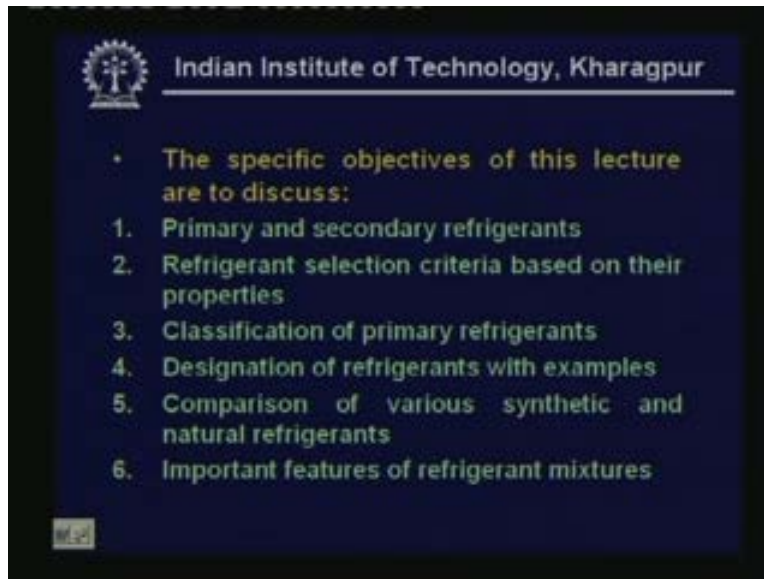


Refrigeration and Air-Conditioning
Prof. M. Ramagopal
Department of Mechanical Engineering
Indian Institute of Technology, Kharagpur
Lecture. No # 33
Refrigerants

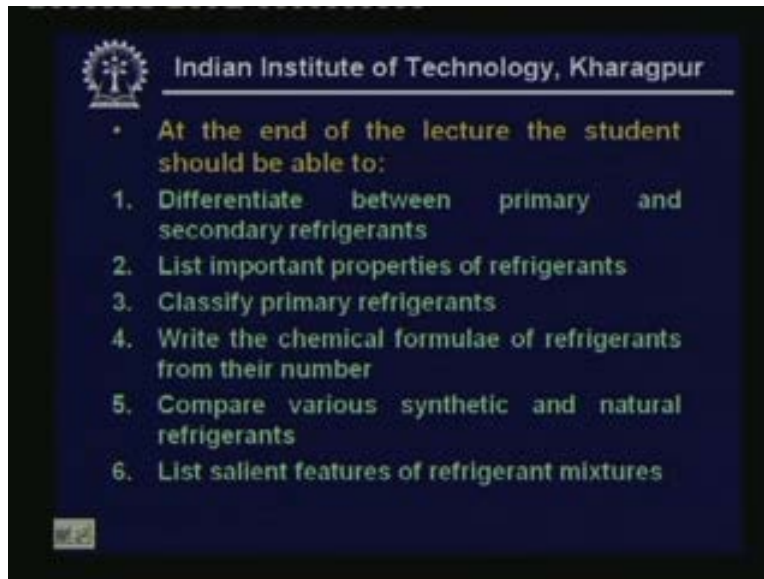
Welcome back in this lecture.

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I shall discuss refrigerants. So the specific objectives of this particular lecture are to discuss primary and secondary refrigerants, refrigerant selection criteria based on their properties, discuss classification of primary refrigerants designation of refrigerants with examples, comparison of various synthetic and natural refrigerants and finally some important features of refrigerant mixtures.

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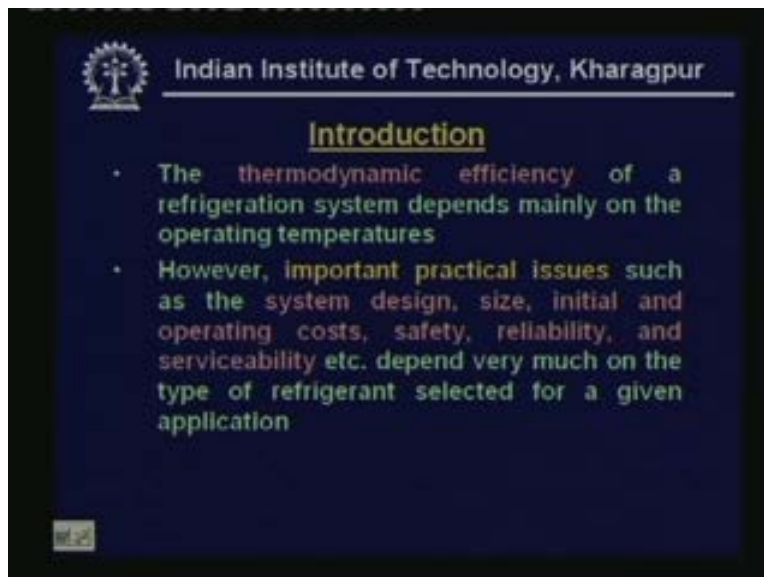


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- At the end of the lecture the student should be able to:
 1. Differentiate between primary and secondary refrigerants
 2. List important properties of refrigerants
 3. Classify primary refrigerants
 4. Write the chemical formulae of refrigerants from their number
 5. Compare various synthetic and natural refrigerants
 6. List salient features of refrigerant mixtures

At the end of the lecture you should be able to differentiate between primary and secondary refrigerants, list important properties of refrigerants, classify primary refrigerants, write the chemical formula of refrigerants from their number, compare various synthetic and natural refrigerants and list salient features of refrigerant mixtures.

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Introduction

- The thermodynamic efficiency of a refrigeration system depends mainly on the operating temperatures
- However, important practical issues such as the system design, size, initial and operating costs, safety, reliability, and serviceability etc. depend very much on the type of refrigerant selected for a given application

Let me give a brief introduction. You know that the thermodynamic efficiency of a refrigeration system depends mainly on the operating temperatures. That means the heat source and sink temperatures. However important practical issues such as the system

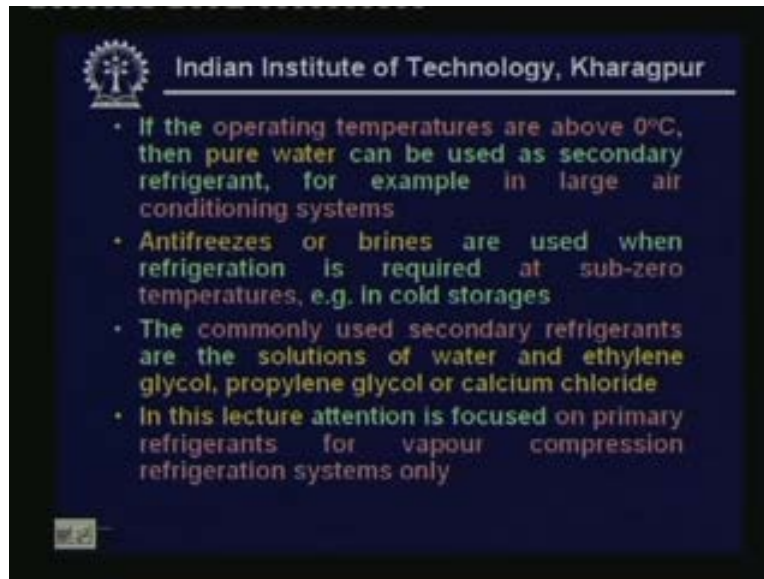
design size initial operating costs safety reliability and serviceability etcetera depend very much on the type of refrigerant selected for a given application and selection of a suitable refrigerant is a very important step in the designing of any refrigerant system okay.

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Refrigerants can be broadly divided into primary and secondary refrigerants. Primary refrigerants are used directly as working fluids. In refrigeration systems they undergo phase change while providing refrigeration. That means while flowing through the evaporator vaporization takes place and while flowing through the condenser these refrigerants condense okay. So that they involve phase change processes whereas secondary refrigerants are those liquids that are used to transfer energy from one one location to another unlike primary refrigerants these secondary refrigerants do not undergo any phase change. And water and brines are the commonly used secondary refrigerants.

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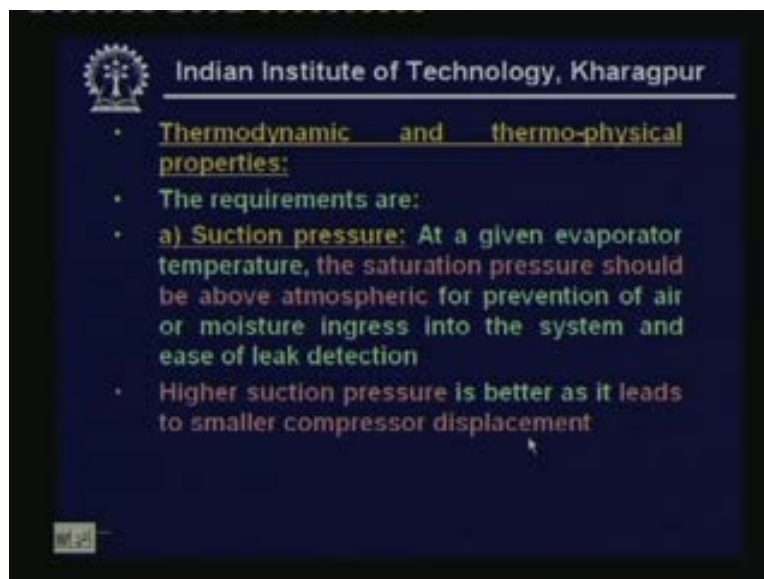
If the operating temperatures are above zero degree centigrade's. Then we can use pure water as a secondary refrigerant. For example pure water is widely used in our chilled water system for air conditioning for air applications etcetera. However if the operating temperature is below zero degree centigrade. That means for sub zero temperatures we cannot use water because water freezes at zero degree centigrade. So we have to use other secondary refrigerants namely anti freezers and brines. And these kind of applications we encounter in cold storages or other frozen food processing applications etcetera. The commonly used secondary refrigerants are the solutions of water and ethylene glycol or the solution of water and propylene glycol or the solution of water and salt such as calcium chloride etcetera. In this lecture I shall not discuss secondary refrigerants for attention is primary focused on primary refrigerants for vapour compression refrigeration systems only.

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Let us look at refrigerant selection criteria selection of refrigerant for a particular application is based on the following requirements. The first requirement is thermo dynamic and thermo-physical properties. Second requirement is environmental and safety properties and finally the third requirement is economics.

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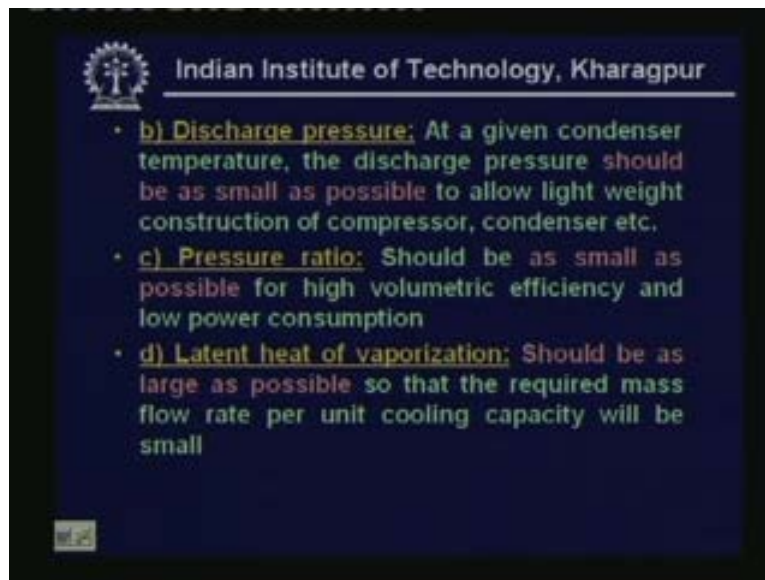


So first let us look at the first requirement. That is thermo dynamic and thermo-physical properties. The requirements are like this, first the suction pressure at a given evaporator temperature. The saturation pressure should be above atmospheric for prevention of air or moisture ingress into the system and ease of leak detection. This is an important

requirement and also for higher suction pressure is better as it leads to smaller compressor displacement. That means at a given evaporated temperature the refrigerant selected should have a positive pressure. That means the operating pressure or evaporated pressure should be above atmospheric. This is required because if there is any leakage takes place from the system to surrounding. That means refrigerant leaks out from the system okay. This is easier to handle than the reverse scale. That means the system is operating under vacuum then either moisture from outside leaks into the system okay.

This is difficult to handle. Because in order to remove the air or moisture we have to do complete over oiling of the system also if the system is operating under vacuum then the detection of leak is difficult okay. So as far as possible the refrigerant should have a positive pressure at evaporated temperature okay. Also we know that when the suction pressure is high at a given temperature. Then the density will be high or the specific volume will be low okay. That means for the given mass storage the required size of the compressor will be small okay. For these reasons the suction pressure should always be as high as possible okay, this is the first requirement.

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The second requirement discharge pressure at a given condenser temperature. The discharge pressure should be as small as possible to allow light weight construction of compressor condenser etcetera. So unlike suction pressure at a given condenser temperature discharge pressure should have a obviously be as low as possible okay. This

is because ones it is low we get maximum operating pressure of the system will be low because that is decided by the condenser pressure okay. Ones the maximum operating pressure is low means the tube stores in for the condensers and the material chosen for compressors etcetera need not be heavy weight right. That means you can go for thinner tubes etcetera okay. This reduces the cost and this reduces the weight of the system okay. So this is a very important requirement also the pressure ratio will also be small when the condenser pressure is small okay that is the third requirement. That means the pressure ratio which is nothing but the ratio to the condenser pressure to the evaporator pressure should be as small as possible for high volumetric efficiency and low power consumption. And the fourth requirement is that the latent heat of vaporization should be as large as possible. So that the required mass flow rate per unit cooling capacity will be small.

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- The above requirements are somewhat contradictory as the operating pressures, temperatures and latent heat of vaporization are related by Clausius-Clapeyron Equation:

$$\ln(P_{sat}) = -\frac{h_{fg}}{RT} + \frac{S_{fg}}{R}$$

- Since entropy of vaporization is almost constant:

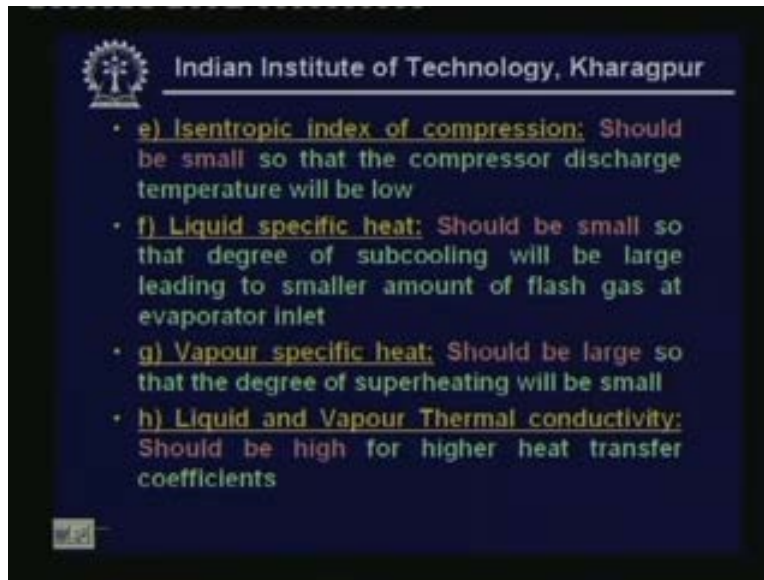
$$\frac{P_e}{P_s} = \exp\left[\frac{h_{fg}}{R}\left(\frac{1}{T_e} - \frac{1}{T_s}\right)\right]$$

However we find that the above requirements are somewhat contradictory because operating pressures temperature latent heats of vaporization are related by Clausius Clapeyron equation. And you know that Clausius Clapeyron equation that is given by this expression $\ln P_{sat}$ is equal to minus h_{fg} by RT plus S_{fg} by R where H_{fg} is the latent heat of vaporization S_{fg} is the entropy of vaporization R is the gas constant and T is the absolute temperature okay. So using this equation we find that this term that is entropy of vaporization does not really change much okay. If we assume that it is constant then you

can show that the pressure ratio. That is the condenser pressure divided by the evaporated pressure is equal to exponential $\frac{H_{fg}}{R}$ multiplied by one by T_e minus one by T_c okay. So, if that evaporator and condenser temperature are fixed. So let us say these temperatures are fixed by the application and by the available heat sink. Then you see that the pressure ratio increases as the latent heat of vaporization increases okay. That means if you want to have a refrigerant with high latent heat of vaporization the penalty you have to pay is in the in the form of high compression ratio or high pressure ratio okay.

And high pressure ratio as you know leads to low volumetric efficiency and low volumetric capacity okay. So on the other hand if you want to have very low pressure ratio then the latent heat of vaporization will be low. That means the required mass of weight for the given capacity of the refrigerant system will be high okay. That means you have to handle large amount of mass okay this is again a disadvantage okay. This shows that certain trade off is required between pressure ratio and latent heat of vaporization in other words the is required between the COP and volumetric capacity okay.

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Next comes isentropic index of compression the isentropic index of compression should be small. So that the compressor discharge temperature will be low we know that the discharge temperature is linked to isentropic index of compression by the formula. For example $T_{discharge}$ is given by $T_{suction} \left(\frac{P_c}{P_e} \right)^{\frac{\gamma - 1}{\gamma}}$

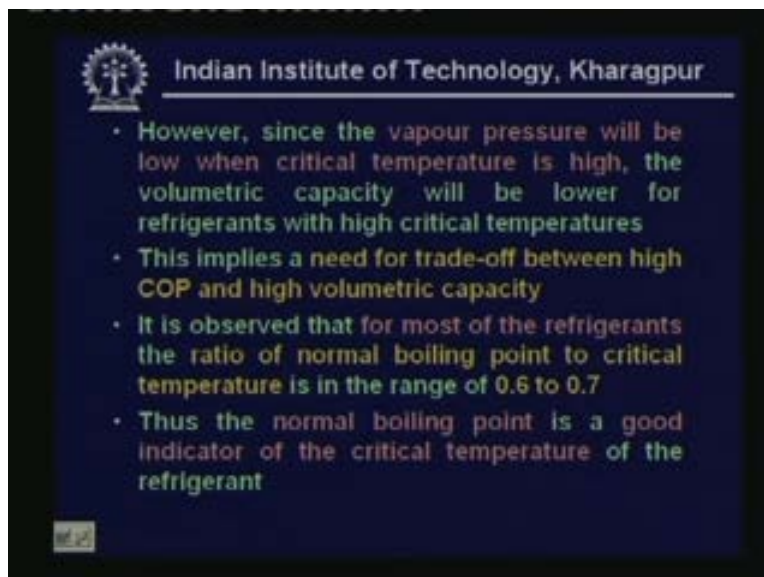
gamma this formula we have used while discussing compressors etcetera. So here gamma is isentropic index of compression. So you can see that for given pressure this compressor condenser and evaporator pressures and given suction temperatures discharge temperature increases as your index of compression increases okay. So this is not good from the compressor life point of view. So in order to have a load discharge temperature value of gamma should be as small as possible. So next requirement is the liquid specific heat liquid specific heat should be small. So that the degree of sub cooling will be large leading to smaller amount of flash gas at evaporator inlet okay, so we need small liquid specific heat.

Next vapour specific heat vapour specific heat should be large. So that the degree of super heating will be small. We know that when the degree of super heating is large the suction temperature will be high okay. Ones the suction temperature is high the density of the refrigerant and the entry to the compressor will be low. That means we require a larger compressor for a given mass per rate okay this is not really good for a particle consideration okay. So as far as vapour specific heat is concerned we should have a high value of specific heat. But the liquid specific heat should be low again you find that this is contradictory okay. It is not possible to have a very high vapour specific heat and low liquid specific heat okay. Next liquid and vapour thermal conductivity both liquid and vapour thermal conductivity should be as high as possible for higher heat transfer coefficient okay.

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Next requirement is liquid and vapour viscosity the viscosity of both liquid and vapour should be as small as possible for smaller frictional pressure drop. We find that thermodynamic properties are actually inter related and they are mainly dependent on normal boiling point critical temperature and the molecular structure. The normal boiling point indicates the useful temperature levels as it is directly related to the operating pressures okay. This is a very very important property next comes the critical temperature. So what is the effect of critical temperature if the of critical temperature is very high it yields higher COP due to smaller compressor superheat and smaller flash gas losses okay. So this is the advantage of having high critical temperature.

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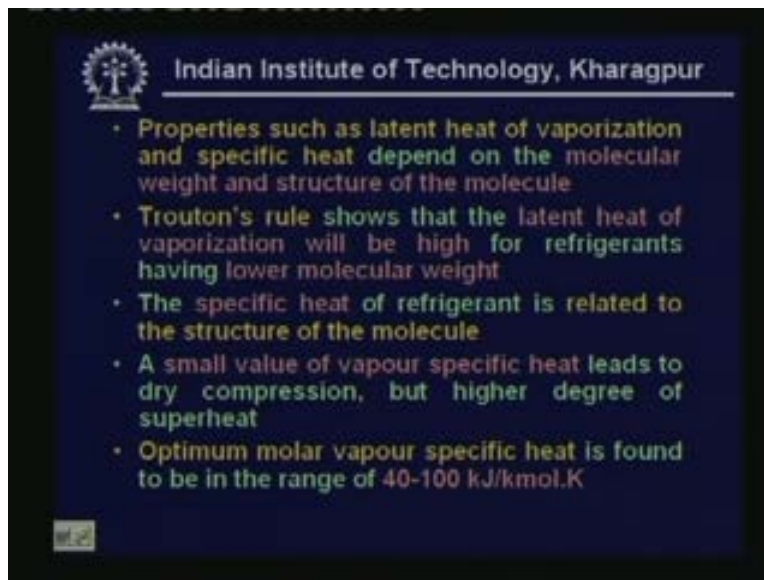
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- However, since the vapour pressure will be low when critical temperature is high, the volumetric capacity will be lower for refrigerants with high critical temperatures
- This implies a need for trade-off between high COP and high volumetric capacity
- It is observed that for most of the refrigerants the ratio of normal boiling point to critical temperature is in the range of 0.6 to 0.7
- Thus the normal boiling point is a good indicator of the critical temperature of the refrigerant

On the other hand when the critical temperature is high we find the vapour pressure will be low ones vapour pressure is low volumetric capacity will be low okay. So this is the disadvantage of having high critical temperature see you find high critical temperature gives rise to higher COP at the same it give rise to lower volumetric capacity okay. Again you have to do a tradeoff between the volumetric capacity and the COP okay. And choose the critical temperature accordingly this implies need for a trade-off between high COP and high volumetric capacity. And it is observed that for most of the refrigerants the ratio of normal boiling point to the critical temperature is in the range of point six to point seven. That means the ratio is almost constant for most of the fluids okay.

This means that the normal boiling point is also a good indicator of the critical temperature of the refrigerant. And this ratio is in the temperatures are in Kelvin okay. Only then this ratio holds good. That means we have to use absolute temperature scale okay. When we are using absolute temperature scale for the normal boiling point and the critical temperature we find that ratio is about point six to point seven okay.

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- Properties such as latent heat of vaporization and specific heat depend on the molecular weight and structure of the molecule
- Trouton's rule shows that the latent heat of vaporization will be high for refrigerants having lower molecular weight
- The specific heat of refrigerant is related to the structure of the molecule
- A small value of vapour specific heat leads to dry compression, but higher degree of superheat
- Optimum molar vapour specific heat is found to be in the range of 40-100 kJ/kmol.K

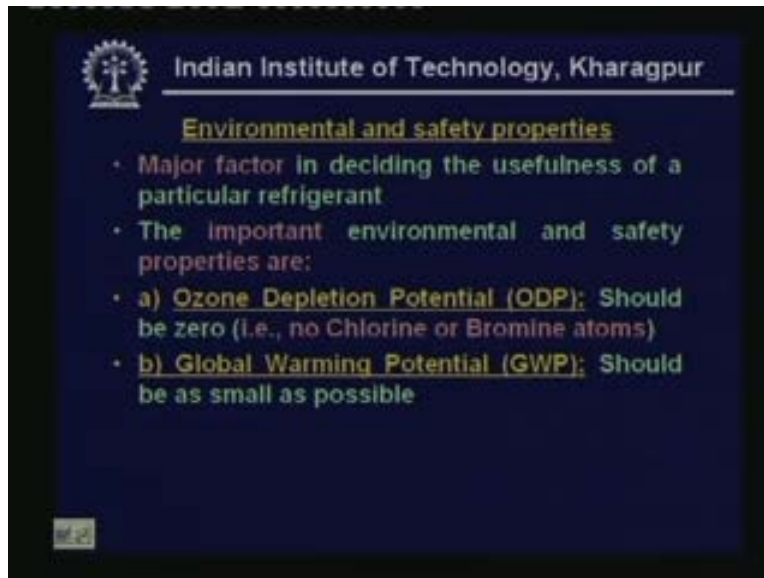
Now properties such as latent heat of vaporization and specific heat depend on the molecular weight. And structure of the molecule and Trouton's rule shows that the latent heat of vaporization will be high for refrigerants having lower molecular weight okay. We have discussed Trouton's rule when, while discussing thermodynamics okay. So according to the Trouton's rule if the molecular weight of the fluid is low. That means it

gives rise to higher latent heat of vaporization okay. This is an advantage or this is the reason why inorganic refrigerants inorganic fluids such as water and ammonia which have low molecular weight always gives rise to high latent heats of vaporization.

On the other hands synthetic refrigerants have high molecular weight. So their latent heat of vaporization is low okay. So that is how the molecular weight and latent heat of vaporization are related. Now the specific heat of the refrigerant is related to the structure of the molecule. And a small value of vapour specific heat leads to dry compression but higher degree of super heat okay. That means when you have a small specific heat for vapour when you find that when you are starting the compression if the inlet to the compression forces is in the saturated line. Then you find that exit is always in the super heated region. That means compression will always be a dry compression process okay. So this is a requirement if you are talking about reciprocating compressors and many other compressor okay. So from this point of view the low value of specific heat is good okay. But if the specific heat is low we find that the degree of super heat will be high okay this is not desirable okay. So again you have to do some kind of trade off and again you find that there is an optimum value of vapour specific heat where the performance will be best and it is also shown that specific heat of vapour is related to specific heat of liquid okay.

Normally it is not possible to have, as I have already mentioned a high value of specific heat for the vapour and a low value of specific heat for the liquid all these vice-versa okay. And it is observed that optimum molar vapour specific heat is found to be in the range of forty two hundred kilo Joule per kilo mol Kelvin okay.

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Next comes environmental and safety properties before I go to environmental and safety properties. There are also other thermodynamic properties which need to be considered. For example one of the important properties especially when we are dealing with very low temperature refrigeration is the freezing point okay. The freezing point of the fluid should be lower than the lowest temperature that you encountered while operating the refrigeration system okay. This is required otherwise the refrigerant may freeze while flowing through the system okay. So the freezing point should be as low as possible all right. Now let us look at the environmental and safety properties. This is the major factor in deciding the usefulness of a particular refrigerant normally the efficiency of the system normally depends on the thermodynamic and thermo physical refrigerant. And we have discussed the requirements right. But it is observed that the finally whether the refrigerant can be used or not is decided not only by thermo dynamical thermo and physical properties but mainly by environmental and safety issues. This is the reason why refrigerants such as carbon dioxide or ammonia sulphur dioxide which give reasonably good performance are faced out or thought to be not good because they have certain safety related problems okay.

So in especially the refrigerants used in the olden days they were good as far as the performance is concerned. But most of them used to have or used to create safety related problems okay such as toxicity etcetera. That is the reason why they were faced out that is the reason why synthetic refrigerants were invented okay. So safety related properties

are very important okay. Now let us look at what are the environmental and safety related properties these properties are the first property is ozone depletion potential the ozone depletion potential or the ODP should be zero okay. And the ODP of the refrigerant or the ODP of the fluid depends mainly on the number of chlorine or bromine atoms in the molecule okay.

If the number of chlorine, if the molecule contains chlorine or bromine atoms then it will have non zero ODP value okay. And as per its mandatory protocol we have discussed this while discussing the history of refrigerants as per mandatory protocol we cannot use any refrigerant which has non zero ODP value okay. That means all ozone depleting substances have been faced out or has to be faced out okay. So in the future the refrigerants should be off non ODP i mean non ODS. That means non ozone depleting substances okay. And the second important property is global warming potential global warming potential or GWP GWP will be it should be as small as possible. That means refrigerants having high GWP are not recommended in fact the Kyoto protocol or the mandatory protocol federal relations mated protocol.

And under the Kyoto protocol several refrigerants which have high GWP values have come under the substances to be regulated okay. Because high global warming potential means you have green house effect and we have discussed this issue also earlier. So the global warming is an environmental issue on global scale. So it is not recommended to use refrigerants having high GWP values okay. Even though there is no final decision as account of using refrigerants having high GWP values we really do not know but in future they may be faced out okay. Next is what is known as total equivalent warming index or TEWI or T E W I this is the new index. And this index takes into account the direct as well as indirect contributions of refrigerants to global warming okay. So global warming potential considers only the direct contribution of refrigerant to global warming what are the direct contributions of refrigerant when the refrigerant leaks out into the atmosphere. That means when you release a refrigerant to atmosphere what are its contribution to global warming okay. This is the considered while estimating the global warming potential okay.

But the refrigerant can also contribute indirectly to the global warming and what is the indirect contribution this indirect contribution depends upon its energy consumption

okay. If a refrigerant, if or a system using a particular refrigerant consumes higher amount of energy compared to another refrigerant. Then this particular refrigerant contributes to global warming indirectly because higher energy consumption means higher burning of coal etcetera okay. So this is the indirectly contribution of refrigerant. So these direct as well as indirect contribution of refrigerant have been taken into a single index and this index is called as total warming TEWI okay. Total warming total equivalent warming index and obviously the total equivalent warming index should be as small as possible for refrigerants okay. Next comes the toxicity obviously the refrigerant should be should non preferably be non toxic.

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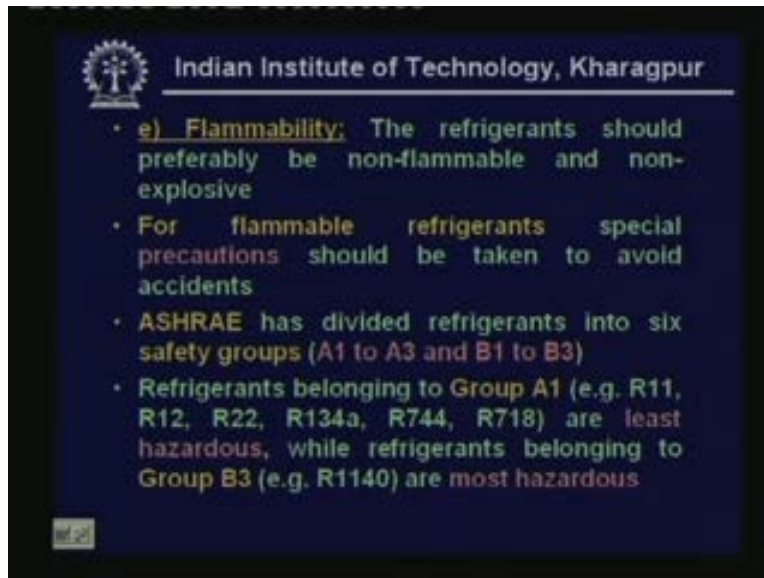
Toxicity means this is, this is related to the hazard, hazardous nature of the refrigerant as for as human beings are concerned okay. Refrigerants is toxic then if the person is exposed to such refrigerant he will be suffocated okay. So obviously the refrigerant should not be toxic toxic right but we find that toxicity is a relative term. So what do you mean by toxicity is a relative term except air all the fluids theoretically all the fluids are toxic. That means when you are exposed to all the fluids other than air in sufficiently large concentration then people will suffocate okay. So in that way all the fluids are toxic. But some of the fluids are more toxic than others okay. So how do we rate the toxicity the toxicity mainly depends upon what is the degree of concentration at which the human beings begin to get suffocated okay. So concentration is important okay. Second factor is

time of exposure okay. How long a human being has to be exposed to a particular concentration of a particular fluid. So that he will begin to get suffocated okay so these two aspects have to be considered right.

So as I said that toxicity is a relative term which becomes meaningful only when the degree of concentration and the time of exposure required to produce harmful effects are specified okay. Refrigerants such as R twelve and R twenty-two are non toxic in the presence of air. However in the presence of an open flame they decompose and release harmful gases such as phosgene okay. This is again an important issue. So if you release R twelve into atmosphere or R twenty-two into atmosphere. If there are no open flame and there are no heating elements etcetera. Then there is no problem provided. Of course if its concentration is not too high right. But if there is an open flame then the R twelve decomposes in the presence of open flame and air. And it releases very dangerous gases such as phosgene okay.

They are poisonous gases then human being is exposed to such condition then he is he will get affected drastically okay. So ultimately the toxicity depends on many other issues right the concentration and the time of exposure and the conditions right. And normally whether the particular refrigerant poses the problem of toxicity or not depends upon what is the amount of refrigerant we are using in what space okay. So if you are using a small amount of refrigerant in a large space even then if all the refrigerant is released into the space then the concentration will be small. So it will really not give rise to any serious problem. On the other hand if you are releasing large amount of refrigerant into a small volume of small space then obviously the danger will be greater okay. So as I said the amount of total refrigerant used verses space is also important.

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Next comes the flammability obviously the refrigerant should be non flammable preferably it should also be non explosive okay. But we find sometimes, we cannot word using flammable refrigerants okay. So in such cases special precautions should be taken to avoid accidents okay. So design is also different when you are using flammable refrigerant okay. So you have to make sure that there are no ignition sources okay. And also you have to take higher precaution to prevent the leakage of refrigerant okay. So basically the way you handle flammable refrigerant will be different from the way you handle non flammable refrigerant okay. And ASHRAE that is American Society for Heating Refrigerants and Air Conditioning Engineers has divided refrigerants into six safety groups and these six safety groups are A one A two A three and B one B two B three okay.

These are the six groups and refrigerants belong to group A one okay. For example R eleven R twelve R twenty-two R one thirty-four a R seven four four R seven a one eight are least hazardous while refrigerants belonging to belonging to group B three. For example R one one four zero are most hazardous okay. So if you look at if you know to what group a particular refrigerant belongs then you know whether it is really dangerous or hazardous or not okay. So these are the advantages of knowing to which group a particular refrigerant belongs okay.

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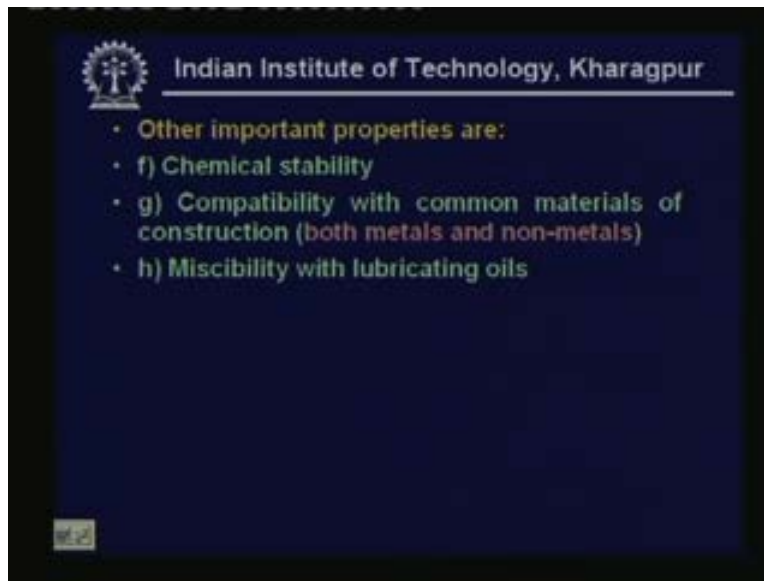
Other important properties are chemical stability okay. As far as possible the refrigerant used should be chemically stable as long as it is within the system okay. So if it is released ones it is released into the atmosphere even if it breaks down that is not a problem okay. Even aftermath of your ozone depletion it is observed that if it breaks down and when it is released to the atmosphere it is good. Because the refrigerant will not go to the stratosphere or anything but as long as the refrigerant is within the system it should not break down okay. Under any circumstances that means even if it is exposed to higher temperature. For example in the compressor okay, that means it should be chemically stable right.

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Second requirement is the compatibility with the common materials of construction. The common materials of construction are both metallic metals as well as non metals. This is a very important practical requirement the refrigerant that we use should be compatible with all materials of construction such as materials used for constructing heat exchangers various shields used in the system. Various plastics used in the system etcetera okay. It should not react with any of these materials okay.

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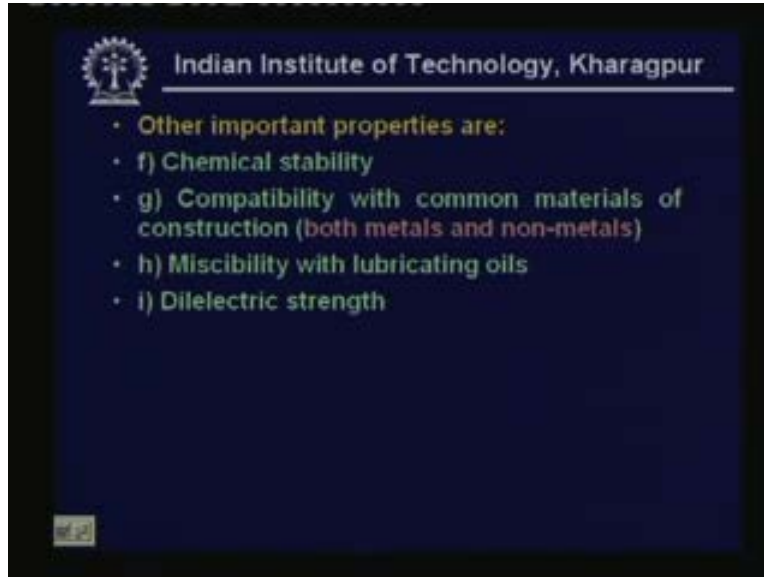


And next, miscibility with lubricating oils miscibility with lubricating oils is a very complex issue. Because it is not necessary that the refrigerant should be completely miscible with a lubricating oil okay. If a refrigerant is not at all miscible with a lubricating oil for example ammonia. Ammonia is not at all miscible with lubricating oil then what we have to do is install an oil separator at the exit of the compressor. So that you can collect oil from the refrigerant vapour and send it back to the compressor okay. so that the oil does not circulate through the system all right.

On the other hand if you have a refrigerant such as R twelve which is completely miscible in the refrigerant then also it is no problem. Because since it is miscible oil is miscible with refrigerant oil will circulate along with the refrigerant. And if you take care of design of the evaporator tubes etcetera then the oil will come back to the compressor okay. So in principle there is no problem with refrigerant which are completely miscible and which are not completely miscible okay. But the problem comes with refrigerants

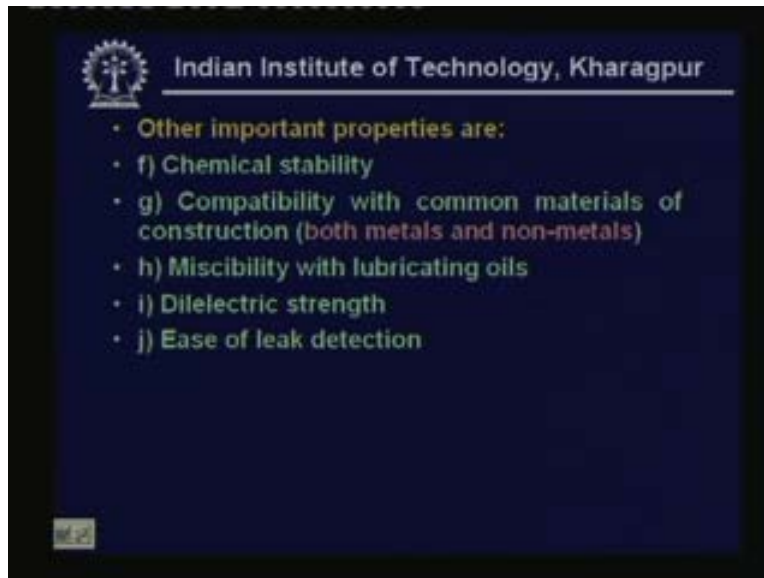
which are partially miscible okay. Partially miscible refrigerants such as R twenty-two you have to take extra care to make sure that the lubricating oil is coming back to the compressor okay. So you must know the relationship between the lubricating oil and the refrigerant okay. So this has the bearing on the design of the system.

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Then dielectric strength dielectric strength is very important in systems using hermetic compressors. We know that in hermetic compressors the refrigerant comes in contact with the winding electric winding of the motor okay. So the dielectric strength of the refrigerant should be high. So that it will not break down okay. This is not very important when you are talking about open type of compressors okay.


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Next important practical property is the ease of leak detection okay. If the refrigerant leaks out of the system you should be able to detect it immediately using some means okay. If you are not able to detect the leak then you do not know that refrigerant is leaking out of the system okay. What happens if the refrigerant is leaking out of the system and if you are not able to detect it first effect you see is that performance of the refrigerant system gets affected okay. And second problem is that it may lead to other problems like suffocation etcetera. And third problem is that you cannot take, if you know there is a leakage immediately you can take some preventive some measure.

So that before it is too late you can correct the problem. On the other hand if you cannot detect the leak then all the refrigerants leak out and that may lead to major over oiling of the system okay. So the refrigerant used should be such that you must be able to detect its leak okay. There are various methods of detecting leak of a refrigerant okay. For example if you are using ammonia then you do not need anything because your nose itself is the best leak detector because ammonia has a very strong odor. So immediately you know that it is leaked out okay. On the other hand some of the refrigerants such as R twelve R one thirty-four etcetera. You have to use some special leak detectors okay. Like detectors electronic leak detectors etcetera to detect the leak okay. So this is again an important practical requirement.

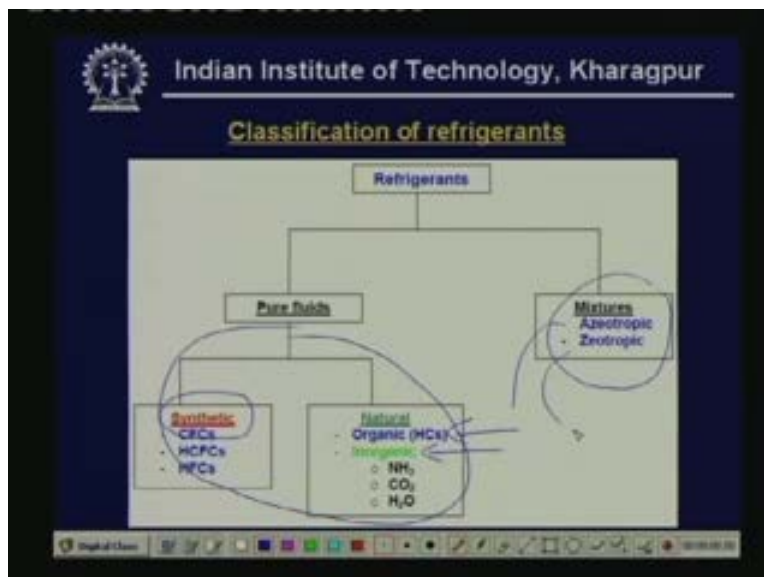
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- Other important properties are:
- f) Chemical stability
- g) Compatibility with common materials of construction (both metals and non-metals)
- h) Miscibility with lubricating oils
- i) Dielectric strength
- j) Ease of leak detection
- Important economic properties are:
- A) Refrigerant cost
- B) Availability

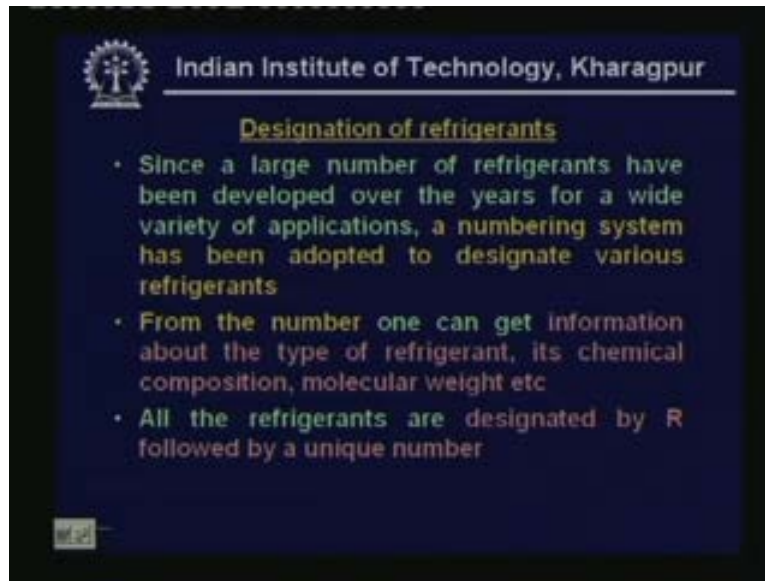
Then what are the important economic properties? Important economic properties are obviously the refrigerant cost it should be as cheap as possible. So that your initial cost will be low and it should be easily available okay. So availability is also an important practical issue right. So these are the important properties which decide the selection of a particular refrigerant for a given application okay. There are so many requirements and then ideal refrigerants should meet all these requirements, all these requirements okay. But you find that in practice there is nothing like an ideal refrigerant. So do not have an ideal refrigerant at all okay. So you always have to balance between various requirements and ultimately you do some kind of optimization and select a suitable refrigerant okay.

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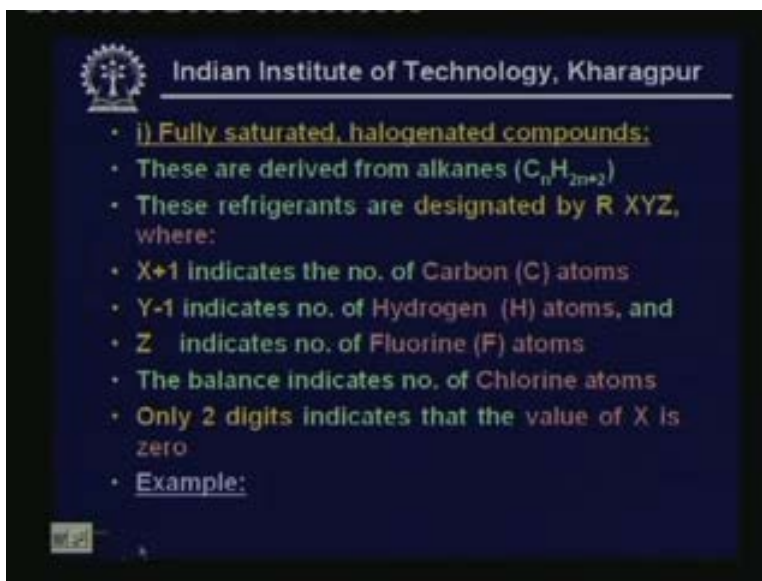
So let us look at the classification of refrigerants. Refrigerants can be broadly classified into pure fluids and mixtures okay. So under pure fluids again you can have synthetic refrigerants okay, for example chlorofluorocarbons CFC hydrochloroflouro carbons HCFC or hydro fluoro carbons these are synthetic pure fluids okay. You can also have natural refrigerants again natural refrigerants can be organic. That means they are typically hydro carbons or inorganic. Inorganic means you have ammonia carbon dioxide or water sulphur dioxide etcetera okay. So all these are pure fluids okay. Under mixtures you have azeotropic mixtures and you have zeotropic mixtures okay. So this is how you can broadly classified refrigerants.

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Now let us look at designation of refrigerants. Since a large number of refrigerants have been developed over a years for a wide variety of applications a numbering system has been adopted to designate various refrigerants okay. There are, in fact hundreds of refrigerants which are used for wide variety of applications okay. So it is very difficult to identify them all to designate by the chemical composition or anything okay. So as a result people have device a numbering system. So if you look at the number or you know the number of a refrigerant then you can get some very useful information regarding the refrigerant okay. So from the number one can get information about the type of refrigerant its chemical composition molecular weight etcetera. All the refrigerants are designated by a R followed by a unique number.

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- i) Fully saturated, halogenated compounds;
- These are derived from alkanes (C_nH_{2n+2})
- These refrigerants are designated by R XYZ, where:
- X+1 indicates the no. of Carbon (C) atoms
- Y-1 indicates no. of Hydrogen (H) atoms, and
- Z indicates no. of Fluorine (F) atoms
- The balance indicates no. of Chlorine atoms
- Only 2 digits indicates that the value of X is zero
- Example:

So first let us look at fully saturated halogenated components. So these are derived from alkanes. Alkanes you know have the general formula C_nH_{2n+2} . And examples for alkanes are for example methane okay. As we said we were fully saturated halogenated components that means they are derivatives of either methane okay, ethane, propane etcetera okay. So what do you mean by halogenated? what is done here is hydrogen atom if partially or fully replaced by other atoms for example chlorine fluorine bromine etcetera okay. And always the formula will be something like this. That means if you look at the total number of atoms in the molecule you will find that it is equal to $n + 2$ okay. So these are fully saturated halogenated compounds okay.

These refrigerants are designated by R XYZ okay, where XYZ are numbers okay. Where X plus one indicates the number of carbon atoms Y minus one indicates number of hydrogen atoms and Z indicates number of fluorine atoms and the balance indicates number of chlorine atoms okay. If there are only two digits that means the value of X is zero. That means if you have R twelve there are X in XYZ if you have R twelve okay. That means X is equal to zero okay, let me give an example.

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- Ex: R 22
- $X = 0 \Rightarrow$ No. of C atoms = $0+1 = 1 \Rightarrow$ derivative of methane (CH_4)
- $Y = 2 \Rightarrow$ No. of Hydrogen atoms = $2-1 = 1$
- $Z = 2 \Rightarrow$ No. of Fluorine atoms = 2
- The balance = $4 - \text{no. of (H+F) atoms} = 4-1-2 = 1 \Rightarrow$ No. of Chlorine atoms = 1
- \therefore The chemical formula of R 22 = CHClF_2
- Similarly it can be shown that the chemical formula of:
- R12 = CCl_2F_2
- R134a = $\text{C}_2\text{H}_2\text{F}_4$ (derivative of ethane)
etc.

Let us say that the number is R twenty-two there are only two numbers. That means X is equal to zero okay, X is zero means number of carbon atoms is zero plus one that is equal to one okay. Number of carbon atoms is one means this refrigerant that it is the derivative of methane okay that means it will have a formula like CH four okay. Next Y is equal to two that means number of hydrogen atoms is equal to two minus one that is one okay. Next Z is equal to two okay. So hope you are getting this you are saying R twenty-two here X this is nothing but R XYZ okay. Since there are only two numbers, so this is will be R zero two two okay. Zero is a number is nothing but X zero is omitted.

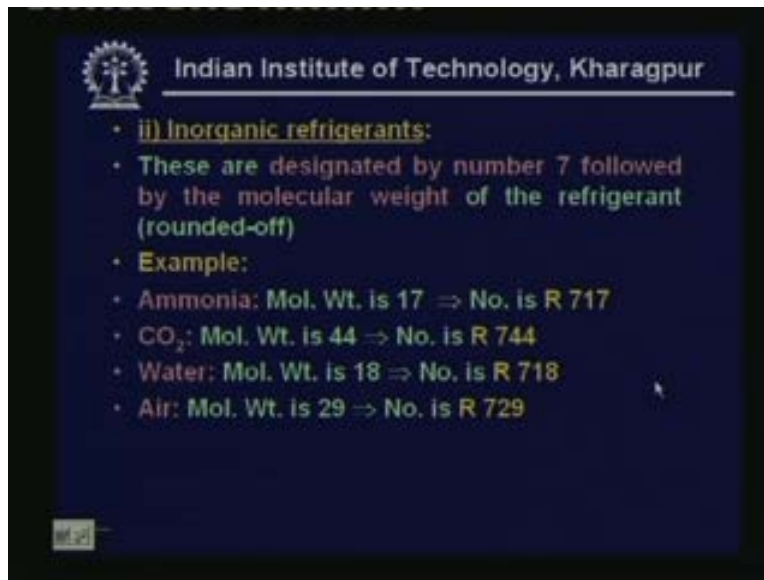
So we are simply showing it as R twenty-two okay so X equal to zero Y is equal to two and Z is equal to two okay. So from the general formula you find that X is Y is two means number of hydrogen atoms is one and Z is two means number of fluorine atoms equal to two and balance. What are the balance? There are there should be four hydrogen atoms. That means balance is four minus number of hydrogen atoms plus fluorine atoms okay? So here number of hydrogen atoms is one and number of fluorine atoms is two. So the balance is four minus one minus two that is one okay so number of chlorine atoms is one okay. So that means this particular refrigerant R twenty-two will have one carbon atom one hydrogen atom two fluorine atoms and one chlorine atom.

So that means its chemical formula is CHClF_2 okay. So it is very easy ones. You know the basic rule then just by looking at the number you can get its chemical composition okay. This is the advantage of dividing in this kind of number system okay.

So using the same rule you can show that for example the formula of R twelve is CCl₂F₂. That means it is a chlorofluoro carbon and chemical composition of R one thirty-four a is C₂H₂F₄ okay. This is the derivative of ethane because you have two atoms of carbon okay. Here a stands for example R one thirty-four a okay. The letter a stands for an isomer that means you can have a refrigerant R one thirty-four and a refrigerant R one thirty-four a okay. Both R one thirty-four and R one thirty-four a have same chemical composition but different atomic arrangement okay. That means the arrangements of atoms will be different.

So the molecule weight and chemical composition everything will be same but the atomic arrangement will be different and such kind of molecules is called as isomers okay. You know that they are called as isomers and because of different molecular arrangements they give different properties okay.

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The slide features the IIT Kharagpur logo and name at the top. It lists the following information:

- ii) Inorganic refrigerants:
- These are designated by number 7 followed by the molecular weight of the refrigerant (rounded-off)
- Example:
- Ammonia: Mol. Wt. is 17 ⇒ No. is R 717
- CO₂: Mol. Wt. is 44 ⇒ No. is R 744
- Water: Mol. Wt. is 18 ⇒ No. is R 718
- Air: Mol. Wt. is 29 ⇒ No. is R 729

Next comes your inorganic refrigerants. These are designated by number seven followed by the molecular weight of the refrigerant okay. The molecular weight is rounded-off for example ammonia. Ammonia has a molecular weight of seventeen. So its number is R seven one seven okay the seven shows that it is a inorganic refrigerant okay. Similarly carbon dioxide CO₂ its molecular weight is forty four. So its number is R seven four four water water molecular weight is eighteen. So its number is R seven one eight okay. So that means the last two digits shows its molecular weight air has a molecular weight of

twenty-nine. So its number is R seven two nine. Similarly sulphur dioxide for example its molecular weight is sixty four. So its number is R seven six four okay.

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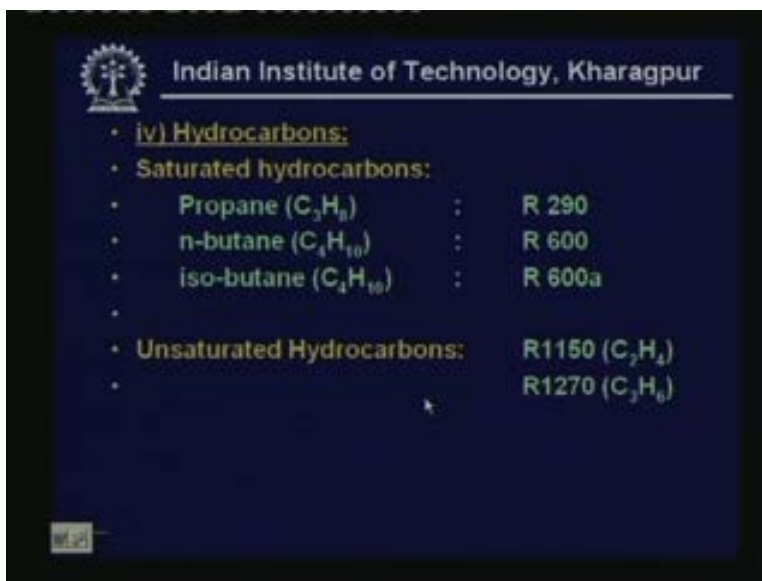


Next third category is mixtures all azeotropic mixtures come under five hundred series that means R five hundred R five hundred one R five hundred two etcetera okay. So letters five or five hundred series means that it is a mixture and it is an azeotropic mixture okay. All zeotropic mixtures have been given four hundred series okay. That means R four not four four not seven for ten etcetera okay. Let me give an example azeotropic mixtures R five hundred this is a mixture of R twelve and R one fifty two a okay. Of course looking at the number five hundred you cannot say that it is a mixture of what but you all that you can say that it is an azeotropic mixture. Because it starts with five okay, you cannot say its composition or its weight percent or anything okay.

Similarly R five not two is a mixture of R twenty-two and R one one five okay. Here this is weight percent for example R five not two R twenty-two has forty eight point eight percent by weight and R one one five its fifty one point two percent by weight. Next comes zeotropic mixtures, say, for example R four not four A again the letter four. That means the four hundred series. That means it is a zeotropic mixture it is a mixture of R one twenty-five R one forty three a and R one thirty-four okay. Here the letter A that means the capital letter A does not mean that it is an isomer okay. To distinguish between isomer and others. If you find that it is a small letter a or b or okay. Small letters a b

etcetera indicate isomers okay where as capital letter A means it's a mixture okay. Then you can again have R four naught seven A it is a mixture of R thirty-two R one thirty five and R one thirty-four a.

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(iv) Hydrocarbons:		
Saturated hydrocarbons:		
Propane (C ₃ H ₈)	:	R 290
n-butane (C ₄ H ₁₀)	:	R 600
iso-butane (C ₄ H ₁₀)	:	R 600a
Unsaturated Hydrocarbons:		
		R1150 (C ₂ H ₄)
		R1270 (C ₃ H ₆)

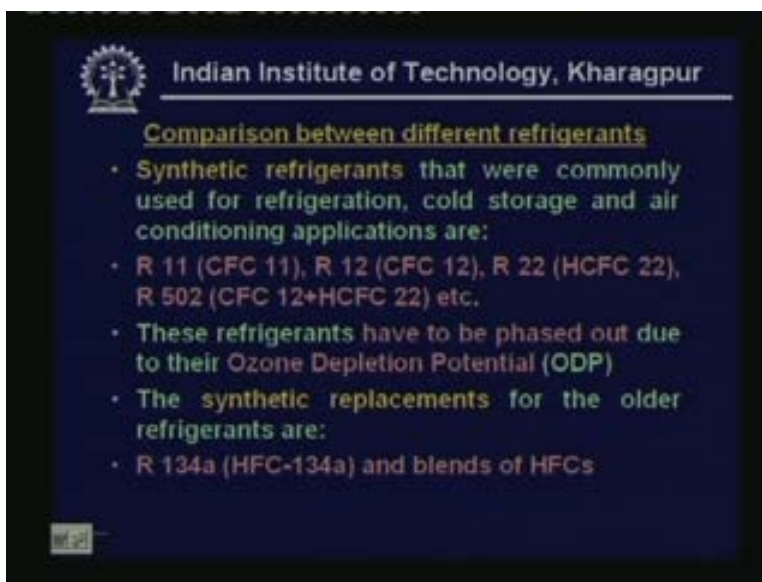
So last category is hydrocarbons, saturated hydrocarbons, for example propane okay. Propane is as you know it has a formula chemical formula of C three H eight. See you can apply the same rule that you have applied for fully halogenated hydrocarbons. And you can show that its number is R two nine zero okay. Because here the number of carbon atoms is three. So this two is, you have two here. So X is two right X is two means number of carbon atoms is two plus one that is three okay. And Y is nine here that means number of hydrogen atoms is nine minus one that is eight okay. Here Z is zero that means it does not consist of any fluorine atoms okay. Since this is balanced you do not have any chlorine atoms also okay. So propane follows the rule given earlier.

But problem comes when you have to give a number first n-butane. For example n-butane has a chemical formula of C four H ten okay. So you cannot give the, you cannot apply the earlier rule because if you are applying the earlier rule. You find that number of hydrogen atoms is ten. So the Y value will be eleven okay. So the Y value will be eleven means it has two digits okay. So that leads to confusion. So as a result this n-butane has been given a arbitrary number that is R six hundred okay. Similarly you have iso-butane.

Iso-butane also an isomer of butane and its chemical composition is same as n-butane. That is, it is C four H ten and it is given a number R six hundred a okay.

Again here the small letter a means it's an isomer okay. You can also have unsaturated hydrocarbons for example R one one five zero okay. Here it is four digits unlike other refrigerants you have four digits here four digits indicates that it is an unsaturated hydrocarbon okay. So the first digit one stands for means that it is an unsaturated hydrocarbon and the other letters you can again apply the rule and you can get the chemical composition. For example second letter one means that number of carbon atoms are two third letter Y means that number of hydrogen atoms are four okay. Fourth letter zero means that number of fluorine atoms are zero okay. Similarly R one two seven zero okay this is C three H six that is it is propylene okay.

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So that is how the numbering system is being used and this is the, you have to keep this in mind. So that you can ones, you know the number; you can immediately nobody when you talk about refrigerant. Normally we designated in terms of numbers only because chemical formula or chemical names are very long okay. And always so mentioning in terms of chemical names can be confusing okay.

Next let us look at comparison between different refrigerants synthetic refrigerants okay. Synthetic refrigerants that were commonly used for refrigeration cold storage and air-conditioning applications are R eleven it is a CFC eleven chlorofluoro carbon R twelve.

That means CFC twelve R twenty-two HCFC that is hydro chlorofluoro carbon twenty-two R five not two is an azeotropic mixture of CFC twelve CFC twenty-two. I am sorry, okay. There is a mix mistake here R five not two is a mixture of CFC twenty-two and CFC one one five okay. Then these were used very widely but these refrigerant have to be faced out due to the ozone depleting potential. That means all these refrigerants have non-zero ODP values okay. So due to this Montreal proto protocol all these refrigerants were already faced out or they have to be faced out okay.

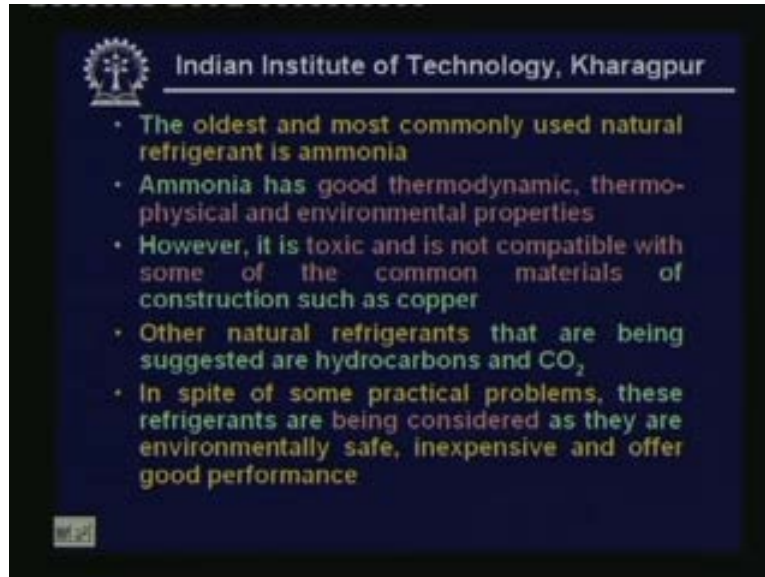
The synthetic replacements for the older refrigerants are R one thirty-four a, this is HFC. That means it is a hydrofluoro carbon. It does not contain chlorine okay. So its ODP value is zero. So it can be used right. So this is one of the synthetic replacements for the older refrigerants in addition to that various blends of hydro fluoro carbons are also being used as synthetic replacements.

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Generally synthetic refrigerants are non-toxic non-flammable and are compatible with various materials of construction. These are the main advantages of synthetic refrigerants. However compared to the natural refrigerants these synthetic refrigerants offer lowered performance and they also have higher global warming potential okay. Normally we find that COP COP values are much lower than the natural refrigerants okay. That means the efficiencies are lower okay, also thermo physical properties are also not as good as that of the natural refrigerants okay. And in addition to this they also possess high global


warming potential okay. As a result all the synthetic refrigerants face an uncertain future okay. Even though right now there is no ban on them we do not know in future they may be banned okay, they may be faced out okay.

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The oldest and most commonly used natural refrigerant is ammonia okay. It is more than hundred year old and it is still being used very widely ammonia has excellent thermodynamic thermo physical and environmental properties. It is in-expensive, it is easily available. However it is toxic and it is not compatible with some of the common materials of construction such as copper or brass okay. These are the disadvantages of ammonia okay. Toxicity incompatibility with common materials it can also be flammable under certain curve condition. Other natural refrigerants that are being suggested are hydrocarbons and carbon-di-oxide okay. Hydrocarbons and carbon dioxide are used in the olden days okay. So remember our lecture on history of refrigerants these were very widely used in the early days of refrigeration okay. But later they were faced out because of some perceive problems such as flammability and high critical low critical temperature etcetera okay. But they have made a excellent strong come back because of its thermodynamic and thermo physical properties and mainly because of their environmental friendly nature okay. So in spite as said in spite of some practical problems these refrigerants are being considered as they are environmentally safe inexpensive and offers good performance.

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Commonly used refrigerants & their properties

Refrigerant	Application	Substitute suggested Retrofit(R)/New (N)
R 11(CFC) NBP = 23.7°C h_g at NBP=162.5 kJ/kg T_c = 157.98°C C _p /C _v = 1.13 ODP = 1.0 GWP = 3500	Large air conditioning systems Industrial heat pumps As foam blowing agent	R 123 (R,N) R 141b (N) R 245fa (N) n-pentane (R,N)
R 12 (CFC) NBP = -29.8°C h_g at NBP=165.8 kJ/kg T_c = 112.04°C C _p /C _v = 1.125 ODP = 1.0 GWP = 7300	Domestic refrigerators Small air conditioners Water coolers Small-cold storages	R 22 (R,N) R 134a (R,N) R 227ea (N) R 401A, R 401B (R,N) R 411A, R 411B (R,N) R 717 (N)


Now let me show some commonly used refrigerants and their salient features and properties okay. So first refrigerant is R eleven R eleven is a chlorofluoro carbon okay. If it is a CFC right. It has a normal boiling point of twenty three point seven degree centigrade. Since its normal boiling point is quite high. That means it is twenty three point seven degree centigrade that means its operating pressure will be low. That means we want to use it for air conditioning applications say seven degree evaporator temperature. That means evaporator will be operating at under vacuum condition. That means the pressure will be sub atmospheric okay. So this is a disadvantage of R eleven okay. And the specific volume of the refrigerant will be very high because of pressures are low okay. So these are the two disadvantages of this particular refrigerant.

However since it has other advantages, this is still used and it is mainly used along with centrifugal compressors okay. It is used with centrifugal compressors because of its high specific volume okay. And its latent heat of vaporization as normal boiling point is one eighty two point five kilo joule per kg. Its critical temperature is almost one ninety eight degree centigrade which is good and its synthetic index of compression is around one point one three okay. And its ODP is one and its GWP is three thousand five hundred okay. Since its ODP is one this is banned okay its ozone depleting substance right. So it is no longer used. And what were its applications its applications were in large air

conditioning systems in industrial heat pumps. Because of its high critical temperature and it is also used very widely as a foam blowing agent in polyethylene foams etcetera. Since it is phased out, substitutes suggested in its place are R-123 and R-133. It can be used in older level systems or in new systems also okay. That means it can be retrofitted and also be used in new systems. Then R-141b, R-245fa and n-pentane okay. Mainly R-141b and n-pentane are used as foam blowing agents in place of R-11 okay. Next you have R-12, another very popular refrigerant, this is also a chlorofluoro carbon. It has a low normal boiling point of minus twenty-nine point eight degrees centigrade. That means its evaporator pressure will be higher than atmospheric if its evaporating temperatures are above almost minus thirty degrees centigrade. Its latent heat of vaporization is one hundred and twenty-four point eight, critical temperature also high, and its Cp/Cv value is one point.

One major problem is it is also having high ODP that means ODP is one and GWP is also very high. So this is also banned okay. And before banned it was widely used in domestic refrigerators, small air-conditioners, water coolers, and small cold storages. Since it has to be phased out, replacements have to be found for it, the most popular replacements for this is R-134a in domestic refrigerators, in small water coolers, air conditioners etcetera. And blends of hydrocarbons okay. In addition to this, there are other refrigerant replacements also shown here like R-22, R-290 etcetera okay.

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Refrigerant	Application	Substitute suggested Retrofit/New (N)
R 22 (HCFC) NBP = -40.8°C h_{fg} at NBP=233.2 kJ/kg T_c = 96.02°C C_p/C_v = 1.166 ODP = 0.05 GWP = 1500	Air conditioning systems Cold storages	R 410A, R 410B (N) R 417A (R,N) R 422C (R,N) R 507, R 507A (R,N) R 409A (R,N) R 717 (N)
R 134a (HFC) NBP = -26.1°C h_{fg} at NBP=222.5 kJ/kg T_c = 101.06°C C_p/C_v = 1.102 ODP = 0.0 GWP = 1200	Used as replacement for R 22 in domestic refrigerators, water coolers, automobile A/Cs etc R12	No replacement required * Immiscible in mineral oils * Highly hygroscopic

Next is R twenty-two this is a hydro fluorochloro carbon. This is another widely used refrigerant and it has a boiling point of minus forty point eight degree centigrade and it also has a relatively high latent heat of vaporization of two thirty-two point two kilo joule per kg but it has a lower critical temperature of ninety-six point zero two centigrade compared to R twelve and its C_p by C_v value is also relatively higher. So that means its discharge temperature will be high and its ODP value is non-zero but it is quite low okay. So it has a ODP value of point zero five. So it is also substance which has to be faced out. But unlike R twelve and R eleven some time is allot for this for faced out for facing out okay. So you can use it till almost twenty thirty okay so you can still use it.

It also has a global warming potential and it is mainly used in air conditioning systems and cold storages okay. And since it also has to be faced out some substitute has to be has to be found okay. Again these are the major substitutes you can see that according to our number numbering system. All these four ten four ten A four ten B four seventeen etcetera are zeotropic refrigerant mixtures okay. Whereas five not seven five not seven are azeotropic refrigerants okay. And you can also replace R twenty by ammonia that is R seven one seven but not as a retrofit of a news new system okay. Another important refrigerant is R one thirty-four a, this is hydro fluoro carbon.

Its properties are almost closest to R twelve okay. It has normal boiling point of minus twenty six point one five degree centigrade. Its latent heat of vaporization is good critical temperature etcetera also shown here and it is mainly used as a replacement for R twelve

in domestic refrigerators water coolers automobile air conditioning systems etcetera okay. No replacement is required as it because its ODP value is zero okay. There are some problems with this the problems are it is immiscible with mineral oils. So you cannot use mineral oils for lubricants. So you have to use synthetic lubricating oils and it is also highly hygroscopic.

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Refrigerant	Application	Substitute suggested Retrofit/R/View (N)
R 717 (NH₃) NBP = -33.35°C h _{fg} at NBP = 1351.5 kJ/kg T _c = 133.8°C Cp/Cv = 1.31 ODP = 0.0 GWP = 0.0	Cold storages Ice plants Food processing Frozen food cabinets	No replacement required * Toxic and flammable * Incompatible with copper * Highly efficient * Inexpensive and available
R 744 (CO₂) NBP = -78.4°C h _{fg} at 40°C = 321.3 kJ/kg T _c = 31.1°C Cp/Cv = 1.2 ODP = 0.0 GWP = 1.0	Cold storages Air conditioning systems Simultaneous cooling and heating (Transcritical cycle)	No replacement required * Very low critical temperature * Eco-friendly * Inexpensive and available

Next comes refrigerant ammonia R seven one say seven and its normal boiling point is almost minus thirty three degree centigrade. It has a very high latent heat of vaporization at normal boiling point because of its low molecular weight okay. Its critical temperature also quite high. Its Cp by Cv value is high which is a disadvantage. So you have to use water cool compressors to keep the compressor temperature low okay. Its excellent aspect is its environment friendly is concerned because its ODP is zero GWP is also zero its major applications are in cold storages ice plants in food processing and in frozen food cabinets etcetera okay. It do not require any replacements for this some problems are, it is toxic and flammable and is incompatible with copper and brass advantages are it is highly efficient and its inexpensive and widely available. Next comes R seven four four this is carbon dioxide.

It has a very low normal boiling point of minus seventy-eight point four degree centigrade. But still its freezing point is about minus fifty degree or sixty degree centigrade. So you cannot use it temperatures below minus fifty sixty degree centigrade

because its freezing point okay. And it also has good latent heat of vaporization major problem with this is its critical temperature is very low okay. That is the reason why it was faced out but alternate cycles have been devised that is trans critical cycle where the condensation process is replaced by gas cooling process. And this has made a strong comeback because of this reason that means because of the modification of cycle okay. And other important properties are it has low ODP and it also has it has non zero ODP okay sorry and it also has very low GWP okay. And its major applications are in cold storages. In air conditioning systems in simultaneous cooling and heating if you are using trans critical cycle. We do not need any replacements and its major disadvantages are low critical temperature and high operating pressures okay. I did not mention it but its operating pressures are very high and it is eco friendly and it is inexpensive and easily available.

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Refrigerant	Application	Substitute suggested Retrofit(R)/New (N)
R718 (H_2O) NEP = $100^\circ C$ h_g at NEP = 2257.9 kJ/kg $T_c = 374.15^\circ C$ $C_p/C_v = 1.33$ ODP = 0.0 GWP = 1.0	Absorption systems Steam jet systems HC	No replacement required * High NEP * High freezing point * Large specific volume * Eco-friendly * Inexpensive and available
R600a (iso-butane) NEP = $-11.7^\circ C$ h_g at NEP = 367.7 kJ/kg $T_c = 135.0^\circ C$ $C_p/C_v = 1.086$ ODP = 0.0 GWP = 3.0	Replacement for R 12 Domestic refrigerators Water coolers	No replacement required * Flammable * Eco-friendly

Next okay, next is water that is R seven one eight major problem with water. Its high normal boiling point hundred degree centigrade okay. That means your operating pressures will be under high vacuum okay. It is a, it is since, it is having low molecular weight. Its latent heat of vaporization is very high. It is an excellent its critical temperature also very high its very good the problem. Of course in C_p by C_v value is high. It is perfectly environmental friendly because its ODP is zero and GWP is very low and its major applications are as refrigerants in absorption system and as refrigerants in

steam jets systems okay. And its features are, you do not require any replacements because of its excellent environmental properties its disadvantage is high normal boiling point okay, and high freezing point.

So you cannot use for sub zero temperatures large specific volume. So you cannot use reciprocating compressors or anything with this large specific volume is because you are operating the system at very low pressures its main advantages are eco friendliness inexpensive and availability. Next is R six hundred a which is iso-butane is a hydrocarbon okay. So its normal boiling point is minus eleven point seven three degree centigrade. Its latent heat of vaporization is reasonably high. Its critical temperature is very high Cp by Cv value is low. Its good its ODP is zero. So it is safe as far as ozone depletion is concerned its GWP also very low okay. So this is used as a replacement for R twelve in new systems you have to change the compressor in domestic refrigerators water coolers etcetera okay. Its features are, we do not require any replacements its main problem or main concern is it is highly flammable and its main advantage is it is eco friendly okay.

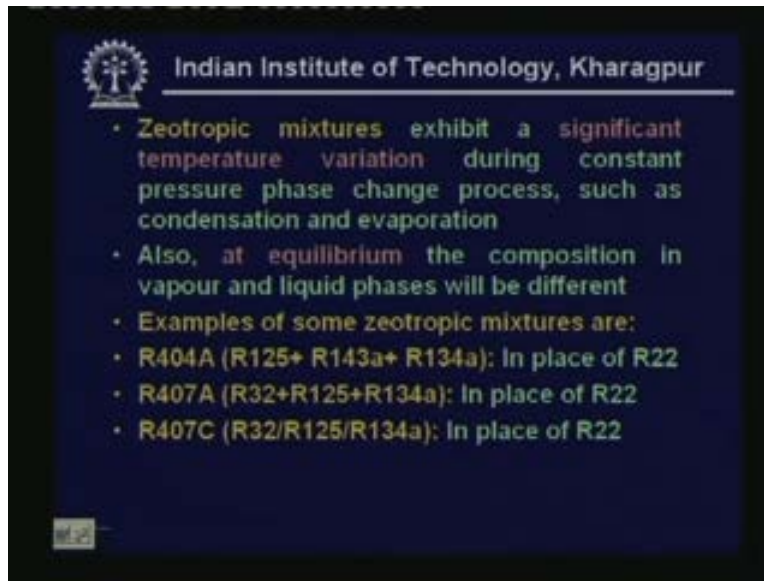
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So these, this table is not actually comprehensive. Because there are many other refrigerants with many other features and many other problems also okay. Now let us briefly look at refrigerant mixtures refrigerant mixtures are mixtures of two or more refrigerant fluids the refrigerant mixtures can be divided into as I said azeotropic

mixtures zeotropic mixtures. The azeotropic mixtures are usually binary mixtures that behave like a pure fluid okay. For all practical purposes they behave like a pure fluid pure fluid okay. The example is R five naught two which is a mixture of R twenty-two and R one one five these may be mainly used in cold storage etcetera. But this mainly banned because of R one one five which is a ozone depleting substance. Then you also have R four one zero A okay. This is R thirty-two plus R one twenty-five even though this I am calling it as azeotropic mixture. Its number is four this, what is known as nearer to azeotropic mixture. That means its temperature variation during phase change is very small okay it's a replacement for R twenty-two.

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Zeotropic mixtures exhibit a significant temperature variation during constant pressure phase change process. That means when evaporation and condensation is taking place at constant pressure temperature does not remain constant okay. But pure phase pressure remains constant. That means the process is iso thermal whereas for zeotropic mixtures temperature of refrigerant varies during phase change okay, that will make the difference. Also at equilibrium the composition in vapour and liquid phases will be different okay. So these are the differences between zeotropic and azeotropic mixtures. Examples of some zeotropic mixtures are R four not four A which is a mixture of R one twenty-five R one forty three a and R one thirty-four a okay. This is mainly used in place of R twenty-two then you also have R four not this is a mixture of thirty-two one twenty-five and one

thirty-four a okay. These are used in place of R twenty-two then you also have R four not seven C which is used in place of R twenty-two okay.

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Then mixtures offer the advantage of tailoring the composition to suit various temperature requirements. These is the major advantage of mixtures it is also possible to control the properties such as toxicity flammability oil miscibility by manipulating the composition hence they are finding greater use okay. However since the composition of zeotropic mixtures change due to leakage this is a major problem use of these substances require greater care okay. And design of equipment such as evaporators and condenser is also complex. Because of the temperature variation during evaporation condensation etcetera. In the next lecture I shall take up air conditioning okay.

Thank you