Advanced Thermodynamics and Combustion

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Module - 03
Thermodynamic Property Relations
Lecture - 14
Joule - Thomson Coefficient and Liquefaction of Gases

Dear learners, greetings from IIT Guwahati. I welcome you to this course Advanced Thermodynamics and Combustions. We are in module 3: Thermodynamic Property Relations.

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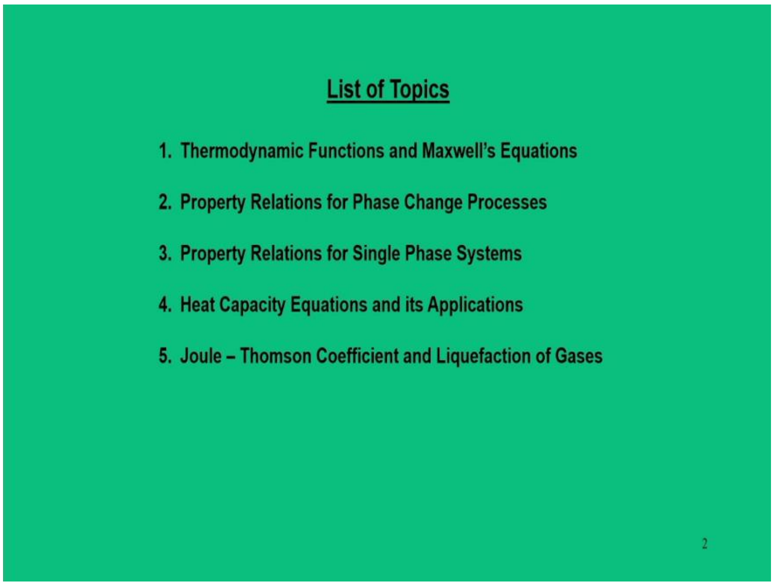

List of Topics

1. Thermodynamic Functions and Maxwell's Equations
2. Property Relations for Phase Change Processes
3. Property Relations for Single Phase Systems
4. Heat Capacity Equations and its Applications
5. Joule – Thomson Coefficient and Liquefaction of Gases

Till today we covered 4 lectures on this model and today we will cover the last lecture that is Joules Thomson coefficients and liquefaction of the gas. This is in fact, one of the practical applications for the thermodynamic functions and relations that we have learnt so far.

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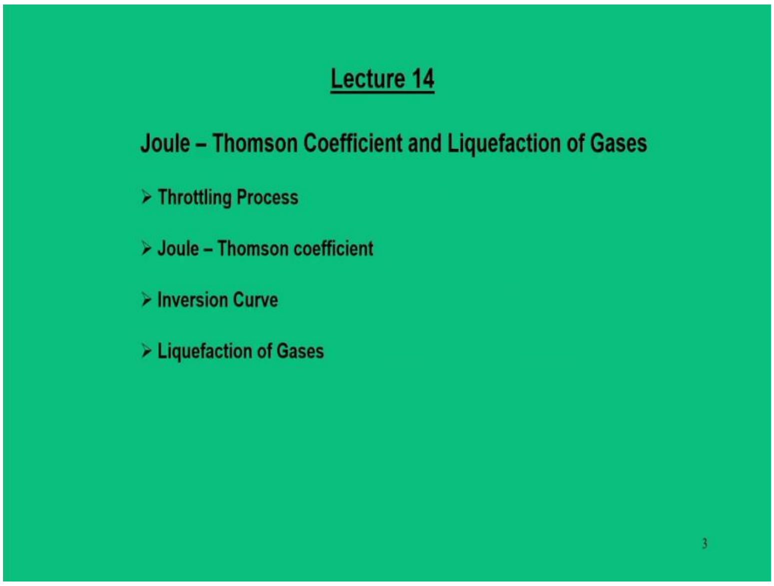

Lecture 14

Joule – Thomson Coefficient and Liquefaction of Gases

- Throttling Process
- Joule – Thomson coefficient
- Inversion Curve
- Liquefaction of Gases

In this lecture, we are going to learn the Joule Thomson coefficient that is one of the vital practical parameter which is used for liquefaction of gases. In fact, gases at certain pressure and temperatures, they are available in the form of gas. So, it is considered as one of the pure substance. But, if you want to liquefy then what concept we are going to use?

So, here the word Joule Thomson coefficient comes into picture and it is considered as the critical parameters. Now, where this parameter is useful? So, this parameter is useful in a thermodynamic process what we call as throttling. Now, under the roof of Joule Thomson coefficients, we will discuss about this graphical representations and what we call as inversion curve. Now, after learning all these things we will try to give the concepts of liquefaction for gases.

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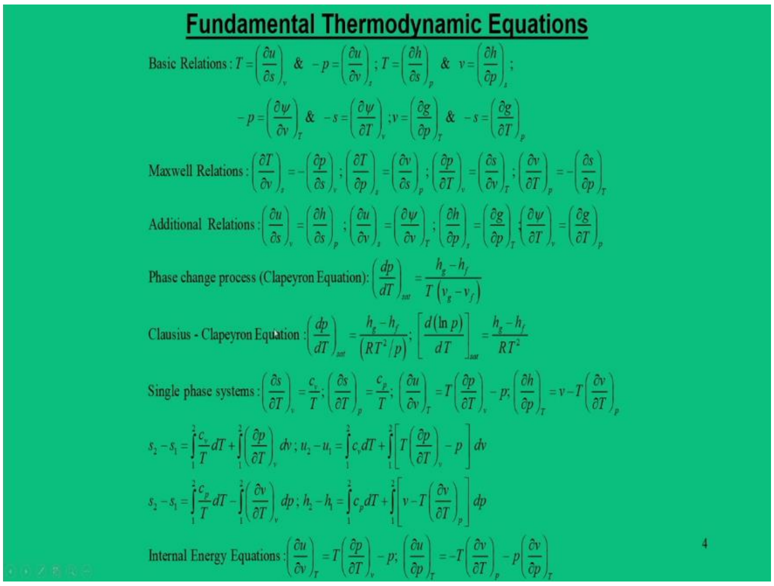

Fundamental Thermodynamic Equations

Basic Relations : $T = \left(\frac{\partial u}{\partial s}\right)_v$ & $-p = \left(\frac{\partial u}{\partial v}\right)_s$; $T = \left(\frac{\partial h}{\partial s}\right)_p$ & $v = \left(\frac{\partial h}{\partial p}\right)_s$;

$-p = \left(\frac{\partial \psi}{\partial v}\right)_T$ & $-s = \left(\frac{\partial \psi}{\partial T}\right)_v$; $v = \left(\frac{\partial g}{\partial p}\right)_T$ & $-s = \left(\frac{\partial g}{\partial T}\right)_p$

Maxwell Relations : $\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v; \left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p; \left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T; \left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T$

Additional Relations : $\left(\frac{\partial u}{\partial s}\right)_v = \left(\frac{\partial h}{\partial s}\right)_p; \left(\frac{\partial u}{\partial v}\right)_s = \left(\frac{\partial \psi}{\partial v}\right)_T; \left(\frac{\partial h}{\partial p}\right)_s = \left(\frac{\partial g}{\partial p}\right)_T; \left(\frac{\partial \psi}{\partial T}\right)_v = \left(\frac{\partial g}{\partial T}\right)_p$

Phase change process (Clapeyron Equation): $\left(\frac{dp}{dT}\right)_{sat} = \frac{h_g - h_f}{T\left(v_g - v_f\right)}$

Clausius - Clapeyron Equation : $\left(\frac{dp}{dT}\right)_{sat} = \frac{h_g - h_f}{\left(RT^2/p\right)}; \left[\frac{d(\ln p)}{dT}\right]_{sat} = \frac{h_g - h_f}{RT^2}$

Single phase systems : $\left(\frac{\partial s}{\partial T}\right)_v = \frac{c_v}{T}; \left(\frac{\partial s}{\partial T}\right)_p = \frac{c_p}{T}; \left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p; \left(\frac{\partial h}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p$

$$s_2 - s_1 = \int_1^2 \frac{c_v}{T} dT + \int_1^2 \left(\frac{\partial p}{\partial T}\right)_v dv;\ u_2 - u_1 = \int_1^2 c_v dT + \int_1^2 \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right] dv$$

$$s_2 - s_1 = \int_1^2 \frac{c_p}{T} dT - \int_1^2 \left(\frac{\partial v}{\partial T}\right)_v dp;\ h_2 - h_1 = \int_1^2 c_p dT + \int_1^2 \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp$$

Internal Energy Equations : $\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p; \left(\frac{\partial u}{\partial p}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_p - p\left(\frac{\partial v}{\partial p}\right)_T$

So, before I start these things, the fundamental thermodynamic equations what you have learned so far. There are 16 thermodynamic relations; basic relations, Maxwell relations and we used it for phase change process, single phase systems, internal energy equations. In fact, some of these equations will be useful for the definition of Joule Thomson coefficients. So, that is the idea that these are the very vital relations we are going to use as and when we recall it for any kind of practical applications.

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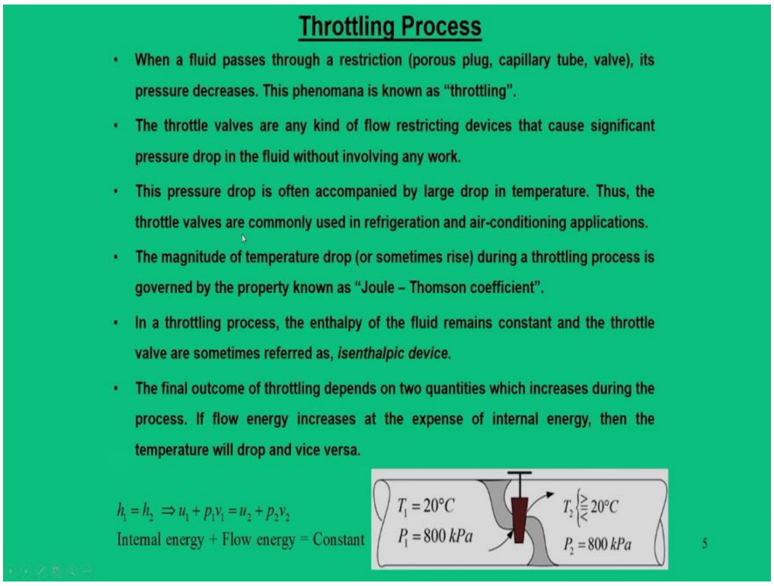

Throttling Process

- When a fluid passes through a restriction (porous plug, capillary tube, valve), its pressure decreases. This phenomana is known as "throttling".
- The throttle valves are any kind of flow restricting devices that cause significant pressure drop in the fluid without involving any work.
- This pressure drop is often accompanied by large drop in temperature. Thus, the throttle valves are commonly used in refrigeration and air-conditioning applications.
- The magnitude of temperature drop (or sometimes rise) during a throttling process is governed by the property known as "Joule – Thomson coefficient".
- In a throttling process, the enthalpy of the fluid remains constant and the throttle valve are sometimes referred as, *isenthalpic device.*
- The final outcome of throttling depends on two quantities which increases during the process. If flow energy increases at the expense of internal energy, then the temperature will drop and vice versa.

$h_1 = h_2 \Rightarrow u_1 + p_1 v_1 = u_2 + p_2 v_2$

Internal energy + Flow energy = Constant

So, before you go for this Joule Thomson coefficients, let us try to first understand throttling process. In fact, we all know what a throttling process is all about, in our basic thermodynamic courses. In fact, at some point of time also during the consideration of refrigeration, we use some valve what we call as throttle valve. But, the very basic essential fact is that what does this throttle valve do? So, basically this comes under the broad heading what we call as throttling process.

So, when a fluid passes through a restrictions, this restriction I mean it can be kind of a porous block or a capillary tube means a very small tube or it can be any kind of valve, then its pressure decreases. And, such phenomena is known as throttling. Then, for example, when the gas expands in the turbine pressure also decreases there. But there we do not call it at the throttling, but there we call it as a work output that we get from a turbine.

So, what is the basic considerations that we have here that during the expansion of gas in a turbine we say it is a isentropic process. But, if the process is not an isentropic process, it is something else and in this case it is a throttling. And, in fact, this isentropic process is a reversible adiabatic process. And, when you say throttling we are trying to reduce this pressure. But, at what cost and what parameter remains constants? So, that is the idea or the throttling process is all about.

So, the throttling valves are of any kind of flow restricting device that causes significant pressure drop of the fluid without involvement any work. And, this pressure drop normally is accompanied by temperature drop. So, that is the reasons this throttling process is a very common phenomena or throttle valves are mainly used for refrigeration and air conditioning applications. Now, question arises we are saying that there is a drop in pressures, but what happens to temperatures? Can the temperature always drop or it can increase?.

So, that is governed by the Joules Thomson coefficients. So in fact, we said that in a throttling process, the thermodynamic parameter that is enthalpy of the fluid remains constants. Enthalpy involves the internal energy plus flow work. So, if this has to remain constant, if you look at this equation when enthalpy remains constant and if we can expand this equation that is $u_1 + p_1 v_1 = u_2 + p_2 v_2$. As you can see here in this figure, that we have a tube or pipe and there is a valve sitting onto it.

So, in one conditions, let us say inlet condition is 800 kPa, 20 C, pressure drop may be 400 kPa. So, that is a drop in pressure. But what will happen? Can temperature increase, can temperature remain same or can temperature drop? So, all these uncertainty conditions still are not known to us so far.

So, under what circumstances whether temperature will increase or decrease or remains constants that depends on the parameter what we call as a Joules Thomson coefficients. And in fact, in our entire lecture today, we will be concentrating on these particular parameters.

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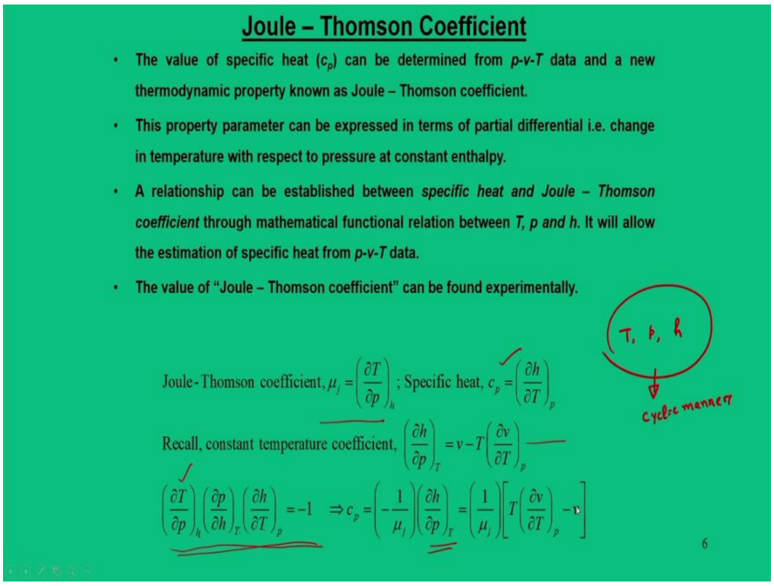

Joule – Thomson Coefficient

- The value of specific heat (c_p) can be determined from *p-v-T* data and a new thermodynamic property known as Joule – Thomson coefficient.
- This property parameter can be expressed in terms of partial differential i.e. change in temperature with respect to pressure at constant enthalpy.
- A relationship can be established between *specific heat and Joule – Thomson coefficient* through mathematical functional relation between *T, p and h*. It will allow the estimation of specific heat from *p-v-T* data.
- The value of "Joule – Thomson coefficient" can be found experimentally.

$$\text{Joule-Thomson coefficient}, \underline{\mu_j = \left(\frac{\partial T}{\partial p}\right)_h}\ ; \text{Specific heat}, c_p = \left(\frac{\partial h}{\partial T}\right)_p$$

$$\text{Recall, constant temperature coefficient}, \left(\frac{\partial h}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p$$

$$\underline{\left(\frac{\partial T}{\partial p}\right)_h \left(\frac{\partial p}{\partial h}\right)_T \left(\frac{\partial h}{\partial T}\right)_p = -1} \Rightarrow c_p = \left(-\frac{1}{\mu_j}\right)\underline{\left(\frac{\partial h}{\partial p}\right)_T} = \left(\frac{1}{\mu_j}\right)\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right]$$

T, p, h

cyclic manner

Now, let us see thermodynamically how does this parameter comes. So, one way of looking at these things, we define a parameter Joule Thomson coefficient μ_j; change in the temperature with respect to pressure at constant enthalpy. So, the Joule Thomson coefficient is defined as the change in the temperature with respect to pressure at constant enthalpy.

And in fact, this is one such parameters we have come across when you derive this mathematical equations involving thermodynamic relations. And, we also know another term that is specific heat which is also defined in terms of h and T and that is change in enthalpy with respect to temperature at constant pressures. So, these two parameters becomes vital to form a relationship and this relationship we can establish from the mathematical functions we have learnt so far.

$$\text{Joule} - \text{Thomson coefficient}, \mu_j = \left(\frac{\partial T}{\partial p}\right)_h ; \text{Specific heat}, c_p = \left(\frac{\partial h}{\partial T}\right)_p$$

And, one such expressions that we have derived from this thermodynamic relation is known as constant temperature coefficient; $\left(\frac{\partial h}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p$. This is one of the relations we have learnt from this thermodynamic equation. Now, if you say the 3 parameters that is temperature, pressure and enthalpy.

And, if these 3 independent parameters are functionally related in a cyclic manner, then we can frame a equation what is called as cyclic relations that is $\left(\frac{\partial T}{\partial p}\right)_h \left(\frac{\partial p}{\partial h}\right)_T \left(\frac{\partial h}{\partial T}\right)_p = -1$. Now, in this equations so far we have defined $\mu_j = \left(\frac{\partial T}{\partial p}\right)_h$, this first term is defined. Last term that is $c_p = \left(\frac{\partial h}{\partial T}\right)_p$ and what we do not know is $\left(\frac{\partial p}{\partial h}\right)_T$.

So, we can write this $c_p = \left(-\frac{1}{\mu_j}\right)\left(\frac{\partial h}{\partial p}\right)_T$. Then, we use this relation here and after putting this we get a fundamental relations $c_p = \left(\frac{1}{\mu_j}\right)\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right]$. So, this is a very fundamental relation that we are going to use in our analysis.

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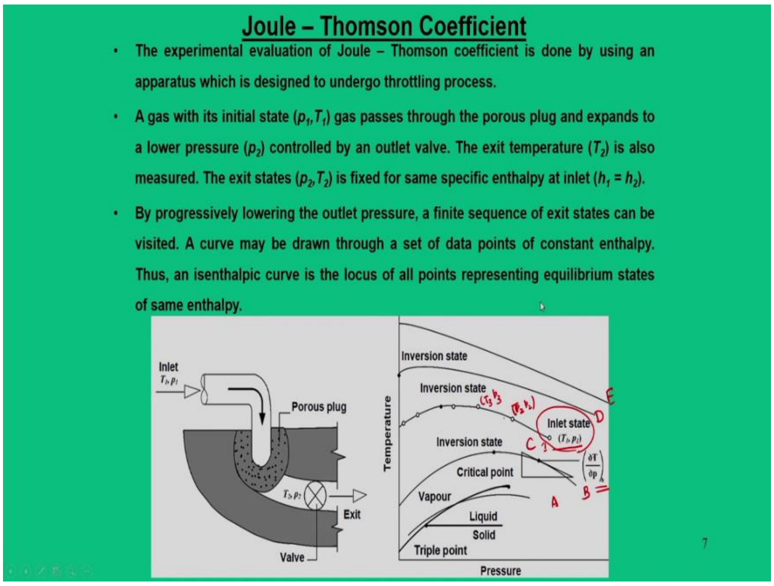

Joule – Thomson Coefficient

- The experimental evaluation of Joule – Thomson coefficient is done by using an apparatus which is designed to undergo throttling process.
- A gas with its initial state (p_1,T_1) gas passes through the porous plug and expands to a lower pressure (p_2) controlled by an outlet valve. The exit temperature (T_2) is also measured. The exit states (p_2,T_2) is fixed for same specific enthalpy at inlet ($h_1 = h_2$).
- By progressively lowering the outlet pressure, a finite sequence of exit states can be visited. A curve may be drawn through a set of data points of constant enthalpy. Thus, an isenthalpic curve is the locus of all points representing equilibrium states of same enthalpy.

Now, let us go towards this experimental evaluation of these Joules Thomson coefficients. We mentioned that for a given inlet conditions that means, when a gas or fluid enters into a throttling device and final pressure and temperatures, we say that final pressure is going to reduce. But, what happens to temperatures?

So, to do that we can do this control part in a regulated manner, in a precise manner. So, what you do is that we consider a gas which enters into a systems and it is passing through a porous block and followed by a valve. So, basically the conditions of the gas which is at the inlet is known that is T_1 and p_1. And condition at the exit; that means, exit pressure is regulated by a valve and that p_2 is regulated by this valve. But, inlet condition is fixed, exit condition p_2 we are fixing it and at that p_2 what is the temperature we are going to measure.

So, basically we have a set of data and that means, gas passes through this porous block and for a given set of initial conditions and for a given outlet exit pressure, we are going to measure T_2. And, such process we can define this in a graphical form. So, for example, in this particular graph you are starting with initial state T_1, p_1 that is this point 1, another point; we have subsequent p_2.

So, we say for same initial conditions you have one set of data p_2, T_2 and T_3, p_3 and so on. So, we can generate this data points on this pressure temperature curve and keep on doing this. So, this is at one particular inlet state. Now, we can change this inlet state to another value. So, when the inlet states are another value; so, different set of curves can be formed that is inlet state A, B, C, D, E and so on.

So, for many inlet state corresponding exit state we can plot it. But, what is more important here this form, for each of this curve there is a parameter what is called as $\left(\frac{\partial T}{\partial p}\right)_h$. This parameter we are going to measure for each of this curve. And, one the characteristics features of all these curves is that they are isenthalpic curve and it is the locus of all the points representing equilibrium states of same enthalpy.

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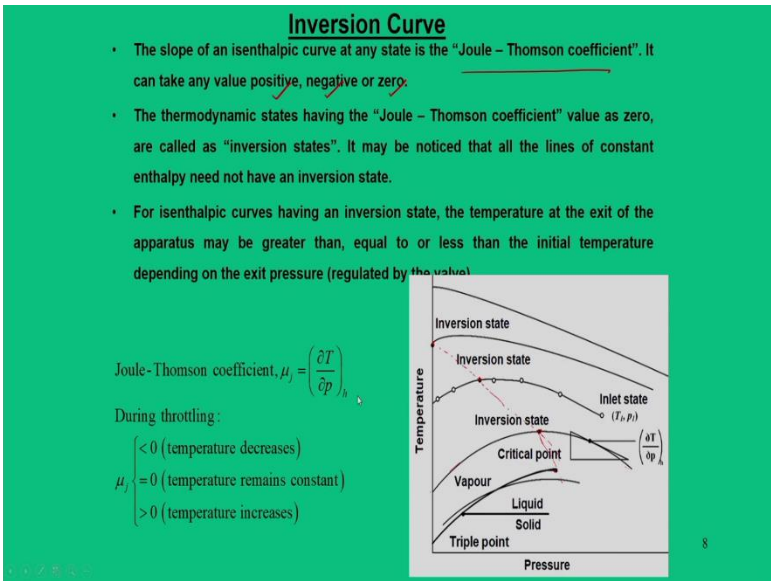

Inversion Curve

- The slope of an isenthalpic curve at any state is the "Joule – Thomson coefficient". It can take any value positive, negative or zero.
- The thermodynamic states having the "Joule – Thomson coefficient" value as zero, are called as "inversion states". It may be noticed that all the lines of constant enthalpy need not have an inversion state.
- For isenthalpic curves having an inversion state, the temperature at the exit of the apparatus may be greater than, equal to or less than the initial temperature depending on the exit pressure (regulated by the valve)

Joule-Thomson coefficient, $\mu_j = \left(\frac{\partial T}{\partial p}\right)_h$

During throttling:

$$\mu_j \begin{cases} < 0 \text{ (temperature decreases)} \\ = 0 \text{ (temperature remains constant)} \\ > 0 \text{ (temperature increases)} \end{cases}$$

Now, when I calculate the slope for this isenthalpic curve and we call this as a Joules Thomson coefficients. And, this value can take a positive number or it can take a negative number or it can be zero. Now, what is the characteristics of the curve? That when I say positive to negative number; that means, there is a inversion; that means, negative value to positive value means it passes through zero and there is a inversion. So, for each of this curve there is an state of inverse point.

So; that means, for each initial state of this curve we can in fact, join all these points where there is a inversion. For example, if I am on this curve and I am moving towards left; that means, if I am going in the direction of decreasing the pressure. We can see temperature first increases then followed by drop in temperatures. So, when $\mu_j < 0$, the temperature drops and when the $\mu_j > 0$, the temperature increases. And, this particular curve and the state point we call this as a inversion state.

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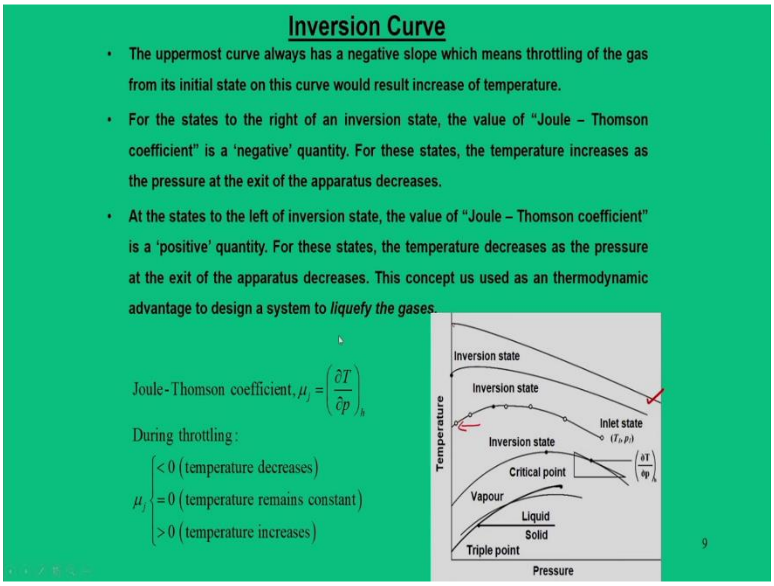

Inversion Curve

- The uppermost curve always has a negative slope which means throttling of the gas from its initial state on this curve would result increase of temperature.
- For the states to the right of an inversion state, the value of “Joule – Thomson coefficient” is a ‘negative’ quantity. For these states, the temperature increases as the pressure at the exit of the apparatus decreases.
- At the states to the left of inversion state, the value of “Joule – Thomson coefficient” is a ‘positive’ quantity. For these states, the temperature decreases as the pressure at the exit of the apparatus decreases. This concept us used as an thermodynamic advantage to design a system to *liquefy the gases*.

$$\text{Joule-Thomson coefficient}, \mu_j = \left(\frac{\partial T}{\partial p}\right)_h$$

During throttling:

$$\mu_j \begin{cases} < 0 \ (\text{temperature decreases}) \\ = 0 \ (\text{temperature remains constant}) \\ > 0 \ (\text{temperature increases}) \end{cases}$$

And, one of the other important aspect of this curves is that if you look at this particular figure, the topmost figure if you look at, there is no inversion point. So, decrease in pressure will always increase in the temperatures. So, there is no rate of inversions; that means, for this particular situation we do not have any inversion point.

So, we can say that the uppermost curve has always a negative slope which means throttling of the gas from its initial state for this case on this curve would result in increase in the temperature. And, for the states right to this inversion curve, the value of Joule Thomson coefficient will be negative quantity. And that means, the temperature increases as the pressure of the exit of the apparatus decreases.

For the states to the left of the inversion state; that means, if you fix this inversion state anything you go towards the left, what is going to happen? The temperature decreases as the pressure at the exit of the apparatus decreases. So, we can take this advantage, that temperature can decrease as the pressure decreases. We can use this concept to as a liquefaction of gases. We will see more details towards the later part of this lecture.

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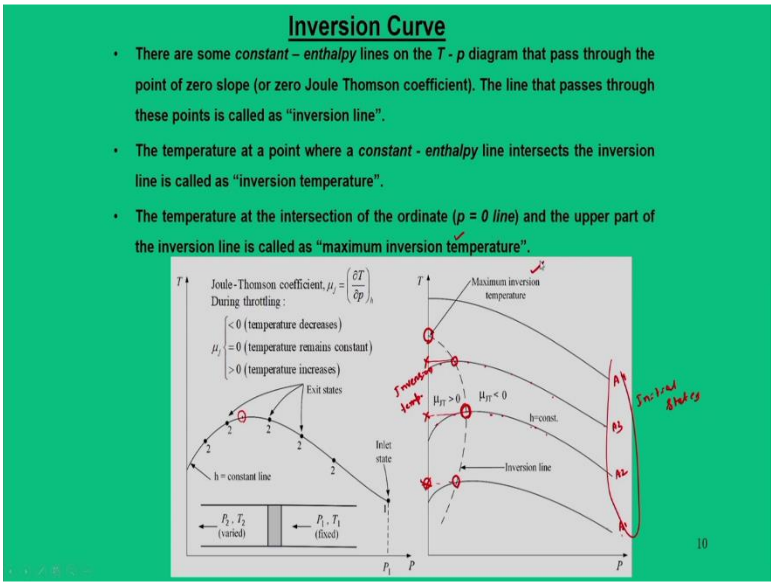

Inversion Curve

- There are some *constant – enthalpy* lines on the *T - p* diagram that pass through the point of zero slope (or zero Joule Thomson coefficient). The line that passes through these points is called as "inversion line".
- The temperature at a point where a *constant - enthalpy* line intersects the inversion line is called as "inversion temperature".
- The temperature at the intersection of the ordinate (*p = 0 line*) and the upper part of the inversion line is called as "maximum inversion temperature".

Now, let us understand more closely about this inversion curve. So, we are now going to introduce the inversion curve or we can say inversion lines. So, a more clear picture what I can say that from a fixed initial condition p_1 to p_2, we can get a varied conditions p_2 and T_2. And, we can put this curve in this manner on a temperature and pressure diagrams.

So, when we say $\mu_j < 0$ temperature decreases, $\mu_j = 0$, temperature remains constant, with $\mu_j > 0$, temperature increases. Now, what you do is this is one set of the curve for a given initial states, for different initial states that like A_1 A_2 A_3 A_4, we can locate the corresponding state point 2 on each of this curve. And, for each of this curve we can also locate at what point this $\mu_j = 0$. So, that is the slope is 0.

So, once you locate all these points, if you can draw a continuous curve joining these points. This line, we call this as a inversion line and many times we call this as also inversion curve. And, this is the line where we can say enthalpy is 0.

So, the temperature at a point where the constant enthalpy line intersects the inversion curve is known as the inversion temperatures. So, basically these are constant h lines and it intersects this inversion line at this point and we call this as inversion temperatures. So, if you drop this particular line on the temperature axis, we can say these are inversion temperatures.

So, these are known as inversion temperature and one interesting fact is that this inversion temperature for the ordinate; that means, when $p = 0$ line, on the temperature axis this is known as maximum inversion temperatures.

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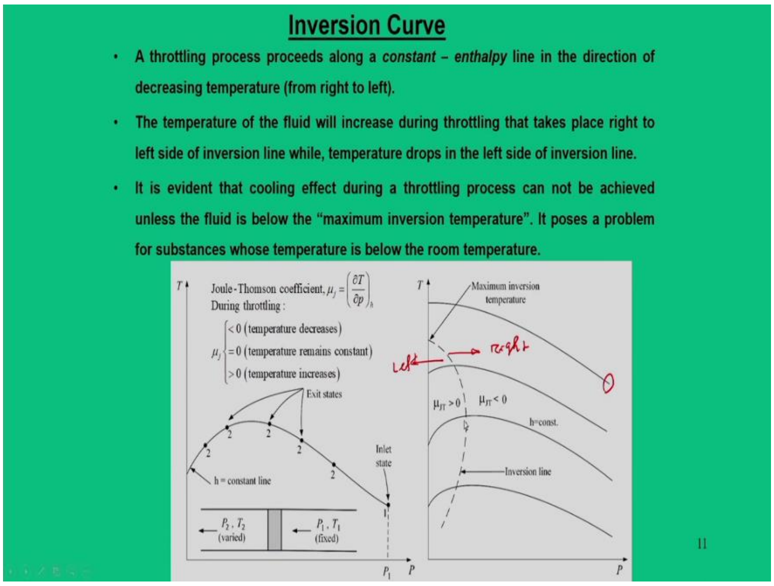

Inversion Curve

- A throttling process proceeds along a *constant – enthalpy* line in the direction of decreasing temperature (from right to left).
- The temperature of the fluid will increase during throttling that takes place right to left side of inversion line while, temperature drops in the left side of inversion line.
- It is evident that cooling effect during a throttling process can not be achieved unless the fluid is below the “maximum inversion temperature”. It poses a problem for substances whose temperature is below the room temperature.

Another some of the physical interpretation also we can say that the throttling process proceeds along the constant enthalpy line in the direction of decreasing the temperature, that is right to left. Temperature of the fluid will increase during throttling process that takes place right to the left side of the inversion line, while the temperature drops in the left side of the inversion line. That means, if this is your inversion line and we are moving towards right and we are moving towards left.

And, when you move from right to left; then the temperature increase and the temperature drops in the left side of the inversion line. It is also evident that the cooling effect during a throttling process cannot be achieved unless this fluid is below the inversion temperatures. So in fact, this is a well known fact that for example, if you look at this topmost curve and this topmost curve does not have a $\mu_j = 0$.

So, it does not have this inversion curve; that means, starting from this initial state, we cannot reach a value for which $\mu_j = 0$. So that means, if you are starting from this curve, we cannot reach this inversion line. So, if you are not reaching this inversion line, it is quite clear that you cannot achieve cooling during throttling.

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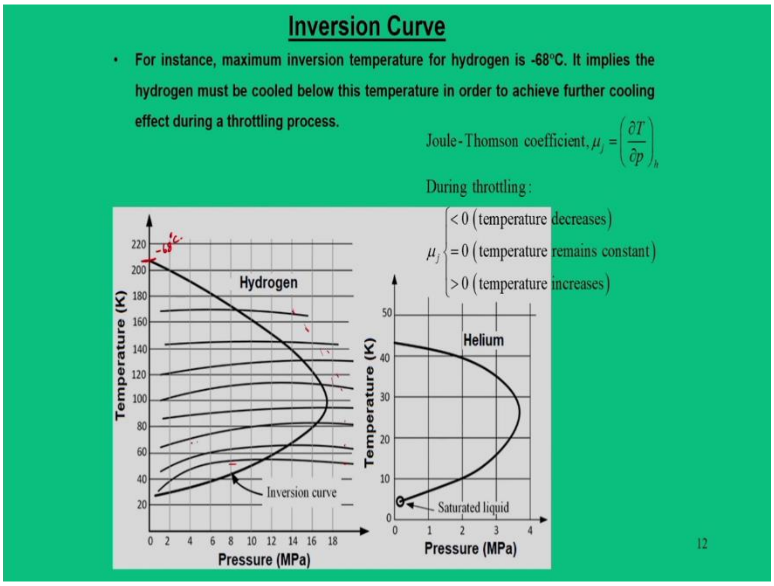

Inversion Curve

- **For instance, maximum inversion temperature for hydrogen is -68°C. It implies the hydrogen must be cooled below this temperature in order to achieve further cooling effect during a throttling process.**

Joule-Thomson coefficient, $\mu_j = \left(\frac{\partial T}{\partial p}\right)_h$

During throttling:

$$\mu_j \begin{cases} < 0 \; (\text{temperature decreases}) \\ = 0 \; (\text{temperature remains constant}) \\ > 0 \; (\text{temperature increases}) \end{cases}$$

So, this particular concept, let us see that how this inversion curve is useful for certain fluids. Now, the fluids that are much of importance is like many a times you use liquid hydrogen, liquid helium. So, basically helium and hydrogen they are available in gas form, but we store them in the liquid form. Now, while storing them you can see that for example, you have to find out that their actual values of pressure and temperature we have to draw first this inversion curve.

So, this typical picture shows that the nature of inversion curve for hydrogen, another curve gives it for helium. So, for instance if I say, the maximum inversion temperature of hydrogen is - 68 C which means, if you want to get the cooling effect; then only we can liquefy it. That means, your throttling process should start anywhere which is below on this line.

So, all this throttling process, the initial state point which has to happen from any of this initial state so that during throttling process we can reach into this inversion curve so as to get the cooling effect.

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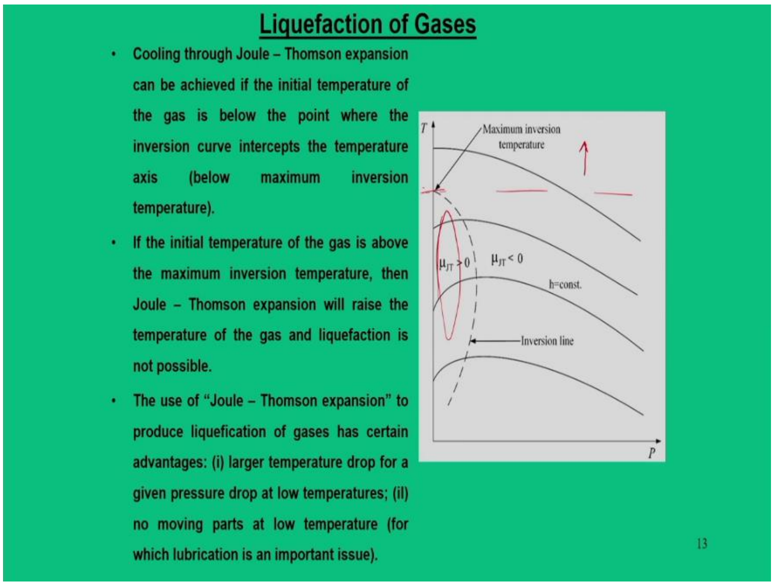

Liquefaction of Gases

- Cooling through Joule – Thomson expansion can be achieved if the initial temperature of the gas is below the point where the inversion curve intercepts the temperature axis (below maximum inversion temperature).
- If the initial temperature of the gas is above the maximum inversion temperature, then Joule – Thomson expansion will raise the temperature of the gas and liquefaction is not possible.
- The use of "Joule – Thomson expansion" to produce liquefication of gases has certain advantages: (i) larger temperature drop for a given pressure drop at low temperatures; (ii) no moving parts at low temperature (for which lubrication is an important issue).

Now, this particular concept is extended for liquefaction of gases. Now, one of the important consideration for liquefaction of the gases that we should get the cooling effect. So, means cooling through Joules Thomson expansion can be achieved if the initial temperature of the gas is below the point, where the inversion curve intersects the temperature axis, that is below maximum inversion temperatures.

That means, if you want to have this cooling effect, then we must be within this region, within this inversion line. But, if the initial temperature is above the maximum inversion temperatures. So, for example, if you have this maximum inversion temperature is this for a given gas, then your initial state should be much above. And, if you have above this, then we cannot raise the temperature. If the initial temperature of the gas is above the maximum temperature, then Joule Thomson effect will raise the temperature of the gas and liquefaction is not possible.

And, another point I need to emphasize that there are certain advantages of this Joule Thomson coefficients. Because, this Joules Thomson coefficient to produce liquefaction of gases has many advantage; few of them are like this. First one is the larger temperature drop for a given pressure at low temperature; that means, when you are looking at the gas at low temperatures for a given pressure drop, we can also get the larger temperature drop.

That means, when you do this throttling process at low initial temperatures, we can get a larger drop in temperature for given pressure drop. And, moreover here we just have to reduce the temperature. There is no moving part; that means, the other issues like lubrication of the devices is not required. So, these two advantages help us, the using the concept of Joule Thomson coefficient as a mechanism to liquefy the gases.

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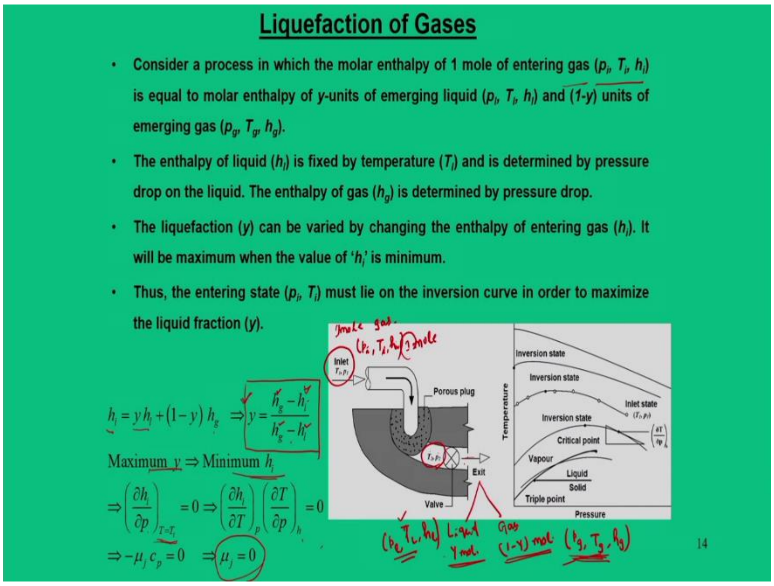

Liquefaction of Gases

- Consider a process in which the molar enthalpy of 1 mole of entering gas (p_i, T_i, h_i) is equal to molar enthalpy of *y*-units of emerging liquid (p_l, T_l, h_l) and (*1-y*) units of emerging gas (p_g, T_g, h_g).
- The enthalpy of liquid (h_l) is fixed by temperature (T_l) and is determined by pressure drop on the liquid. The enthalpy of gas (h_g) is determined by pressure drop.
- The liquefaction (*y*) can be varied by changing the enthalpy of entering gas (h_i). It will be maximum when the value of 'h_i' is minimum.
- Thus, the entering state (p_i, T_i) must lie on the inversion curve in order to maximize the liquid fraction (*y*).

$$h_i = y h_l + (1-y)\, h_g \Rightarrow \boxed{y = \frac{h_g - h_i}{h_g - h_l}}$$

$$\text{Maximum } y \Rightarrow \text{Minimum } h_i$$

$$\Rightarrow \left(\frac{\partial h_i}{\partial p}\right)_{T=T_i} = 0 \Rightarrow \left(\frac{\partial h_i}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_h = 0$$

$$\Rightarrow -\mu_j c_p = 0 \quad \Rightarrow \mu_j = 0$$

Now, let us understand with respect to some realistic number how I should approach while doing this liquefaction process. So, you can recall our previous figure as if that we are having a throttling process which is happening through this mechanism in which we have some inlet gas. So, if I say this inlet gas which is entering to this throttling device which is at the state p_1, T_1. And, exit state is regulated by a valve; that means, we are regulating pressure p_2 and finding the temperature T_2.

Now, what our given situation here that we have the initial state would say 1 mole of gas. And, here I say its initial condition is p_i, T_i and h_i. And, its molar enthalpy of y unit of emerging fluid initially it is in gas state and at the outlet, we have two parts. One is a liquid and we have other is gas. So, 1 mole of gas if it is entering and we are getting y unit of liquid; that means, y mole of liquid and 1-y mole of gas. So, the conditions that we are getting in the liquid phase is p_L.

And, it is governed by its saturated temperature and pressure T_L and h_L, that is enthalpy of saturated liquid and for the gas phase that is for which 1-y mole of gas is being produced. So, we have p_g, T_g and h_g. So, these are the saturated values. Now, if I say this the fundamental equations that is $h_i = yh_l + (1-y)h_g$.

So, this equation can be formed that $y = \frac{h_g - h_i}{h_g - h_l}$. So, this is a fundamental equation, normally we use in the steam table as a dryness fractions. But, here we are interpreting this y as a amount of liquid that comes out. Now, here in this equation if you look at closely the values of h_g is limited by the conditions at the exit state, that is saturated pressure and temperature values. And, that is again is fixed what condition we are exiting this gas and liquid. And, if liquid state is fixed by its own saturated state.

So, we do not have much control of h_g and h_l, but we should have the initial situation h_i. Now, where I should start? My initial enthalpy; that means, if you want to liquefy this gas; that means, we need to have more and more quantities of y, we need to maximize y. So, for maximum y we should have minimum value of h_i from this equation. Then, one condition you can impose because in this process, what is going to happen?

We can write this equation that $\left(\frac{\partial h_i}{\partial p}\right)_{T=T_i} = 0$. Now, this equation can be expanded as $\left(\frac{\partial h_i}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_h = 0$. And, through this cyclic relation between h, p and T. And, by definition we can say it is it becomes $\Rightarrow -\mu_j c_p = 0$. Now, c_p for this gas cannot be 0.

So, one condition you must have that $\mu_j = 0$. So, in other words in order to have maximum quantity of liquefaction, we must start, the initial state should be fixed for a conditions where $\mu_j = 0$. So, this is the starting point. In fact, that we also proved that you should start the initial state for which the state should be lower than the inversion temperature in the curve. So, this is the very basic bottom line for liquefaction of gases.

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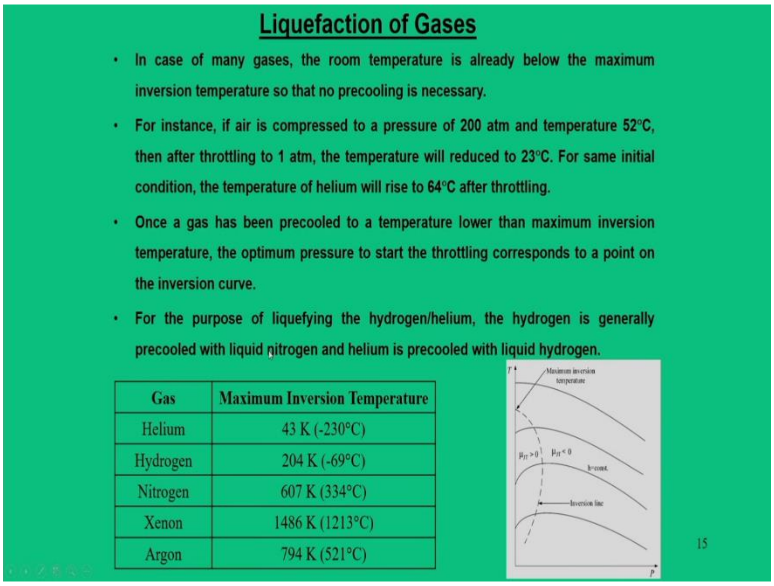

Liquefaction of Gases

- In case of many gases, the room temperature is already below the maximum inversion temperature so that no precooling is necessary.
- For instance, if air is compressed to a pressure of 200 atm and temperature 52°C, then after throttling to 1 atm, the temperature will reduced to 23°C. For same initial condition, the temperature of helium will rise to 64°C after throttling.
- Once a gas has been precooled to a temperature lower than maximum inversion temperature, the optimum pressure to start the throttling corresponds to a point on the inversion curve.
- For the purpose of liquefying the hydrogen/helium, the hydrogen is generally precooled with liquid nitrogen and helium is precooled with liquid hydrogen.

Gas	Maximum Inversion Temperature
Helium	43 K (-230°C)
Hydrogen	204 K (-69°C)
Nitrogen	607 K (334°C)
Xenon	1486 K (1213°C)
Argon	794 K (521°C)

Now, in the end I will just try to give some realistic number. What is the significance; that means, why we require liquefaction for certain gases? One thing in this picture you can say that maximum inversion temperature for helium is 43 K, hydrogen it 204 K, nitrogen is 607 K. But, what we say all these numbers; for hydrogen and helium they are much more below this room temperature.

Whereas, for nitrogen there is no issue of initial state because its inversion state is maximum inversion temperature is 607. That means, they are much above the atmospheric and these are much below the atmospheric conditions. So, what does this signify? If air is compressed to a pressure 200 atmosphere and 22 C, then we throttle this air to 1 atmosphere that means, we are reducing the pressure.

Subsequently, for this such initial conditions the air temperature will be reduced. And; that means, we get a in this case a cooling effect. But, when you do this same thing for some initial conditions for helium, this temperature will rise. That means, initially it was 52 and this temperature will rise; that means, we cannot achieve this cooling effect for helium, but same thing we can get it for air. So, this is the significance of how different gases behave when you start from its initial state.

So; that means, for many gases room temperature is already below the maximum inversion temperature; so, that no pre-cooling is necessary. Now, once the gas has been precooled to a temperature lower than maximum temperature, the optimum pressure to start the throttling corresponds to the point on the inversion curve. Now, there are some issues like if you want to store this hydrogen or helium in liquid form.

Then, what type people try to use is that hydrogen is generally precooled with liquid nitrogen to achieve its initial state and helium is normally precooled with liquid hydrogen to achieve its initial states. So, for these cases there is a challenge that how you are going to store them in the liquid form.

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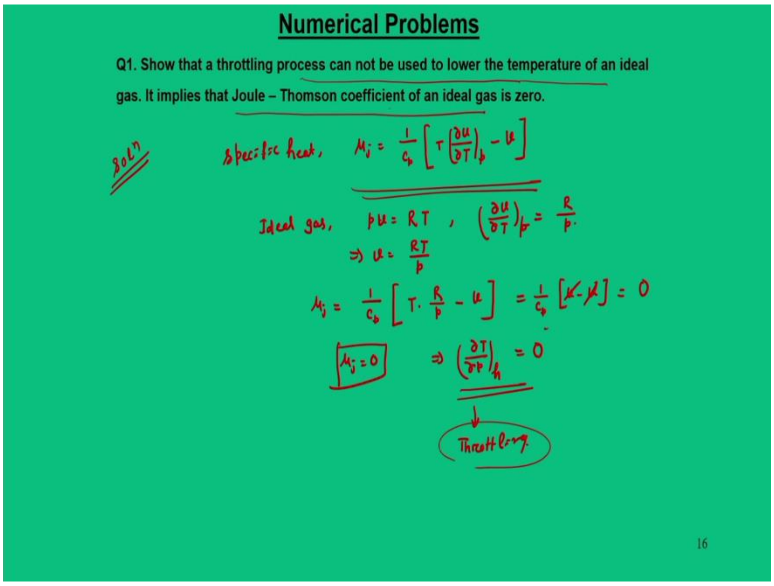

Numerical Problems

Q1. Show that a throttling process can not be used to lower the temperature of an ideal gas. It implies that Joule – Thomson coefficient of an ideal gas is zero.

Soln

Specific heat, $\mu_j = \frac{1}{c_p}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right]$

Ideal gas, $pv = RT$, $\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p}$

$\Rightarrow v = \frac{RT}{p}$

$\mu_j = \frac{1}{c_p}\left[T\cdot\frac{R}{p} - v\right] = \frac{1}{c_p}\left[\cancel{v}-\cancel{v}\right] = 0$

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

$\downarrow$

Throttling

So, with this I come to the end of this lecture. And it towards the end, I will just try to solve a simple problem. Most of this content of this lecture are more towards the physical natures. But, many times we use that the Joule Thomson coefficient for an ideal gas is zero. So, in other words it means what will happen if I use the throttling process to lower the temperature for an ideal gas? Can you throttle it? If at all I throttle it, what is going to happen?

This is the physical significance or physical consequence. But, the very basic bottom line that we should give our attention to Joule Thomson coefficient for an ideal gas what is happening. And, this number will tell you whether we can throttle an ideal gas or not. So, to start with we can recall our fundamental expressions that we derived, $c_p = \left(\frac{1}{\mu_j}\right)\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right]$.

This is one of the expressions that we derived in this lecture. Now, for an ideal gas we have this relations $pv = RT; v = \frac{RT}{p}$; $\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p}$. Now, when I substitute this, we can write $c_p = \left(\frac{1}{\mu_j}\right)\left[\frac{TR}{p} - v\right]$. Now $\frac{TR}{p}$ is nothing, but v. So, I can say $\mu_j = \left(\frac{1}{c_p}\right)(v - v) = 0$. So, $\left(\frac{\partial T}{\partial p}\right)_h = 0$. This is we are going to achieve through throttling.

And, throttling happens at constant enthalpy, what happens if you drop the temperatures. This makes us the understanding that in a throttling process, since $\mu_j = 0$; the throttling process cannot be used to lower the temperature. But, it can lower the pressure, but throttling process cannot be used to lower the temperature of an ideal gas. So, this is the fundamental concept for the Joules Thomson coefficients. With this I come to the end of this lecture and also, I come to this end of this module.

Thank you for your attention.