

Upstream LNG Technology
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Lecture – 70
Cryogenic refrigeration and liquefaction in natural gas systems – II

Welcome, we have started learning about the principles and analysis of the various types of refrigeration and liquefaction cycles.

(Refer Slide Time: 00:28)

What we shall learn

- ✓ Principle and performance parameters of gas liquefaction
- ✓ Factors affecting gas liquefaction
- ✓ Isenthalpic expansion
- ✓ Inversion temperature, and inversion curve
- ✓ Adiabatic expansion

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So, this is now the second in the series that, we shall be learning about the principle and performance of the parameters of gas liquefaction and the factors affecting gas liquefaction, isenthalpic expansion, inversion temperature, inversion curve and the adiabatic expansion.

(Refer Slide Time: 00:43)

Gas liquefaction

- ✓ Is an open system.
- ✓ Ideal liquefaction is based on Carnot cycle, using reversible isothermal compression and reversible isentropic expansion.
- ✓ Very high pressure (about 70-80 GPa) is needed to liquefy the gas by isothermal compression – this is impractical, and hence ideal process is not used in practice.

$$-\dot{W}_{id}/\dot{m}_f = T(s_1 - s_f) - (h_1 - h_f)$$

Isenthalpic Compression
 $W_c = h_2 - h_1 + Q$

Isentropic Expansion—
 Work Produced
 $W_e = h_2 - h_f$

P_2 Selected so that Gas Will Become a Liquid on Expansion

Temperature

Entropy

Liquid

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So, first we see the gas liquefaction, again I shall not be going into detail of the derivations, which are available in any standard thermodynamics book or the references I have given at the end of lecture. So, here I shall be just highlighting the salient features and the equations which are needed for the analysis.

So, the liquefaction unlike the refrigeration is an open system and here we have seen what is open system that some mass is coming and this part of this mass will be liquefied. So, this mass will be coming and some of we liquefied. So, we find that this becomes a open, because if I say closed system that means, nothing can go out of the system see from closed system.

So, the open system and the ideal liquefaction is based on Carnot cycle, we using reversible isothermal compression and reversible isentropic or adiabatic expansion and here we find that very high pressure is needed to liquefy the gas, if we use isothermal compression and this pressure is about 70 to 80 GigaPascal.

And GigaPascal is 10 to the power 9 Pascal is 1 GigaPascal. So, we need very high pressure for if we want to convert the gas into the liquid isothermal by a compression. So, it is not feasible, because there is no compressor, which can generate such high amount of pressure. So, but this is ideal work process cycle and ideal process is never used in practice. So, here first let us understand the process, here we have the total mass, which is going into the compressor and this Q dot represents the heat of compression,

that is rejected to keep the compression isothermal and then this compressed mass is taken here and this is expanded and we are getting out some work, if we are using turbine and then finally, we find that we get some kind of liquefaction here and here this represents the liquid portion out of this thing.

So, this is how this liquefaction works and if we are making this looking putting the temperature entropy diagram, we start with some particular state 1 here and then we when we move on the left side from right, we are increasing the pressure and then it is this pressure is increased isothermally and this P_2 is selected. So, that the gas will become a liquid on expansion, so that is how we are putting this thing and then what will happen that now we are expanding it.

So, you can see that if we go to some other pressure on the left hand side, we can also go here and if we say I compress up to this then and then I expand it here, I will never reach the liquid side. So, we have to see that whenever this dome is there, we have to cross this dome to ensure that on the isentropic expansion, this gas is converted to liquid that is why we need such a high pressure ok. So, that is and then once we go to this pressure then we come to this and this is isentropic expansion and this work produced is $h_2 - h_f$; this $h_2 - h_f$ is the work produced.

So, this is how the ideal cycle ideal liquefaction is represented on a T-s diagram and if we apply the first law of thermodynamics on this particular cycle, we find this is how we will get the ideal work needed and this m_f is per unit mass of the amount liquefied. This m_f is the amount if out of this total \dot{m} m_f is liquefied this is m_f and this is coming as T into $S_i - S_1 - S_f - S_1 - S_f - h_1 - h_f$. So, this is how in terms of the temperature and the entropy and the enthalpy, we are getting the ideal work.

(Refer Slide Time: 04:47)

Performance parameters for gas liquefaction system

- ✓ Work required for unit mass of gas compressed, $-\dot{W}/\dot{m}$
- ✓ Work required for unit mass of gas liquefied, $-\dot{W}/\dot{m}_f$
- ✓ Fraction of the total mass of the gas liquefied, $y = \dot{m}_f/\dot{m}$

$$-\frac{\dot{W}}{\dot{m}} = y \left(-\frac{\dot{W}}{\dot{m}_f} \right)$$
$$\text{FOM} = \frac{\dot{W}}{\dot{W}_{id}} = \frac{-\dot{W}/\dot{m}_f}{-\dot{W}_{id}/\dot{m}_f}$$

- ✓ In ideal system, whole of the gas is liquefied, that is, $\dot{m}_f = \dot{m}_g$ or $y = 100\%$

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Now, there are various performance parameters used for this liquefaction systems and one is this work required for unit mass gas compressed. So, here we are representing the total work required and this total work required, maybe the if else suppose we are not taking the turbine work to run the compressor then, this work representing the work where inputting for the compressor and if we are taking the work from the turbine and putting it to the compressor then it will mean the net-work which is inputted externally in addition to the work obtained from the turbine ok.

So, that is how we are talking about the work required for the unit mass of gas compressed and this is the \dot{m} is the total mass of the gas, which is going into the system. There is another parameter that is the work required for unit mass of gas liquefied. So, this is compressed liquefied. So, this is the amount which is getting liquefied out of this amount.

So, again we can represent this, another way of representing the process performance and third way is the fraction of the total mass, that gets liquefied we call it yield. So, yield defined as the amount that has gone into liquid phase and divided by the total amount that has been taken into the system and these two works can be represented easily. You can see this if you put this definition over here and you can see that this work amount, this work that is needed for unit mass of the gas compressed is equal to the product of the

yield and the amount of the work per unit mass of the gas liquefied. Now, this why we are putting negative? Because the net-work has to be given to the system, ok.

So; that means, whenever we have work is done on the system in thermodynamics, we use the convention, that we put the worker as negative and when the work is produced by the system we put as positive. So, in this particular thing we have net-work has to be given to the system. So, it is negative. Suppose in case of turbine, the work is positive, because turbine is producing the work and then we are putting the figure of merit by comparing the actual work needed and the ideal work, which is calculated.

So, this is how we are getting the actual work needed per unit mass of the gas liquefied and the ideal work needed for the unit mass of the gas liquefied. In an ideal system, what you mean by ideal system? The whole gas is liquefied that means, we are not leaving any gas un-liquefied. So, in that case what happens? This m_f is become equal to m dot and then y becomes 100 percent, but this is never achieved and not also needed in practice.

(Refer Slide Time: 07:45)

Ideal work requirement for gas liquefaction at 294 K and 0.101 MPa

Gas	$\dot{W}_i/\dot{m}_f \times 10^{-3}$ (kJ/kg)
Helium	6.67
Hydrogen	11.62
Neon	1.30
Nitrogen	0.747
Air	0.718
Argon	0.467
Oxygen	0.616
Methane	1.053

Now, in this particular table, what we are showing that we are showing that depending on the type of gas, we are showing that how much work ideal work, this W_i is the ideal work, how much ideal work per unit mass of the gas liquefied is needed for the gas liquefaction at this particular temperature and the pressure? Now, you see that with temperature pressure as we have seen that this h_1 value S_1 value h_f S_f this all these h

values change with temperature. So, we find these things that for the various types of gases, because this enthalpy and entropy values depend on the type of the substance.

So, we find that we are getting the difference different types of ideal work and we find that here this hydrogen is leading the greatest amount of work, whereas we find that these nitrogen, air, they have and this argon is still quite less. So, that is why we find that the cost of hydrogen production is also quite high rather than these work from the function point of view.

(Refer Slide Time: 08:51)

Factors affecting performance parameters for gas liquefaction system

- ✓ Adiabatic efficiencies of the compressor and expander.
- ✓ Mechanical efficiencies of the compressor and expander.
- ✓ Heat exchanger efficiencies.
- ✓ Pressure drop through pipe lines, heat exchangers etc.
- ✓ Heat transfer between system and surroundings.

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And here we have the various factors, which affect the performance parameters of the liquefaction cycle because in the cycle we have found that, we have the compressors, we have heat exchangers. So, all individual equipment, how good how well they are working, they also dictate the overall performance of the system.

So, here we say that the adiabatic efficiency of compressor and expander. Then mechanical efficiencies of the compressor and expander and the heat exchanger efficiencies, then we have we assume that there is no pressure drop in the pipelines but in reality we find there will be some finite pressure drop in the pipelines, heat exchangers and the various set of fittings, valves, etcetera we are using and then there could be some heat transfer between the systems and their surroundings.

Even though we try to ensure that there is no heat exchanged between system surroundings by providing insulation, but there is no perfect insulation. So, whatever insulation we are using, we will find that; however, small, but some finite amount of heat exchange will always be there. Heat exchange means that it could be either from the system to the ambient or ambient into the system, in both ways it can take place and these factors are not only dictating the liquefaction performance, but they also dictate the efficient performance because refrigeration cycle also we are using all this compressors, expanders, heat exchangers, pipelines, valves, etcetera.

(Refer Slide Time: 10:23)

Production of low temperature: Joule-Thomson effect

- ✓ Neglecting changes in kinetic- and potential energies, assuming no heat exchange between the system and the surroundings (adiabatic) and zero shaft work, First law of thermodynamics gives for JT valves, $h_1 = h_2$, where 1 and 2 denote the inlet and outlet conditions of the valve.
- ✓ Within the valve, the flow is irreversible and not isentropic.
- ✓ Change in temperature with a change in the pressure for an isenthalpic process is represented by *Joule-Thomson coefficient*, μ_{JT} , defined as

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_h$$

For an ideal gas, $\mu_{JT} = 0$, that is, an ideal gas does not experience any temperature change during its expansion. Hence ideal gas behavior is not desirable for cooling.

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Now, let us come to ways of the producing low temperature and this is also true for the refrigeration cycle. So, here we find that the low temperature first we learnt about the Joule Thomson effect and in this means that in this we are using some kind of expansion valve to carry out the Joule Thomson expansion.

If we neglect the kinetic and the potential energy changes and we assume that there is no heat exchange between the system and the surroundings, that is it is completely adiabatic process and there is no shaft work involved, that is your system is not producing any work then, if we apply the first law of thermodynamics across the expansion device then we will get what?

Then we will get as h_1 is equal to h_2 that is the enthalpy at the inlet is equal to the enthalpy at the outlet and even though the in the within the valve, the flow is irreversible

and it is not isentropic. So, this is all irreversibility inside the valve, but on the outside, we are getting it to be an isenthalpic process. Now, due to this expansion what happens?

There will be some change in the temperature and this change in temperature may either increase or it may decrease. So, this particular change in the temperature due to the change in the pressure is given by some parameter, which is called the Joule Thomson coefficient by μ and this JT is Joule Thomson and this Joule Thomson coefficient is defined like this; that how the pressure change affects the temperature change keeping the enthalpy constant. So, we are assuming the isenthalpic process because of the h_1 is equal to h_2 .

So, $\frac{dT}{dP}$ at constant enthalpy. So, this is the coefficient of expansion for Joule Thomson effect and again without deriving any this thing, we can find out that for the ideal gas, this value of the μ_{JT} is equal to 0 and μ_{JT} equal to 0 means, we will not be able to change the temperature of the fluid, if we change the pressure. So that means, is unaffected by the change in the pressure in this case expansion.

So, if that is the case if we are not able to generate any temperature change that would mean that, any ideal gas will not be suitable to produce cooling or refrigeration ok. So, we do not want the gas to behave ideally under the given condition, because it will not be able to generate the low temperature and fortunately under the cryogenic conditions, because cryogenic means very low temperature. Under cryogenic conditions all the gases will behave non-ideally and that is why we will be able to produce some amount of refrigeration by using any of the cryogenic gases.

(Refer Slide Time: 13:31)

Isenthalpic expansion of real gases

- ✓ On expansion, a real gas may either get heated up or get cooled down.
- ✓ **Inversion temperature:** The temperature at a given enthalpy, expansion below which will produce cooling and above which will cause heating.
 - It first increases and then decreases with a decrease in the enthalpy.
 - May be more or less than ambient temperature.
- ✓ **Inversion curve:** Locus of inversion temperatures at different enthalpies.
- ✓ Expansion valve should be operated below inversion temperature in liquefaction or refrigeration.

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Now, let us look into this isenthalpic expansion a little bit more. So, as I said that due to the expansion depending on the value of the μ_{JT} , the gas may either get heated up or it may get cooled down ok.

Now for to know that means how it will be? So, let us see the inversion temperature. So, this is the temperature at a given enthalpy that expansion below which will produce cooling and above which will cause heating. So, if we on this temperature versus pressure diagram, we put these are various lines of constant enthalpy ok. So, if we choose any enthalpy randomly, suppose, I choose this isenthalpic curve and in this particular curve we find there is a certain temperature, if we are expand if we have the gas initially at this particular in this region and if we are going for any kind of expansion, we will find it is always we are going to raise the temperature.

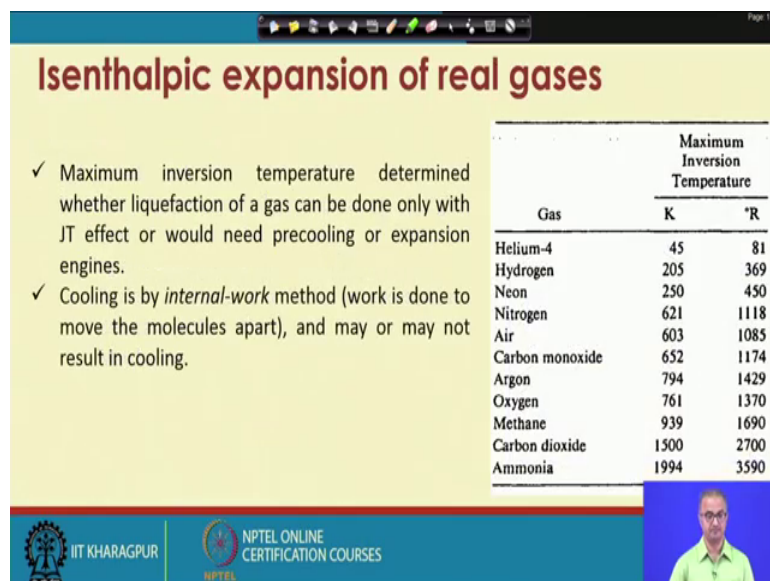
On the other hand, if we go below it we will find that it is going to lower the temperature. So, we would always like to operate the particular expansion below this particular temperature. So, we will find that this particular temperature is the inversion temperature and this inversion temperature will be changing with the different enthalpies. So, that is what you see the temperature at which at a given enthalpy and the expansion below which will produce cooling and above which will cause heating and as if it is experimentally found that as we changed this enthalpy, this temperature will be first increasing and then decreasing with decrease in the enthalpy and what happens that it

reaches certain maximum. So, that is the maximum inversion temperature for that particular gas.

So, we must always make sure that we are always below the maximum inversion temperature, whenever we want to have some refrigeration and this inversion temperature may be more or less than the ambient. So, for some gases if the inversion temperature is less than ambient temperature then, we first we need to cool down the gas and then carry out expansion ok, but if the inversion temperature is more than the ambient temperature, then we need not need any kind of pre cooling. So, then we have inversion curve and what are these curve? These are locus of the inversion temperatures at different enthalpies.

So, this particular curve, which is joining the inversion temperature at different enthalpies, this is the inversion curve, the locus of the inversion temperatures and this expansion valve should be operated below this inversion temperature in liquefaction or refrigeration. So, that is the importance of knowing the inversion temperature and inversion curve. And here we can see that when there is a heating this μ_{JT} will be less than 0 and when it is cooling this μ_{JT} will be more than 0 and as you can see from the definition of the μ_{JT} .

(Refer Slide Time: 16:43)



Isenthalpic expansion of real gases

- ✓ Maximum inversion temperature determined whether liquefaction of a gas can be done only with JT effect or would need precooling or expansion engines.
- ✓ Cooling is by *internal-work* method (work is done to move the molecules apart), and may or may not result in cooling.

Gas	Maximum Inversion Temperature	
	K	°R
Helium-4	45	81
Hydrogen	205	369
Neon	250	450
Nitrogen	621	1118
Air	603	1085
Carbon monoxide	652	1174
Argon	794	1429
Oxygen	761	1370
Methane	939	1690
Carbon dioxide	1500	2700
Ammonia	1994	3590

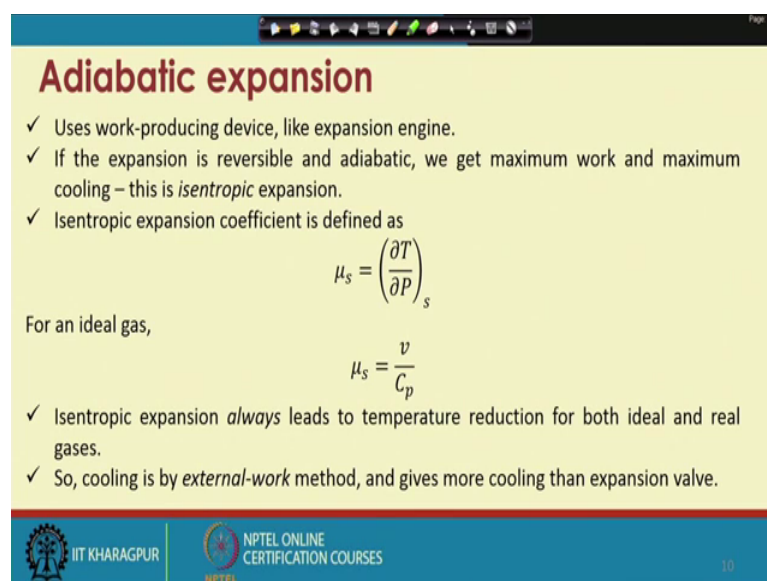
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And here we find that this maximum inversion temperature determined by from whether liquefaction of a gas can be done only with JT effect or would need pre cooling or expansion engines.

So, this is what saying that it will depend on the inversion temperature and this isenthalpic expansion works on the internal work method, that is there is no shaft work involved; that means, we cannot get any useful work that can be used for driving some other devices, which is only internally there is a work happening and this internal work is basically, that they are moving the molecules apart during the expansion and this may or may not result in cooling.

And in this particular table, we find for the different types of gases we have this maximum inversion temperature and here, we will see that like helium, hydrogen, neon this maximum temperature is less than the ambient temperature. So, for these gases we need to cool down the pre cool the gases before expanding them if you want cooling, but on the other than nitrogen, air, carbon monoxide, argon, oxygen, methane, carbon dioxide, ammonia we find there inversion maximum inversion temperatures are way above the ambient temperatures. So that means, we do not need to pre cool these gases before we take them for expansion to produce cooling. So, this is that is the importance of knowing this maximum inversion temperature.

(Refer Slide Time: 18:23)



Adiabatic expansion

- ✓ Uses work-producing device, like expansion engine.
- ✓ If the expansion is reversible and adiabatic, we get maximum work and maximum cooling – this is *isentropic* expansion.
- ✓ Isentropic expansion coefficient is defined as

$$\mu_s = \left(\frac{\partial T}{\partial P} \right)_s$$

For an ideal gas,

$$\mu_s = \frac{v}{C_p}$$

- ✓ Isentropic expansion *always* leads to temperature reduction for both ideal and real gases.
- ✓ So, cooling is by *external-work* method, and gives more cooling than expansion valve.

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Next way that is another way of producing the work is adiabatic expansion and in this adiabatic expansion produces some external work which may be used for driving some other machines. And if the expansion is reversible and adiabatic that means, it is not just adiabatic, but also reversible, in that case, we get the maximum work and then we maximize the work, we get the maximum cooling and this kind of system which is reversible and as well as adiabatic is called isentropic expansion.

So, in this case also we defined another kind of expansion coefficient that is called the isentropic expansion coefficient and it is defined in a similar manner that here, we are instead of JT are using s to represent the equal entropy before and after the expansion and here, we define in a similar fashion to μ_{JT} by $\frac{dT}{dT} \frac{dP}{dP}$ but instead of h we are writing s ; so this is a difference and it can be also derived and shown that for ideal gas this μ_s is equal to $\frac{v}{c_p}$ that is a specific volume and the specific heat.

Now, here it is something different from the Joule Thomson effect. In Joule Thomson for the ideal gases it was coming to 0, but in this case, it is nonzero and this shows that isentropic expansion will always lead to cooling, whether the gas is real or gas is ideal. It does not matter. Every time, it will be producing cooling and why because this cooling is dependent external work method, and because it is generating work, which can be used to drive some other machines and that is why the isentropic expansion will always lead to better cooling than the isenthalpic expansion valves.

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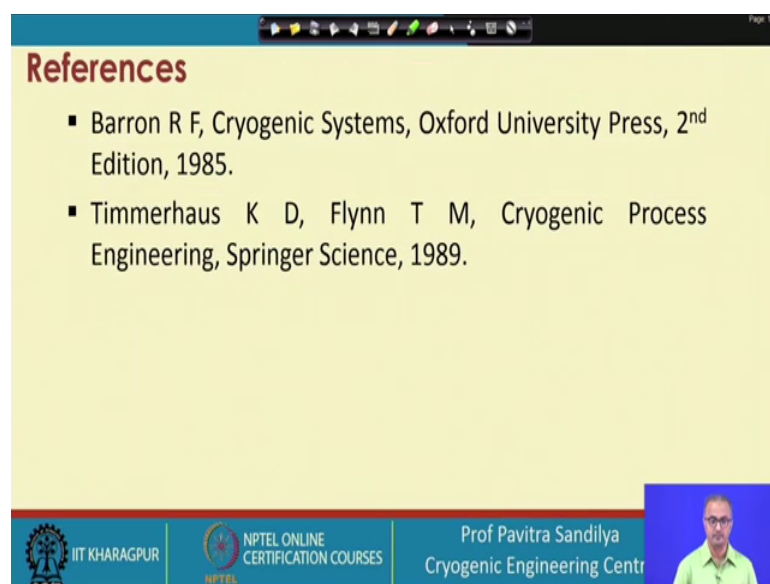
Expansion valve	Adiabatic expansion
May cool down or may heat up the gas after its expansion	Always will result in cooling of gas after its expansion
Does not change temperature for ideal gases on expansion	Ideal gases undergo cooling on expansion
Based on internal work method (no work is produced)	Based on external work method (work produced may be used to drive compressor)
Can handle two phase (vapor-liquid) fluid, and hence used for final liquefaction	Cannot handle two-phase vapor-liquid system

Now, here is a comparison between the expansion valve and the adiabatic expansion for producing the cold. First is that in this expansion valve it may cool down or it may heat up after expansion depending on whether the gas is below or above the inversion temperature, but adiabatic expansion will always lead to cooling and these does not change the temperature of ideal gas of expansion. So, ideal gases will remain the temperature will remain unchanged in ideal gases, but ideal gases undergo cooling on expansion adiabatically. Then this is based on the internal work, that is all the molecules are separated, but this is based on the external work which may be used to drive a machine for example, a compressor.

And then these can handle 2 phases; liquid and vapour phases and hence used for final liquefaction, but this adiabatic expansion is so, generally they cannot handle 2 phases even though, some standards these turbines are also being designed for handling, 2 phases in general they cannot handle 2 phases, because the turbine rotate at a very high speed. So, any kind of liquid will damage the blades of the turbine. So, that is not used. So, that is the limitation of using the adiabatic expansion for liquefaction.

So, what happens? These adiabatic expanders are generally used to pre cool the gas before it is taken for the expansion valve for isenthalpic expansion to produce the liquefaction. So, that is how these two both these types of expansion devices are used.

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References

- Barron R F, Cryogenic Systems, Oxford University Press, 2nd Edition, 1985.
- Timmerhaus K D, Flynn T M, Cryogenic Process Engineering, Springer Science, 1989.

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And these are the references, which we may refer to for further detail and the derivations of the various types of equations I have shown you in this particular lecture.

Thank you.