

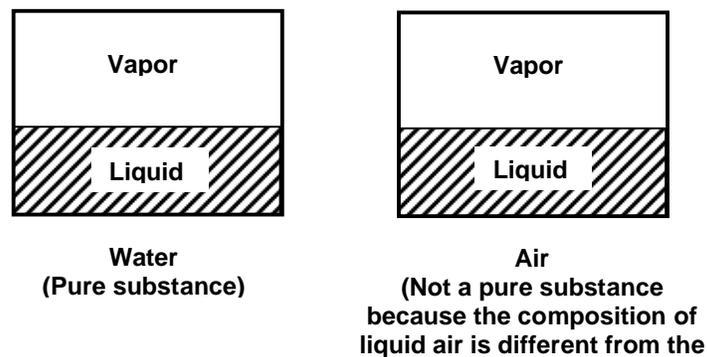
THERMODYNAMICS

PROPERTIES OF PURE SUBSTANCES

Pure Substance

A substance that has a fixed chemical composition throughout is called pure substance. Water, helium carbon dioxide, nitrogen are examples.

It does not have to be a single chemical element just as long as it is homogeneous throughout, like air. A mixture of phases of two or more substance is can still a pure substance if it is homogeneous, like ice and water (solid and liquid) or water and steam (liquid and gas).



Phases of a Pure Substance

There are three principle phases – solid, liquid and gas, but a substance can have several other phases within the principle phase. Examples include solid carbon (diamond and graphite) and iron (three solid phases). Nevertheless, thermodynamics deals with the primary phases only.

In general:

- Solids have strongest molecular bonds.
- Solids are closely packed three dimensional crystals.
- Their molecules do not move relative to each other

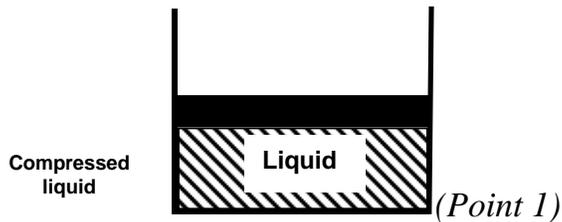
- Intermediate molecular bond strength
- Liquid molecular spacing is comparable to solids but their molecules can float about in groups.
- There is molecular order within the groups

- Weakest molecular bond strength.
- Molecules in the gas phases are far apart, they have no ordered structure
- The molecules move randomly and collide with each other.
- Their molecules are at higher energy levels, they must release large amounts of energy to condense or freeze.

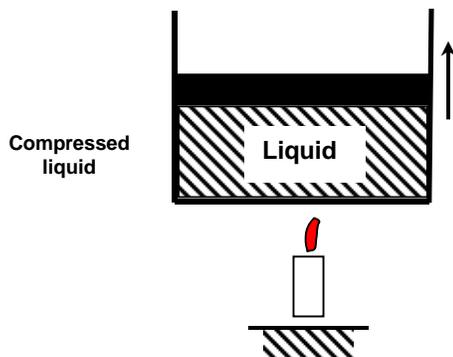
Phase – Change Processes Of Pure Substances

At this point, it is important to consider the liquid to solid phase change process. Not so much solid to liquid because thermodynamics deals only with liquid to gases (or vice versa) to generate power.

Consider water at room temperature (20°C) and normal atmospheric pressure (1 atm) in a piston-cylinder device. The water is in liquid phase, and it is called **compressed liquid** or subcooled liquid (not about to vaporize).

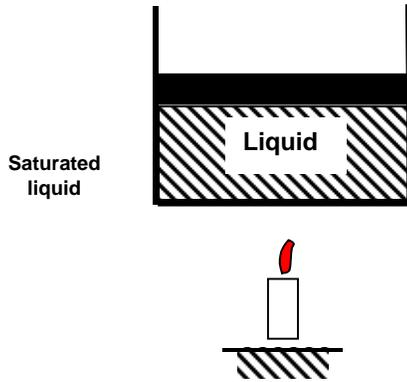


If we add heat to water, its temperature will increase; let us say until 50°C. Due to the increase in temperature, the specific volume v will increase. As a consequence, the piston will move slightly upward therefore maintaining constant pressure (1 atm).



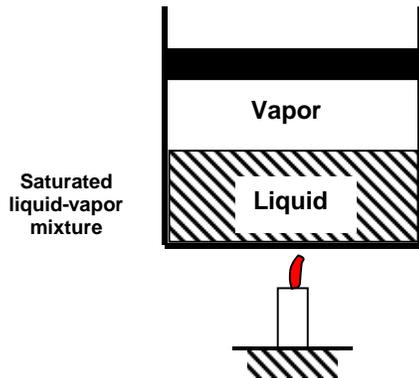
Now, if we continue to add heat to the water, the temperature will increase further until 100°C. At this point, any additional addition of heat will vaporize some water. This specific point where water starts to vaporize is called **saturated liquid**.

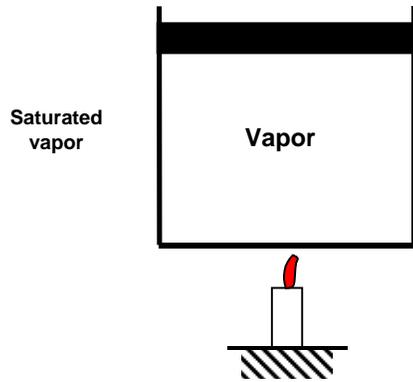
(Point 2)



If we continue to add heat to water, more and more vapor will be created, while the temperature and the pressure remain constant ($T = 100^{\circ}\text{C}$ and $P = 1 \text{ atm}$). The only property that changes is the specific volume. These conditions will remain the same until the last drop of liquid is vaporized. At this point, the entire cylinder is filled with vapor at 100°C . This state is called **saturated vapor** (*Point 4*)

The state between saturated liquid (only liquid) and saturated vapor (only vapor) where two phases exist is called saturated liquid-vapor mixture. (*Point 3*)





After the saturated vapor phase, any addition of heat will increase the temperature of the vapor, this state is called **superheated vapor** (Point 5)

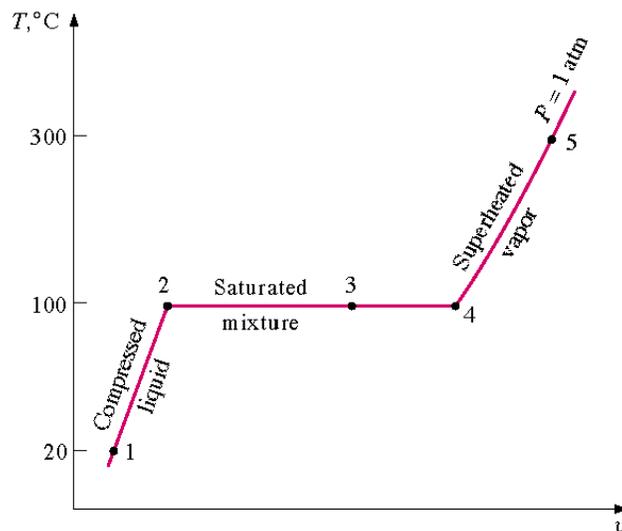


Figure 3: T-v diagram representing phase change for water at constant pressure.

This concept can be applied to pure substance other than water.

Saturation Temperature And Saturation Pressure

Recall that during a phase change, pressure and temperature are not independent intensive properties. As a consequence, the temperature at which water starts boiling depends on the pressure. In other words, water starts boiling at 100 °C but only at 1 atm. At different pressures, water boils at different temperatures.

At a given pressure, the temperature at which a pure substance changes phase is called the saturation temperature (T_{sat}).

Likewise, at a given temperature, the pressure at which a pure substance changes phase is called the saturation pressure (P_{sat}).

Property Diagrams for Phase Change Processes

T-v Diagram

If we increase the pressure of water in the piston-cylinder device, the process from compressed liquid to superheated vapor will follow a path that looks like the process for $P = 1$ atm, the only difference is that the width of the mixture region will be shorter.

Then, at a certain pressure, the mixture region will be represented only by one point. This point is called the **critical point**. It is defined as the point at which the saturated liquid and saturated vapor states are identical.

At the critical point, the properties of a substance are called critical properties (critical temperature (T_{cr}), critical pressure (P_{cr}) and critical specific volume (v_{cr})).

Example

Water $P_{\text{cr}} = 22.09 \text{ MPa}$
 $T_{\text{cr}} = 374.148^\circ\text{C} = 647.298 \text{ K}$
 $v_{\text{cr}} = 0.003155 \text{ m}^3/\text{kg}$

Air $P_{\text{cr}} = 3.77 \text{ MPa}$
 $T_{\text{cr}} = 132.5^\circ\text{C} = 405.65 \text{ K}$
 $v_{\text{cr}} = 0.0883 \text{ m}^3/\text{kg}$

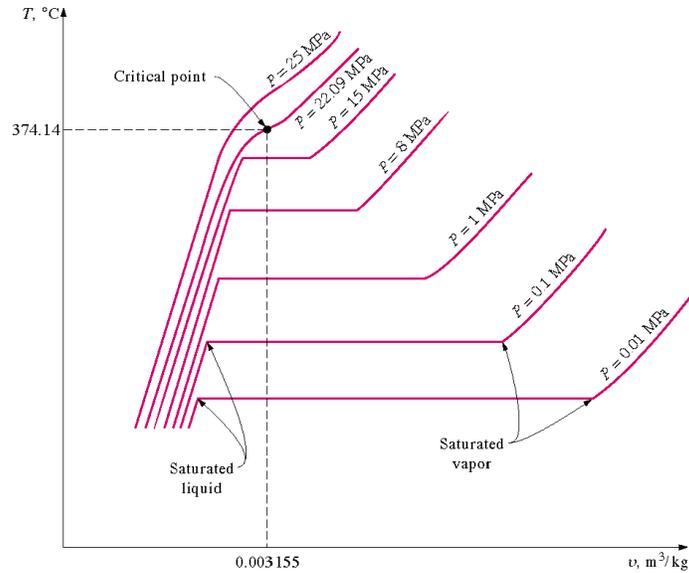


Figure 4: T-v diagram.

If we connect all the points representing saturated liquid we will obtain the saturated liquid line.

If we connect all the points representing saturated vapor we will obtain the saturated vapor line.

The intersection of the two lines is the critical point.

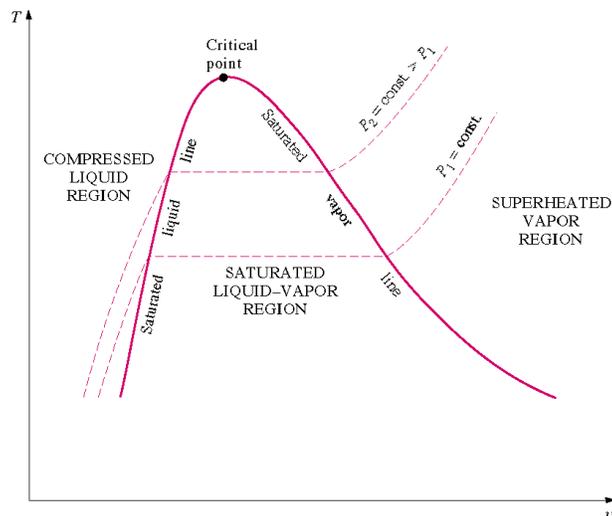


Figure 5: T-v diagram and saturation lines.

P-v Diagram

If we consider the pressure-cylinder device, but with some weights above the piston, if we remove the weights one by one to decrease the pressure, and we allow a heat transfer to obtain an isothermal process, we will obtain one of the curves of the P-v diagram.

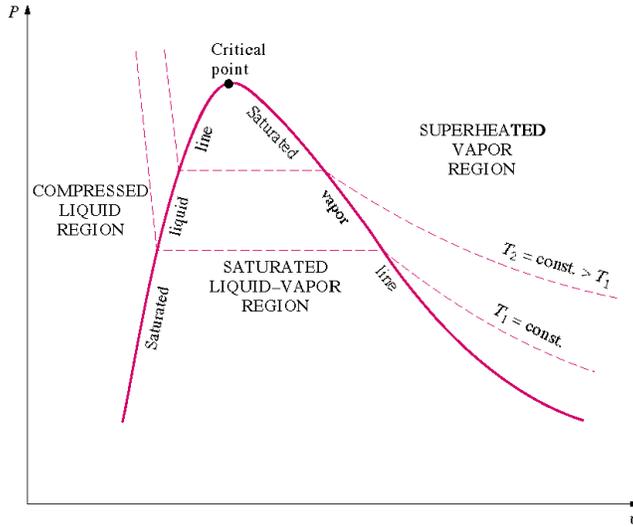


Figure 6: P-v diagram.

The P-v diagram can be extended to include the solid phase, the solid-liquid and the solid-vapor saturation regions.

As some substances, as water, expand when they freeze, and the rest (the majority) contracts during freezing process, we have two configurations for the P-v diagram with solid phase.

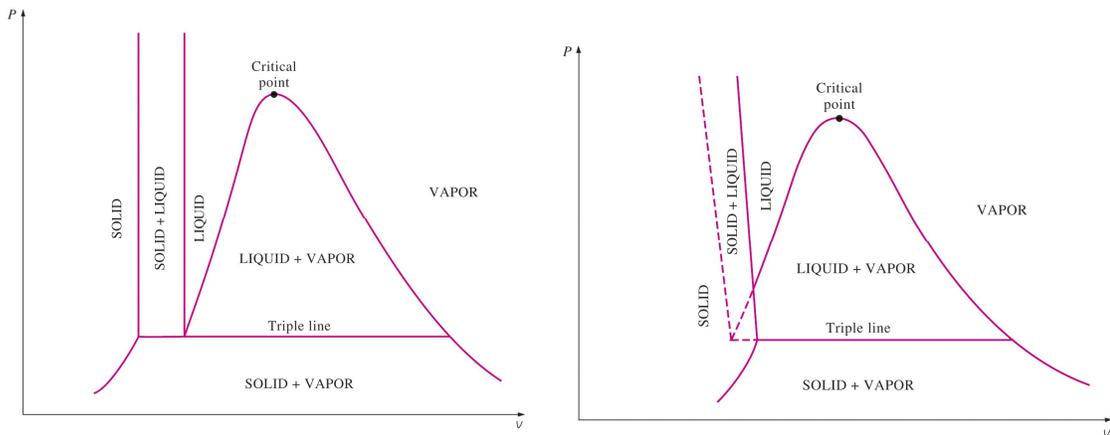


Figure 7: P-v diagram for a substance that contracts during freezing (left) and for a substance that expands during freezing (right).

Triple point

Until now, we have defined the equilibrium between two phases. However, under certain conditions, water can exist at the same time as ice (solid), liquid and vapor. These conditions define the so called triple point.

On a P-T diagram, these conditions are represented by a point.

Example

Water $T = 0.01^{\circ}\text{C} = 273.16\text{ K}$ and $P = 0.6113\text{ kPa}$

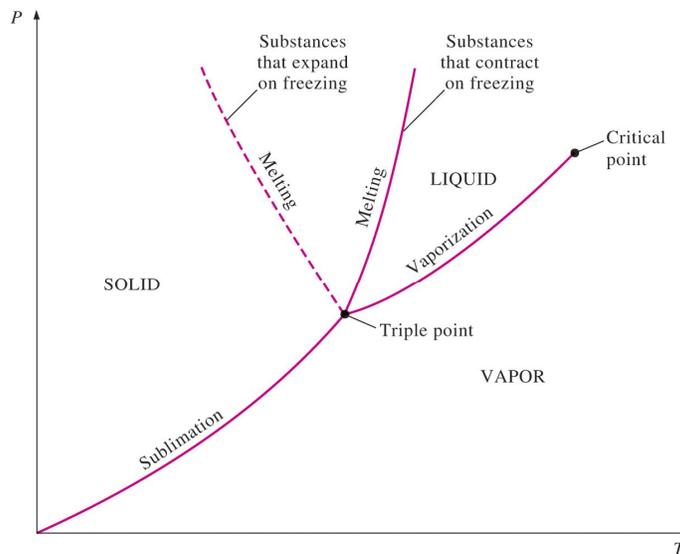


Figure 8: P-T diagram and the triple point.

The P-T diagram is often called the phase diagram since all three phases are separated by three lines.

- Solid → vapor sublimation
- Solid → liquid melting
- Liquid → vapor vaporization

P-T-v Diagram

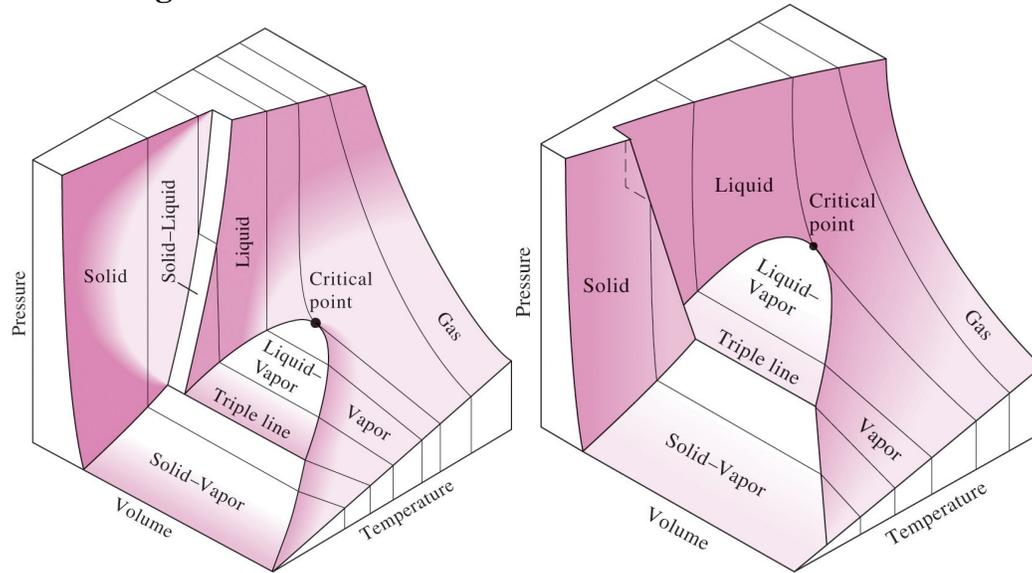


Figure 9: P-T-v diagram for a substance that contracts during freezing (left) and for a substance that expands during freezing (right).

Property Tables

In addition to the temperature, pressure, and specific volume data, tables contain data for the **specific internal energy u** , the **specific enthalpy h** , and the **specific entropy s** .

In thermodynamics analysis, we will encounter the combination of properties $U + PV$ frequently. For simplicity this combination is defined as a new property called enthalpy.

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

The enthalpy per unit mass is

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

Saturated Water Tables

Since temperature and pressure are dependent properties using the phase change, two tables are given for the saturation region. Table A-4 has temperature as the independent property; Table A-5 has pressure as the independent property. These two tables contain the same information.

TABLE A-4

Saturated water-Temperature table

The last entry is the critical point at 373.95 °C.

TABLE A-5

Saturated water-Pressure table

The last entry is the critical point at 22.064 MPa.

The subscript fg used in Tables A-4 and A-5 refers to the difference between the saturated vapor value and the saturated liquid value region. That is,

$$u_{fg} = u_g - u_f$$

$$h_{fg} = h_g - h_f$$

$$s_{fg} = s_g - s_f$$

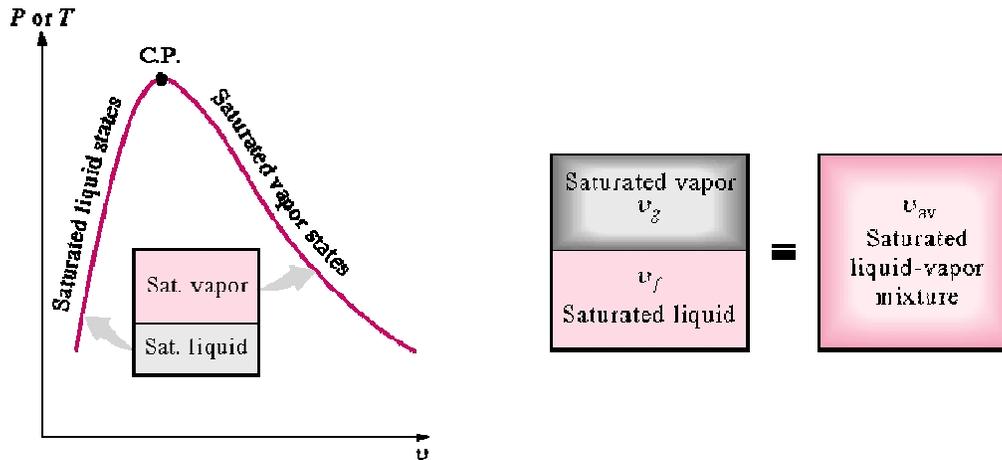
The quantity h_{fg} is called the enthalpy of vaporization (or latent heat of vaporization). It represents the amount of energy needed to vaporize a unit of mass of saturated liquid at a given temperature or pressure.

Quality and Saturated Liquid-Vapor Mixture

Now, let's review the constant pressure heat addition process for water shown in Figure 3 (pg 4). Since state 3 is a mixture of saturated liquid and saturated vapor, how do we locate it on the T-v diagram? To establish the location of state 3 a new parameter called the quality x is defined as:

$$x = \frac{\text{mass of saturated vapor}}{\text{total mass}} = \frac{m_g}{m_f + m_g}$$

The quality is zero for the saturated liquid and one for the saturated vapor ($0 \leq x \leq 1$). The average specific volume at any state 3 is given in terms of the quality as follows. Consider a mixture of saturated liquid and saturated vapor. The liquid has a mass m_f and occupies a volume V_f . The vapor has a mass m_g and occupies a volume V_g .



We note

$$V = V_f + V_g$$

$$m = m_f + m_g$$

$$V = mv, \quad V_f = m_f v_f, \quad V_g = m_g v_g$$

$$mv = m_f v_f + m_g v_g$$

$$v = \frac{m_f v_f}{m} + \frac{m_g v_g}{m}$$

Using the definition of the quality x

$$x = \frac{m_g}{m} = \frac{m_g}{m_f + m_g}$$

Then

$$\frac{m_f}{m} = \frac{m - m_g}{m} = 1 - x$$

Note, quantity $1 - x$ is often given the name moisture. The specific volume of the saturated mixture becomes

$$v = (1 - x) v_f + x v_g$$

The form that we use most often is

$$v = v_f + x (v_g - v_f)$$

It is noted that the value of any extensive property per unit mass in the saturation region is calculated from an equation having a form similar to that of the above equation. Let Y be any extensive property and let y be the corresponding intensive property, Y/m , then

$$y = \frac{Y}{m} = y_f + x(y_g - y_f)$$

$$y = y_f + x y_{fg}$$

$$\text{where } y_{fg} = y_g - y_f$$

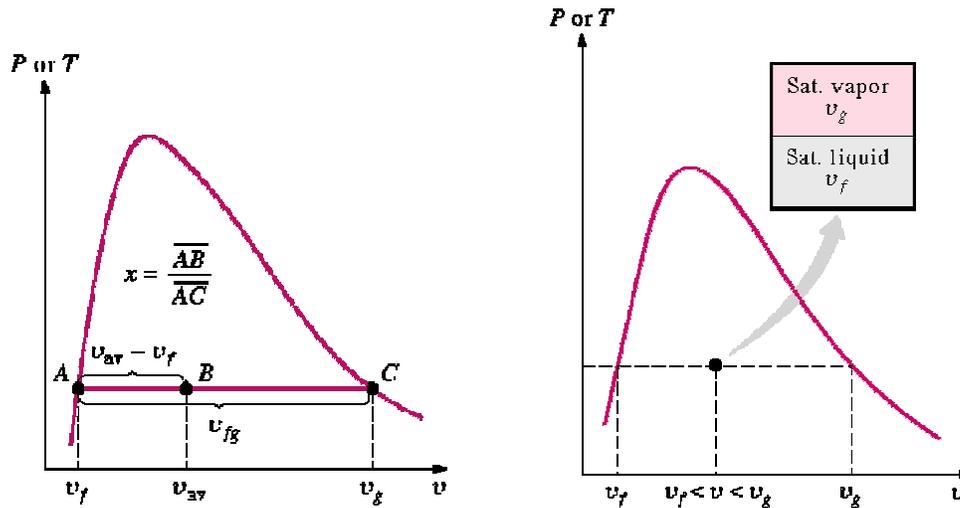
The term y_{fg} is the difference between the saturated vapor and the saturated liquid values of the property y ; y may be replaced by any of the variables v , u , h , or s .

We often use the above equation to determine the quality x of a saturated liquid-vapor state.

The following application is called the Lever Rule:

$$x = \frac{y - y_f}{y_{fg}}$$

The Lever Rule is illustrated in the following figures.



Superheated Water Table

A substance is said to be superheated if the given temperature is greater than the saturation temperature for the given pressure.

State 5 in Figure 2-3 (page 3) is a superheated state.

In the superheated water Table A-6, T and P are the independent properties. The value of temperature to the right of the pressure is the saturation temperature for the pressure. The first entry in the table is the saturated vapor state at the pressure.

Superheated vapor is characterized by:

- Lower pressure ($P < P_{\text{sat}}$ at a given T)
- Higher temperature ($T > T_{\text{sat}}$ 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)

Compressed Liquid Water Table

A substance is said to be a compressed liquid when the pressure is greater than the saturation pressure for the temperature.

It is now noted that state 1 in Figure 2-3 (page 3) is called a compressed liquid state because the saturation pressure for the temperature T_1 is less than P_1 .

Data for water compressed liquid states are found in the compressed liquid tables, Table A-7. Table A-7 is arranged like Table A-6, except the saturation states are the saturated liquid states. Note that the data in Table A-7 begins at 5 MPa or 50 times atmospheric pressure.

At pressures below 5 MPa for water, the data are approximately equal to the saturated liquid data at the given TEMPERATURE. We approximate intensive parameter y , that is v , u , h , and s data as

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

The enthalpy is more sensitive to variations in pressure; therefore, at high pressures the enthalpy can be approximated by

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

For our work, the compressed liquid enthalpy may be approximated by

$$h \cong h_{f@T}$$

Compressed liquid is characterized by:

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

Lower temperature ($T < T_{sat}$ at a given P)

Lower specific volumes ($v < v_g$ at a given P or T)

Lower internal energies ($u < u_g$ at a given P or T)

Lower enthalpies ($h < h_g$ at a given P or T)

How to Choose the Right Table

The correct table to use to find the thermodynamic properties of a real substance can always be determined by comparing the known state properties to the properties in the saturation region. 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,

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

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

$$\text{is } v > v_g ?$$

The answer to one of these questions must be yes. If the answer to the first question is yes, the state is in the compressed liquid region, and the compressed liquid tables are used to find the properties of the state. If the answer to the second question is yes, the state is in the saturation region, and either the saturation temperature table or the saturation pressure table is used to find the properties. Then the quality is calculated and is used to calculate the other properties, u , h , and s . If the answer to the third question is yes, the state is in the superheated region and the superheated tables are used to find the other properties.

Some tables may not always give the internal energy. When it is not listed, the internal energy is calculated from the definition of the enthalpy as

$$u = h - Pv$$

Equations of State

The tables with which we have been working provide an accurate relationship between temperature, pressure and other important thermodynamic properties. If we restrict consideration to only the vapor state, then we may often find a simple algebraic relationship between temperature, pressure and specific volume; such a relationship is called an equation of state.

For gases at low pressure it has been observed that pressure, P , is directly proportional to temperature, T , (this is known as Charles' law) and inversely proportional to specific volume, v (Boyle's law).

$$P = R \cdot \frac{T}{v}$$

Here, R is known as the gas constant.

It is further found that there is a relationship between the various gas constants and the molecular weight of the particular gas. Specifically, it is found that the product of the gas constant and the gas molecular weight yields the same constant for all gases. This product is known as the Universal Gas Constant.

Jacques Alexandre César Charles ([November 11, 1746](#) - [April 7, 1823](#)) was a French inventor, scientist, mathematician, and balloonist. Circa 1787 he discovered [Charles' Law](#), which states that under constant pressure, an [ideal gas](#)' volume is proportional to its temperature. The volume of a gas at constant pressure increases linearly with the temperature of the gas. The formula he created was $V_1/T_1 = V_2/T_2$. His discovery anticipated [Joseph Louis Gay-Lussac's](#) published law of the expansion of gases with heat (1802). Charles was elected to the [Institut Royal de France, Académie des sciences](#), in 1793, and subsequently became professor of physics at the [Conservatoire des Arts et Métiers](#). He died in [Paris](#) on April 7, 1823.



Robert Boyle ([January 25, 1627](#) – [December 30, 1691](#)) was an [Irish natural philosopher](#), chemist, physicist, inventor, and early [gentleman scientist](#), noted for his work in [physics](#) and [chemistry](#). Although his research and personal philosophy clearly has its roots in the alchemical tradition, he is largely regarded today as the first modern chemist. Among his works, [The Sceptical Chymist](#) is seen as a cornerstone book in the field of chemistry.



Therefore, the gas constant for a specific (R) gas is equal to:

$$R = \frac{R_u}{M}$$

The Universal gas constant is considered a fundamental constant, similar to the gravitational constant.

$$R_U = 8.314 \text{ kJ/kmol K}$$

Alternate forms of the ideal gas law:

$$P \cdot v = R \cdot T$$

$$P = \rho \cdot R \cdot T$$

$$P \cdot V = m \cdot R \cdot T$$

$$P \cdot V = N \cdot R_u \cdot T$$

Remember that: mass (m) = Number of moles (N) × Molecular Mass (M)

Following the ideal gas law, for a process from (1) to (2), we can write:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$