MSE 321
ENGINEERING THERMODYNAMICS AND HEAT TRANSFER

- Properties of Pure Substances (Chapter 4)
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.**

Note: 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. For example, a mixture of ice and liquid water is a pure substance because both phases have the same chemical composition. A mixture of liquid air and gaseous air, however, is not a pure substance since the composition of liquid air is different from the composition of gaseous air, and thus the mixture is no longer chemically homogeneous.

PHASES OF A PURE SUBSTANCE

A pure substance may exist in different phases, i.e., solid, liquid, and gas which are dictated by the microscopic structure (Fig. 1).

**Figure1:** The microscopic arrangement in different phases: (a) 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, (b) 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, and (c) in a 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.

**Definition of phase**

A phase is identified as having a distinct molecular arrangement that is homogeneous throughout and separated from the others by easily identifiable boundary surfaces. The two phases of H₂O in iced water (solid and liquid) represent a good example of this.

**Note:** 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 pressures.
Phase-Change Processes of Pure Substances

Compressed liquid and saturated liquid
Consider a piston–cylinder device containing liquid water at \( T = 20^\circ C \) and \( P = 1 \) atm (state 1 in Fig. 2). Under these conditions, water exists in the liquid phase, and it is called a “compressed liquid”, or a “subcooled liquid”, meaning that it is not about to vaporize.

Heat is now transferred to the water until its temperature rises to \( T = 40^\circ C \). As the temperature rises, the liquid water expands slightly, and so its specific volume increases. To accommodate this expansion, the piston moves up slightly. The pressure in the cylinder remains constant at \( P = 1 \) atm during this process since it depends on the outside barometric pressure and the weight of the piston, both of which are constant. Water is still a compressed liquid at this state since it has not started to vaporize.

As more heat is transferred, the temperature keeps rising until it reaches \( T = 100^\circ C \) (state 2 in Fig. 2). At this point water is still a liquid, but any further heat addition would cause some of the liquid to vaporize (phase-change). A liquid that is about to vaporize is called a “saturated liquid”. Therefore, state 2 is a saturated liquid state.

![Figure 2: Phase change process of water at constant pressure.](Image)

Saturated vapor and superheated vapor
Once boiling starts, the temperature stops rising until the liquid is completely vaporized. The temperature remains constant during the entire phase-change process if the pressure is held constant. During a boiling process (state 3 in Fig. 2) the only change we observe is a large increase in the volume and a steady decline in the liquid level as a result of more liquid turning to vapor. As we continue transferring heat, the vaporization process continues until the last drop of liquid is vaporized (state 4 in Fig. 2). At this point, the entire cylinder is filled with vapor that is on the borderline of the liquid phase. Any heat loss from this vapor would cause some of the vapor to condense (phase change from vapor to liquid). A vapor that is about to condense is called a “saturated vapor”. Therefore, state 4 is a saturated vapor state.

A substance at states between 2 and 4 is referred to as a “saturated liquid–vapor mixture” since the liquid and vapor phases coexist in “thermal equilibrium” at these states. Once the phase-change process is completed, we are back to a single-phase region again (this time vapor), and further transfer of heat results in an increase in both the temperature and the specific volume (state 5 in Fig. 2).
At state 5, the temperature of the vapor is $T = 300^\circ \text{C}$; and if we transfer some heat from the vapor, the temperature may drop somewhat but no condensation takes place. A vapor that is not about to condense (i.e., not a saturated vapor) is called a “superheated vapor”. Therefore, water at state 5 is a superheated vapor.

This constant-pressure phase-change process is illustrated on a $T - \nu$ diagram in Fig. 3. If the entire process described here is reversed by cooling the water while maintaining the pressure at the same value, the water will go back to state 1, retracing the same path.

![Figure 3: $T - \nu$ diagram for the heating process of water at constant pressure.](image)

**SATURATION TEMPERATURE AND SATURATION PRESSURE**

During a phase-change process, pressure and temperature are dependent properties, which means, once the value for one of them is known, the other takes a certain value.

- At a given pressure, the temperature at which a pure substance changes phase is called the “saturation temperature” $T_{\text{sat}}$.
- At a given temperature, the pressure at which a pure substance changes phase is called the “saturation pressure” $P_{\text{sat}}$.

For example, at a pressure of 1 atm (101.325 kPa), $T_{\text{sat}}$ for water is 99.97°C. Conversely, at a temperature of 99.97°C, $P_{\text{sat}}$ for water is 101.325 kPa.

**Note:** Saturation tables that list the saturation pressure against the temperature (or the saturation temperature against the pressure) are available for practically all substances.

**Note:** A plot of $T_{\text{sat}}$ versus $P_{\text{sat}}$, such as the one given for water in Fig. 4, is called a liquid–vapor saturation curve. A curve of this kind is characteristic of all pure substances.
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. Here, we discuss the diagrams based on intensive properties, i.e., $T - \nu$, $P - \nu$, and $P - T$ diagrams for pure substances.

- The $T - \nu$ diagram
  Consider the process of liquid water evaporation at a constant atmospheric pressure (inside a piston-cylinder system) as we discussed above in Fig. 3.
Assume that we add weights on top of the piston until the pressure inside the cylinder reaches 1 MPa. At this pressure, water has a somewhat smaller specific volume than it does at 1 atm pressure (although, we always refer to liquids as incompressible substances, but in reality they can be compressed very slightly). As heat is transferred to the water at this new pressure, the process follows a path that looks very much like the process path at 1 atm pressure, as shown in Fig. 3, but there are some noticeable differences.

- **First:** water starts boiling at a much higher temperature (179.9°C) at this pressure.
- **Second:** the specific volume of the saturated liquid is larger, and the specific volume of the saturated vapor is smaller than the corresponding values at 1 atm pressure. That is, the horizontal line that connects the saturated liquid and saturated vapor states is much shorter (See Fig. 5).

**Critical point**

As the pressure is increased further, this saturation line continues to shrink, as shown in Fig. 5, and it becomes a point when the pressure reaches 22.06 MPa for the case of water. This point is called “the critical point”, and it is defined as the point at which the saturated liquid and saturated vapor states are identical!

**Note:** At pressures above the critical pressure, there is not a distinct phase-change process, and there is only one phase present.

**Saturated liquid line and saturated vapor line**

The saturated liquid can be connected by a line called the “saturated liquid line”, and also saturated vapor states can be connected by another line, called the “saturated vapor line”. These two lines meet at the critical point, forming a dome as shown in Fig. 6. All the compressed liquid states are located in the region to the left of the saturated liquid line, called the compressed liquid region. All the superheated vapor states are located to the right of the saturated vapor line, called the superheated vapor region. In these two regions, the substance exists in a single phase, a liquid or a vapor. All the states that involve both phases in equilibrium are located under the dome, called the saturated liquid–vapor mixture region, or the wet region.

Figure 6: Saturated liquid and vapor lines in $T - \nu$ diagram for a pure substance.
**The $P–\nu$ diagram**

The general shape of the $P–\nu$ diagram of a pure substance is very much like the $T–\nu$ diagram, but the $T = \text{constant}$ lines on this diagram have a downward trend, as shown in Fig. 7.

![Figure 7: $P–\nu$ diagram for a pure substance.](image)

**The $P–T$ diagram**

Figure 8 shows the $P–T$ diagram of a pure substance. This diagram is often called “the phase diagram” since all three phases are separated from each other by three lines. The sublimation line separates the solid and vapor regions, the vaporization line separates the liquid and vapor regions, and the melting (or fusion) line separates the solid and liquid regions. These three lines meet at the triple point, where all three phases coexist in equilibrium. The vaporization line ends at the critical point because no distinction can be made between liquid and vapor phases above the critical point. Substances that expand and contract on freezing differ only in the melting line on the $P–T$ diagram.

![Figure 8: $P–T$ diagram for a pure substance.](image)
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.

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:

\[ v_f = \text{specific volume of saturated liquid} \]
\[ v_g = \text{specific volume of saturated vapor} \]
\[ v_{fg} = \text{difference between } v_g \text{ and } v_f \ (v_{fg} = v_g - v_f) \]

ENTHALPY: A COMBINATION PROPERTY

Enthalpy denoted by \( H \) is a property defined as \( H = U + PV \) (kJ) or

\[
\frac{h}{m} = \frac{H}{m} = \frac{U + PV}{m} = \frac{u + pV}{kg}
\]  

SATURATED LIQUID–VAPOR MIXTURE

During a vaporization process, a substance exists as part liquid and part vapor (see Fig. 9). That is, it is a mixture of saturated liquid and saturated vapor (Fig. 9). To analyze this mixture properly, we need to know the proportions of the liquid and vapor phases in the mixture. This is done by defining a new property called the quality “\( x \)” as the ratio of the mass of vapor to the total mass of the mixture:

\[
x = \frac{m_{\text{vapor}}}{m_{\text{total}}} \]

where

\[
m_{\text{total}} = m_{\text{liquid}} + m_{\text{vapor}} = m_f + m_g
\]

Note: The value of quality \( x \) changes between 0 and 1, i.e., \( 0 \leq x \leq 1 \). The quality \( x = 1 \) represents a saturated vapor and \( x = 1 \) represents a saturated liquid.

Note: In saturated mixtures, quality can serve as one of the two independent intensive properties needed to describe a state. Note that the properties of the saturated liquid and vapor are the same whether they exist alone or in a mixture.
Figure 9: The relative amounts of liquid and vapor phases in a saturated mixture are specified by the quality $x$.

The properties of the “mixture” are the volume-averaged properties. To perform volume averaging we start with the volume,

$$ V_{\text{total}} = V_{\text{liquid}} + V_{\text{vapor}} = V_f + V_g $$  \hspace{1cm} (4)

Since $V = mV$ then the above equation can be written as

$$ m_fV_{\text{avg}} = m_fV_f + m_gV_g = (m_f - m_g)V_f + m_gV_g $$  \hspace{1cm} (5)

Dividing by $m_f$ gives

$$ V_{\text{avg}} = (1-x)V_f + xV_g $$

$$ = V_f - xV_f + xV_g $$

$$ = V_f + x(V_g - V_f) $$

$$ = V_f + xV_{fg} $$

or

$$ x = \frac{V_{avg} - V_f}{V_{fg}} $$  \hspace{1cm} (6)

Figure 10: Graphical presentation for $V_f$, $V_g$, $V_{fg}$, and $V_{avg}$ in a $P-v$ diagram.
Similarly for other properties of a mixture, such as energy and enthalpy, we can write,

\[ u_{\text{avg}} = u_f + xu_{fg} \]  

\[ h_{\text{avg}} = h_f + rh_{fg} \]  

**SUPERHEATED VAPOR**

In the region to the right of the saturated vapor line and at temperatures above the critical point temperature, a substance exists as “superheated vapor”.

Since the superheated region is a single-phase region (vapor phase only), temperature and pressure are no longer dependent properties and they can conveniently be used as the two independent properties in the tables.

**COMPRESSED LIQUID**

Variation of properties of compressed liquid with pressure is very mild (incompressible). A general approximation is to treat compressed liquid as saturated liquid at the given temperature. Thus,

\[ y_{\text{avg}} \approx y_{f@T} \quad \text{where} \quad y = V, u, \text{or } h \]  

The property most affected by pressure is enthalpy \( h \). For enthalpy of compressed liquids use the following approximation

\[ h_{\text{avg}} \approx h_{f@T} + \nu_{f@T} \left( P - P_{\text{sat}@T} \right) \]  

**THE IDEAL GAS EQUATION OF STATE**

Any equation that relates the pressure \( P \), temperature \( T \), and specific volume \( \nu \) 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.

**Note:** 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, and this proportionality can be expressed via “the ideal-gas equation of state”

\[ P\nu = RT \quad \text{or} \quad P = \rho RT \]  

where \( R \) (kJ/kg K) is a constant called “gas constant” which is different for each gas, and is defined as
\begin{equation}
R = \frac{R_u}{M} \left[ \frac{\text{kJ}}{\text{kg} \cdot \text{K}} \right]
\end{equation}

where \( R_u \) is the universal gas constant \( R_u = 8.314 \) (kJ/kmol K) which is constant for all gases, and \( M \) (kg/kmol) is the molar mass.

The values for the universal gas constant in different units are:

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

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

\[ m = M N \quad [\text{g}] \]  

For air the molar mass is \( M = 28.97 \) (kg/kmol), then \( R_{\text{air}} = 0.287 \) (kJ/kg K).

**Note:** The values of \( R \) and \( M \) for several substances are given in Table A–1.

In general, at low pressures and high temperatures, the density of a gas decreases, and the gas behaves as an ideal gas under these conditions.

**Note:** Temperature in the ideal gas law should be absolute temperature (i.e., in Kelvin and NOT in °C).

Since \( R \) is a constant for a gas, for two different states of a gas (state 1 and state 2) one can write

\[ R = \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \]  

- In the range of practical interest, many familiar gases such as air, nitrogen, oxygen, hydrogen, helium, argon, neon, and \( \text{CO}_2 \) can be treated as ideal gases with negligible error.
- Water vapor and 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.

**IS WATER VAPOR AND IDEAL GAS?**

At pressures below 10 kPa, water vapor can be treated as an ideal gas, regardless of its temperature, with negligible error (less than 0.1 percent). At higher pressures, however, the ideal gas assumption yields unacceptable errors, particularly in the vicinity of the critical point and the saturated vapor line (over 100 percent error). Therefore, in air-conditioning applications, the water vapor in the air can be treated as an ideal gas with essentially no error since the pressure of the water vapor is very low. In steam power plant applications, however, the pressures involved are usually very high; therefore, ideal-gas relations should not be used, see Fig. 11.

![Figure 11: Percentage of error for considering water vapor as an ideal gas is calculated and shown from \( \left( \frac{v_{	ext{true}} - v_{\text{ideal}}}{v_{\text{true}}} \right) \times 100 \) for different pressures and temperatures. The region where steam can be treated as an ideal gas with less than 1 percent error is the shadowed area.](image)
**COMPRSSIBILITY EFFECTS**

The assumption of ideal gas relation implies that forces between gas molecules is small, and thus, gas particles act independent of one another.

However, in reality, due to forces between gas molecules, 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 $Z$ defined as

$$Z = \frac{P_\text{v}}{RT}$$

or

$$P_\text{v} = ZRT$$

(15)

It can be expressed as

$$Z = \frac{\nu_\text{actual}}{\nu_\text{ideal}}$$

where

$$\nu_\text{ideal} = \frac{RT}{P}$$

(16)

For real gases $Z$ can be greater than or less than unity. The farther away $Z$ is from unity, the more the gas deviates from ideal-gas behavior.

*Figure 12: Comparison of $Z$ factors for various gases.*
Gases behave very much the same at temperatures and pressures normalized with respect to their critical temperatures \( T_{\text{cr}} \) and critical pressures \( P_{\text{cr}} \). The normalization is done (always using absolute pressure and temperature) as

\[
P_R = \frac{P}{P_{\text{cr}}} \quad \text{and} \quad T_R = \frac{T}{T_{\text{cr}}} \tag{17}
\]

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. 12).

From the \( Z \) chart, one can conclude:
- at very low pressure \( (P_R < 1) \), 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**

Determine the specific volume of refrigerant-134a at 1 MPa and 50°C, using (a) the ideal-gas equation of state and (b) the generalized compressibility chart. Compare the values obtained to the actual value of 0.021796 m³/kg and determine the error involved in each case.

Solution:

a) To use the ideal gas law \( PV = RT \), we need to find the value of \( R \) for R-134a from Table A-1,

For Tetrafluoroethane (R-134a), Table A-1 gives: \( R = 0.08149 \) kJ/kg K

Then the specific volume from ideal gas law reads:

\[
\nu = \frac{RT}{P} = \frac{(0.08149 \text{kJ/Kg K}) (50 + 273 \text{ K})}{1000 \text{ kPa}} = 0.0263213 \text{ [m}^3/\text{kg]}
\]

Therefore, treating the refrigerant-134a vapor as an ideal gas would result in an error of

\[
\text{Error} = \left| \frac{\nu_{\text{actual}} - \nu_{\text{ideal}}}{\nu_{\text{actual}}} \right| \times 100 = \left| \frac{0.021796 - 0.0263213}{0.021796} \right| \times 100 = \frac{0.0045253}{0.021796} \times 100 = 20.8\%
\]

b) From Table A-1 for R-134a we read, \( P_{\text{cr}} = 4.059 \) MPa and \( T_{\text{cr}} = 374.2 \) K.

In order to use the compressibility chart we need to calculate \( P_R \) and \( T_R \):

\[
P_R = \frac{P}{P_{\text{cr}}} = \frac{1 \text{MPa}}{4.059 \text{MPa}} = 0.249
\]

\[
T_R = \frac{T}{T_{\text{cr}}} = \frac{323 \text{K}}{374.2 \text{K}} = 0.863 \quad \Rightarrow \quad Z = 0.84
\]
Then \( \nu = Z \nu_{\text{ideal}} = (0.84)(0.0263213 \text{ m}^3/\text{kg}) = 0.02211[\text{m}^3/\text{kg}] \)

\[
\text{Error} = \left| \frac{\nu_{\text{actual}} - \nu_{\text{chart}}}{\nu_{\text{actual}}} \right| \times 100 = \left| \frac{0.021796 - 0.02211}{0.021796} \right| \times 100 = 1.4\%
\]

The error obtained from compressibility chart is very small, less than 2%. Therefore, in the absence of actual data, the generalized compressibility chart can be used with confidence.