

MODULE 4

Availability, Irreversibility and General Thermodynamic relations: Introduction, Availability (Exergy), Unavailable energy, Relation between increase in unavailable energy and increase in entropy. Maximum work, maximum useful work for a system and control volume, irreversibility, second law efficiency.

Pure Substances: P-T and P-V diagrams, triple point and critical points. Sub-cooled liquid, saturated liquid, mixture of saturated liquid and vapor, saturated vapor and superheated vapor states of pure substance with water as example. Enthalpy of change of phase (Latent heat). Dryness fraction (quality), T-S and H-S diagrams, representation of various processes on these diagrams. Steam tables and its use. Throttling calorimeter, separating and throttling calorimeter.

AVAILABILITY, IRREVERSIBILITY AND GENERAL THERMODYNAMIC RELATIONS

OBJECTIVE: To determine the amount energy available for work in a system and the thermodynamic relations applied to a system

STRUCTURE:

4. Introduction

4.1. Available energy referred to a cycle

4.2. Decrease in available energy

4.3. Availability in non-flow systems

4.4. Helmholtz and gibbs functions

4.5. Irreversibility**4.6. Effectiveness****4.7. The Maxwell relationships****4. Introduction:**

There are many forms in which an energy can exist. But even under ideal conditions all these forms cannot be converted completely into work. This indicates that energy has two parts: Available part, Unavailable part

Available energy: is the maximum portion of energy which could be converted into useful work by ideal processes which reduce the system to a dead state (a state in equilibrium with the earth and its atmosphere). Because there can be only one value for maximum work which the system alone could do while descending to its dead state, it follows immediately that 'Available energy' is a property.

Unavailable energy: A system which has a pressure difference from that of surroundings, work can be obtained from an expansion process, and if the system has a different temperature, heat can be transferred to a cycle and work can be obtained. But when the temperature and pressure becomes equal to that of the earth, transfer of energy ceases, and although the system contains internal energy, this energy is

4.1. Available energy referred to a cycle:

The available energy (A.E.) or the available part of the energy supplied is the maximum work output obtainable from a certain heat input in a cyclic heat engine (Fig. 6.1). The minimum energy that has to be rejected to the sink by the second law is called the unavailable energy (U.E.), or the unavailable part of the energy supplied.

$$Q_1 = \text{A.E.} + \text{U.E.}$$

$$\text{or } W_{\max} = \text{A.E.} = Q_1 - \text{U.E.}$$

For the given values of the source temperature T_1 and sink temperature T_2 , the reversible efficiency,

$$\eta_{rev} = 1 - \frac{T_1}{T_2}$$

For a given T_1 , η_{rev} will increase with the decrease of T_2 . The lowest practicable temperature of heat rejection is the temperature of the surroundings, T_0 .

$$\eta_{max} = 1 - \frac{T_0}{T_2}$$

$$W_{max} = \eta_{max} \left(1 - \frac{T_0}{T_2} \right)$$

And

$$W_{max} = \eta_{max} \left(1 - \frac{T_0}{T_2}\right) \cdot Q_1$$

Consider a finite process l-m, in which heat is supplied reversibly to a heat engine (Fig. 6.2). Taking an elementary cycle, if dQ_1 is the heat received by the engine reversibly at T_1 ,

Then
$$dW_{max} = \eta_{max} \left(1 - \frac{T_0}{T_1}\right) \cdot dQ_1 = A.E$$

For the heat engine receiving heat for the whole process l-m, and rejecting heat at T_0 .

$$\int dW_{max} = \int_l^m dQ_1 - \int_l^m \frac{T_0}{T_1} dQ_1$$

$W_{max} = A.E. = Q_{l-m} - T_0 (S_1 - S_m)$
 or unavailable energy, U.E. = $Q_1 - m - W_{max}$
 or U.E. = $T_0 (S_1 - S_m)$

Thus unavailable energy is the product of the lowest temperature of heat rejection, and the change of entropy of the system during the process of supplying heat

4.2. Decrease in available energy when heat is transferred through a finite temperature difference:

When transfer of heat takes place through a finite temperature difference, there is a decrease in the availability of energy so transferred. Consider a reversible heat engine operating between temperatures T_1 and T_0

$Q_1 = T \cdot \Delta s$

$Q_2 = T_0 \Delta s$

and $W = A.E. = [T_1 - T_0] \Delta s$

Assume that heat Q_1 is transferred through a finite temperature difference from the reservoir or source at T_1 to the engine absorbing heat at T_1' , lower than T_1 . The availability of Q_1 as received by the engine at T_1' can be found by allowing the engine to operate reversibly in a cycle between T_1' and T_0 receiving Q_1 and rejecting Q_2' .

Now, $Q_1 = T_1 \Delta s = T_1' \Delta s'$

– $T_1 > T_1'$

$\therefore \Delta s' > \Delta s$

$Q_2 = T_0 \Delta s$

$Q_2' = T_0 \Delta s'$

– $\Delta s' > \Delta s$

$\therefore Q_2' > Q_2$

$$\therefore W' = Q_1 - Q_2' = T_1' \Delta s' - T_0 \Delta s'$$

$$\text{and } W = Q_1 - Q_2 = T_1 \Delta s - T_0 \Delta s$$

$$\therefore W' < W, \text{ because } Q_2' > Q_2$$

The loss of available energy due to irreversible heat transfer through finite temperature difference between the source and the working fluid during the heat addition process is given as :

$$W - W' = Q_2' - Q_2 = T_0 (\Delta s' - \Delta s)$$

i.e., Decrease in available energy, A.E.

$$= T_0 (\Delta s' - \Delta s)$$

Thus the decrease in A.E. is the product of the lowest feasible temperature of heat rejection and the additional entropy change in the system while receiving heat irreversibly, compared to the case of reversible heat transfer from the same source. The greater is the temperature difference ($T_1 - T_1'$), the greater is the heat rejection Q_2' and the greater will be the unavailable part of the energy supplied.

Energy is said to be degraded each time it flows through a finite temperature difference. That is, why the second law of thermodynamics is sometimes called the law of the degradation of energy, and energy is said to 'run down hill'.

4.3 Availability in non-flow systems:

Let us consider a system consisting of a fluid in a cylinder behind a piston, the fluid expanding reversibly from initial condition of p_1 and T_1 to final atmospheric conditions of p_0 and T_0 . Imagine also that the system works in conjunction with a reversible heat engine which receives heat reversibly from the fluid in the cylinder such that the working substance of the heat engine follows the cycle O1LO as shown, where $s_1 = s_1$ and $T_0 = T_L$ (the only possible way in which this could occur would be if an infinite number of reversible heat engines were arranged in parallel, each operating on a Carnot cycle, each one receiving heat at a different constant temperature and each one rejecting heat at T_0). The work done by the engine is given by :

$$W_{\text{engine}} = \text{Heat supplied} - \text{Heat rejected} = Q - T_0 (s_1 - s_0) \dots(i)$$

The heat supplied to the engine is equal to the heat rejected by the fluid in the cylinder. Therefore, for the fluid in the cylinder undergoing the process 1 to 0, we have

$$-Q = (u_0 - u_1) + W_{\text{fluid}}$$

$$\text{i.e., } W_{\text{fluid}} = (u_1 - u_0) - Q \dots(ii)$$

Adding eqns. (i) and (ii), we get

$$\begin{aligned} W_{\text{fluid}} + W_{\text{engine}} &= [(u_1 - u_0) - Q] + [Q - T_0 (s_1 - s_0)] \\ &= (u_1 - u_0) - T_0 (s_1 - s_0) \end{aligned}$$

The work done by the fluid on the piston is less than the total work done by the fluid, since there is no work done on the atmosphere which is at constant pressure p_0

$$\text{i.e., Work done on atmosphere} = p_0 (v_0 - v_1)$$

Hence, maximum work available

$$= (u_1 - u_0) - T_0 (s_1 - s_0) - p_0 (v_0 - v_1)$$

Note. When a fluid undergoes a complete cycle then the net work done on the atmosphere is zero.

$$W_{\max} = (u_1 + p_0 v_1 - T_0 s_1) - (u_0 + p_0 v_0 - T_0 s_0) \dots (6.3)$$

$$\therefore W_{\max} = a_1 - a_0$$

The property, $a = u + p_0 v - T_0 s$ (per unit mass) is called the non-flow availability function.

4.4 Helmholtz and gibbs functions:

The work done in a non-flow reversible system (per unit mass) is given by :

$$W = Q - (u_0 - u_1)$$

$$= T \cdot ds - (u_0 - u_1)$$

$$= T (s_0 - s_1) - (u_0 - u_1)$$

$$\text{i.e., } W = (u_1 - Ts_1) - (u_0 - Ts_0)$$

The term $(u - Ts)$ is known as Helmholtz function. This gives maximum possible output when the heat Q is transferred at constant temperature and is the case with a very large source. If work against atmosphere is equal to $p_0 (v_0 - v_1)$, then the maximum work available,

$$W_{\max} = W - \text{work against atmosphere}$$

$$= W - p_0 (v_0 - v_1)$$

$$= (u_1 - Ts_1) - (u_0 - Ts_0) - p_0 (v_0 - v_1)$$

$$= (u_1 + p_0 v_1 - Ts_1) - (u_0 + p_0 v_0 - Ts_0)$$

$$= (h_1 - Ts_1) - (h_0 - Ts_0)$$

$$\text{i.e., } W_{\max} = g_1 - g_0$$

where $g = h - T \cdot s$ is known as Gibb's function or free energy function.

The maximum possible available work when system changes from 1 to 2 is given by

$$W_{\max} = (g_1 - g_0) - (g_2 - g_0) = g_1 - g_2$$

Similarly, for steady flow system the maximum work available is given by

$$W_{\max} = (g_1 - g_2) + (KE_1 - KE_2) + (PE_1 - PE_2)$$

where K.E. and P.E. represent the kinetic and potential energies.

It may be noted that Gibb's function $g = (h - Ts)$ is a property of the system where availability function $a = (u + p_0 v - T_0 s)$ is a composite property of the system and surroundings.

$$\text{Again, } a = u + p_0 v - T_0 s$$

$$b = u + p v - T_0 s$$

$$g = u + p v - T s$$

When state 1 proceeds to dead state (zero state)

$$a = b = g.$$

4.5. IRREVERSIBILITY:

The actual work which a system does is always less than the idealized reversible work, and

the difference between the two is called the irreversibility of the process.

Thus, Irreversibility, $I = W_{\max} - W \dots(6.8)$

This is also sometimes referred to as ‘degradation’ or ‘dissipation’.

For a non-flow process between the equilibrium states, when the system exchanges heat only with environment, irreversibility (per unit mass),

$$\begin{aligned} i &= [(u_1 - u_2) - T_0(s_1 - s_2)] - [(u_1 - u_2) + Q] \\ &= T_0 (s_2 - s_1) - Q \\ &= T_0 (\Delta s)_{\text{system}} + T_0 (\Delta s)_{\text{surr.}} \end{aligned}$$

i.e., $i = T_0 [(\Delta s)_{\text{system}} + (\Delta s)_{\text{surr.}}] \dots(6.9)$

$\therefore i \geq 0$

Similarly, for steady flow-process

$$\begin{aligned} i &= W_{\max} - W_{\text{(per unit mass)}} \\ &= T_0 (s_2 - s_1) - Q \\ &= T_0 (\Delta s)_{\text{system}} + T_0 (\Delta s)_{\text{surr.}} \end{aligned}$$

i.e., $i = T_0 (\Delta s)_{\text{system}} + T_0 (\Delta s)_{\text{surr.}}$

The same expression for irreversibility applies to both flow and non-flow processes.

The quantity $T_0 (\Delta s)_{\text{system}} + T_0 (\Delta s)_{\text{surr.}}$ represents (per unit mass) an increase in unavailable energy (or energy).

4.6. EFFECTIVENESS

Effectiveness is defined as the ratio of actual useful work to the maximum useful work. The useful output of a system is given by the increase of availability of the surroundings. Effectiveness, $\epsilon = \frac{\text{Increase of availability of surroundings}}{\text{Loss of availability of the system}}$ For a compression or heating process the effectiveness is given by $\epsilon = \frac{\text{Increase of availability of system}}{\text{Loss of availability of the surroundings}}$ The effectiveness of an actual process is always less than unity. Thus effectiveness of a process is the measure of the extent to which advantage has been taken of an opportunity to obtain useful work.

4.7. The Maxwell relationships:

As we have seen, the fundamental thermodynamic relation $dE = TdS - PdV$ implies that the natural variable in which to express E are S and V : $E = E(S, V)$.

That means that on purely mathematical grounds, we can write

$$dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV$$

But comparison with the fundamental thermodynamic relation, which contains the physics, we can make the following identifications:

$$T = \left(\frac{\partial E}{\partial S} \right)_V \quad \text{and} \quad P = - \left(\frac{\partial E}{\partial V} \right)_S$$

These (especially the second) are interesting in their own right. But we can go further, by differentiating both sides of the first equation by V and of the second by S :

$$\left(\frac{\partial T}{\partial V} \right)_S = \left(\frac{\partial}{\partial V} \left(\frac{\partial E}{\partial S} \right)_V \right)_S \quad \text{and} \quad \left(\frac{\partial P}{\partial S} \right)_V = - \left(\frac{\partial}{\partial S} \left(\frac{\partial E}{\partial V} \right)_S \right)_V$$

Using the fact that the order of differentiation in the second derivation doesn't matter, we see that the right hand sides are equal, and thus so are the left hand sides, giving

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V$$

By starting with F , H and G , we can get three more relations.

$dE = TdS - PdV \Rightarrow T = \left. \frac{\partial E}{\partial S} \right _V \quad \& \quad P = - \left. \frac{\partial E}{\partial V} \right _S$	\Rightarrow	$\left. \frac{\partial P}{\partial S} \right _V = - \left. \frac{\partial T}{\partial V} \right _S$
$dF = -SdT - PdV \Rightarrow S = - \left. \frac{\partial F}{\partial T} \right _V \quad \& \quad P = - \left. \frac{\partial F}{\partial V} \right _T$	\Rightarrow	$\left. \frac{\partial P}{\partial T} \right _V = \left. \frac{\partial S}{\partial V} \right _T$
$dH = TdS + VdP \Rightarrow T = \left. \frac{\partial H}{\partial S} \right _P \quad \& \quad V = \left. \frac{\partial H}{\partial P} \right _S$	\Rightarrow	$\left. \frac{\partial V}{\partial S} \right _P = \left. \frac{\partial T}{\partial P} \right _S$
$dG = -SdT + VdP \Rightarrow S = - \left. \frac{\partial G}{\partial T} \right _P \quad \& \quad V = \left. \frac{\partial G}{\partial P} \right _T$	\Rightarrow	$\left. \frac{\partial V}{\partial T} \right _P = - \left. \frac{\partial S}{\partial P} \right _T$

The two equations involving derivatives of S are particularly useful, as they provide a handle on S which isn't easily experimentally accessible.

For non-hydrodynamic systems, we can obtain analogous relations involving, say, m and B

instead of P and V ; for instance by starting with $dE = TdS + mdB$ we get. $(\partial T/\partial B)_S = (\partial m/\partial S)_B$

To fully exploit these relations, some properties of partial derivatives are useful. See [here](#) for a refresher course!

In maths, it's usually quite obvious what the independent variables are: either x, y, z or r, θ, ϕ , for instance, and if you differentiate with respect to one you know that you are keeping the others constant. In thermal physics it isn't obvious at all, so **always** specify what is being held constant. Expressions like

$$\frac{\partial P}{\partial T} \quad \text{and} \quad \frac{dP}{dT}$$

are simply meaningless. (OK, we met the latter in the Clausius-Clapeyron equation, but there it really was the slope of a line: the restriction to points of phase coexistence was understood.)

OUTCOMES:

- Apply the thermodynamic relation for determining the system properties

IMPORTANT QUESTIONS:

1. Derive an expression for work done in a steady flow polytropic process.
2. Explain Maxwell's relation and Clausius-Clapeyron equation
3. Write Maxwell's relation and explain terms involved
4. 0.2 Kg of air with pressure 1.5 bar and temperature 27°C is compressed to a pressure of 15 bar according to the law $PV^{1.25} = C$. Determine i) Work done ii) Heat flow to or from the air iii) Change of entropy.
5. Derive an expression for change in entropy for an ideal gas undergoing isobaric process

FURTHER READING:

- Basic Engineering Thermodynamics, A.Venkatesh, Universities Press, 2008
- Basic and Applied Thermodynamics, P.K.Nag, 2nd Ed., Tata McGraw Hill Pub.
- <http://www.nptel.ac.in/courses/112104113/4#>

THE PURE SUBSTANCE

OBJECTIVE: Introduce the concept of a pure substance and Illustrate the P-v , T-v and P-T property diagrams and P-v-T surfaces of pure substances. Demonstrate the procedures for determining thermodynamic properties of pure substances from tables of property data.

STRUCTURE:

4. Introduction

4.1 Application of 1st law of thermodynamics for a closed system

4. Introduction: The system encountered in thermodynamics is often quite less complex and consists of fluids that do not change chemically, or exhibit significant electrical, magnetic or capillary effects. These relatively simple systems are given the generic name the Pure Substance.

“A system is set to be a pure substance if it is (i) homogeneous in chemical composition, (ii) homogeneous in chemical aggregation and (iii) invariable in chemical aggregation.”

Pure Substances

Define Pure Substance:

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

A pure substance does not have to be of a single element or compound. A mixture of two or more phases of a pure substance is still a pure substance as long as the chemical composition of all phases is the same.

Phases of a Pure Substance

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

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

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

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

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

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

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

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

Phase-Change Processes of Pure Substances:

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

1. Solid
2. Mixed phase of liquid and solid
3. Sub-cooled or compressed liquid (means it is not about to vaporize)
4. Wet vapor or saturated liquid-vapor mixture, the temperature will stop rising until the liquid is completely vaporized.

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

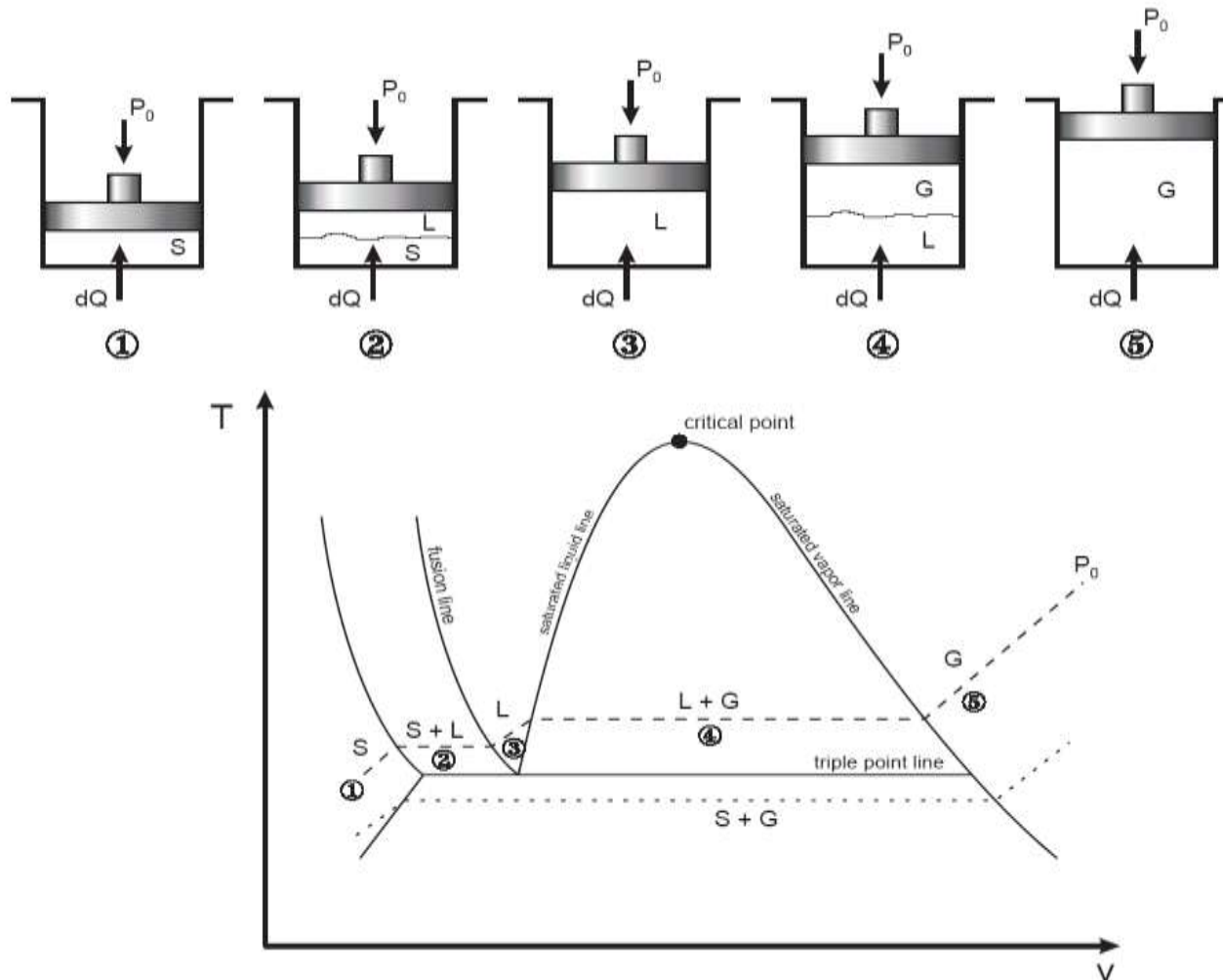


Fig. 1: T-v diagram for the heating process of a pure substance.

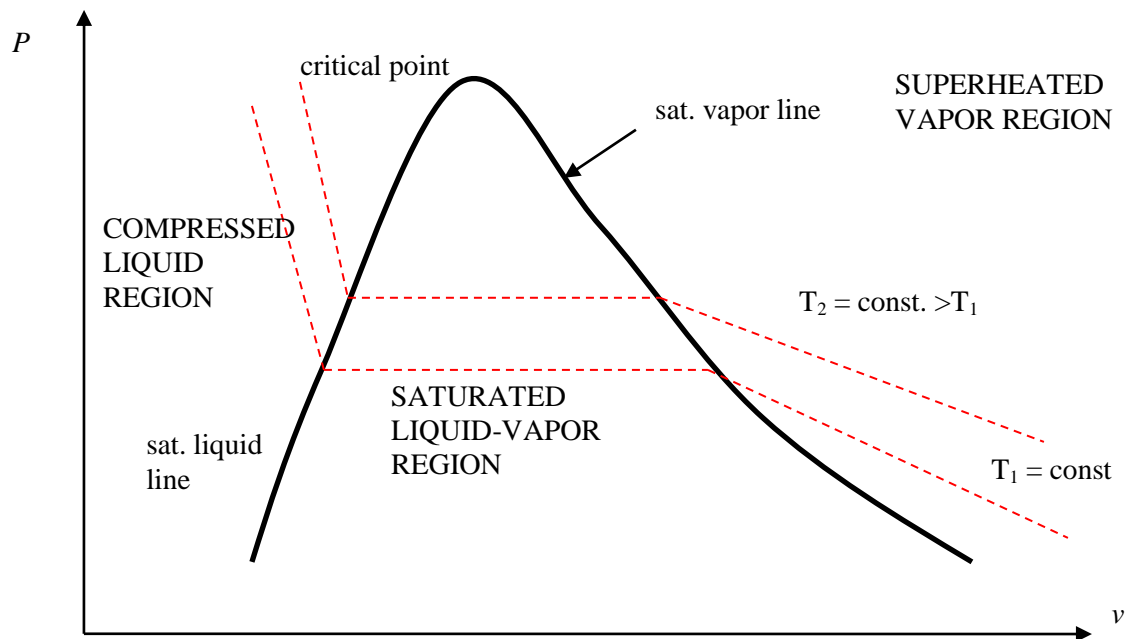
- ◆ At a given pressure, the temperature at which a pure substance starts boiling is called the saturation temperature, T_{sat} .
- ◆ Likewise, at a given temperature, the pressure at which a pure substance starts boiling is called the saturation pressure, P_{sat} .
- ◆ During a phase-change process, pressure and temperature are dependent properties, $T_{\text{sat}} = f(P_{\text{sat}})$.
- ◆ The critical point is the point at which the liquid and vapor phases are not distinguishable
- ◆ The “triple point” is the point at which the liquid, solid, and vapor phases can exist together. On P-v or T-v diagrams, these triple-phase states form a line called the triple line.

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

	Critical Point		Triple Point	
	P (atm)	T (K /°C)	P (atm)	T (K /°C)
H ₂ O	218	647.30/(374.14)	0.006	273.17 (0.01)
O ₂	50.136	154.80/(-118.36)	0.0015	54.16/(-219)

Vapor Dome

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

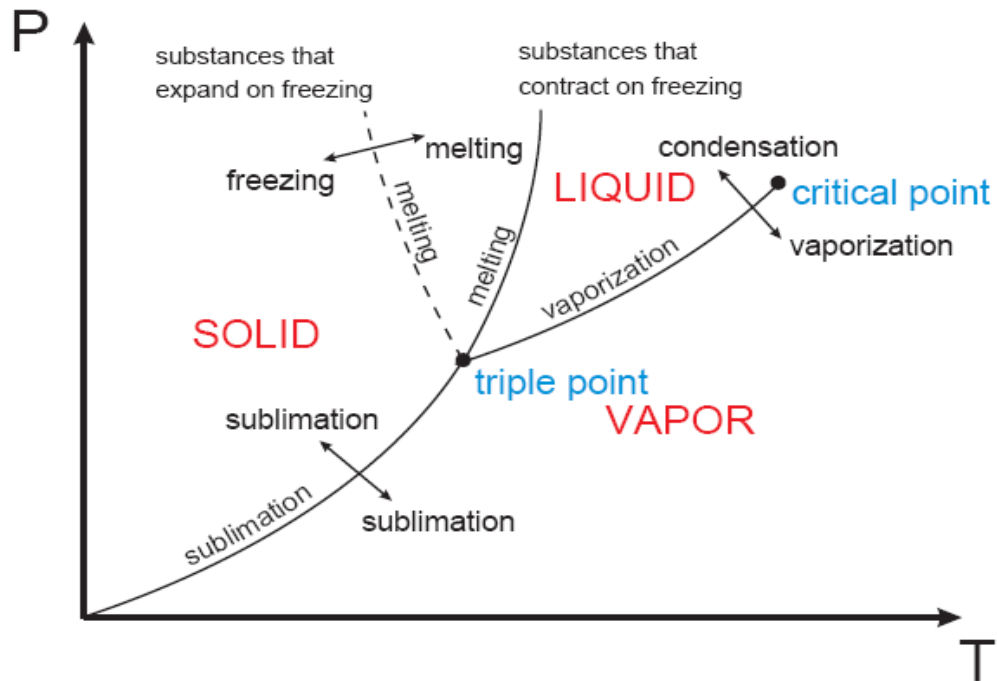


P-v diagram of a pure substance.

The P-T or Phase Change Diagram

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

- ◆ One exception is water. Water expands upon freezing.



phase diagram of pure substances.

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

- ◆ the sublimation line separates the solid and the vapor.
- ◆ the vaporization line separates the liquid and vapor regions
- ◆ the melting or fusion line separates the solid and liquid.
- ◆ these three lines meet at the triple point.
 - if $P < P_{TP}$, the solid phase can change directly to a vapor phase
 - at $P < P_{TP}$ the pure substance cannot exist in the liquid phase. Normally ($P > P_{TP}$) the substance melts into a liquid and then evaporates.
 - matter (like CO_2) which has a triple point above 1 atm sublimate under atmospheric conditions (dry ice)
 - for water (as the most common working fluid) we are mainly interested in the liquid and vapor regions. Hence, we are mostly interested in boiling and condensation.

Property Tables

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

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

For example:

v_f = specific volume of saturated liquid

v_g = specific volume of saturated vapor

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

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

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

1- Saturated Liquid-Vapor Mixture

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

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

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

$$V = V_f + V_g$$

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

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

dividing by m_t

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

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

or,

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

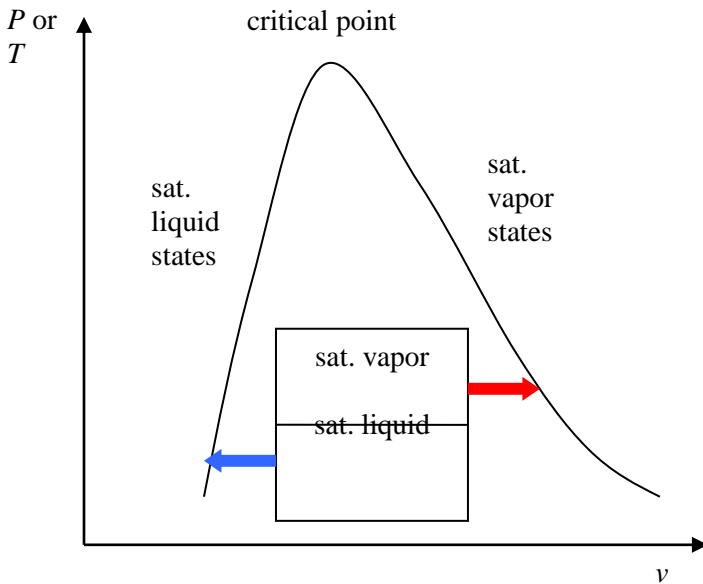


Fig. 4: The relative amounts of liquid and vapor phases (quality x) are used to calculate the mixture properties.

Similarly,

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

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

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

$$0 \leq x \leq 1$$

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

Note: pressure and temperature are dependent in the saturated mixture region.

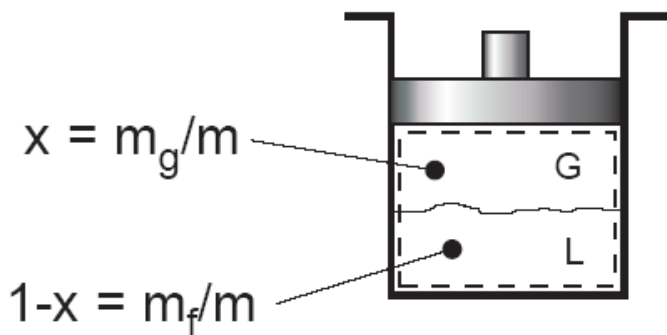


Fig. 5: Quality defined only for saturated liquid-vapor mixture.

Example 1: Saturated liquid-vapor mixture

A closed, rigid container of volume 0.5 m^3 is placed on a hot plate. Initially the container holds a two-phase mixture of saturated liquid water and saturated water vapor at $P_1 = 1 \text{ bar}$ with a quality of 0.5. After heating, the pressure in the container is $P_2 = 1.5 \text{ bar}$. Indicate the initial and final states on a T-v diagram, and determine:

- the temperature, in $^{\circ}\text{C}$, at each state.
- the mass of vapor present at each state, in kg.
- if heating continues, determine the pressure, in bar, when the container holds only saturated vapor.

Solution:

Assumptions:

- Water in the container is a closed system.
- States 1, 2, and 3 are equilibrium states.
- The volume of container remains constant.

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

$$v_1 = v_{f1} + x_1(v_{g1} - v_{f1})$$

From Table A - 5 at $P = 1 \text{ bar} = 100 \text{ kPa}$

$$v_1 = 0.001043 + 0.5(1.694 - 0.001043) = 0.8475 \text{ m}^3 / \text{kg}$$

At state 2, the pressure is known. Volume and mass remain constant during the heating process within the container, so $v_2 = v_1$. For $P_2 = 0.15 \text{ MPa}$, Table A-5 gives $v_{f2} = 0.001053$ and $v_{g2} = 1.1593 \text{ m}^3/\text{kg}$. Since

$$v_{f2} < v_2 < v_{g2}$$

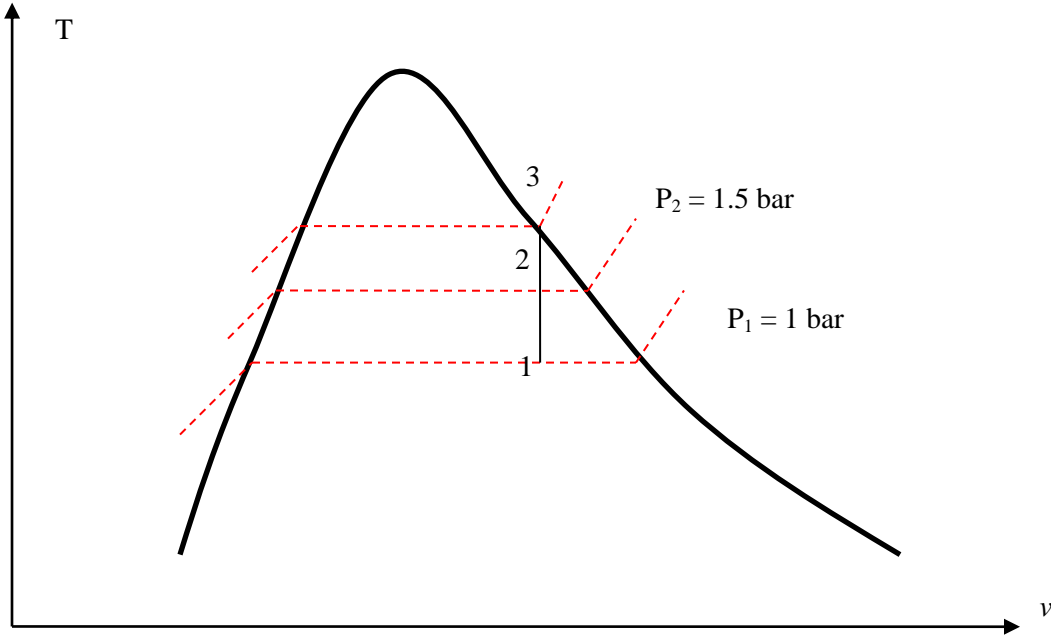
State 2 must be in the two-phase region as well. Since state 1 and 2 are in the two-phase liquid-vapor region, the temperatures correspond to the saturation temperatures for the given. Table A-5:

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

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

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

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



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

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

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

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

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

2- Superheated Vapor

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

If $T \gg T_{\text{critical}}$ or $P \ll P_{\text{critical}}$, then the vapor can be approximated as an “ideal gas”.

3- Compressed (or Sub-cooled) Liquid

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

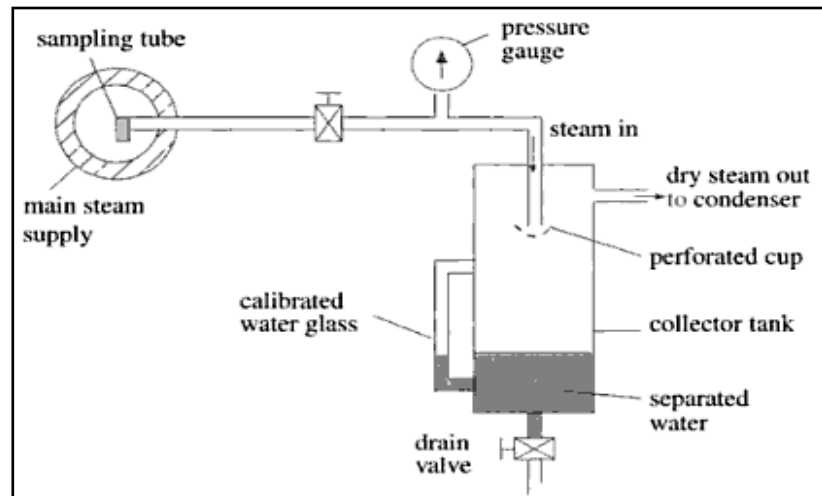
A general approximation is to treat compressed liquid as saturated liquid at the given saturation temperature.

Determination the dryness fraction:

- **Separating calorimeter:**

The quality of wet steam is usually defined by its dryness fraction. When the dryness fraction, pressure and temperature of the steam are known, then the state of wet steam is fully defined. In a steam plant it is at times necessary to know the state of the steam. For wet steam, this entails finding the dryness fraction. When the steam is very wet, we make use of a separating calorimeter.

Construction of separating calorimeter is as shown in figure:



The steam is collected out of the main steam supply and enters the separator from the top. The steam is forced to make a sharp turn when it hits the perforated cup (or any other mechanism that produces the same effect). This results in a vortex motion in the steam, and water separates out by the centrifugal action. The droplets then remain inside the separator and are collected at the bottom, where the level can be recorded from the water glass. The dry steam will pass out of the calorimeter into a small condenser for the collection of the condensate. However, not all the water droplets remain in the collector tank. Some water droplets pass through to the condenser, and hence this calorimeter only gives a close approximation of the dryness fraction of the steam.

From the results obtained from the two collectors, the dryness fraction may then be found from

$$\text{Dryness fraction} = \frac{\text{Mass of dry steam}}{\text{Mass of wet steam containing dry steam}}$$

This can be expressed as:

$$x = \frac{M}{m+M}$$

Where,

M is the mass of dry steam and

m is the mass of suspended water separated in the calorimeter in the same time.

- **Throttling calorimeter:**

If we have steam that is nearly dry, we make use of a throttling calorimeter as shown in figure. This calorimeter is operated by first opening the stop valve fully so that the steam is not partially throttled as it passes through the apparatus for a while to allow the pressure and temperature to stabilize. If the pressure is very close to atmospheric pressure, the saturation should be around 100°C, it may be assumed that the steam is superheated.

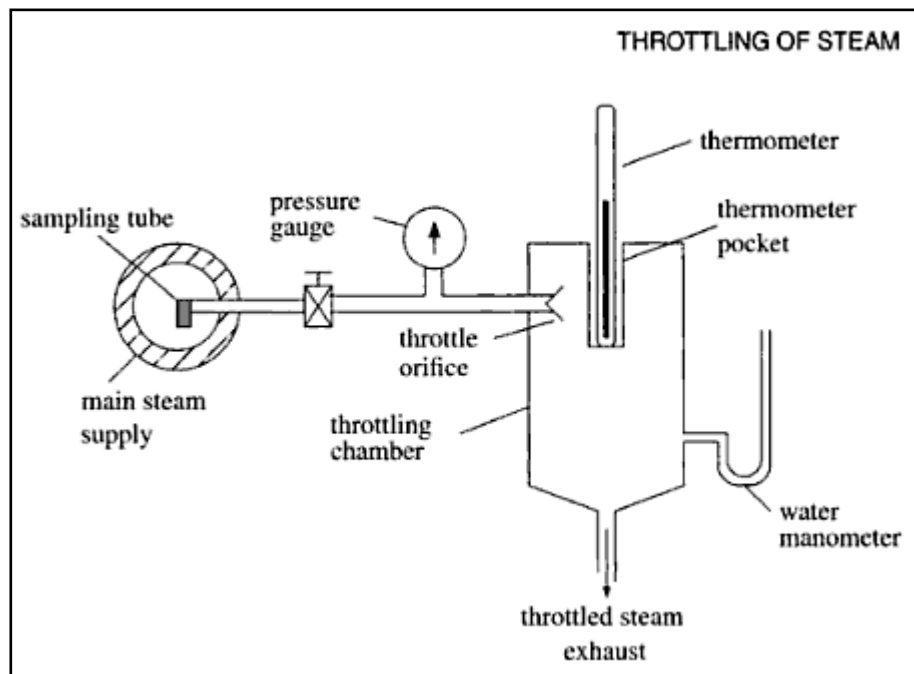
When the conditions have become steady, the gauge pressure before throttling is read from the pressure gauge. After throttling, the temperature and gauge pressure are read from the thermometer and manometer respectively. The barometric pressure is also recorded.

From equation $h_1 = h_2$,

We have

$$h_w \text{ at } p_1 = h_{sup} \text{ at } p_2$$

And thus $x = \frac{h_{g2} + Cp (T_{sup} - T_{sat}) - h_{f1}}{h_{fg1}}$



List of Formulas:

1. Dryness fraction of steam sample entering Separating Calorimeter = $x = \frac{M}{m+M}$

Where, M is the mass of dry steam and

m is the mass of suspended water separated in the calorimeter in the same time.

2. Dryness fraction of steam sample entering Throttling calorimeter

We have h_w at $p_1 = h_{sup}$ at p_2

$$\text{And thus } x = \frac{h_{g2} + C_p (T_{sup} - T_{sat}) - h_{f1}}{h_{fg1}}$$

3. Dryness Fraction = $x = \text{Mass of dry steam} / \text{Mass of wet steam}$

4. Specific Enthalpy of wet steam at Pressure $P = h = h_f + x h_{fg}$ KJ/Kg (Similarly specific entropy, specific volume can be calculated)

5. Enthalpy(h) = Internal energy(u) + ($P.v$)

6. Specific heat at constant volume = $C_v = du/dt$

7. Specific heat at constant pressure = $C_p = dh/dt$

8. Specific heat at constant pressure for dry steam = $C_{ps} = 2.1 \text{ KJ/Kg.K}$

OUTCOME: Demonstrate understanding of key concepts including phase and pure substance, state principle for simple compressible systems, p-v-T surface, saturation temperature and saturation pressure, two-phase liquid-vapor mixture, quality, enthalpy, and specific heats. Apply the closed system energy balance with property data.

IMPORTANT QUESTIONS:

1. With a neat sketch explain how Combined separating and throttling calorimeter can be used to measure the dryness fraction of wet vapour
2. With a neat sketch explain throttling calorimeter can be used to measure the dryness fraction of wet vapour
3. Draw phase equilibrium diagram of water on P-T Coordinates indicating triple and critical point
4. Steam initially at 1.5 MPa 300°C expands reversibly and adiabatically in a steam turbine to 40°C . Determine the ideal work output of the turbine per kg of steam

FURTHER READING:

1. Basic Engineering Thermodynamics, A.Venkatesh, Universities Press, 2008
2. Basic and Applied Thermodynamics, P.K.Nag, 2nd Ed., Tata McGraw Hill Pub.
3. <http://www.nptel.ac.in/courses/112104113/4#>

Problems

Question paper problems

Steam initially at 1.5 Mpa, 300°C expands reversibly & adiabatically in a steam turbine to 40°C. Determine the ideal work output of the turbine per kg of steam

→ SFEE for the control volume

for Turbine $d(K.E) = 0$
 $d(P.E) = 0$
 W is +ve
 $Q = 0$ (adiabatic)

∴ $W = (h_1 - h_2)$

The process is reversible & adiabatic, so it is isentropic hence the line 1-2 will be vertical in T-s & h-s diagram

from steam table (15 bar)
 since at $P_1 = 1.5 \text{ Mpa}$, $T_1 = 300^\circ\text{C}$
 $T_1 > T_s$ (saturation temperature) hence we have to check $P_1 = 15 \text{ bar}$, $T_1 = 300^\circ\text{C}$ in superheated steam table for properties at state 1 (superheated condition)

$h_1 = 3038.9 \text{ kJ/kg} = h_{\text{sup}}$
 $s_1 = 6.9207 \text{ kJ/kg}\cdot\text{K} = s_{\text{sup}}$

for state 2 :- (liquid vapour mixture region)

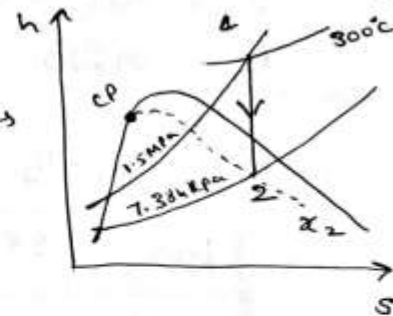
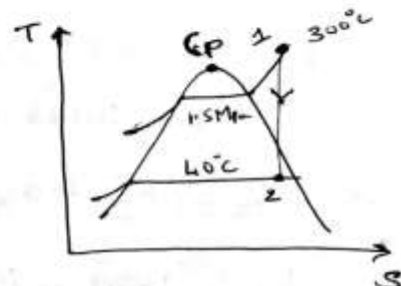
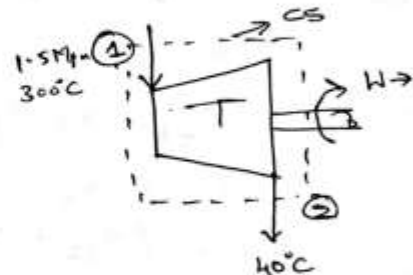
$P_2 = P_{\text{saturation}} = 0.073750 \text{ bar} = 7.375 \text{ kPa}$

$s_f = 0.5721 \text{ kJ/kg}\cdot\text{K}$

$h_f = 167.5 \text{ kJ/kg}$

$s_{fg} = 7.6845 \text{ kJ/kg}\cdot\text{K}$

$h_{fg} = 2406.9 \text{ kJ/kg}$



To find h_2

$$h_2 = h_{f2} + x_2 h_{fg2}$$

To find x_2 which is unknown
we have $S_1 = S_2$ (adiabatic expansion)

$$S_1 = 6.9207 \text{ kJ/kg K}$$

$$S_2 = S_{g2} + x_2 S_{fg2}$$

$$S_1 = S_2$$

$$6.9207 = (S_{g2} + x_2 S_{fg2})_{40^\circ\text{C}}$$

$$6.9207 = 0.5721 + x_2 \times 7.6845$$

$$x_2 = 0.826 \text{ or } 82.6\%$$

$$\therefore h_2 = (h_{f2} + x_2 h_{fg2})_{40^\circ\text{C}}$$

$$h_2 = (167.5 + (0.826 \times 2406.9))$$

$$h_2 = 2152.57 \text{ kJ/kg}$$

$$\therefore W = h_1 - h_2 = (3038.9 - 2152.57) = 885.03 \text{ kJ/kg} //$$

$$\boxed{W = +885.03 \text{ kJ/kg}}$$

2) A rigid vessel of 2 m^3 volume is filled with super heated steam at 20 bar & 300°C . The vessel is cooled until the steam is just dry saturated. Calculate the mass of steam in the vessel, the final pressure of steam & the amount of energy transferred as heat to the surroundings. Represent the process on T-s diagram

(15)

Solution:-

At state point 1,

$$P_1 = 20 \text{ bar}, T_1 = 300^\circ\text{C}, V_1 = 2 \text{ m}^3$$

From steam table

superheated steam table

$$P_1 = 20 \text{ bar}, T_1 = 300^\circ\text{C}$$

$$\text{Specific volume} = v_{\text{sup}} = v_1 = 0.12550 \text{ m}^3/\text{kg}$$

Mass of steam in vessel

$$m = \frac{V_1}{v_1} = \frac{2}{0.12550} = 16 \text{ kg}$$

Since the tank is rigid the volume remains constant

$$\therefore v_2 = v_1 = 0.12550 \text{ m}^3/\text{kg}$$

The steam is just dry & saturated at point 2 & so

$$v_{g2} = v_2 = 0.12550 \text{ m}^3/\text{kg}$$

From steam tables, the pressure of dry saturated steam corresponding to specific volume $0.125 \text{ m}^3/\text{kg}$ is 16 bar

For constant volume process, workdone is zero & therefore from the principle of energy conservation

$$\text{heat transferred} = q_2 = du = u_2 - u_1$$

$$q_2 = (h_2 - P_2 v_2) - (h_1 - P_1 v_1)$$

$$= (h_2 - h_1) - v_1 (P_2 - P_1) \quad \{ \because v_2 = v_1 \}$$

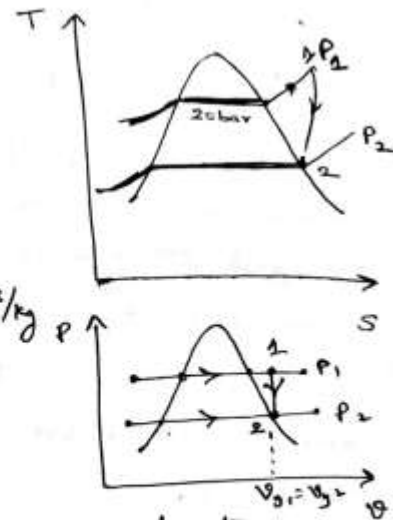
$$\text{At } 20 \text{ bar \& } 300^\circ\text{C} \quad h_1 = 3023.9 \text{ kJ/kg}$$

$$\text{At } 16 \text{ bar \& } x = 1 \quad h_2 = h_g = 2791.7 \text{ kJ/kg (dry saturated)}$$

$$\therefore q_2 = (2791.7 - 3023.9) - [0.12550 (16 - 20) \times 100]$$

$$q_2 = -182.4 \text{ kJ/kg}$$

(16)



∴ Total energy transferred as heat to Surroundings

$$Q_2 = m_1 q_{12} = 16 (-282.4) = \underline{\underline{-4518.4 \text{ kJ}}}$$

⇒ calculate the internal energy per kg of superheated steam at pressure of 10 bar & a temperature of 300°C. Also find the change in internal energy if this steam is expanded to 1.4 bar & dryness fraction 0.8

→ state 1 :- $P_1 = 10 \text{ bar}$, $T_1 = T_{\text{sup}} = 300^\circ\text{C}$

state 2 :- $P_2 = 1.4 \text{ bar}$, $x_2 = 0.8$

To find u_1

$u_1 = h_1 - P_1 v_{g1}$ (superheated steam)
from superheated steam table

$h_1 = 3052.1 \text{ kJ/kg}$, v_{g1} at $P_1 = 10 \text{ bar}$ from ~~superheated~~ superheated steam table

$$v_{g1} = v_{g \text{ sup}} = 0.25798 \text{ m}^3/\text{kg}$$

$$\therefore u_1 = 3052.1 - (10 \times 10^2 \times 0.25798)$$

$$u_1 = 2794.12 \text{ kJ/kg}$$

To find u_2

$$u_2 = h_2 - x_2 P_2 v_{g2}$$

$$u_2 = (h_{f2} + x_2 h_{fg2}) - x_2 P_2 v_{g2}$$

• at $P_2 = 1.4 \text{ bar}$ from Saturated steam table

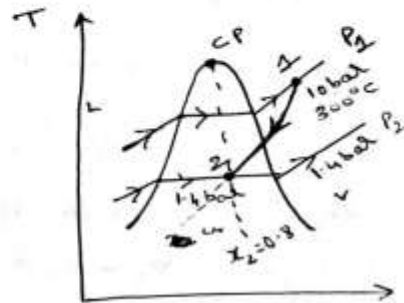
$$h_{f2} = 458.4 \text{ kJ/kg}, x_2 = 0.8 \text{ (Given)}$$

$$h_{fg2} = 2231.9 \text{ kJ/kg}, P_2 = 1.4 \times 10^2 \text{ kPa}$$

$$v_{g2} = 1.2363$$

$$\therefore u_2 = 2105.4544 \text{ kJ/kg}$$

$$\text{Change in internal energy} = u_2 - u_1 = 688.66 \text{ kJ/kg}$$



Process 1-2 represents the expansion process

4) The following data were obtained with a separating & throttling calorimeter
 pressure in pipeline = 1.5 MPa

condition after throttling = 0.1 MPa, 110°C

During 5 min, moisture collected in the separator = 0.15 kg at 70°C

steam condensed after throttling during 5 min = 3.24 kg

Find the quality of steam in the pipe line

→ Let m_1 = mass of moisture collected in a separator in 5 min
 & m_2 = mass of steam condensed after throttling in 5 min

$$\text{then } x_1 = \frac{x_2 m_2}{m_1 + m_2}$$

from h-s diagram & steam table

• To find x_2 :-

at state 3, at 0.1 MPa & 110°C

$$h_3 = 2696.2 \text{ kJ/kg}$$

we know that for a throttling process
 enthalpy at inlet = enthalpy at outlet

$$h_2 = h_3 =$$

$$(h_f + x_2 h_{fg})_{1.5 \text{ MPa}} = h_3 = 2696.2$$

$$844.87 + x_2 \times 1947.3 = 2696.2$$

$$\boxed{x_2 = 0.955}$$

• To find m_1 :-

at 70°C moisture collected in the

$$\text{separator} = V_1 = 0.150 \text{ m}^3 = 0.150 \times 10^{-3} \text{ m}^3$$

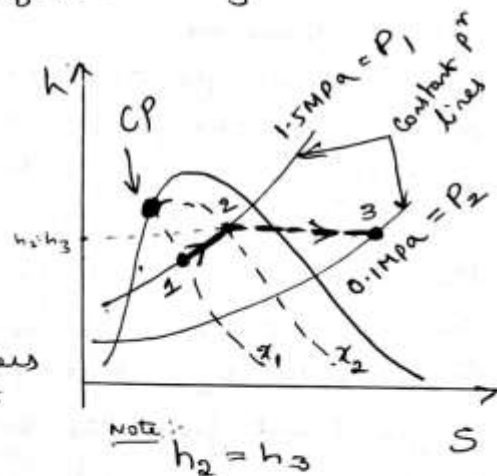
to convert m^3 to kg

$$\text{at } 70^\circ\text{C}, v_f = 0.001023 \text{ m}^3/\text{kg}$$

$$\therefore m_1 = \frac{0.150 \times 10^{-3} \text{ m}^3}{0.001023 \text{ m}^3/\text{kg}} = 0.1462 \text{ kg}$$

$$m_2 = 3.24 \text{ kg (Given)}$$

$$\therefore \boxed{x_1 = 0.915}$$



5) Steam flows in a pipeline at 1.5 Mpa. After expanding to 0.1 Mpa in a throttling calorimeter, the temperature is found to be 120°C. Find the quality of steam in the pipeline. What is the maximum moisture at 1.5 Mpa that can be determined with this setup if at least 5°C of superheat is required after throttling for accurate readings?

→ At state 2, when $P = 0.1 \text{ Mpa}$, $t = 120^\circ\text{C}$ by interpolation

superheated table & by interpolation we get

$$h_2 = 2716.2 \text{ kJ/kg}$$

At pressure 1.5 Mpa = 15 bar from saturated steam table

$$h_f = 844.89 \text{ kJ/kg} \quad \& \quad h_{fg} = 1947.3 \text{ kJ/kg}$$

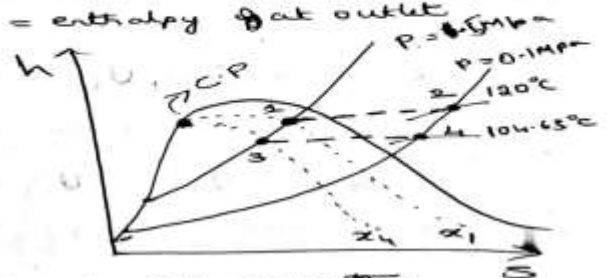
To find x_1 , we know that across throttling valve during throttling process enthalpy at inlet = enthalpy at outlet

$$\therefore h_1 = h_2$$

$$[h_{d1} + x_1 h_{fg}]_{P_1=15 \text{ bar}} = 2716.2$$

$$844.89 + x_1 \times 1947.3 = 2716.2$$

$$\boxed{x_1 = 0.963}$$



To find x_2 :-

It's given that the exit temperature is 5°C more than the saturation temperature at pressure $P_2 = 0.1 \text{ Mpa} = 1 \text{ bar}$

∴ Temperature at exit of the valve for condition 2 is

at $P = 1 \text{ bar}$ from saturated steam table $T_s = 99.63$

∴ Exit temperature = superheated temperature = $99.63 + 5$ at exit

$$T_{\text{sup}} \text{ for condition 2} = 104.63^\circ\text{C}$$

∴ from superheated steam table at 1 bar & 104.63°C

$$h_{\text{sup}} = h_{31} = 2685.5 \text{ kJ/kg}$$

Since $h_{31} = h_3$

$$2685.5 = [h_{f3} + x_2 h_{fg3}]_{P=1 \text{ bar}}$$

from saturated steam table

$$2685.5 = 844.89 + x_2 \times 1947.3$$

$$x_2 = 0.9218$$

$$\left. \begin{aligned} \text{dryness fraction} &= 0.948 \\ &= 94.8\% \end{aligned} \right\}$$

$$\left. \begin{aligned} \text{moisture fraction} &= 1 - 0.948 \\ &= 0.052 \\ &= 5.2\% \end{aligned} \right\}$$

The maximum moisture that can be determined with the setup = 5.2%

6) A steam boiler initially contains 5 m^3 of steam & 5 m^3 of water at 1 Mpa . Steam is taken out at constant pressure until 4 m^3 of water is left. What is the heat transferred during the process

$$\rightarrow \left\{ \begin{array}{l} \text{heat transferred} \\ \text{during the process} \end{array} \right\} = \left\{ \begin{array}{l} \text{Final energy} \\ \text{stored in saturated} \\ \text{water \& steam} \end{array} \right\} - \left\{ \begin{array}{l} \text{Initial} \\ \text{energy} \\ \text{stored} \end{array} \right\} + \left\{ \begin{array}{l} \text{Energy going} \\ \text{out with} \\ \text{steam removed} \\ \text{of } (m_s) \text{ mass} \end{array} \right\}$$

$$Q = (m_2 U_2 - m_1 U_1) + m_s h_g$$

Assuming that steam taken out is dry ($x=1$) $\therefore Q_s = m_s h_g$
or we can write:-

$$Q (m_2 U_2 - m_1 U_1) = Q_s - m_s h_g \rightarrow \textcircled{1}$$

$$\left\{ \begin{array}{l} \text{change in internal energy} \end{array} \right\} = \left\{ \begin{array}{l} \text{heat input} \\ \text{to the system} \\ \text{from external} \\ \text{source} \end{array} \right\} - \left\{ \begin{array}{l} \text{heat or energy leaving} \\ \text{with dry steam} \end{array} \right\}$$

At $1 \text{ Mpa} = 10 \text{ bar}$ from saturated steam table

$$v_f = 0.001127, \quad v_g = 0.1944 \text{ m}^3/\text{kg}, \quad h_g = 2778.1 \text{ kJ/kg}$$

To find m_s :-

The initial mass of saturated water & steam in the boiler is given by, at 10 bar

$$m_{f1} = \frac{V_{f1}}{v_{f1}} = \frac{5}{0.001127} = 4436.5 \text{ kg} \quad v_{g1} = 0.1944 \text{ m}^3/\text{kg}$$

$$m_{g1} = \frac{V_{g1}}{v_{g1}} = \frac{5}{0.1944} = 25.72 \text{ kg}$$

\therefore The final mass of saturated water & steam in the boiler is given by

$$m_{f2} = \frac{V_{f2}}{v_{f2}} = \frac{4}{0.001127} = 3549.2 \text{ kg}$$

$$m_{g2} = \frac{V_{g2}}{v_{g2}} = \frac{6}{0.1944} = 30.86 \text{ kg}$$

\therefore pressure is constant

\therefore at $P = 10 \text{ bar}$

$$v_{f2} = v_{f1}$$

$$v_{g2} = v_{g1}$$

Mass of steam taken out of the boiler (m_s)

$$= \text{Total mass of mixture at state 1} - \text{Total mass of mixture at state 2}$$

$$= (m_{f1} + m_{g1}) - (m_{f2} + m_{g2})$$

$$m_s = \cancel{894.9 \text{ kg}} \times 882.16 \text{ kg}$$

Equation (1) can be written as

$$U_2 - U_1 = Q - m_s h_g$$

$$[U_{f2} + U_{g2}] - [U_{f1} + U_{g1}] = Q - m_s h_g$$

$$(m_{f2} u_{f2} + m_{g2} u_{g2}) - (m_{f1} u_{f1} + m_{g1} u_{g1}) = Q - m_s h_g \rightarrow (3)$$

to find $u_{f2} = h_{f2} - p v_{f2} = 762.6 - 1.127 = 761.473 \text{ kJ/kg}$

$$u_{f1} = h_{f1} - p v_{f1} = 761.473 \text{ kJ/kg}$$

$$u_{g2} = h_{g2} - p v_{g2} = 2776.2 - 0.1944 = 2581.8 \text{ kJ/kg}$$

$$u_{g1} = h_{g1} - p v_{g1} = 2581.8 \text{ kJ/kg}$$

Substituting in (3) we get

$$(3549.2 \times 761.473 + 30.86 \times 2581.8) - (4436.5 \times 761.473 + 25.72 \times 2581.8) = Q - 808.9 \times 2778.1$$

$$\boxed{Q = 1752.676 \text{ MJ}} = 1.805 \text{ KJ} //$$