Basic Thermodynamics

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Lecture - 15
Joule-Kelvin Expansion; Properties of Pure Substances

Good morning. Last class, we started the discussion on Joule-Kelvin expansion or Joule-Kelvin effect. We just started the discussion, let us continue that. What is Joule-Kelvin expansion?

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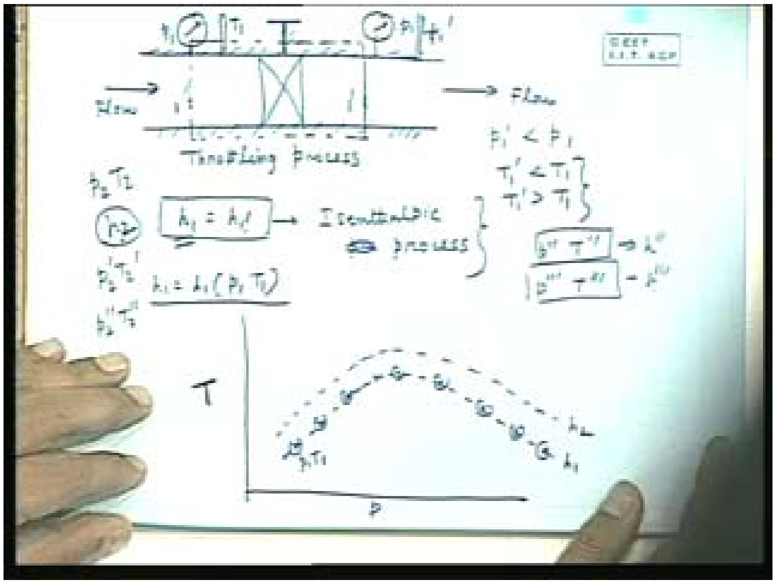

Joule-Kelvin expansion is like that if there is a constant area pipe, for example, it is like this; A fluid flows in this direction and if we have a valve in between which restricts the flow by closing the flow area by providing restricted passage and if the valve is completely closed, there is no passage for the flow to take place. If the valve is gradually opened, the flow commences through restricted passages. So, by various opening of the valve, we can create various flow passages across this through which the fluid flow takes place. By that, we can control the flow at different levels.

So, in this situation, if we just recognize some section one, upstream to this valve which is undisturbed by this valve and if we measure both the pressure; This is the pressure $p_{1,}$ section one and the temperature T_1.

If we recognize another downstream section, far from the valve which is undisturbed section when the fluid flow has become again steady and uniform, and if we measure both the pressure, let this section is p_1 dash and temperature T_1 dash. We recognize that, if there is no heat transfer, heat is not allowed to flow; that means, the entire pipe is insulated along with the valve. Then in these situations, we have recognized experimentally that p_1 dash is always less than $p_{1.}$ Pressure is reduced while flowing through, because of the friction flowing through the restricted area of flow provided by the valve.

About T_1 dash, let us define it with $T_{1.}$ T_1 dash may be less than T_1 or may be greater than $T_{1,}$ depending upon the situation. Now, this process is known as throttling process. This is the practical terminology, throttling process. Fluid is throttled that means it is coming with some high pressure. It is throttled to a lower pressure p_1 dash. So, while throttling the fluid the entire flow rate is set to a reduced value. So, by setting the valve at different positions, we can go on reducing the flow rate.

When the valve is fully closed, no flow and when the valve is wide open, the full flow so that at various levels we can set the flow by regulating the valve. This is one of the very practical ways of controlling the flow. There are different types of valves which we will come across in practice. There is nothing much to understand fluid flow, but how to analyze this process thermodynamically?

Now, if we consider a control volume, comprising one and one dash section, then from thermodynamic point of view, this is a control volume which does not have any heat and work interaction with the surrounding.

If we write the steady flow energy equations then the enthalpy plus the kinetic and potential energy section one must be equal to those quantities at one dash. But the kinetic energy at one and one dash is the same. Since the cross sectional area is the same, the flow rate is the same.

Therefore, per unit mass basis we can write, the specific enthalpies remain the same at the two sections one and one dash. In the last class, I designated the section downstream by two. Now, I designate it by one dash.

We see this is an isenthalpic process. Therefore, throttling process is an isenthalpic process; that means, the process where the initial and final enthalpies are same. But this is an irreversible process. This is because of friction. Unless and until there is friction, the pressure cannot be lower than this. If this could have been an in viscid flow, if we allow an in viscid flow to flow through a restricted passage area, then what will happen? There will be no change in pressure, because if we write the Bernoulli's equation across these two sections as we have read in fluid mechanics, the pressure at these two points will be same.

If we write the Bernoulli's equation, even if the velocities are same, pressures are not same which is known as head loss that means the energy loss. The sum of the pressure energy is a part of mechanical energy which is being converted in to intermolecular energy which we call as loss of mechanical energy.

As such energy cannot be lost. That is why the loss of energy in Bernoulli's equation is, the loss of mechanical energy. A part of the mechanical energy, here the pressure energy is being converted. Loss means it being converted from mechanical energy. The loss from the account to the mechanical energy goes to the intermolecular energy which raises the temperature of the fluid. It may or may not, but increases the intermolecular energy of the fluid. It is the friction of the fluid by virtue of which there is a difference in pressure.

The pressure is reduced at the downstream from that of the upstream; this is a process from one to one dash executed by an open system, or a steady or a flow process which is highly irreversible in nature. Friction is the dominating factor in reducing the pressure. Therefore, isenthalpic process means initial and final enthalpies are same, but it is an irreversible process.

Now, if we do an experiment like this, we fix this quantity p_1 T_1 so that h_1 is fixed because h_1 is a function of p_1 T_1. If we fix p_1T_1 then h_1 is fixed. We set the valves at different positions that means throttle the fluid at different levels so that we arrive at different pressures and temperatures at the outlet. So, we can do the experiment.

We get a pair of points like p double dash, T double dash, p triple dash; these are all outlet pair of pressure and temperatures at outlet which we get after throttling at different valve settings. Because of the fact the enthalpy has to remain same, from the steady flow energy equation applied to this control volume, all the enthalpies which correspond to this pressure; let these enthalpies are h double dash, h triple dash, but they become equals to h.

We can generate equal enthalpy state points. If we draw this in a curve or a plane Tp plane, we can get a curve which represents the locus of constant enthalpy. So, this curve looks like this. Actually, this is not the curve or the line representing this process because throttling is an irreversible process. So, this curve is not the representation of the process. An irreversible process can never be described or shown in a thermodynamic coordinate diagram.

So, it is very important to note in this context that this is a curve showing a constant enthalpy h_1, constant enthalpy line; that is, locus of the constant the enthalpy points. If we join the points, we will get this curve. One of the points corresponds to p_1 T_1 that is the inlet. For example, we see that we have a maximum if we repeat the experiment in this way. We now change this inlet conditions from some other value.

Let p_2 T_2 be corresponding to another enthalpy h_2. We set the valves at different levels to generate different other points that means p_2 dash, T_2 dash, p_2 double dash, T_2 double dash. Then we will be able to generate state points of enthalpy which equals to h_2 which is said by the fixed values of the inlet state point. Then we can generate another curve. This way we can generate different families of curves of constant enthalpies in Tp diagram.

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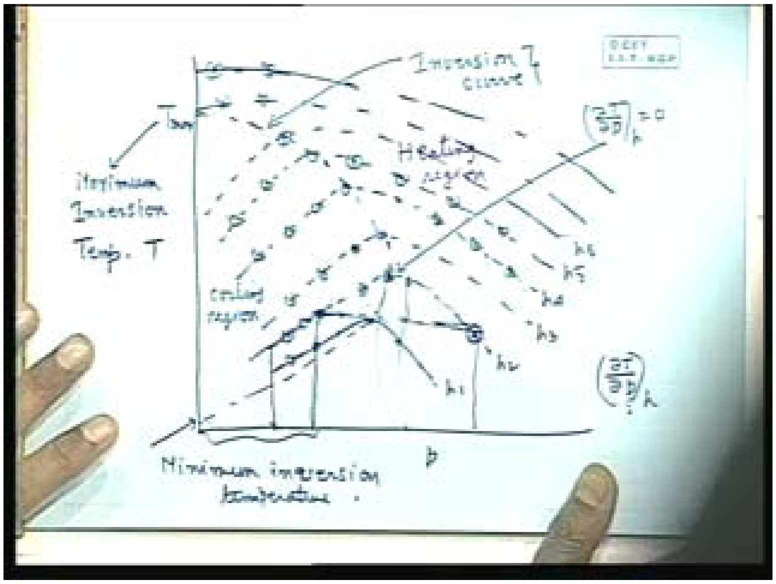

If we do so, we will come across such a curve. Let me draw this. Then I will explain this. We should come across such a curve. These are the families of curves. Now, as we have already noted, let us do like this. I will explain these things. Let me draw the diagram. This is the family of curves we obtained.

What are these things? Now this is Tp. These are all constant enthalpy curve. Let h_1, h_2, h_3 they are same. All the points h_5, h_6 are constant enthalpy curves. All the points on this curve represent same enthalpy. There are different interesting features. These points are all constants. We just join these experimental points, the way we draw the experimental curve.

I am sorry. These lines also will be dotted, this part of the line. There are few interesting points now. Any curve, if we follow at any constant enthalpy curve, there is a maximum and then it is falling; that means, there is a maximum on the curve. So, some part of the curve, this slope is positive and some part of the curve, the slope is negative. This del T divided by del p. If we define this slope is del T divided by del p slope is positive on some part the curve has a maximum and the slope is negative. This way this goes.

Another interesting fact we see, as we go on increasing the temperature, the maximum point shifts towards the right, towards this increasing p value. Then again, it shifts towards the left. If we join these maximum points which are given by del T divided by del $p_{0;}$ that means, all these points corresponds to del T divided by del p. This point which corresponds to del T divided del p at constant h is zero. If we join the maximum of all these constant enthalpy curves in Tp plane, if we join the del T divided del p at zero point, we get a locus as shown by this red dotted line which is known as inversion curve.

Now, our main question was that this is our experimental findings. Whatever we have generated that we have done the experiments in the laboratory as a worker and we plot the data. Now, we will explain these things. This is the data generated from the laboratory experiments. Now, we see that each and every curve has a maximum which goes on shifting in the right direction in Tp plane and again on the left direction. If we join, we will see that the locus of this maximum point, del T divided by del p at constant h is zero. It is like that at some point it cuts on T axis here and here. Therefore, from this point onwards the curve has only negative slope.

When the curve has a positive slope there, only the throttling process can reduce the temperature. What is throttling process? The pressure has to be reduced. In the positive part of the slope and in the positive slope part of the curve, what is the value of del T divided by del p positive?

If we decrease the pressure, temperature will be decreased. Therefore, this positive slope part of the curve represents always a cooling effect or cooling region; that means, if we start at any point here and throttle, the starting part is here and we throttle up to this. So, there will be always a cooling. So, this region is the cooling region. Throttling means, if we start at initial point while we throttle, we have to move in a direction where the pressure is reduced.

If the initial point, initial state lies on this positive slope part then if we throttle, that means if we go along the direction where pressure is reduced, always temperature will be reduced. Because this part of the curve shows a positive value of del T divided by del p at constant h. So, it is a cooling region.

If the initial point is somewhere here or here and if we go along this line in a direction where pressure is reduced, temperature will be increased. Because this part of this curve is having a negative del T divided by del p at constant h, negative slope; that means, when the pressure is reduced temperature is increased. So, this part is the heating region.

It is the inversion point. This is known as inversion curve which demarcates the cooling and heating region. Let us analyze few other interesting things. If we have a maximum cooling effect due to throttling then the initial point should be at the top point; that means the maximum point lie on the inversion curve.

For example, at this enthalpy, if we start at this point and throttle up to this point, we get a cooling of this much. This much temperature drop. But if our point is at the inversion point then if we have to throttle up to this point then we get the maximum cooling. To have the maximum cooling, we have this initial state point at the point of del T divided by del p at constant h_0; that means at the inversion curve.

Now, the question is that is it so, if the initial point for example, here some initial point I consider at this enthalpy line is in the heating region, there will be no cooling? That we cannot tell. That is because it depends upon the extent up to which we can throttle; that means, if we throttle up to a pressure of this point up to this pressure that means we arrive at this point. So, there is a heating.

If we throttle up to this pressure, I draw a horizontal line. There will be neither cooling nor heating same temperature. But if we throttle up to this point, so from this pressure to this pressure that means we go along this part and this come here. So this temperature is lower than this temperature.

If the initial point is on the negative slope part in the heating region part of the curve, we cannot tell conclusively that there will be no cooling. Usually there is no cooling. That depends upon the level of throttling.

If we throttle to a very low pressure so that this point can come up to this part of this curve in such a way that there is a drop in temperature. That is also possible. But usually it is not so. Usually this much throttle is not done. If the throttling is done up to some pressure, that means, if we draw a horizontal line, so this is the pressure. If this is the starting point below which if we throttle then only we will get the cooling.

If we throttle up to this pressure or to a pressure higher than this pressure then we will never get cooling. But if the initial point lies in the positive slope part of the curve, we will always get cooling effect. The cooling effect is maximum if the initial point is on the inversion curve.

[Conversation between Student and Professor – Not audible ((17:29 min))]

Heating and cooling. Another interesting thing is that if this point is known as T_{max}, this point is known as maximum inversion temperature.

Similarly, where it cuts is known as minimum inversion. Now, from the type of the curves above the maximum inversion temperature, the curve is having only negative slope. So, there is no way cooling is possible. Similarly, below the maximum inversion temperature. Also, if the initial state always corresponds to such a temperature which is more than the maximum inversion temperature, the point has to be in either of these curves anywhere here. So, we can never have a throttling effect; that means, if the initial point is somewhere here, throttling will not be done; that means cooling cannot be made with throttling.

These points will be always on the negative slope of the curve and there is no positive slope part of this curve. So, this is another interesting point of this curve. Let me discuss, what is the mathematical expression for this del T divided by del p at constant h.

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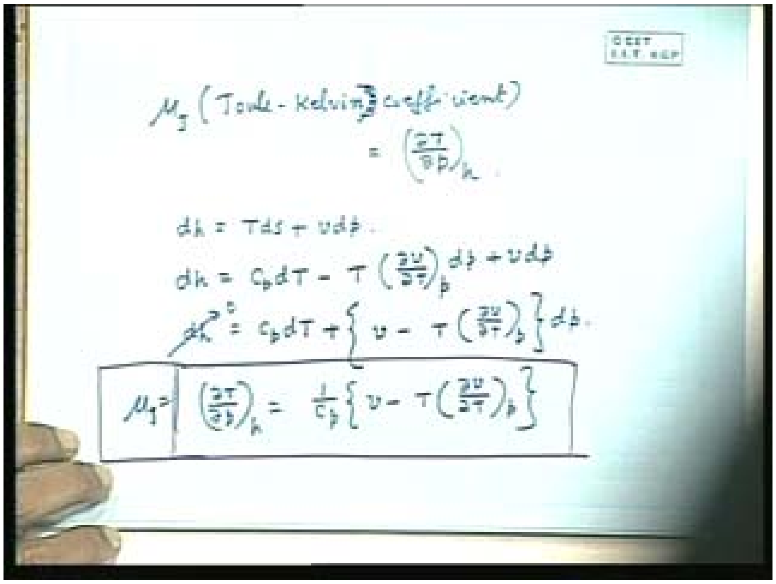

μ_J (Joule-Kelvin coefficient)

$$= \left(\frac{\partial T}{\partial p}\right)_h$$

$$dh = Tds + vdp$$

$$dh = c_p dT - T\left(\frac{\partial v}{\partial T}\right)_p dp + vdp$$

$$\cancel{dh}^{0} = c_p dT + \left\{v - T\left(\frac{\partial v}{\partial T}\right)_p\right\} dp$$

$$\boxed{\mu_J = \left(\frac{\partial T}{\partial p}\right)_h = \frac{1}{c_p}\left\{v - T\left(\frac{\partial v}{\partial T}\right)_p\right\}}$$

Now, this del T divided del p at constant h, the slope of the isenthalpic curve is known as Joule Thomson coefficient or Joule-Kelvin, Thomson and Kelvin are the same man. Joule-Kelvin coefficient mu J is given by del T divided by del p at constant h. This is known as Joule-Kelvin. So, this is zero on the inversion point.

So, I want to have an expression of this Joule-Kelvin coefficient in terms of other property how is it done? We write the equation per unit mass basis, dh is T ds plus v dp. This equation is the basic property relation.

If any problem you ask me. Is there any problem? Is there any question?

Now, if we recollect the first T ds equation and second T ds equation which expresses T ds in terms of dp and dT. What is this expression? c_p per unit mass basis dT. If we see your earlier class notes minus this is T into del v divided by del T, v specific volume at constant p dp plus v dp.

I can write this as c_p into dT plus v minus T del v divided by del T at p into dp that is dh, this expression. Now at constant h, dh is zero. From this equation, we get del T divided by del p. Therefore, at constant h is 1 by c_p into v minus T into del v divided by del T at constant p. Therefore, this is one of the very useful expression; that means, this is mu J del T divided by del p; that means, del T divided by del p is mu$_J$. I should write mu$_J$ is equal del T divided by del p at constant h. Therefore, this is a very useful expression for the Joule-Kelvin coefficient.

Clear?

[Conversation between Student and Professor – Not audible ((21:42 min))]

Any question? Please ask me.

Mu$_J$ is del T divided by del p at constant h. One very important application comes out. If we consider a system which obeys the ideal gas equation that means for ideal gas, let us see what happens for ideal gas? What is the value of Joule-Kelvin coefficient for an ideal gas? 0.

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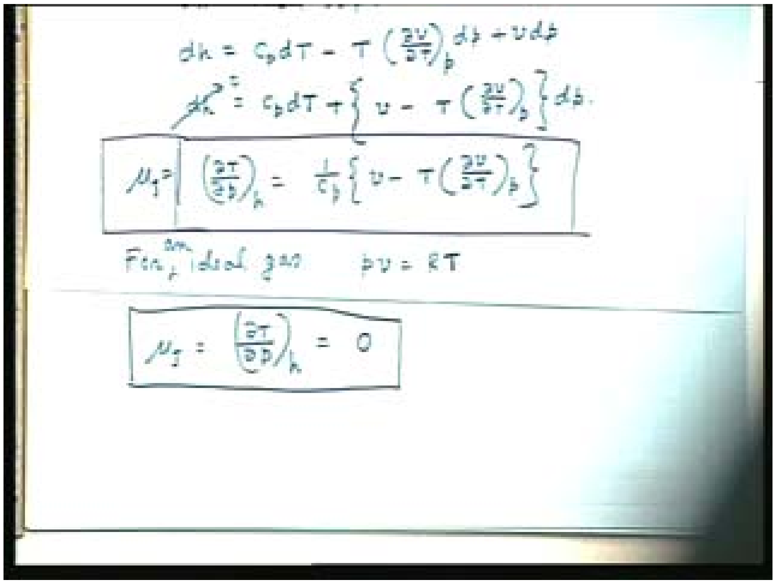

$$dh = c_p dT - T\left(\frac{\partial v}{\partial T}\right)_p dp + v\,dp$$

$$\cancel{dh} = c_p dT + \left\{v - T\left(\frac{\partial v}{\partial T}\right)_p\right\} dp.$$

$$\boxed{\mu_J = \left(\frac{\partial T}{\partial p}\right)_h = \frac{1}{c_p}\left\{v - T\left(\frac{\partial v}{\partial T}\right)_p\right\}}$$

For an ideal gas $pv = RT$

$$\boxed{\mu_J = \left(\frac{\partial T}{\partial p}\right)_h = 0}$$

[Conversation between Student and Professor – Not audible ((22:08 min))]

How do we get it? For an ideal gas the equation of state is pv is equal to RT, v is the specific volume. R is the characteristic gas constant. Therefore, if we equate this quantity v minus T into del v divided by del T at constant p, this will become 0.

So, for an ideal gas, therefore mu$_J$ is equal del T divided by del p at constant h is equal to 0 which means that at constant enthalpy, there is no change in the temperature with pressure . That means if enthalpy remains constant, temperature remains constant. That is one of the corollaries of the ideal gas laws which will be again told afterwards that enthalpy is a function of temperature.

When the enthalpy remains same as the function of temperature only that means when enthalpy remains same, temperature also remains same; that means, isenthalpic process is equals to isothermal process. The change in temperature with pressure is 0 if the enthalpy remains the same. We cannot change the temperature by throttling, if the enthalpy remains constant. Throttling means the constant enthalpy process.

Therefore, for an ideal gas mu$_J$ is zero. Therefore, if a gas is perfectly ideal which is a hypothesis, then the gas can never be cooled by making a Joule-Kelvin expansion or Joule Thompson expansion.

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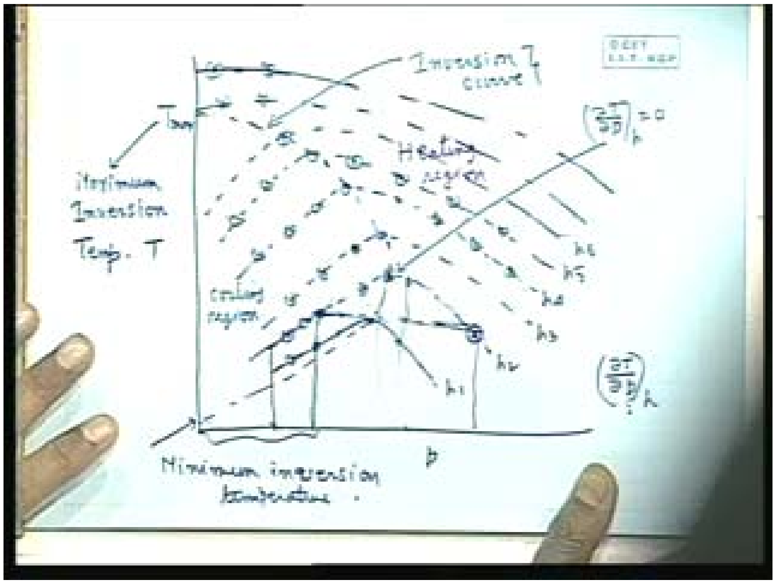

After this, I again comeback, that a gas can be cooled. Now, Joule-Kelvin expansion is one of the methods by which a gas is cooled. So, if we look into this curve, if a gas, because the non-idealities of a gas; that means, no gas is an ideal gas is a clue to its cooling. Because when the gas is non-ideal, then only Joule Thomson effects will have a cooling effect, because del T divided by del p at constant h is not 0.

But in the ideal gas, hypothesis is equal to zero. Therefore, all gases are non-ideal. So, there is a value del T divided by del p at constant h is non-zero. So, cooling can be made, but now we have to be particular to which region of the curve the initial state one should be there, so that we get a cooling effect. So, that will be decided by this curve that the initial state point should be on the left of this inversion point, inversion curve; that means, this is the inversion point where the slope is zero.

So, the left side of the inversion point that means the initial state should lie on the positive slope part of the isenthalpic curve. Again, one has to be very careful whether the initial temperature is below the maximum inversion temperature or not. If it not so, then we can never get it cooled by Joule Thompson expansion.

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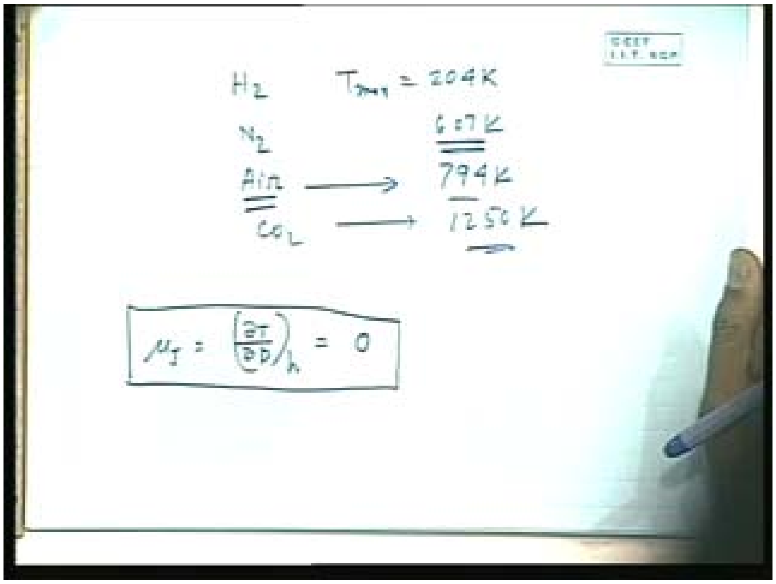

H_2 $T_{max} = 204 K$

N_2 $\underline{\underline{607 K}}$

$\underline{\underline{Air}} \longrightarrow 794 K$

$CO_2 \longrightarrow \overline{1250} K$

$$\boxed{\mu_J = \left(\frac{\partial T}{\partial p}\right)_h = 0}$$

The typical example is hydrogen whose maximum inversion temperature is 204 K. Usually the maximum inversion temperatures are very high for most of the gases. Therefore, we can choose the state, the corresponding pressure so that we can have a cooling effect but unfortunately hydrogen, the maximum inversion temperature is 204 K.

So, if we have a compressed hydrogen gas even at the ambient temperature of 273 K or even more. Then its temperature is more than the maximum inversion temperature; it can never be cooled. Therefore, always when hydrogen is cooled, by Joule Thompson's or Joule-Kelvin expansion, the basic requirement is a primary cooling by some other coolant not by expansion. To reduce this temperature from the existing temperature down to a temperature below to 204 K, this is the maximum inversion temperature. For nitrogen, the value for nitrogen 60, temperature is 607 K.

For air, as we know though air is not a single component system, but air behaves as a pure substance. Pure substance means, it is almost equivalent to a single component system which is homogeneous in its composition. So, that is why we consider air as a single component system. Pure substance, its behavior is almost like a substance. So, air is a pure substance and it has maximum inversion temperature. So, for air, nitrogen, there are other gas, carbon dioxide, I exactly cannot recall it is like 1250 K.

So, the maximum inversion temperature is pretty high. If we compress the gas at some high pressure, but its temperature is below that, then if we cool it, we can make a cooling effect.

What is done in practice? Compress the gas at some high pressure then the gas will be compressed and because of its increasing pressure, the temperature will increase.

Now, if we cool the gas by a coolant at constant pressure, keeping the pressure same; that means, the gas temperature comes down to the initial value; for example, the ambient temperature. Then if we throttle the gas that means expand, the gas reduces its pressure from higher one to a lower one. We get a cooling effect that means the temperature goes below that of the ambient. But unfortunately, with hydrogen we cannot do it even if we compress it. We have to cool down to a temperature below 204K so that the cooling will be effective. That means we will have to precool it in such a way that below the ambient temperature it should come.

Otherwise hydrogen gas cannot be cooled by Joule-Kelvin or Joule Thompson expansion until and unless it is precooled to a degree, where its temperature comes below the inversion temperature. This is very important practical information. This is all about Joule-Kelvin or Joule Thompson expansion.

So, we learn that in a throttling process, pressure is reduced definitely because of the friction, but temperature may or may not reduce. It may increase or it may reduce. The physical concept is there that there are two countering effects; one is that because of the friction, pressure is being reduced. That means a part of the pressure energy is converted to intermolecular energy whose effect is to increase the temperature of the fluid, as we are rotating a paddle wheel or impeller in a fluid.

For example, in a liquid its temperature will increase, but at the same time, because of the expansion the reduction in pressure, there will be a reduction in temperature depending upon its equation of state. These two countering effects will decide whether the temperature will increase or decrease. That depends upon the inversion point of a particular system. So, this is all about the Joule-Kelvin effect. Now, I will start a new chapter, properties of pure substances.

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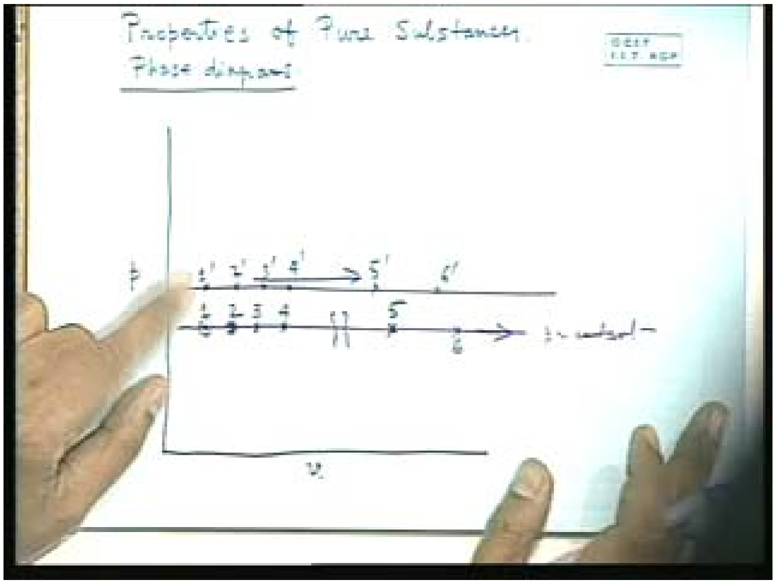

Properties of Pure Substances.

Phase diagrams

Properties of pure substances and we first do the phase diagram which is very important. What is a pure substance? Pure substance is a substance that it is a single component substance, but it is not always true that single component substance is a pure substance. Very first line is a single component substance. But what is that? Always a single component substance is a pure substance.

Pure substance is a substance which is homogeneous in its chemical composition throughout its mass. For example, air is a pure substance because air's composition is homogeneous throughout a mass. We can represent any mass or we can describe a system by any representative mass which has the same composition of its constituents. Then also, it is a pure substance.

Now let us consider a pure substance first; the properties of pure substance. We will cover the ideal gas. Mixture of ideal gases all are pure substance afterwards. But before that, we deal with the phase diagram of a pure substance.

Let us consider a pure component first. Pure component, single component and how to draw the phase diagram. There are three neutral phases of a substance; solid, liquid and gases. As we go on heating from the solid state, it first comes to a saturated state. With increase in temperature, it absorbs sensible heat. These are the common information at basic primary school level I am recapitulating it

It gains heat and it increases the temperature which is the representation of the molecular kinetic energy. So, molecular disorder increases; along with that entropy increases, as we know heating process entropy increases. It comes to a stage depending upon the pressure. That stage is represented by the temperature, when it melts and changes its phase from solid to liquid at the constant temperature. If the pressure is maintained constant, temperature will also be maintained constant. Until and unless the entire solid melts to liquid, the temperature remains constant, but it takes heat. That heat is known as latent heat.

Again, a sensible heating is there, where the liquid phase is heated. It absorbs the heat and then its temperature increases. That means the molecular kinetic energy increases. Again, it comes to a point when the liquid is converted into vapor. That point is represented by a temperature corresponding to a pressure. These are known as saturation states. Then they absorb the latent heat required for converting the entire amount of liquid to the vapor. Then again if it absorbs heat, it goes on increasing its temperature. As we go on heating it, the temperature will go on increasing which increases the intermolecular energy or the kinetic energy of the molecules.

When it reaches the gaseous state, if we go on increasing supplying heat, temperature will go on increasing. So, there will be no other change or phase in its neutral position until and unless the gases are ionized and goes to the plasma state which is beyond the scope of this course. Therefore, there are three states: solid, liquid and gases. How do we represent the thermodynamic properties of a pure component when they undergo such phase changes? Now, let us see that. Let us first consider a pv diagram.

All know one thing, I tell you here as a teacher you do not need to draw the entire diagram by doing. So I am telling, you lose some interest in studying these things and you following the lecture. At the same time this is my suggestion to other teachers also and to me also. A teacher should not do all the diagrams so meticulously without speaking much or telling, describing much in drawing the phase diagram all these things. I have come with some prepared diagram so that I lose the explanation part of it.

Why I am telling you this is because all these diagrams are available in all standard textbooks, you can consult there. But try to understand the thing here. So if we observe all taking this phase diagram drawing, how to do it? How a teacher draws that thing?

Then your concentration will be mainly in drawing the diagram. Not in understanding the thing because, these are the very simple diagrams and very popular diagram which are available in books.

Let us consider this plane; specific volume and pressure and consider a certain mass of gas which we heat at a constant pressure. So, let us consider a constant pressure line. Let us denote the constant pressure line by this. Let us consider even this pressure is one atmospheric pressure. It may be one atmospheric pressure, p is equal to constant. pv plane is a line horizontal parallel to v axis.

Now, we start at a solid state one. If we give heat then its specific volume will increase. Obviously, when it gets heated its temperature is increased. So, it goes to a state two so long.

Now, when we go to a state two, state two is a state where the solid starts melting. Then while melting again, its specific volume increases except water. It is an exception. So, specific volume will increase and go to three. So, three is a state point where the solid is being melted into liquid.

Now, if we still go on giving heat, liquid will go to another point four, where the specific volume will increase because of the increase in temperature. Then four is a point where the liquid starts vaporizing, boiling to the vapor phase taking heat at constant temperature.

This is not being manifested in pv diagram, but the specific volume increases. Abruptly, there is a cut when it comes to a vapor. Why there is such a gap? Because we know the specific volume of a vapor is much higher corresponding to the specific volume of the water.

Therefore, this is the heating process. Then we go on increasing the temperature; go on more heat, increasing the temperature supplying more heat. It will go to 0.6; then onwards go to the superheated vapor region. So, now if these experiments are carried out to designate or to find out these state points, to mark these state points at different pressure, we can do it at another pressure.

So, I want to find out this one dash, two dash corresponding points, three dash, four dash five dash and they may be different. So, I can generate the same points on different constant pressure lines. and if we do so, what I will get is see here.

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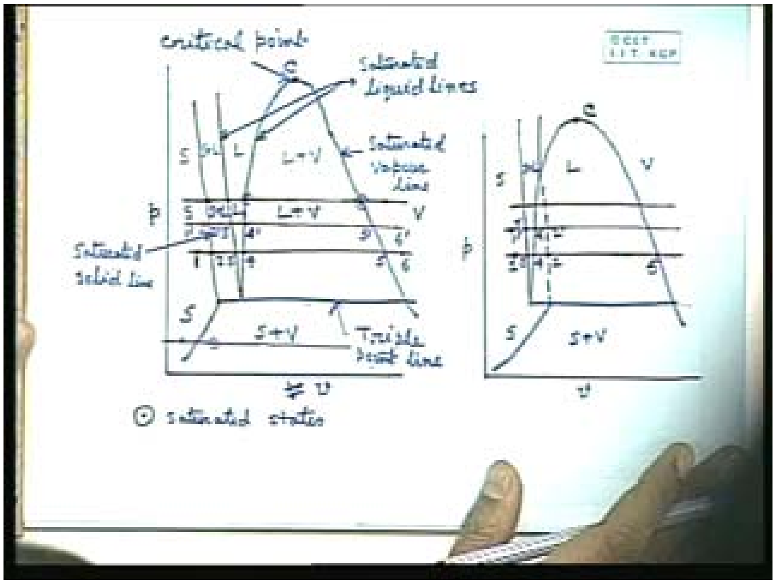

One, two, three, four, here is this solid state. Now, two is a point where solid starts melting and three is a point when entire solid has been melted. Therefore, this is the region which is the mixture of solid plus liquid. I have not written that solid. So this is solid plus liquid this is liquid plus vapor. oh! It is written solid so solid plus liquid.

Then from three to four is the sensible heating of the liquid. From four to five is the vaporization. There is an enormous change in the specific volume. Then six is gas. So, if we consider this in case of water, it is a special case. Then one to two, then two to three; there is a reduction in the volume. So, the three points come here then again three to four and four to five. Therefore, this line shifts here. So, this is for the water .Now if we do so

[Conversation between Student and Professor – Not audible ((36:35 min))]

please,

[Conversation between Student and Professor – Not audible ((36:37 min))]

Last part from water but that is one to two. That means, it gains the specific volume then specific volume is reduced to two to three. So, it is not drawn in scale that means there is a reduction in specific volume. Again, there is an increase in specific volume because of the heating then again from four to five.

Only thing is that we will have to consider that from two to three, there is an increase in specific volume. But for water, it is a decrease. Now, if we draw these diagrams at different pressures, we will be getting the curves like this. We are not much more interested at the present moment with the solid liquid line rather than liquid vapor.

We will see if we join all these points. Now, before that, these points for example, in a particular pressure, constant pressure, what are these points two, three, four, and five? Let us discuss. Two is a point where solid is ready for melting. For example, ice. If I state either simple example I am giving. At one atmospheric pressure I am heating an ice. So, at minus 10 degree Celsius, here temperature is not coming, I go on heating its specific volume increases and its temperature also increases.

When the specific volume attains a value, where the temperature is 0 degree Celsius then solid is ready for transforming into water, with addition of heat and the change in the specific volume which is a reduction in this case. But the temperature will remain constant that is the melting will start. This point is known as saturation state; this state two, saturation state with respect to melting. Similarly, when the entire melting will be finished at three that means all the ice is now melted at 0 degree Celsius water; then this state is also saturation state. 0 degree Celsius water at 0 degree Celsius ice at one atmospheric pressure, both are saturation state. One is saturation state with respect to melting. Another is saturation state with respect to Solidification.

[Conversation between Student and Professor – Not audible ((38:33 min))]

These are the state where this is unstable state; that means, the little perturbation of heat flux will change its phase. These are known as saturation states. Similarly, here in this figure, four is a saturated liquid state for vaporization. Similarly, five is a saturated vapor state for liquefaction or condensation. Better we tell condensation, it is a condensation, liquefaction is alright, but condensation is more popular term.

So, one, two, three, four, five are the saturated states. not sorry I am sorry two, three, four, five not one, not six, or not any point within the two, three or beyond the point five. That means only two, three, four, five are the saturation states. So, if we draw this saturation states at different pressure lines, we will see that this locus of the saturation states look like this; that means if we are much more interested on the liquid vapor region, the locus of all these four states in pv diagram is very steep. But hilling little towards right increasing specific value, whereas this locus of these five points that means saturated vapor points are very curvy. That means these are not very steep, much less steep, but these hills in this direction, if we go up, there is a decrease in the specific volume. I am explaining this thing physically.

These lines are therefore known as saturated solid lines which are the locus of all saturated solid points. Similarly, the locus of all saturated liquid points is known as saturated liquid line. So, this line is the saturated liquid line with respect to solidification and this line is the saturated liquid line with respect to vaporization. Similarly, this line is the saturated vapor line and this dome is known as vapor dome. The beauty is that from the nature's experiment that from the nature which we get from experiment that this dome merges; that means this creates the dome. The saturated liquid line and saturated vapor line merge together and meet at a point C which is known as the critical point. First of all this is the observation.

Immediately do not ask much question. This will take two complete classes. To explain all those things. I will do, I will see that whether it can be completed this class or not. So that this is known as critical point and if we see here, we will see, this joins here, there is a straight line which is known as triple point line.

Point is a state. Normally, that one we are writing point lying together. How they can be, point cannot be a line, but in science, this physical science or thermodynamics, point means a state. That means a triple point state line is used as a state. There is a particular state, critical state; similarly, triple state critical point means that is not the geometrical point. It is a critical state line. This is the line. Now here this is the solid, this is the solid vapor line that means if we construct a constant pressure line in this zone, solid will directly be converted into vapor, without going to liquid phase. That is known as sublimation.

First of all, we are not much interested with the solid-liquid line. We are rather interested mostly in the liquid and vapor line. So that for an explanation, I think it will be better if we concentrate only on the okay that diagram is not there. We disregard liquid and vapor zone.

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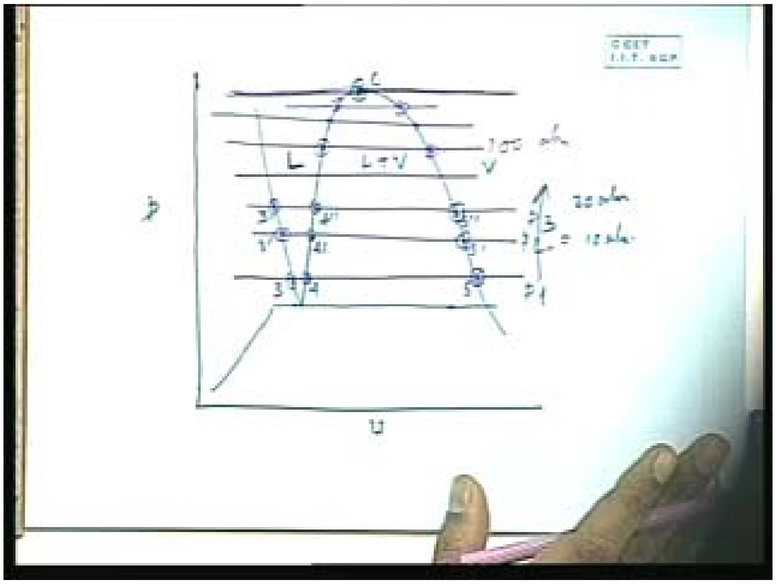

Now, if we do that only this liquid and this thing. Let us consider this as if this is the dome. Let us draw this line, the liquid line that means this is c, this is p, this is v.

We are now interested only in the liquid vapor, liquid plus vapor and liquid. I am not disregarding the solid part, this is vapor. Now this is the point, saturated liquid for melting. So, this is the liquid line. So, this is the point; that means, in our earlier notation, these points are the three points; three double dash, three dash, different three. So, this point is our four, four dash, four double dash, this point is our five, five dash, five double dash. Now, this line is very steep.

Yes, any question?

This is the liquid. I am discarding the solid part. Why this line is very steep little hilling towards this? Can anybody guess? Okay! I will explain. What are the differences between these different points? These are the saturated states at higher pressure. This is the increasing pressure. This is p_1, this is p_2, and this is p_3. Let us consider a very complete example. This is one atmospheric pressure. What is this temperature at the point four, if p_1 is one atmospheric pressure for water?

[Conversation between Student and Professor – Not audible ((43:45 min))]

What is that?

[Conversation between Student and Professor – Not audible ((43:46 min))]

Please

100 degree Celsius, 373 K. Now, if this pressure p_2 is 10 atmospheric pressure, what will be this temperature? It will be roughly, we do not know the temperature. It will be more than the 100 degree Celsius. Let us consider the temperature is 150 degree Celsius. That means all these points correspond to a higher temperature point. Because these saturation states at higher pressure, where the liquid will convert itself from liquid state to gaseous state will occur at a higher temperature. So, with the increase in temperature, there is an increase in the specific volume of the liquid.

At the same time, we argue that this state point is at a higher pressure. Therefore, the four dash, four double dash. So in this direction, the state points are at higher temperature and higher pressure since liquid is incompressible. So, the influence of pressure on the volume is not being dominated, whereas the influence of temperature on the volume is being dominated which makes a slight hill there.

There is a countering effect. Because of higher pressure, volume should be reduced; because of higher temperature, volume should be more. These two countering effects make this thing very steep, but little inclined in the right direction; just the reverse. Here five, the saturated vapor that means it is steamed at 100 degree Celsius. It is steam at 10 atmospheric pressure but at 150 degree Celsius.

Here, steam maybe at 20 atmospheric pressure, but the corresponding temperature at which it should condensed to liquid maybe 200 degree Celsius, but the influence of pressure on steam being much compressible. So, this shows a reduction in the volume because of higher pressure so that the locus saturated vapor state point hills much towards to the left on this v axis.

While this hills little towards the right because of which there is an opportunity that this meets at this point c. So, if I draw a curve like that, one thing I can see that I go on drawing the curve. Now, when we change the state from liquid to vapor, if we go on increasing the pressure, what is happening? This temperature is increased. This is not being manifested here. This will be manifested in some other pT diagram, Ts diagram.

But one thing is that, the changes in the specific volume due to change in phase is getting reduced. That means difference between the specific volume of vapor and that of the water is getting reduced slowly. If we try to boil water at a very high pressure, for example, 100 atmospheric pressure. The specific volume of the saturated water and the specific volume of the saturated vapor are very close to each other. In 150 degrees, they are very close to each other. So, specific volume changes are becoming lesser and lesser.

If consider an isobar through the critical point, we see there is virtually no change in the specific volume. That means saturated liquid, saturated vapor almost have the same specific volume. It is very difficult to distinguish liquid from the vapor.

How do you distinguish a liquid from the vapor because of the assembling of the molecules? So, liquids have a much lower specific volume than of the gases. Its density is higher than the gases so that visually, this is a liquid and this is a gas.

A much verified liquid, where the densities are very low, the specific volume is very high. Then it seems to be the vapor itself. There is no distinguishing between liquid and vapor. Therefore, we see that there is no change in the specific volume. Virtually the change in the specific volume will be between the saturated liquid and vapor phase is going to be diminished. This is the change in the specific volume due to vaporization. This is going to be reduced. So, up to this let us consider the pv diagram finished. I will comeback it to this again. Before that let me consider a diagram in Ts plane. Now, let us see that, how can I generate a diagram in Ts plane? Then I will go to pT, one by one.

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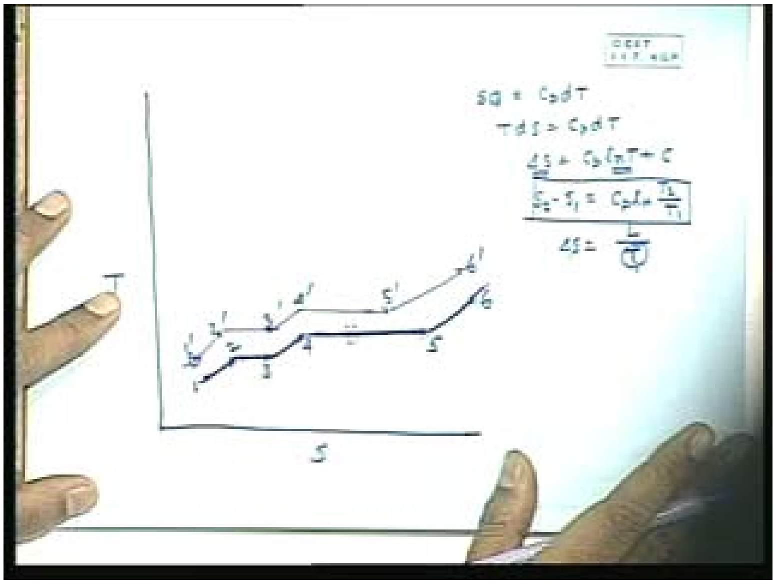

Let us now think that we want to draw the Ts plane, the same diagram which we did and we do the experiments at a constant pressure. One thing was simple that in pv diagram constant pressure. Immediately we drew a line which is parallel to this abscissa, because ordinate was p. But here Ts diagram, constant pressure; that means, if we consider the solid substance of a given mass and we go on heating the way we consider, there we observed how the specific volume changes at constant pressure.

But here we have to observe, how the temperature and entropy changes at constant pressure so that we can draw the locus of the constant pressure line and mark the saturation states.

Now at constant pressure, if we add heat reversible, without any work transfer, we can write first del Q is c_p dT, and at constant, at reversible heat addition T ds is c_p dT. That means we write delta s is c_p ln T plus some constant.

That means change in entropy is a logarithmic function. One can write this way; the final minus initial is $c_p$ln into T_2 by $T_{1;}$ that means, as we supply heat, the entropy will change, but in a logarithmic manner.

Now, when it comes to the saturation states, what happens? There also at constant pressure, if we give heat, its temperature remains same but entropy increases. Because it gets the heat that means, there the increase in entropy will be equal to the latent heat by constant temperature at which the phase change is taking place.

So, there will be always a change in entropy but temperature remains constant. Therefore, if we now draw this, we will see that state one. This will be a little difficult. So, we get a point like this two, while this is the solid heating, then heating of the solid from a state one to the saturated state two, where both temperature and entropy increases according to this relationship. I am showing some qualitative trend.

So, when it reaches the state two, then all the states are corresponding to the earlier one as I defined. The nomenclature remaining same that means state two will be saturated state of the state. Then it melts. Then the entropy changes, but at a constant temperature; that means this will follow like this, until and unless the state three.

Again, three to four is the sensible heating. Both the entropy and temperature change by this equation. But from four to five, again, there is a large change. Because the entropy takes huge heat as the latent heat of vaporization. So, there is a huge change in entropy whose value is also equal to the latent heat divided by the temperature, latent heat of vaporization divided by the temperature so that again this goes like this.

Therefore this is the isotherm. So therefore by red this is the sorry isobar I am sorry isotherm isobar. But in this region, the isobar and isotherm coincides; constant pressure and constant temperature curves remain same. Here, we distinctly see that this becomes horizontal line.

So, one, two, three, four, five, six; this curve shows a typical isobar in Ts plane. The part of the isobar two, three and four, five shows a constant temperature. This temperature and this temperature are different.

For example, water this temperature is 0 degree Celsius and this temperature four, five is 100 degree Celsius.

In this way, we do the experiments sorry. That means if I draw this two, then this is three, then this is four dash. Similar way, I did five dash, six dash at different pressure, we arrive at this diagram.

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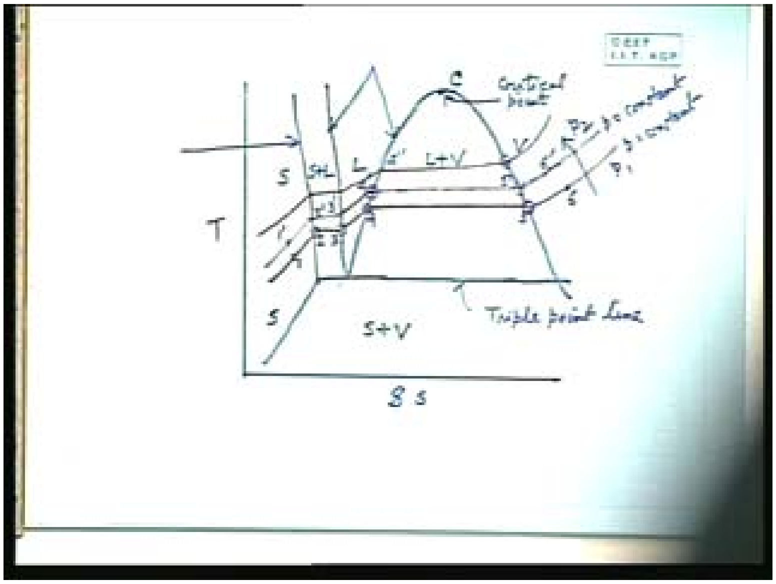

This diagram shows that these are the constant pressure lines. These are the state points. These are the saturated solid, saturated liquid with respect to solidification, saturated liquid with respect to vaporization, saturated vapor with respect to condensation. So, these red lines are the constant pressure line. This way the constant pressure lines are increasing.

Now here, we see just if we discard the solid-liquid part, this is the saturated four dash, four double dash, saturated liquid straight points, the locus; they are hilling much towards right this is not much steep. As we obtained in pv diagram. So this way, if one draws the pv and Ts diagram from its drawing qualitative, one can understand whether this concept is clear or not. This is hilling much.

This is because this point and this point are having a higher temperature and entropy, for example, in water this point is at 100 degree Celsius, if this pressure is the 1 atmospheric pressure if this pressure is 1.5 atmospheric pressure, then this temperature will be a little higher. This temperature will be, for example, 150 degree Celsius.

So, this temperature is higher and at the same time, this absorbs more heat. So, the entropy will be more so that this hills towards right. This saturated vapor point locus hills towards left as usual, because these are at higher pressures. The specific volume of the steam which is a vapor is reduced .So, that also creates a vapor dome meeting at a point c. This is the critical point.

Now this is all for today, because time is not there this is almost Ts plane. So next class, I will again continue all the diagrams and their comparisons. But one thing at the last time probably I do not know whether by mistake told 150 atmosphere or something like that. It is 1.5 atmospheres.

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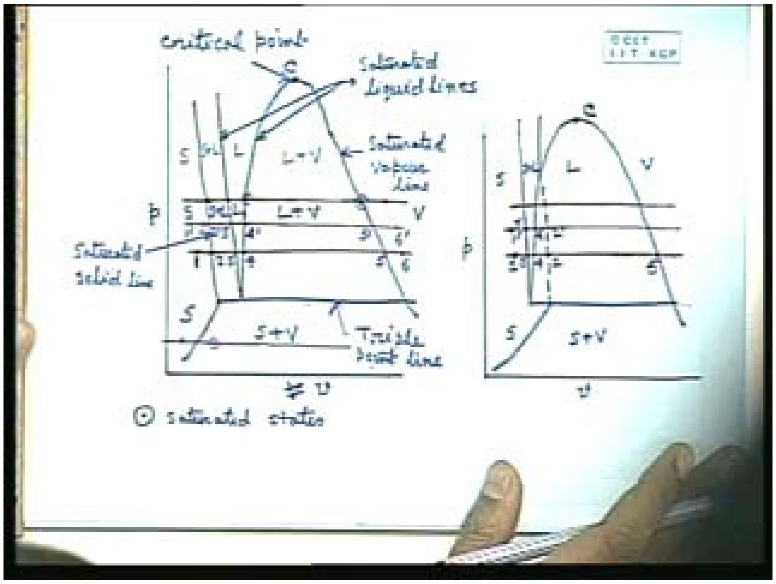

When we discuss this figure, let us consider this is at 1 atmospheric pressure, this is 1.5 atmospheric pressure.

Like that okay!

Thank you.

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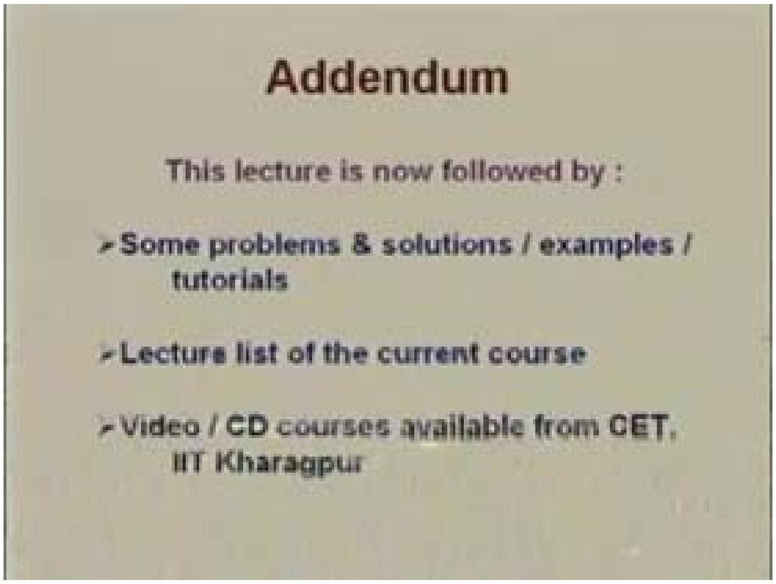

Addendum

This lecture is now followed by :

- Some problems & solutions / examples / tutorials
- Lecture list of the current course
- Video / CD courses available from CET, IIT Kharagpur

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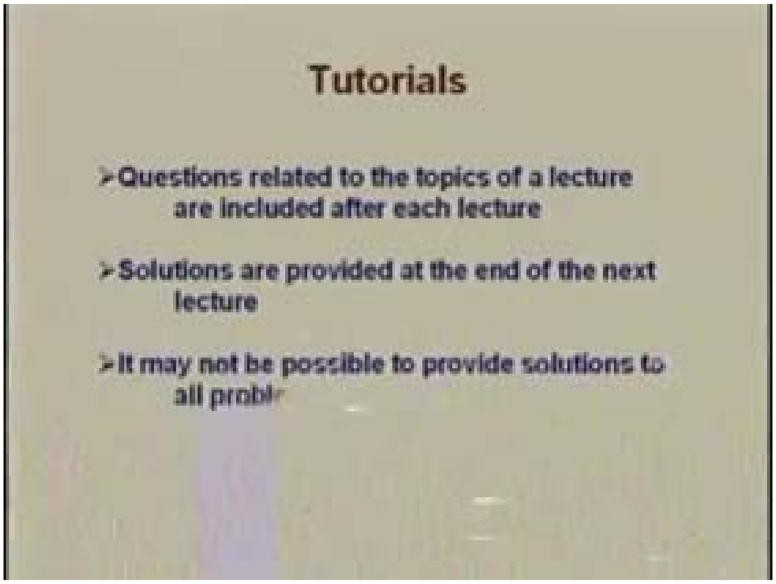

Tutorials

- Questions related to the topics of a lecture are included after each lecture
- Solutions are provided at the end of the next lecture
- It may not be possible to provide solutions to all probl

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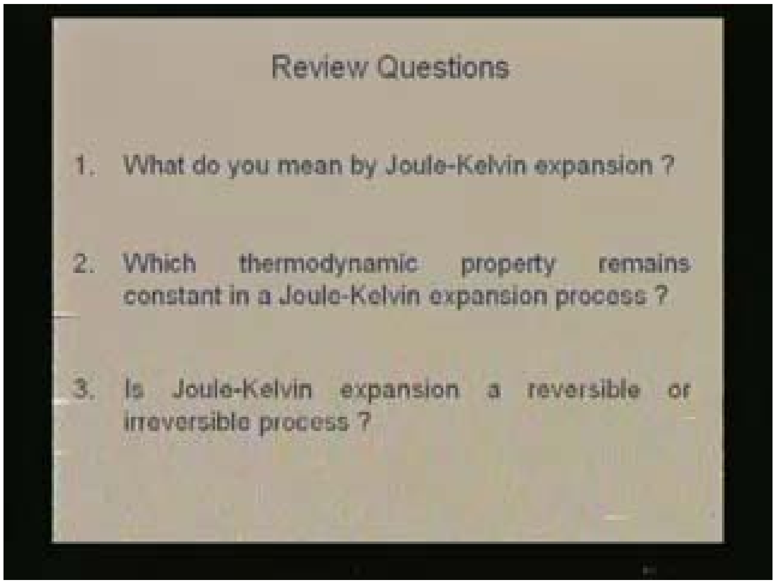

Review Questions

1. What do you mean by Joule-Kelvin expansion ?
2. Which thermodynamic property remains constant in a Joule-Kelvin expansion process ?
3. Is Joule-Kelvin expansion a reversible or irreversible process ?

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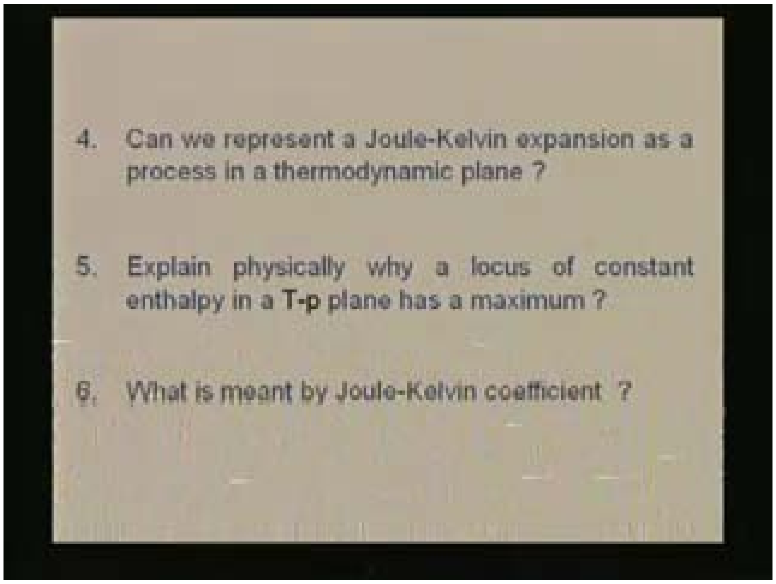

4. Can we represent a Joule-Kelvin expansion as a process in a thermodynamic plane ?
5. Explain physically why a locus of constant enthalpy in a **T-p** plane has a maximum ?
6. What is meant by Joule-Kelvin coefficient ?

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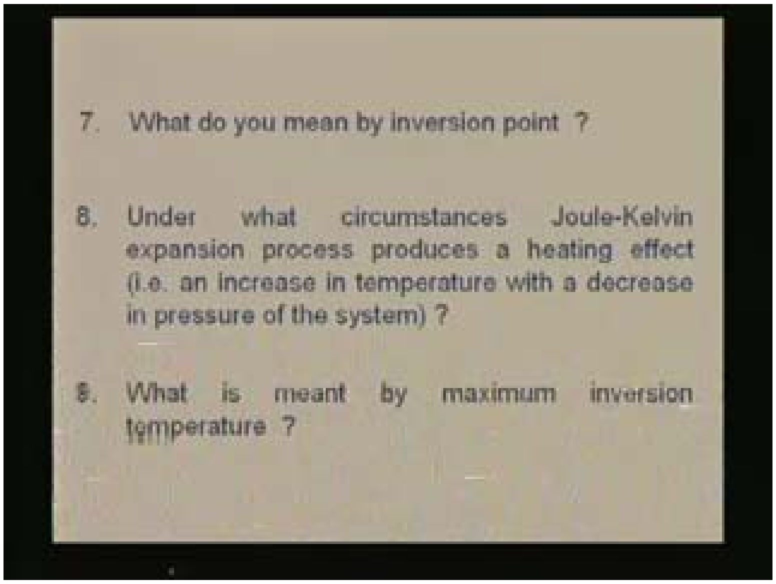

7. What do you mean by inversion point ?

8. Under what circumstances Joule-Kelvin expansion process produces a heating effect (i.e. an increase in temperature with a decrease in pressure of the system) ?

9. What is meant by maximum inversion temperature ?

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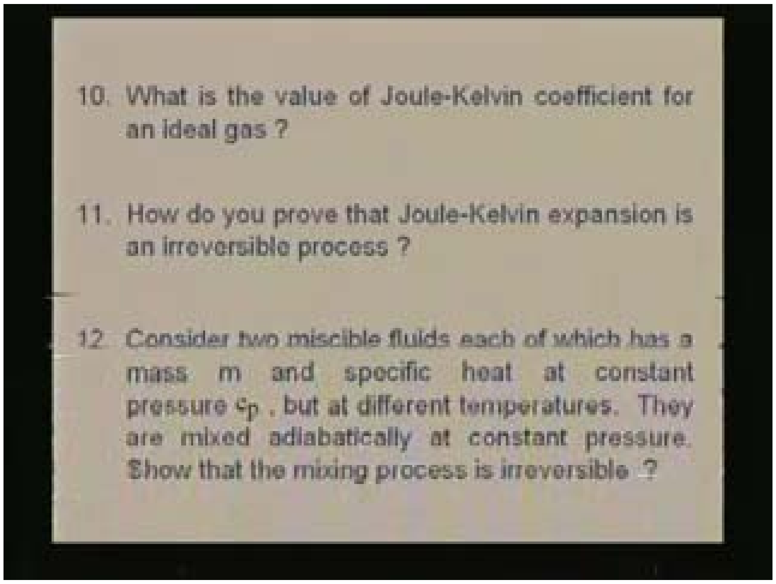

10. What is the value of Joule-Kelvin coefficient for an ideal gas ?

11. How do you prove that Joule-Kelvin expansion is an irreversible process ?

12. Consider two miscible fluids each of which has a mass m and specific heat at constant pressure c_p , but at different temperatures. They are mixed adiabatically at constant pressure. Show that the mixing process is irreversible ?

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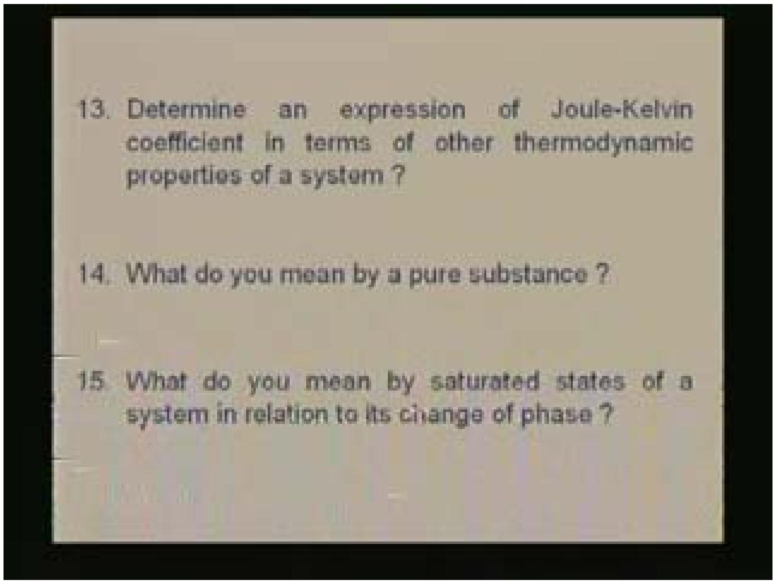

13. Determine an expression of Joule-Kelvin coefficient in terms of other thermodynamic properties of a system ?

14. What do you mean by a pure substance ?

15. What do you mean by saturated states of a system in relation to its change of phase ?

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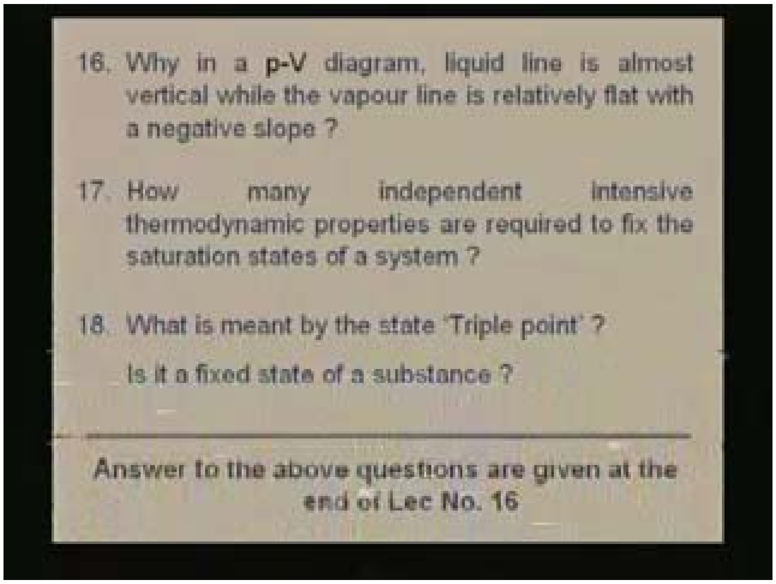

16. Why in a **p-V** diagram, liquid line is almost vertical while the vapour line is relatively flat with a negative slope ?

17. How many independent intensive thermodynamic properties are required to fix the saturation states of a system ?

18. What is meant by the state 'Triple point' ?
    Is it a fixed state of a substance ?

Answer to the above questions are given at the end of Lec No. 16

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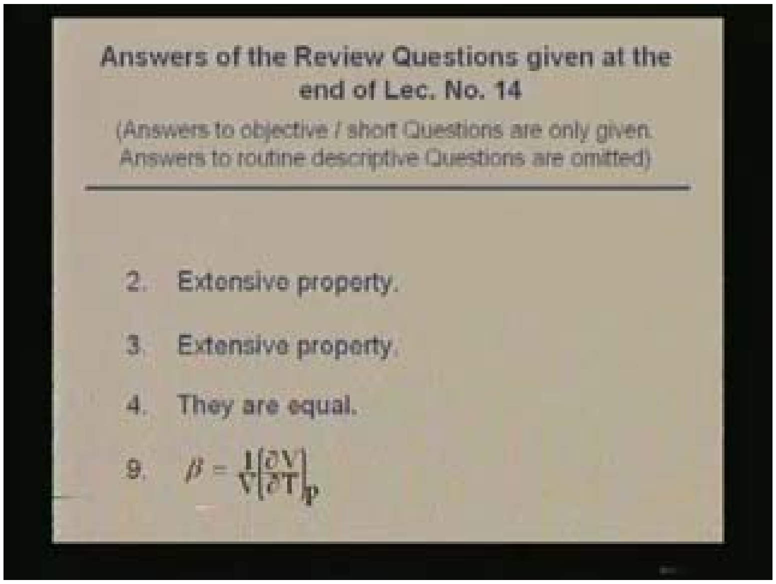

Answers of the Review Questions given at the end of Lec. No. 14

(Answers to objective / short Questions are only given. Answers to routine descriptive Questions are omitted)

2. Extensive property.
3. Extensive property.
4. They are equal.
9. $\beta = \frac{1}{V}\left[\frac{\partial V}{\partial T}\right]_P$