Preface

Important Thermodynamic Properties

Independent properties: Temperature (T), Pressure (P), Volume (V)
Dependent properties: Internal energy (U), Enthalpy (H), Entropy (S)

Internal energy (U): is a property consisting of the combined molecular kinetic and potential energies. This property is derived from the first law of thermodynamics.

Enthalpy (H): is a thermodynamic quantity equivalent to the total heat content of a system. It is equal to the internal energy of the system plus the product of pressure and volume.

Entropy (S): is a thermodynamic quantity representing the unavailability of a system's thermal energy for conversion into mechanical work, often interpreted as the degree of disorder or randomness in the system. This property is derived from the second law of thermodynamics.

Intensive and Extensive Properties

An intensive property is a bulk property, meaning that it is a physical property of a system that does not depend on the system size or the amount of material in the system. Examples of intensive properties include (temperature, pressure and density). By contrast, an extensive property is additive for subsystems. This means the system could be divided into any number of subsystems. Examples of extensive properties include (volume, internal energy, enthalpy and entropy). Extensive properties have two values (Total and Specific), total values have the usual units of that property while specific values have the same units divided by the units of mass. For example: Volume (V) has the units (m^3) in SI system, while specific volume (v) has the units (m^3/kg). So that:

$$\text{Specific value of a property} = \frac{\text{Total value}}{\text{Mass}}$$

Classification of Thermodynamic Processes

1. According to flow:

• Non-flow processes

• Flow processes

     Steady flow processes $\left(\frac{dm}{dt} = 0\right)$

     Unsteady flow processes $\left(\frac{dm}{dt} \neq 0\right)$

2. According to reversibility:

• Reversible processes

• Irreversible processes

Gas Laws and Thermodynamic Processes

Perfect gas equation of state $PV = mRT$

$$PV = NR_oT$$

The universal gas constant $R_o = 8.314 \text{ kJ/kmol.K}$

Generally for processes, $\frac{PV}{T} = C$ and depending on the type of process:
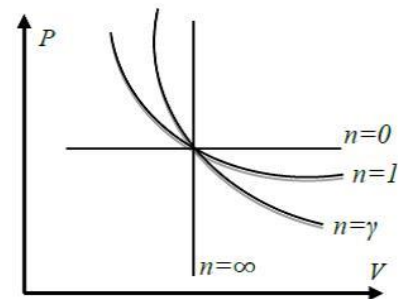
1. Polytropic process (general process) $(n = 0, \infty)$

For polytropic processes:

$$\left(\frac{P_2}{P_1}\right) = \left(\frac{V_1}{V_2}\right)^n$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{n-1}$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}}$$

2. Adiabatic (Isentropic) process (no heat transfer) $(n = \gamma)$

3. Constant volume (isochoric) process $\frac{P}{T} = C$ $(n = \infty)$

4. Constant pressure (isobaric) process $\frac{V}{T} = C$ $(n = 0)$

5. Constant temperature (isothermal) process $PV = C$ $(n = 1)$

Specific Heats

C_p Specific heat at constant pressure

C_v Specific heat at constant volume

For a perfect gas:

$h = C_P . T$

$u = C_v . T$

The gas constant $R = C_p - C_v$, $\frac{C_p}{C_v} = \gamma$ where the adiabatic index $\gamma > 1$

1. Pure Substance

It is the substance that has a homogenous and invariable chemical composition. It may exist in more than one phase, but the chemical composition is the same in all phases, such as a mixture of ice and liquid water or a mixture of water and steam. Sometimes a mixture of gases such as air is considered a pure substance as long as there is no change of phase, since it exhibits the same characteristics as a pure substance.

Equilibrium in a Pure Substance

Consider as a system of 1 kg of water contained in the piston-cylinder arrangement shown in figure below. Suppose that the piston maintains a pressure of 0.1 MPa in the cylinder and that the initial temperature is 20°C. As heat is transferred to the water, the temperature increases appreciably, the specific volume increases slightly, and the pressure remains constant. When the temperature reaches 99.6°C, additional heat transfer results in a change of phase. That is, some of the liquid becomes vapor, and during this process both the temperature and pressure remain constant, but the specific volume increases considerably. When the last drop of liquid has vaporized, further transfer of heat results in an increase in both the temperature and specific volume of the vapor.
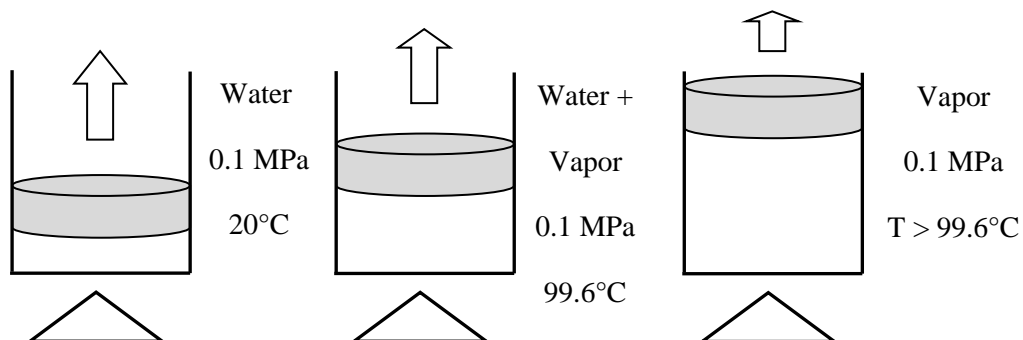
The term **saturation temperature** designates the temperature at which vaporization takes place at a given pressure. This pressure is called the **saturation pressure** for the given temperature. Thus, for water at 99.6°C the saturation pressure is 0.1 MPa, and for water at 0.1 MPa the saturation temperature is 99.6°C. For a pure substance there is a definite relation between saturation pressure and saturation temperature.

If a substance exists as liquid at the saturation temperature and pressure, it is called a **saturated liquid**. If the temperature of the liquid is lower than the saturation temperature for the existing pressure, it is called either a **subcooled liquid** (implying that the temperature is lower than the saturation temperature for the given pressure) or a **compressed liquid** (implying that the pressure is greater than the saturation pressure for the given temperature).

When a substance exists as part liquid and part vapor at the saturation temperature, its **quality** is defined as the ratio of the mass of vapor to the total mass. The quality may be

considered an intensive property and has the symbol *x*. Quality has meaning only when the substance is in a saturated state, that is, at saturation pressure and temperature.

If a substance exists as vapor at the saturation temperature, it is called **saturated vapor** (sometimes the term dry saturated vapor is used to emphasize that the quality is 100%). When the vapor is at a temperature greater than the saturation temperature, it is said to exist as a **superheated vapor**. The pressure and temperature of superheated vapor are independent properties, since the temperature may increase while the pressure remains constant. Actually, the substances we call gases are highly superheated vapors.

The (*T-V*) Diagram

Let us consider a temperature-volume (*T-V*) diagram for a heating process at constant pressure for a pure substance.

at A
$T = 20^{\circ}C$
$P = 0.1$ MPa

at B
$T = 99.6^{\circ}C$
$P = 0.1$ MPa

at D
$T > 99.6^{\circ}C$
$P = 0.1$ MPa
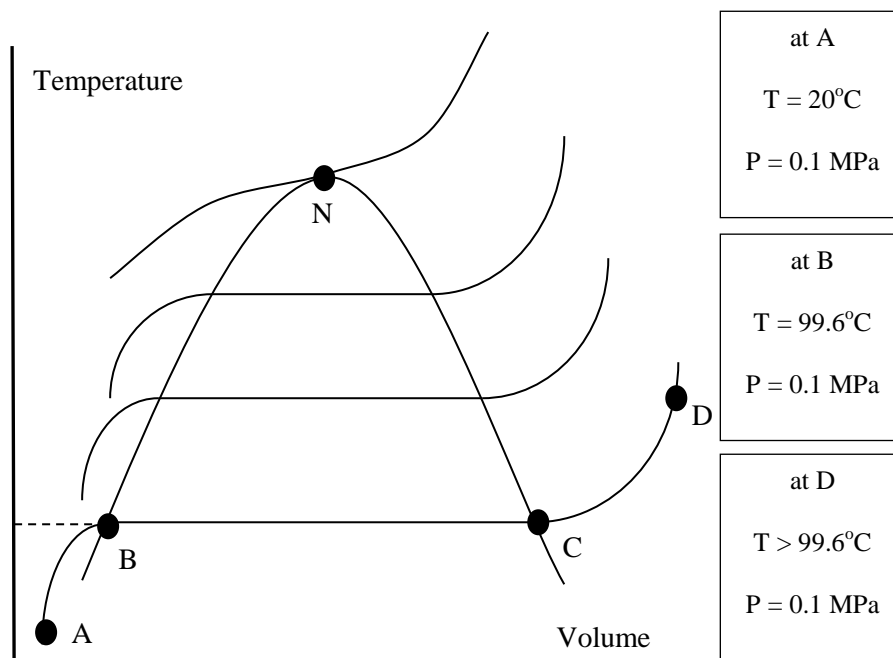
• Point A represents the initial state, point B is the saturation temperature at 0.1 MPa (99.6°C). Line AB represents a heating process with no change of phase.

• Point C is the saturated vapor state. Line BC is the constant temperature and pressure (change of phase; evaporation).

• Line CD represents the process during which the steam becomes superheated. During this process the temperature and specific volume increases and the pressure remains constant.

• Line ABCD represents a constant pressure line on the (*T-V*) diagram; i.e. heating process of constant pressure with change of phase.

Similar lines may be drawn for heating processes at other pressure values. At a pressure of 22.09 MPa, we find that there is no constant temperature vaporization process. Instead point N is a point of inflection with zero slop. This point is called the critical point

which is the point where the saturated vapor and liquid can coexist. At the critical point the temperature, pressure and specific volume are called critical temperature, critical pressure and critical specific volume.

The line joining the saturated liquid temperatures is called the **saturated liquid line**, and the line joining the saturated vapor temperatures is called the **saturated vapor line**.

The (*P-T*) Diagram

Assume that a system consisting of 1 kg of ice at -20°C and 100 kPa is contained in a piston-cylinder arrangement as in the previous example. When the system is heated the pressure remains constant. The specific volume increases slightly and it reaches 0°C. At this point the ice melts while the temperature remains constant and in this state the ice is called saturated solid. When all the ice melts, any further heating results in an increase in the temperature of the liquid.

Let the initial state of the ice be -20°C and 0.26 kPa. The heating would result in increasing the temperature until -10°C. At this point the ice would pass directly from solid phase to vapor phase in a process known as **Sublimation**. Any further heating results in superheating the vapor.
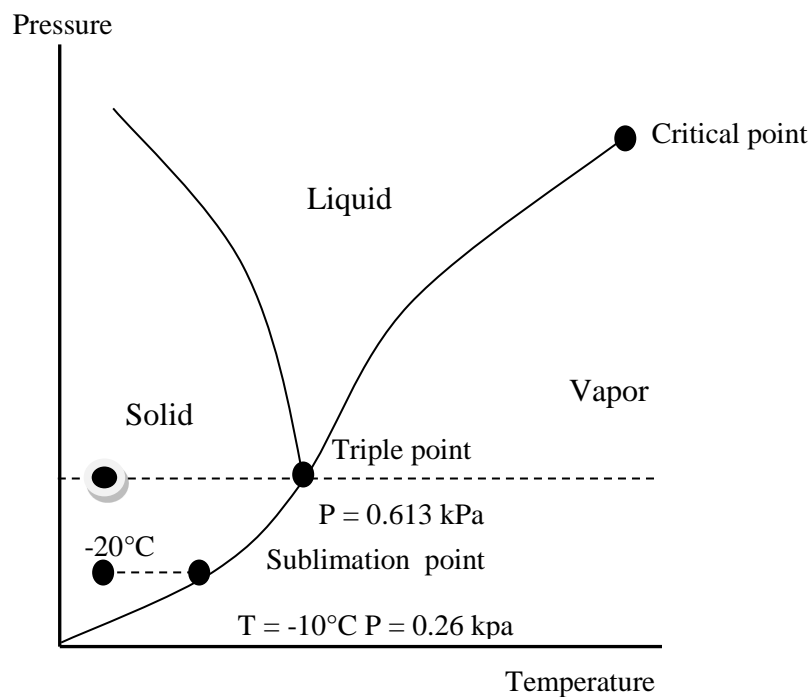

When the initial state of the system is -20°C and 0.613 kPa, the heating process results in increasing the temperature until it reaches 0.01°C. Further heating may result in some of the ice becoming vapor and some becoming liquid. Therefore at these conditions it is possible to have three phases in equilibrium. This point is called **triple point**; which is defined as the state in which the three phases of a pure substance may be present in equilibrium.

When the heating process is carried out at a pressure higher than the triple point pressure, the substance would pass from solid phase to liquid phase and then from liquid phase to vapor phase at higher temperature.

Water Properties Tables

The term steam is solely used for water vapor. 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. Some thermodynamic properties can be measured easily, but others cannot and are calculated by using the relations between them and measurable properties. The results of these measurements and calculations are presented in tables in a convenient format. In the following discussion, the steam tables are used to demonstrate the use of thermodynamic property tables.
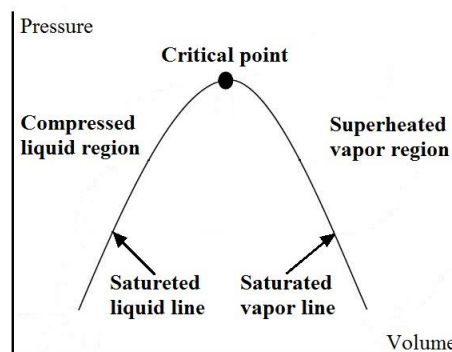
Property tables of other substances are used in the same manner. For each substance, the thermodynamic properties are listed in more than one table. In fact, a separate table is prepared for each region of interest such as the superheated vapor, compressed liquid, and saturated (mixture) regions.

1. Saturated liquid and vapor: when water is in the saturated phase, (table 2) and (table 3) are used to get the required properties. Both tables give the same information, the only difference is that in (table 2) properties are listed under temperature and in (table 3) under pressure. Therefore, it is more convenient to use (table 2) when temperature is given and (table 3) when pressure is given. Knowing only one property of the water, we can extract any other property from these tables. For saturated liquid, the properties with the subscript (f) are used. For saturated vapor, the properties with the subscript (g) are used. The properties with the subscript (fg) are the difference between the two phases ($g - f$). For example: $h_{fg} = h_g - h_f$ which is called the **latent heat**.

2. Wet vapor: it is a state in which a mixture of both saturated vapor and liquid are present. To calculate the properties of water in this phase, a property known as the **dryness fraction** (x) is used alongside the saturation properties of (table 2) and (table 3).

Dryness Fraction can be defined as the mass of dry saturated vapor in 1 kg of a mixture of liquid and vapor. It is also called **vapor quality**.

$$x = \frac{m_v}{m_m} = \frac{m_v}{m_v + m_l} \qquad \ldots \ldots \ldots \ldots \ldots \ldots (1.1)$$

For saturated liquid line $x = 0$ (which is said to have a quality of 0%)

For dry saturated vapor $x = 1$ (which is said to have a quality of 100%)

For mixed region $0 < x < 1$

Wetness Fraction: is defined as the mass of liquid in 1 kg of a mixture of liquid and vapor.

Wetness Fraction $= 1 -$ Dryness Fraction $\quad\quad$ … … … … … … … (1.2)

For one kilogram of wet vapor, there are x kg of vapor, and $(1 - x)$ kg of liquid. Hence to calculate the specific volume at this point:

$$v = (1 - x)v_f + xv_g \quad\quad \text{… … … … … … … (1.3)}$$

The volume of the liquid is negligibly small compared to the volume of dry saturated vapor. Moreover, for practical problems:

$$v = xv_g \quad\quad \text{… … … … … … … (1.4)}$$

The enthalpy of a wet vapor is given by the sum of the enthalpy of the liquid plus the enthalpy of the dry vapor:

$$h = (1 - x)h_f + xh_g$$

$$h = h_f + x(h_g - h_f)$$

$$h = h_f + xh_{fg} \quad\quad \text{… … … … … … … (1.5)}$$

Similarly the internal energy equation is:

$$u = u_f + xu_{fg} \quad\quad \text{… … … … … … … (1.6)}$$

And the entropy equation is:

$$s = s_f + xs_{fg} \quad\quad \text{… … … … … … … (1.7)}$$

3. Superheated vapor: when water is in the superheated vapor phase, (table 4) is used to get the required properties. To use this table, two properties must be known:

$P + T \rightarrow$ Table 4 $\rightarrow$ required property

$P +$ any other property $(v, u, h, s) \rightarrow$ Table 4 $\rightarrow$ required property

$T +$ any other property $(v, u, h, s) \rightarrow$ Table 4 $\rightarrow$ required property

4. Compressed (Subcooled) liquid: when water is in the compressed liquid phase, (table 5) is used to get the required properties. To use this table, two properties must be known. So the same rules as with the superheated vapor are applied here.

Finding the Phase of Water

We can identify the state of water using the saturation tables (i.e. table 2 and table 3). Two known properties are required to identify the state of water as follows:

If $P < P_{sat.}$ at T

          $T > T_{sat.}$ at P

          $v > v_g$ at T or P

          $u > u_g$ at T or P

          $h > h_g$ at T or P

          $s > s_g$ at T or P

then the water is in the superheated vapor state.

If $P > P_{sat.}$ at T

          $T < T_{sat.}$ at P

          $v < v_f$ at T or P

          $u < u_f$ at T or P

          $h < h_f$ at T or P

          $s < s_f$ at T or P

then the water is in the compressed liquid state.

If the property equals the saturation value, then the water is in the saturated state (vapor or liquid).

If ($property_f < property < property_g$), then the water is in the wet vapor state.

Linear Interpolation

When the required property value is located between two known values in the tables, we can calculate the required value by linear interpolation. Assume that $(Y_1, Y_2, Y_3, X_1, X_3)$ are known and (X_2) is the required value. By assuming a linear relationship:

$$Slop = \frac{(X_2 - X_1)}{(Y_2 - Y_1)} = \frac{(X_3 - X_1)}{(Y_3 - Y_1)}$$

$$X_2 = X_1 + \left(\frac{Y_2 - Y_1}{Y_3 - Y_1}\right)(X_3 - X_1)$$
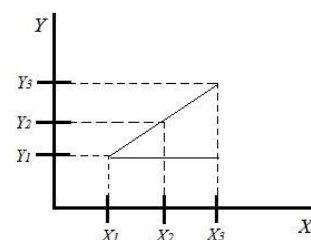
Example (1.1): Determine the specific volume, internal energy, enthalpy and entropy for a mixture of 10% quality at 0.15 MPa.

Solution:

Given, $x = 0.1$

At 0.15 MPa, from table 3:

$v_g = 1.1593 \text{ m}^3/\text{kg}$

$u_f = 466.94 \text{ kJ/kg}, \qquad u_{fg} = 2052.7 \text{ kJ/kg}$

$h_f = 467.11 \text{ kJ/kg}, \qquad h_{fg} = 2226.5 \text{ kJ/kg}$

$s_f = 1.4336 \text{ kJ/kg. K}, \qquad s_{fg} = 5.7897 \text{ kJ/kg. K}$

Specific volume:

$v = x. v_g$

$= 0.1 \times 1.159 = 0.1159 \text{ m}^3/\text{kg}$

Internal energy:

$u = u_f + x. u_{fg}$

$= 466.94 + 0.1 \times 2052.7 = 672.21 \text{ kJ/kg}$

Enthalpy:

$h = h_f + x. h_{fg}$

$= 467.11 + 0.1 \times 2226.5 = 689.759 \text{ kJ/kg}$

Entropy:

$s = s_f + x. s_{fg}$

$= 1.4336 + 0.1 \times 5.7897 = 2.01257 \text{ kJ/kg. K}$

$\boldsymbol{v = 0.1159 \text{ m}^3/\text{kg}} \qquad$ **Ans.**

$\boldsymbol{u = 672.21 \text{ kJ/kg}} \qquad$ **Ans.**

$\boldsymbol{h = 689.759 \text{ kJ/kg}} \qquad$ **Ans.**

$\boldsymbol{s = 2.01257 \text{ kJ/kg. K}} \qquad$ **Ans.**

Example (1.2): Determine the phase for each of the following water states:

a. 120°C, 500 kPa

b. 120°C, 0.5 m³/kg

Solution:

a. From table 2 with 120°C. The saturation pressure is 198.5 kPa, so we have a compressed liquid. We could also have used table 3 with 500 kPa and found the saturation temperature as 151.86°C, so we would say that it is a subcooled liquid.

b. From table 2 with 120°C we notice that:

$$v_f = 0.00106 < v < v_g = 0.89186 \text{ m}^3/\text{kg}$$

So the state is a two-phase mixture of liquid and vapor.

Example (1.3): Determine the temperature and quality (if defined) for water at a pressure of 300 kPa and at each of these specific volumes:

a. 0.5 m³/kg

b. 1 m³/kg

Solution:

a. From table 3 at 300 kPa, we can see that $v_f < v < v_g$, so we have a mixture of liquid and vapor and $\boldsymbol{T = 133.6°C}$ **Ans.**

From table 3 at 300 kPa, $v_g = 0.6058 \text{ m}^3/\text{kg}$

$$v = x. v_g \rightarrow 0.5 = x \times 0.6058$$

$$\boldsymbol{x = 0.826} \qquad \textbf{Ans.}$$

b. From table 3 at 300 kPa, we can see that $v > v_g$, so we have superheated vapor.

From table 4 at 300 kPa and $v = 1 \text{ m}^3/\text{kg}$, we can see that the value of T can be found by interpolation between 300°C and 400°C at 300 kPa.

$$\frac{T - 300}{1 - 0.8753} = \frac{400 - 300}{1.0315 - 0.8753}$$

$$\boldsymbol{T = 379.8°C} \qquad \textbf{Ans.}$$