_g v_g \\
 &= (8 \text{ kg})(0.001 \text{ m}^3/\text{kg}) + (2 \text{ kg})(2.36 \text{ m}^3/\text{kg}) \\
 &= 4.73 \text{ m}^3
 \end{aligned}$$

Another way is to first determine the quality x , then average specific volume v , and finally the total volume:

$$x = \frac{m_g}{m_t} = \frac{2 \text{ kg}}{10 \text{ kg}} = 0.2$$

$$\begin{aligned}
 v &= v_f + x v_{fg} \\
 &= 0.001 \text{ m}^3/\text{kg} + (0.2)[2.361 - 0.001] \text{ m}^3/\text{kg} \\
 &= 0.473 \text{ m}^3/\text{kg}
 \end{aligned}$$

$$V = mv = (10 \text{ kg})(0.473 \text{ m}^3/\text{kg}) = 4.73 \text{ m}^3$$

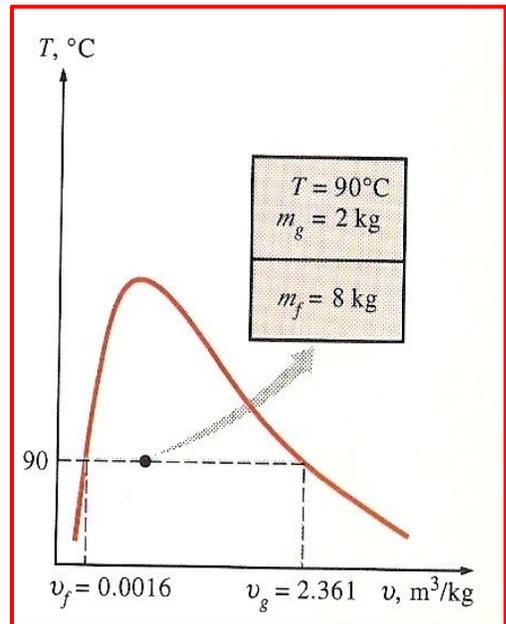


Figure 2-43. Schematic and T - v diagram for **Example 2-4**.

2 Superheated vapor

In the region to the right of the saturated vapor line, a substance exists as superheated vapor. Since the superheat region is a single-phase region (**vapor phase only**), temperature and pressure are no longer dependent properties and they can conveniently be used as two independent properties in the tables. The format of the superheated vapor tables is illustrated in **Fig. 2-45**.

Superheated vapor is characterized by:

Lower pressures ($P < P_{\text{sat}}$ at a given T)

Higher temperatures ($T > T_{\text{sat}}$ 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).

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

Figure 2-45. A partial listing of **Table A-6**.

Example 2-6.

Determine the **internal energy** of water at **200 kPa** and **300°C**?

Solution

At $P = 200 \text{ kPa}$, $T_{\text{sat}} = 120.23$ (Table A-5)

Since $T > T_{\text{sat}}$, the water in superheated region,

Then, $u = 2808.6 \text{ kJ/kg}$

Another way: At $T = 300^\circ\text{C}$, $P_{\text{sat}} = 8.581 \text{ MPa}$ (Table A-4)

Since $P < P_{\text{sat}}$, the water in superheated region,

Then, $u = 2808.6 \text{ kJ/kg}$ (Table A-6)

3 Compressed liquid

There are not many data for **compressed liquid** in the literature, and **Table A-7** is the only compressed liquid table in this text. One reason for the lack of compressed liquid data is the relative independence of compressed liquid properties from pressure.

In the absence of compressed liquid data, a general approximation is to treat compressed liquid as saturated liquid at the given temperature (**Fig. 2-47**). This is because the compressed liquid properties **depend on temperature** more strongly than they do on **pressure**. Thus,

$$y \cong y_f @ T$$

for compressed liquids where y is v , u , or h . In general, a **compressed liquid** is characterized by:

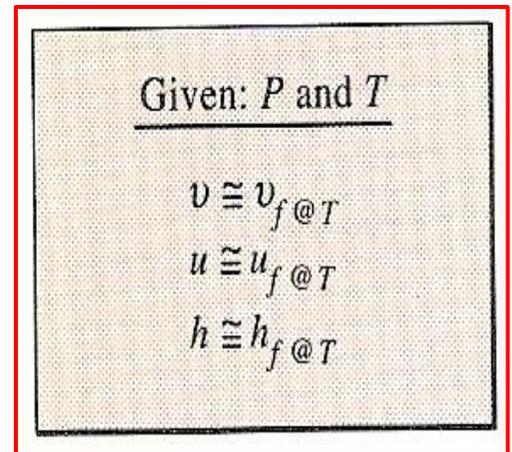
Higher pressures ($P > P_{sat}$ at a given T)

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)



Given: P and T

$$v \cong v_f @ T$$
$$u \cong u_f @ T$$
$$h \cong h_f @ T$$

Figure 2-47. A compressed liquid may be approximation as a saturated liquid at the same temperature.

Example 2-8.

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?

Solution

At 80°C , the saturation pressure of water is 47.39 kPa , and since $5\text{ MPa} > P_{\text{sat}}$, we obviously have compressed liquid as shown in Fig.2-48.

(a) From the compressed liquid table (Table A-7)

$$\left. \begin{array}{l} P = 5\text{ MPa} \\ T = 80^\circ\text{C} \end{array} \right\} u = 333.72\text{ kJ/kg}$$

(b) From the saturation table (Table A-4), we read $u \cong u_f @ 80^\circ\text{C} = 334.86\text{ kJ/kg}$

The error involved is:

$$\frac{334.86 - 333.72}{333.72} \times 100 = 0.34\%$$

Which is less than **1 percent**.

2-7. The ideal-gas equation of state

One way of reporting property data for pure substances is to list values of properties at various states. The property tables provide very accurate information about the properties, but they are very bulky and vulnerable to typographical errors.

Any equation that relates the pressure, temperature, and specific volume of a substance is called an equation of state. They are several equations of state, some simple and other very complex. The simplest and best known equation of state for substances in the gas phase is the ideal-gas equation of state. This equation predicts the P - v - T behavior of a gas quite accurately within some property selected region. In 1802, J. Charles and J. Gay-Lussac, Frenchmen, experimentally

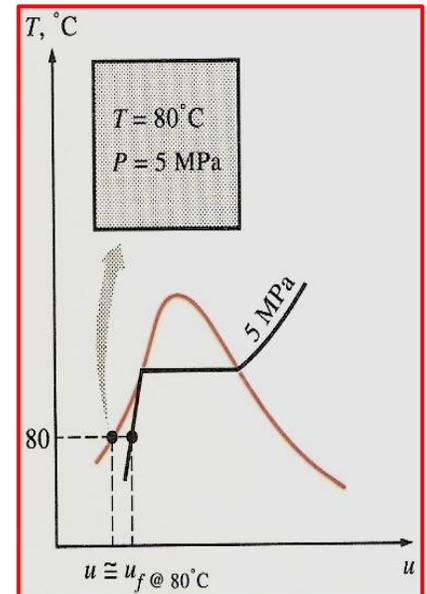


Figure 2-48. Schematic and T - v diagram for Example 2-8.

determined that **at low pressures the volume of a gas is proportional to its temperature.** That is,

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

or $Pv = RT$ (2-9)

Equation 2-9. is called the **ideal-gas equation of state**, or simply the **ideal gas equation**.

Where,

P = absolute pressure

R = gas constant

T = absolute temperature

v = specific volume

The gas constant **R** is different for each gas (**Fig. 2-50.**) and is determined from:

$$R = \frac{R_u}{M} \quad [\text{kJ}/(\text{kg}\cdot\text{K}) \text{ or } \text{kPa}\cdot\text{m}^3/(\text{kg}\cdot\text{K})] \quad (2-10)$$

Where,

R_u = universal gas constant

M = molar mass (**also called molecular weight**) of the gas. Constant **R_u** is the same for all substances and its value is:

<u>Substance</u>	<u>R, kJ/(kg·K)</u>
Air	0.2870
Helium	2.0769
Argon	0.2081
Nitrogen	0.2968

Figure 2-50. Different substances have different gas constants.

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

The **mass** of a system is equal to the product of its molar mass m and the mole number N :

$$m = MN \quad (\text{kg}) \quad (2-12)$$

The values of R and M for several substances are given in **Table A-1**.

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

$$V = mv \longrightarrow PV = mRT \quad (2-13)$$

$$mR = (MN)R = NR_u \longrightarrow PV = NR_u T \quad (2-14)$$

$$V = N\bar{v} \longrightarrow P\bar{v} = R_u T \quad (2-15)$$

Where,

\bar{v} = molar specific volume (m^3/kmol or ft^3/lbmol). A bar above a property will denote values on a unit-mole basis throughout this text (**Fig. 2-51**).

By writing **Eq. 2-13**. twice for a **fixed mass** and simplifying, the properties of an ideal gas at two different states are related to each other by:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad (2-16)$$

Per unit mass	Per unit mole
$v, \text{ m}^3/\text{kg}$	$\bar{v}, \text{ m}^3/\text{kmol}$
$u, \text{ kJ/kg}$	$\bar{u}, \text{ kJ/kmol}$
$h, \text{ kJ/kg}$	$\bar{h}, \text{ kJ/kmol}$

Figure 2-51. Properties per unit mole are denoted with a bar on the top.

Example 2-9.

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

Solution

A sketch of the room is given in **Fig. 2-53**. Air at specified conditions can be treated as an **ideal gas**. From **Table A-1**, the gas constant of air $R = 0.287 \text{ kPa}\cdot\text{m}^3/(\text{kg}\cdot\text{K})$, and the absolute temperature is $T = 25^\circ\text{C} + 273 = 298 \text{ K}$. The volume of the room is:

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

By substituting these into **Eq. 2-13**, the mass of air in the room determined to be:

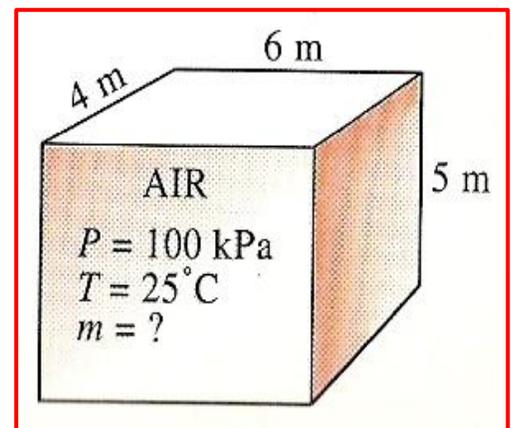


Figure 2-53. Schematic for Example 2-9.

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

2-8. Compressibility factor

The ideal-gas equation is very simple and thus very convenient to use. Gases deviate from ideal-gas behavior significantly at states near the saturation region and the critical point. This deviation from ideal-gas behavior at a given temperature and pressure can accurately be accounted for by the introduction of a correction factor called the compressibility factor Z . It is defined as:

$$Z = \frac{Pv}{RT} \quad (2-17)$$

$$Pv = ZRT \quad (2-18)$$

or, it can also be expressed as:

$$Z = \frac{v_{\text{actual}}}{v_{\text{ideal}}} \quad (2-19)$$

where $v_{\text{ideal}} = RT/P$. Obviously, $Z = 1$

For ideal gases. For real gases Z can be greater than or less than unity (Fig. 2-55).

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 pressures. The normalization is done as:

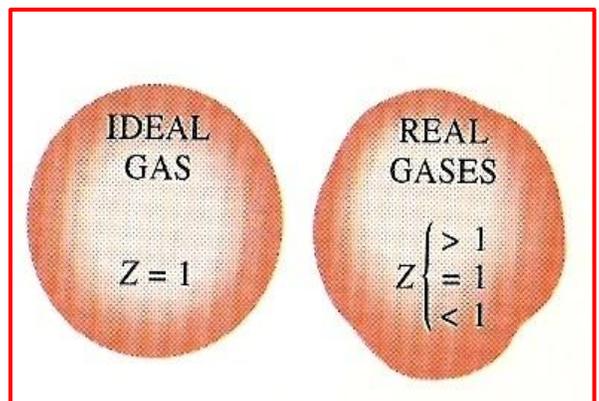


Figure 2-55. The compressibility factor is unity for ideal gases.

$$P_R = \frac{P}{P_{cr}} \quad \text{and} \quad T_R = \frac{T}{T_{cr}} \quad (2-20)$$

Here, P_R = reduced pressure, T_R = reduced temperature

The Z factor for all gases is approximately the same at the same **reduced pressure and temperature** (Fig. 2-56). This is called the **principle of corresponding states**.

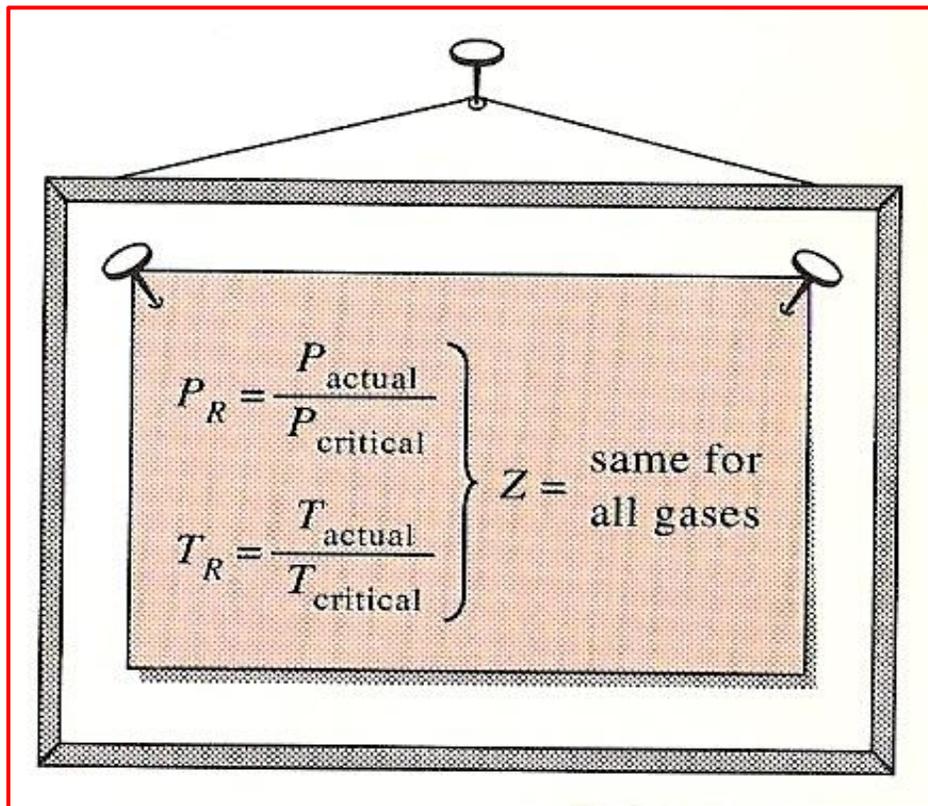


Figure 2-56. The compressibility factor is the same for all gases at the reduced pressure and temperature (principle of corresponding states).

In Fig. 2-57, the experimentally determined Z values are plotted against P_R and T_R for several gases. The gases seem to obey the

principle of corresponding states reasonably well. By curve-fitting all the data, we obtain the generalized compressibility chart which can be used for all gases.

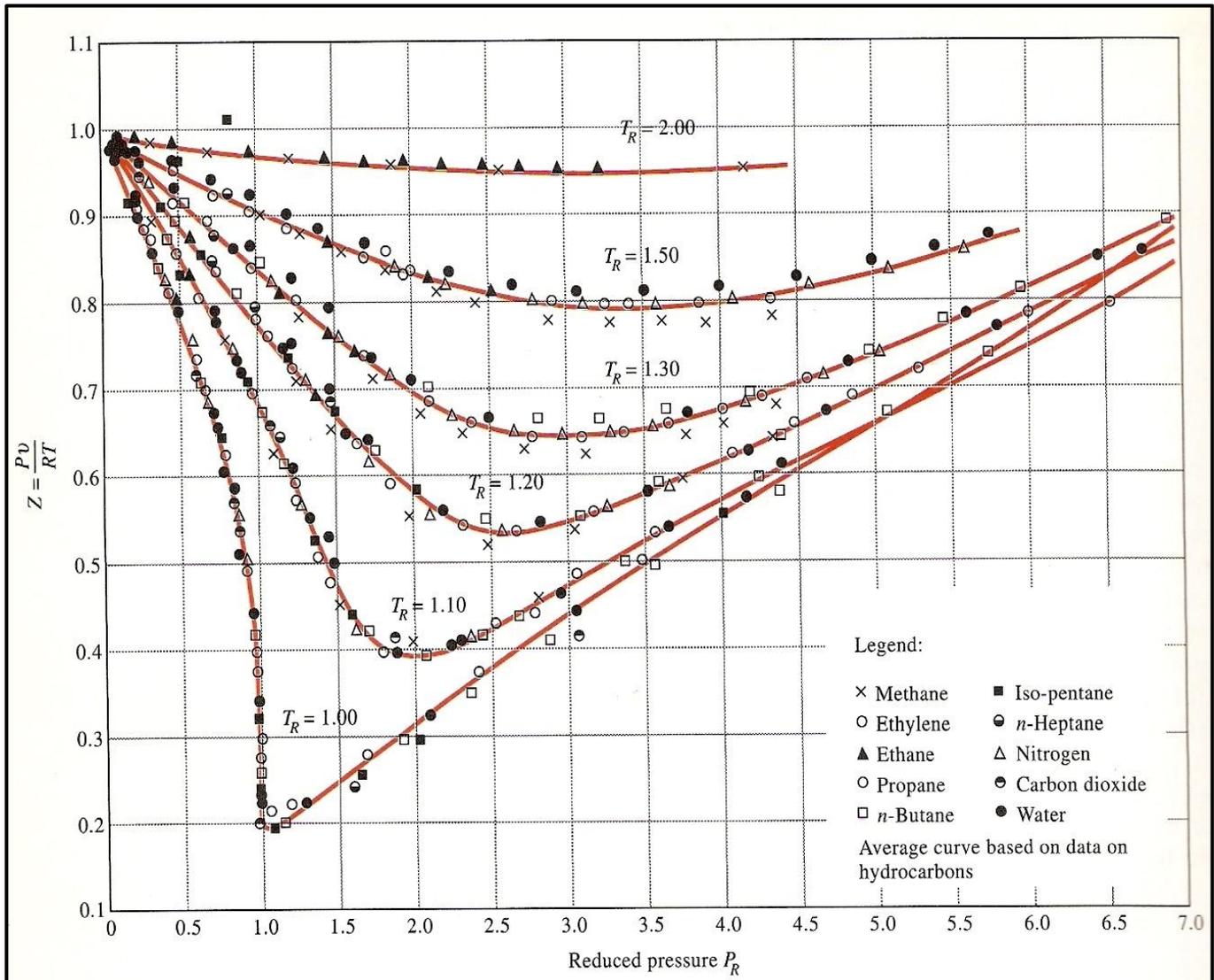


Figure 2-57. Comparison of Z factors for various gases.

The following observations can be made from generalized compressibility chart:

1. At very low pressures ($P_R \ll 1$), the gases behave as an ideal gas regardless of temperature (Fig. 2-58).

2. At **high temperatures** ($T_R > 2$), ideal-gas behavior can be assumed with good accuracy regardless of pressure (except when $P_R \gg 1$).

3. The deviation of a gas from ideal-gas behavior is greatest in the vicinity of the critical point (**Fig. 2-59**).

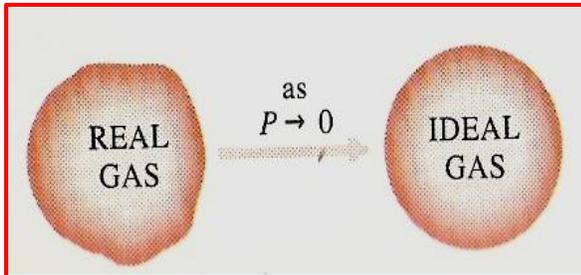


Figure 2-58. At very low pressures, all gases approach ideal-gas behavior (regardless of their temperature).

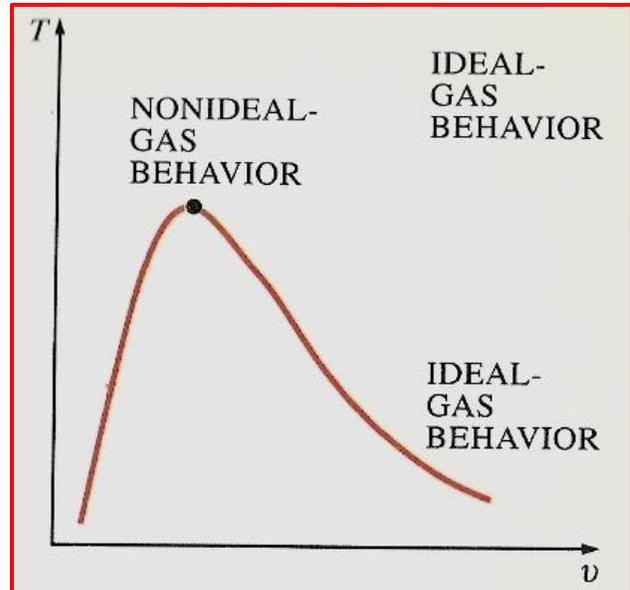


Figure 2-59. Gases deviate from the ideal-gas behavior most in the neighborhood of the critical point.

Example 2-10.

Determine the **specific volume** of refrigerant-12 at **1 MPa** and **50°C**, using (a) the refrigerant-12 tables, (b) the ideal-gas equation of state, and (c) the generalized compressibility chart. Also determine the **error** involved in parts (b) and (c).

Solution

A sketch of the system is given in **Fig. 2-60**. The gas constant, the critical pressure, and the critical temperature of refrigerant-12 are determined from **Table A-1** to be:

$$R = 0.0688 \text{ kPa}\cdot\text{m}^3/(\text{kg}\cdot\text{K})$$

$$P_{cr} = 4.01 \text{ MPa}$$

$$T_{cr} = 384.7 \text{ K}$$

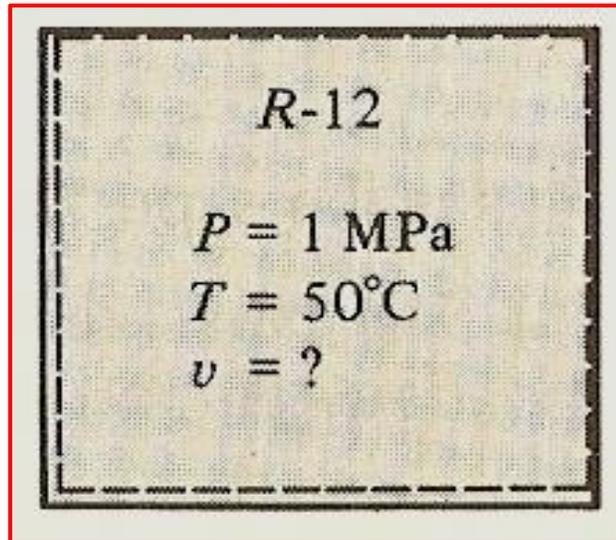


Figure 2-60. Schematic for **Example 2-10**.

(a) **The specific volume** of refrigerant-12 at the specified state is determined from **Table A-13** to be:

$$\left. \begin{array}{l} P = 1 \text{ MPa} \\ T = 50^\circ\text{C} \end{array} \right\} v = 0.01837 \text{ m}^3/\text{kg}$$

This is the experimentally determined value, and thus it is the **most accurate**.

(b) **The specific volume** of the refrigerant-12 under the ideal-gas assumption is determined from the ideal-gas relation (**Eq.2-9**) to:

$$v = \frac{RT}{P} = \frac{[(0.0688 \text{ kPa}\cdot\text{m}^3)/(\text{kg}\cdot\text{K})](323 \text{ K})}{1000 \text{ kPa}} = 0.02222 \text{ m}^3/\text{kg}$$

Therefore, treating the refrigerant-12 vapor as an **ideal gas** would result in an **error** of:

$$\% \text{ error} = \frac{0.02222 - 0.01837}{0.01837} \times 100 = 20.8 \%$$

(c) To determine the correction factor Z from the compressibility chart, we first need to calculate the reduce pressure and temperature:

$$P_R = \frac{P}{P_{cr}} = \frac{1 \text{ MPa}}{4.01 \text{ MPa}} = 0.249$$

$$T_R = \frac{T}{T_{cr}} = \frac{323 \text{ K}}{384.7} = 0.840$$

$Z = 0.83$ (Fig.A-30)

Thus, $v = Zv_{ideal} = (0.83)(0.02222 \text{ m}^3/\text{kg}) = 0.01844 \text{ m}^3/\text{kg}$

$$\% \text{ error} = \frac{0.01844 - 0.01837}{0.01837} \times 100 = 0.38 \%$$

When P and v , or T and v , are given instead of P and T , the generalized compressibility chart can still be used to determine the third property, but it would involve tedious trial and error. Therefore, it is very convenient to define one more reduced property called the **pseudo-reduced specific volume** v_R as:

$$v_R = \frac{v_{actual}}{RT_{cr}/P_{cr}} \quad (2-21)$$

v_R is defined differently from P_R and T_R . It is related to T_{cr} and P_{cr} instead of v_{cr} . Lines of constant v_R are also added to the compressibility charts, and this enables one to determine T or P without having to resort to time-consuming iterations (Fig. 2-61).

Figure 2-61. The compressibility factor can also be determine from a knowledge of P_R and v_R .

$$\left. \begin{aligned} P_R &= \frac{P}{P_{cr}} \\ v_R &= \frac{v}{RT_{cr}/P_{cr}} \end{aligned} \right\} Z = \dots \quad (\text{Fig. A-30})$$

Example 2-11.

Determine the **pressure** of water vapor at **600°F** and **0.514 ft³/lbm**, using (a) the steam tables, (b) the ideal-gas equation, and (c) the generalized compressibility chart?

Solution

A sketch of the system is given in **Fig. 2-62**. The gas constant, the critical pressure, and the critical temperature of steam are determined from **Table A-1E** to be:

$$R = 0.5956 \text{ psia}\cdot\text{ft}^3/(\text{lbm}\cdot\text{R})$$

$$P_{cr} = 3204 \text{ psia}$$

$$T_{cr} = 1165.3 \text{ R}$$

(a) The pressure of steam at the specified state is determined from **Table A-6E** to be:

$$\left. \begin{aligned} v &= 0.514 \text{ ft}^3/\text{lbm} \\ T &= 600^\circ\text{F} \end{aligned} \right\} P = 1000 \text{ psia}$$

This is the experimentally value, and thus it is the **most accurate**.

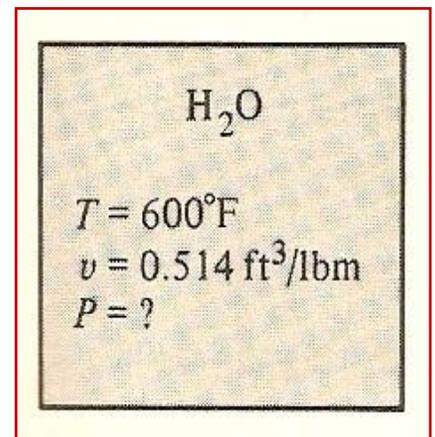


Figure 2-62 Schematic for **Example 2-11**.

(b) The pressure of steam under the ideal-gas assumption is determined from the ideal-gas relation (Eq.2.9) to be:

$$P = \frac{RT}{v} = \frac{[0.5956 \text{ psia.ft}^3/(\text{lbm.R})](1060 \text{ R})}{0.514 \text{ ft}^3/\text{lbm}} = 1228.3 \text{ psia}$$

Therefore, treating the steam as an **ideal gas** would result in an **error** of :

$$\% \text{ error} = \frac{1228.2 - 1000}{1000} \times 100 = 22.8 \%$$

(c) To determine the correction **Z** from the compressibility chart (Fig.A-30), we first need to calculate the **pseudo-reduced specific volume** and the reduced temperature:

$$v_R = \frac{v_{\text{actual}}}{RT_{\text{cr}}/P_{\text{cr}}} = \frac{(0.514 \text{ ft}^3/\text{lbm})(3204 \text{ psia})}{[0.5056 \text{ psia.ft}^3/(\text{lbm.R})](1165.3 \text{ R})} = 2.373$$

$$T_R = \frac{T}{T_{\text{cr}}} = \frac{1060 \text{ R}}{11653 \text{ R}} = 0.91$$

} $P_R = 0.33$

Thus, $P = P_R P_{\text{cr}} = (0.33)(3204 \text{ psia}) = 1057.3 \text{ psia}$

$$\% \text{ error} = \frac{1057.3 - 1000}{1000} \times 100 = 5.7 \%$$

Using the compressibility chart **reduced the error** from **22.8 to 5.7 percent**, which is acceptable for most engineering purposes (Fig. 2-63). A bigger chart, of course, would give better resolution and reduce the reading errors. Notice that we did not have to determine **Z** in this problem since we could read P_R directly from the chart.

Figure 2-63 Results obtained by using the compressibility chart are usually within a few percent of the experimentally determined values.

	<u>P, psia</u>
Exact	1000.0
Z chart	1057.3
Ideal gas	1228.3

(from Example 2-11)

2-9. Other Equations of State

The **ideal-gas equation of state** is **very simple**, but its range of **applicability is limited**. It is desirable to have equations of state that represent the $P-v-T$ behavior of substances accurately over a larger region with **no limitations**. Several equations have been proposed for this purpose (**Fig. 2-64**).

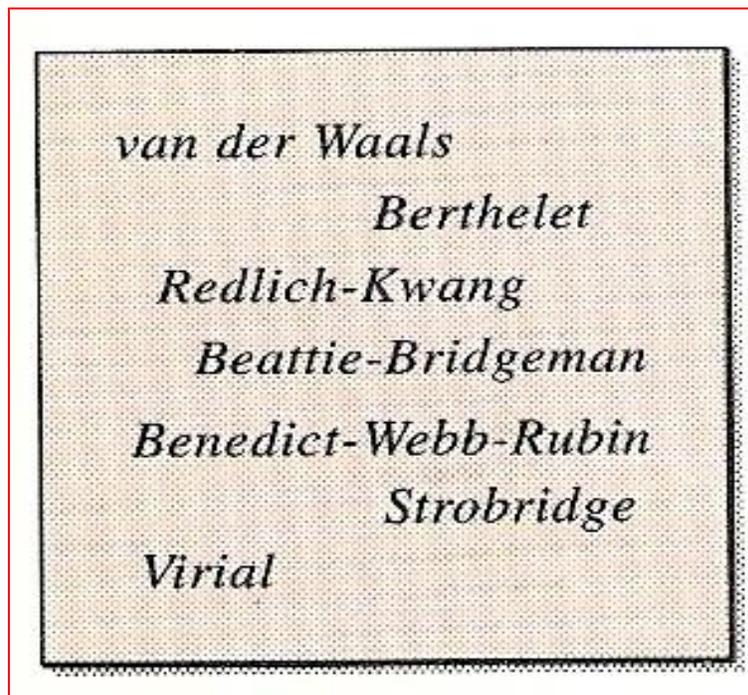


Figure 2-64 Several equations of state are proposed throughout the history.

Van der Waals Equation of State

The van der Waals equation of state is one of the earliest equations was proposed in **1873**, and it has **two constants** which are determined from the behavior of a substance at the critical point. The van der Waals equation of state is given by:

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT \quad (2-22)$$

Van der Waals intended to improve the ideal-gas equation of state by including two of the effects not considered in the ideal-gas model: The intermolecular attraction forces and the volume occupied by the molecules themselves. a/v^2 accounts for the **intermolecular attraction forces**, and b accounts for the **volume** occupied by the gas molecules. Van der Waals proposed to correct this by replacing v in ideal-gas relation with the quality $v - b$, where b represents the volume by the gas molecules per unit mass.

The equation determination of the two constants appearing in this equation is based on the observation that the critical isotherm on a P - v diagram has a **horizontal inflection** point at the **critical point** (Fig. 2-65). Thus the first and second derivatives of P with respect to v at the **critical point** must be zero. That is,

$$\left(\frac{\partial P}{\partial v}\right)_{T=T_{cr}=\text{const}} = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial v^2}\right)_{T=T_{cr}=\text{const}} = 0 \quad (2-23)$$

By performing the differentiations and elimination v_{cr} , constants a and b are determined to be:

$$a = \frac{27R^2T_{cr}^2}{64P_{cr}} \quad \text{and} \quad b = \frac{RT_{cr}}{8P_{cr}} \quad (2-24)$$

The constants a and b can be determined for any substance from the critical-point data alone (Table A-1). The van der Waals equation of state can also be expressed on a unitmole basis by replacing the v in Eq. 2-22 by \bar{v} , and the R in Eq. 2-23 and 2-24 by R_u .

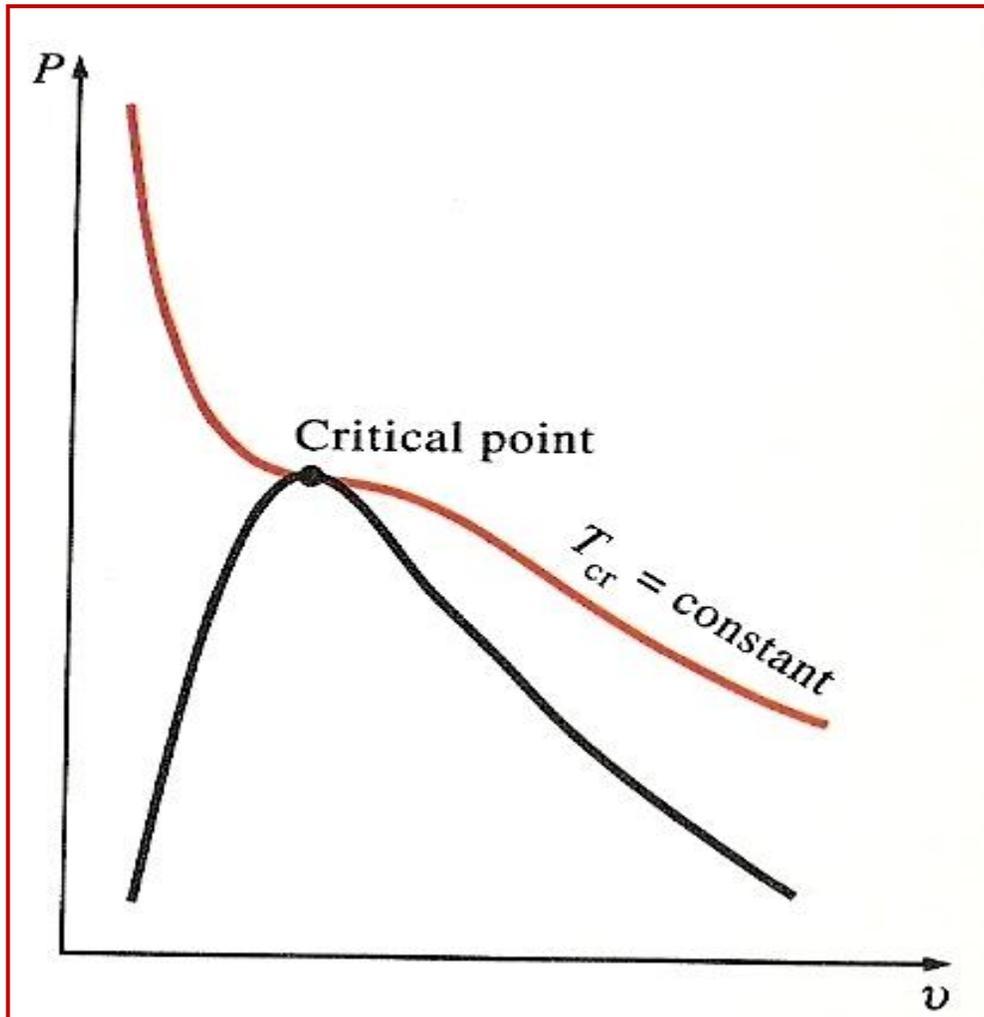


Figure 2-65 Critical isotherm of a pure substance has an inflection at the critical state.

Beattie-Bridgeman Equation of State

The **Beattie-Bridgeman equation of state** was proposed in **1928** as one of the best known equations, and is reasonably accurate.

It is an equation of state based on **five** experimentally determined **constants**. It was proposed in the form of:

$$P = \frac{R_u T}{\bar{v}^2} \left(1 - \frac{c}{\bar{v} T^3} \right) (\bar{v} + B) - \frac{A}{\bar{v}^2} \quad (2-25)$$

where

$$A = A_0 \left(1 - \frac{a}{\bar{v}} \right) \quad \text{and} \quad B = B_0 \left(1 - \frac{b}{\bar{v}} \right) \quad (2-26)$$

The constants appearing in the above equation are given in **Table A-29a** for various substances.

Benedict-Webb-Rubin Equation of State

Benedict, **Webb**, and **Rubin** extended the **Beattie-Bridgeman** equation in **1940** by using the number of constants to **eight**. It is expressed as:

$$P = \frac{R_u T}{\bar{v}^2} + \left(B_0 R_u T - A_0 - \frac{c_0}{T^2} \right) \frac{1}{\bar{v}^2} + \frac{b R_u T - a}{\bar{v}^3} + \frac{a\alpha}{\bar{v}^6} + \frac{c}{\bar{v}^3 T^2} \left(1 + \frac{\gamma}{\bar{v}^2} \right) e^{-\gamma/\bar{v}^2} \quad (2-27)$$

The values of constants of the above two equations are given in **Table A-29b**. In **1962**, **Strobridge** further **extended** this equation by raising the number of **constants** to **16** (**Fig.2-66**).

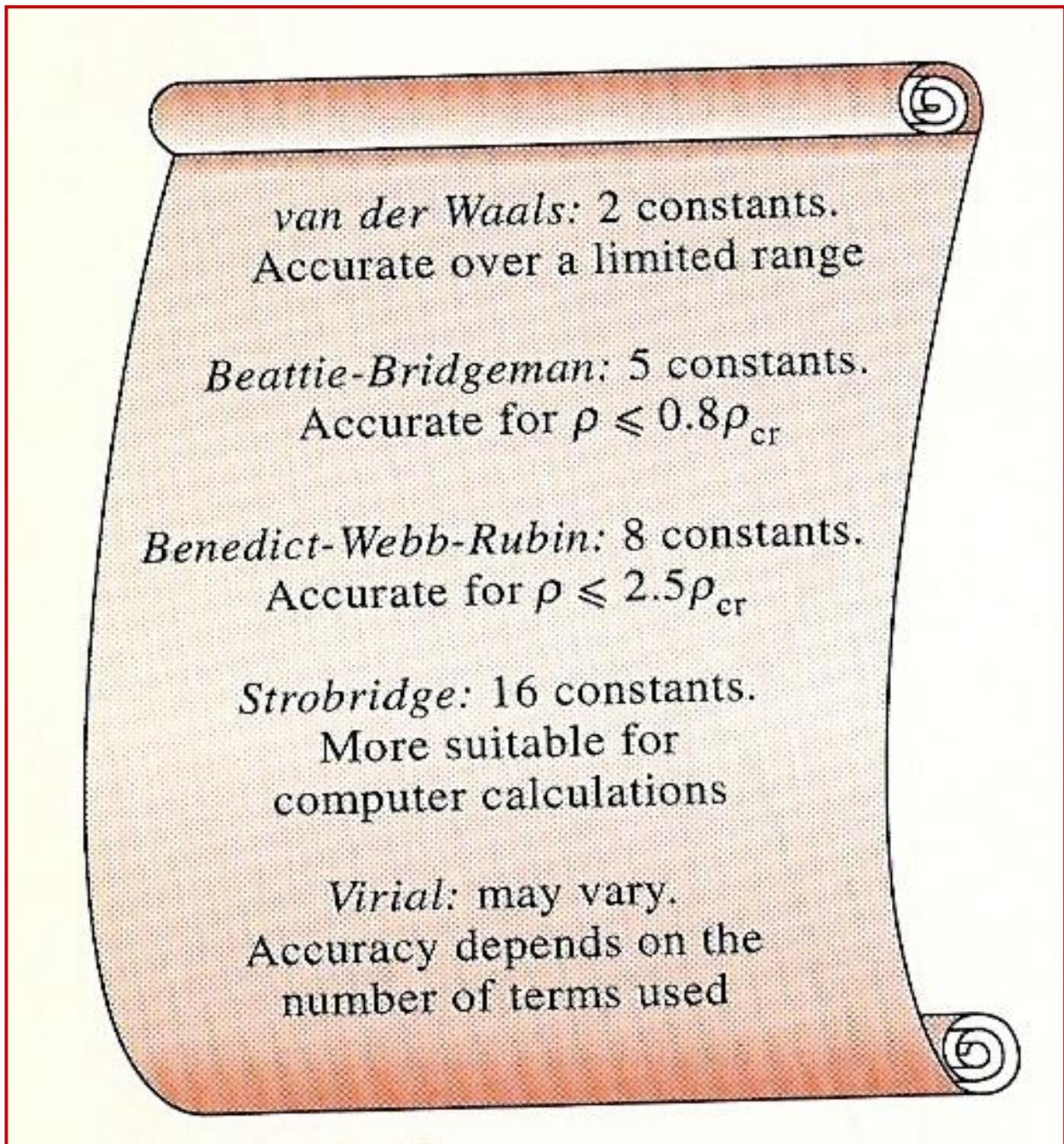


Figure 2-66 Complex equations of state represent the P - v - T behavior of gases more accurately over a wide range.

Virial Equation of State

The equation of state of a substance can also be expressed in a **series** form as:

$$P = \frac{RT}{v} + \frac{a(T)}{v^2} + \frac{b(T)}{v^3} + \frac{c(T)}{v^4} + \frac{d(T)}{v^5} + \dots \quad (2-28)$$

This and similar equations are called the virial equation of state, and the coefficients $a(T)$, $b(T)$, $c(T)$, etc., which are functions of temperature alone are called **virial coefficients**. These **coefficients** can be **determined experimentally** or **theoretically** from **statistical mechanics**.

All equations of state discussed above are **applicable to the gas phase** of the substances **only**, and should **not be used** for **liquids** or **liquid-vapor mixtures**.

The accuracy of the van der Waals, Beattie-Bridgeman, and Benedict-Webb-Rubin equations of state is illustrated in **Fig. 2-65**. It is obvious from this figure that the **Benedict-Webb-Rubin equation** of state is the **most accurate**.

Example 2-11.

Predict the **pressure of nitrogen** gas at $T = 175$ K and $v = 0.00375$ m³/kg on the basis of (a) the ideal-gas equation of state, (b) the van der Waals equation of state, (c) the Beattie-Bridgeman equation of state, and (d) the Benedict-webb-Rubin equation of state. Compare the values obtained to the **experimentally** determined value of 10000 kPa.

Solution

From the superheated nitrogen table (**Table A-16**):

$$\left. \begin{array}{l} T = 175 \text{ K} \\ v = 0.00375 \text{ m}^3/\text{kg} \end{array} \right\} = P = 10 \text{ MPa} = 10000 \text{ kPa}$$

(a) By using **the ideal-gas equation** of state (**Eq. 2-9**), the **pressure** is found to be:

$$P = \frac{RT}{v} = \frac{[0.2968 \text{ kPa}\cdot\text{m}^3/(\text{kg}\cdot\text{K})](175\text{K})}{(0.00375 \text{ m}^3/\text{kg})} = 13860 \text{ kPa}$$

The **error** is:

$$\% \text{ error} = \frac{13860 - 10000}{10000} \times 100 = 38.6 \%$$

(b) For nitrogen: $\left. \begin{array}{l} T_{\text{cr}} = 126.2 \text{ K} \\ P_{\text{cr}} = 3.39 \text{ MPa} = 3390 \text{ kPa} \\ R = 0.2968 \text{ kPa}\cdot\text{m}^3/(\text{kg}\cdot\text{K}) \end{array} \right\} \text{ (Table A-1)}$

The **van der Waals constants** for nitrogen are determined from **Eq. 2-24** to be:

$$\begin{aligned} a &= \frac{27R^2T_{\text{cr}}^2}{64P_{\text{cr}}} = \frac{(27)(0.2968 \text{ kPa}\cdot\text{m}^3/\text{kg}\cdot\text{K})^2(126.2 \text{ K})^2}{(64)(3390 \text{ kPa})} \\ &= 0.175 \text{ m}^6\cdot\text{kPa}/\text{kg}^2 \end{aligned}$$

$$b = \frac{RT_{cr}}{8P_{cr}} = \frac{(0.2968 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(126.2 \text{ K})}{(8)(3390 \text{ kPa} \cdot \text{m}^3)} = 0.00138 \text{ m}^3/\text{kg}$$

From Eq. 2-22,

$$P = \frac{RT}{v-b} - \frac{a}{v^2} = 9465 \text{ kPa}$$

The error is:

$$\% \text{ error} = \frac{10000 - 9465}{10000} \times 100 = 5.4 \%$$

(c) The constants in the Beattie-Bridgemen equation are determined from Table A-29a to be:

$$A = 102.29$$

$$B = 0.05378$$

$$c = 4.2 \times 10^4$$

Also, $\bar{v} = Mv = (28.013 \text{ kg/kmol})(0.00375 \text{ m}^3/\text{kg}) = 0.10505 \text{ m}^3/\text{kmol}$. Substituting these values into Eq.2-25, we obtain:

$$P = \frac{R_u T}{\bar{v}^2} \left(1 - \frac{c}{\bar{v} T^3} \right) (\bar{v} + B) - \frac{A}{\bar{v}^2} = 10110 \text{ kPa}$$

The error is:

$$\% \text{ error} = \frac{10110 - 10000}{10000} \times 100 = 1.1 \%$$

(d) The constants in the Benedict-Webb-Rubin equation are determined from Table A-29b to be:

$$a = 2.54$$

$$A_0 = 106.73$$

$$b = 0.002328$$

$$B_0 = 0.04074$$

$$c = 7.379 \times 10^4$$

$$C_0 = 8.164 \times 10^5$$

$$\alpha = 1.272 \times 10^{-4} \quad \gamma = 0.0053$$

Substituting these values into **Eq. 2-27**, we obtain:

$$P = \frac{R_u T}{\bar{v}^2} + \left(B_0 R_u T - A_0 - \frac{c_0}{T^2} \right) \frac{1}{\bar{v}^2} + \frac{b R_u T - a}{\bar{v}^3} + \frac{a\alpha}{\bar{v}^6} + \frac{c}{\bar{v}^3 T^2} \left(1 + \frac{\gamma}{\bar{v}^2} \right) e^{-\gamma/\bar{v}^2} = 10009 \text{ kPa}$$

$$\% \text{ error} = \frac{10009 - 10000}{10000} \times 100 = 0.09 \%$$

Thus the **accuracy** of the **Benedict-Webb-Rubin** equation of state is rather impressive in this case.