Refrigerants-Classification, Properties & Application

Refrigerant

Classification

properties

Refrigeration & Cold ChainSem

-Dr. Vinkel Kumar Arora

Refrigerants-Classification, Properties & Application

- **Definition of refrigerant its classification- primary refrigerant, secondary refrigerants,**
- **History of refrigerants, Designation and classification of refrigerants,**
- **Properties of refrigerants – thermodynamic properties, chemical properties and physical properties,**
- **Refrigerants in use after 2000,**
- **Ozone layer depletion and global warming potential of CHC refrigerants,**
- **Introduction to eco-friendly refrigerants.**

Definition of Refrigerant and its Classification

- The working substance or heat transferring medium in a refrigeration system is called refrigerant. It absorbs heat from the sink at the low temperature and rejects to a source at the higher temperature.
- In domestic refrigerator, refrigerant absorbs heat in the evaporator and rejects heat to the atmosphere in the condenser.
- The refrigerant changes from liquid phase to vapour phase in the process of absorbing the heat and condenses again to liquid while rejecting the heat. The ideal refrigerant would be one that could reject all the heat it is capable of absorbing.

History of refrigerants

- **The natural ice and mixtures of ice and salt were the first refrigerants used by human beings to produce cold.**
- **Latter either, ammonia, sulphur dioxide, methyl chloride, ethyl chloride, and carbon dioxide were used as the refrigerants. Most of these refrigerants were discarded for safety reasons and for lack of thermal stability.**
- **In 1901—30, hydro-carbon compounds like methane, ethane etc. were used as a refrigerants. However, hydro-carbons were found extremely inflammable.**
- **In 1930s, a great break through occurred. Fluorinated hydro-carbons or freons were developed. These are derived from methane, ethane etc. are called F_{11}, F_{12}, F_{22} etc.**

Refrigerants are classified according the manner of absorption heat from the substance to be refrigerated.

- **1. Primary Refrigerant: are those that produce refrigeration effect by absorption of latent heat and take part directly in the refrigeration system. Such refrigerants are ammonia, carbon dioxide ,freons etc.**
- **Types of primary refrigerants:**
- **A) Halo-carbons B) Azeotropes C) Inorganic D) Hydrocarbons**
- **2. Secondary Refrigerants: are those that produce refrigeration or cooling effect by sensing heat. Secondary refrigerants are liquids used for transporting low-temperature heat energy from one location to another Such refrigerants are air, water, calcium chloride, sodium chloride, brine etc.**

Secondary refrigerants are used in those refrigerating systems where primary refrigerants cannot be used due to safety reasons and high cost of primary refrigerants. For example, toxic refrigerant NH_3 can not be used for air-conditioning of residential buildings. It is usual practice to chill brine over the evaporator coil and then air is cooled by passing it over the brine coil.

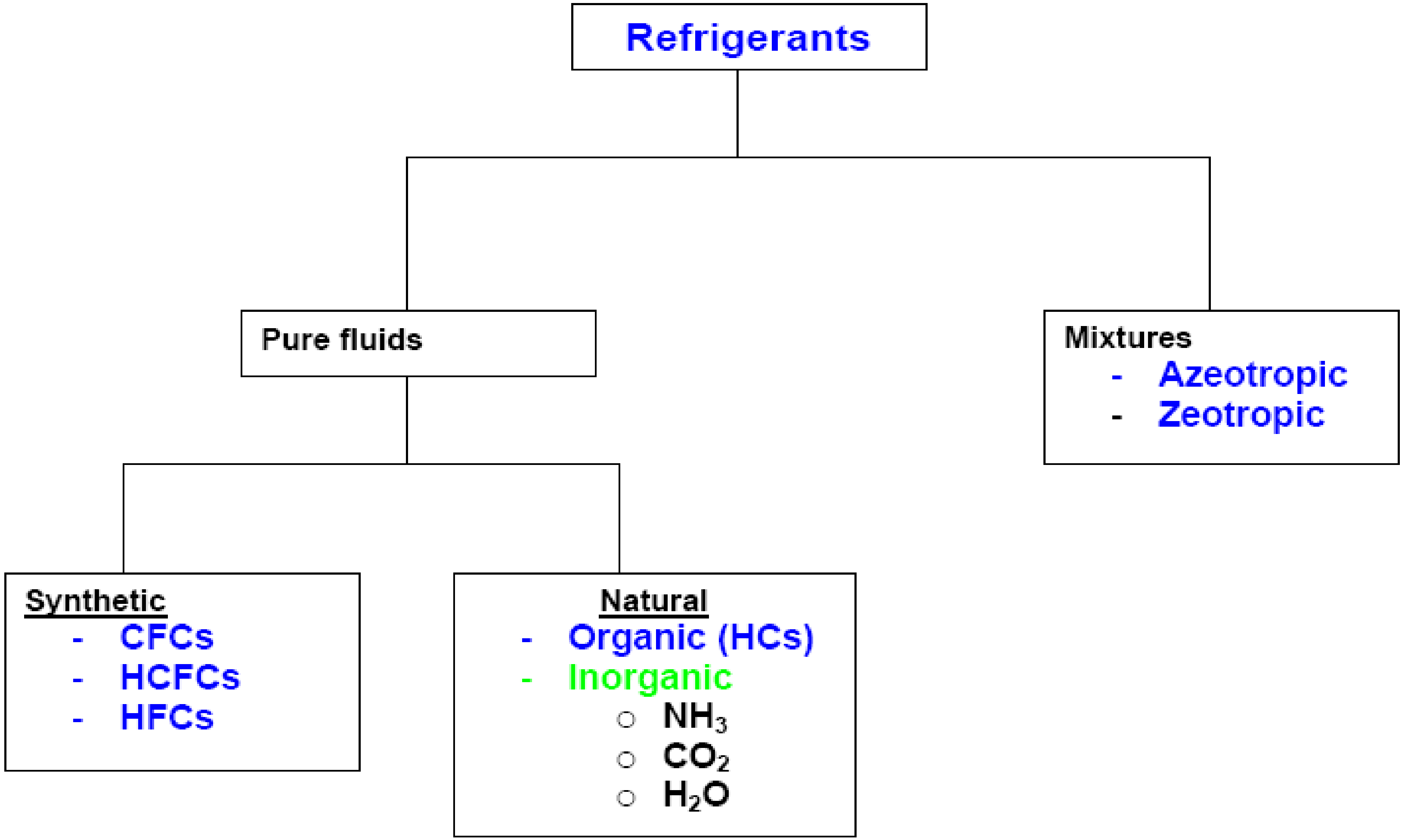
PRIMARY REFRIGERANTS-

- **Take directly part in cooling, phase change take place**
- **Heat absorption by Latent heat**
- **High refrigeration effect**
- **Expensive**
- **Less quantity required**
- **May or may not corrode**
- **No need of anti freeze**
- **Example are, Halocarbon, inorganic, Azeotropes, organic (saturated and unsaturated compounds as discussed further.**

SECONDARY REFRIGERANT

- **Indirect cooling and no phase change take place**
- **Heat absorption by sensible heat**
- **Low refrigeration effect**
- **Comparatively much cheaper**
- **More quantity required**
- **Usually corrosive**
- **Anti freeze required**
- **Example, water, brines(Nacl,$CaCl_2$), $CaCl_2$)+ water, Nacl+water,Glycols (ethylene and propylene glycols are generally mixed with water to reduce the freezing temperature)**

Classification of primary refrigerants



Halocarbons

- **These refrigerants are derivatives of alkanes (C_nH_{2n+2})**

such as methane (CH_4),(2 digit) ethane (C_2H_6). (3-digit)

- **<u>METHANE SERIES</u>**

R-10	**CCl_4**
R-11	**CCl_3 F**
R-12	**CCl_2F_2**
R-13	**$CClF_3$**
R-14	**CF_4**
R-21	**$CHCl_2F_2$**
R-22	**$CHClF_2$**
R-30	**CH_2Cl_2**
R-32	**CH_2F_2**
R-40	**CH_3Cl**
R-50	**CH_4**
R-13B1	**CF_3Br**

- **<u>ETHANE SERIES</u>**

R-100	**C_2H_5Cl**
R-114	**$C_2Cl_2F_4$**
R-113	**$C_2Cl_3F_3$**
R-115	**C_2ClF_5**
R 152a	**CH_3CHF_2**
R 143a	**CH_3CF_3**
R 125	**CHF_2CF_3**
R134	**$C_2H_2F_4$**
R134a	**CH_2F-CF_3**

<u>R134 = $C_2H_2F_4$</u>

<u>R134a = CH_2F-CF_3 (derivative of ethane)</u>

- **(Letter ‘a’ stands for isomer, e.g. molecules having same chemical composition but different atomic arrangement, e.g. R134 and R134a)**

Designation of Refrigerants

- **Chemical Formula: $C_mH_nCl_pF_q$**

m indicates the number of Carbon (C) atoms

n indicates number of Hydrogen (H) atom

P indicates number of Chlorine (Cl) atom

q indicates number of Fluorine (F) atoms

Such that n+p+q =2m+2

These refrigerants are designated by R (m-1)(n+1)q, where:

- **R stands for Refrigerant.**

m-1 indicates the number of Carbon (C) atoms

n+1 indicates number of Hydrogen (H) atoms

q indicates number of Fluorine (F) atoms

Examples

- **For Trichloro-monofluoro-methane ,CCl_3F,**

there is one carbon atom(m=1), no hydrogen atom(n=0), and there is one fluorine atom(q=1),

the corresponding designation is R(1-1) (0+1) (1)or R11.

- **Similarly, dichloro difluoro methane, CCl_2F_2**

there is one carbon atom(m=1), no hydrogen atom(n=0), there are two chlorine atom(p=2), and there are two fluorine atom(q=2),

the corresponding designation is R(1-1) (0+1) (2)or R12.

Monochloro difluoro methane, $CHClF_2$, is designated as R22.

- **Similarly, $C_2Cl_3F_3$ is R113. CH_4 is R50. C_2H_6 is R170**
- **The brominated refrigerants are denoted by putting an additional B and a number to denote as to how many chlorine atoms are bromine atoms. Thus R13B1 is derived from R13($CClF_3$) with the replacement one chlorine atom by bromine atom. Its chemical formula is CF_3Br**

Inorganic Refrigerants

These are designated by number 7 followed by the molecular weight of the refrigerant (rounded-off).
Ex.:
Ammonia: Molecular weight is 17,
∴ The designation is R 717
Carbon dioxide: Molecular weight is 44,
∴ The designation is R 744
Water: Molecular weight is 18,
∴ The designation is R 718

Other inorganic refrigerants are listed below.

R-702	H_2
R-704	**He**
R-717	NH_3
R-718	H_2O
R-720	**Ne**
R-728	N_2
R-729	0.21 O_2 0.78 N_2 0.01 A (AIR)
R-732	O_2
R-740	**A (ARGON)**
R-744	CO_2
R-764	SO_2

Unsaturated organic (HC)Refrigerants

- **Unsaturated organic compound like ethylene C_2H_4 , propylene C_3H_6 , Ethane C_2H_6 etc.**
- **for which (n+p+q) = 2m , are designated by putting digit 1 before (m-1). Thus, ethylene is R1150 and propylene is R1270.**
- **These are not commonly used now days due to highly inflammable nature and explosive.**

Azeotropes

- **Azeotropes are mixtures of two refrigerants whose vapour and liquid phases retains identical composition over a wide range of temperature.**
- **They cannot be separated into its components by distillation and behave like pure substances. These are given arbitrary designations.**
- **Azeotropic mixtures are designated by 500 series, where as zeotropic refrigerants (e.g. non-azeotropic mixtures) are designated by 400 series.**
- **Isomers are compounds with same chemical formula but different molecular structure are called isomers. Subscripts a,b,c are used after the designation.**

- **Azeotropic mixtures:**

R 500: Mixture of R 12 (73.8 %) and R 152a (26.2%)

R 502: Mixture of R 22 (48.8 %) and R 115 (51.2%)

R503: Mixture of R 23 (40.1 %) and R 13 (59.9%)

R507A: Mixture of R 125 (50%) and R 143a (50%)

- **Zeotropic mixtures:**

R404A :Mixture of R 125 (44%), R 143a (52%) and R 134a (4%)

R407A :Mixture of R 32 (20%), R 125 (40%) and R 134a (40%)

R407B : Mixture of R 32 (10%), R 125 (70%) and R 134a (20%)

R410A : Mixture of R 32 (50%) and R 125 (50%)

Properties of Refrigerants

- The properties of refrigerants may be grouped into three categories:

1.Thermodynamic Properties 2.Chemical Properties and 3.Physical Properties

Thermodynamic Properties

(i) **Positive and Low Evaporator and Condenser Pressure**

(a) The operating pressure should be low enough so that light weight material will contain the material. This will result in low cost of the material.

(b) The pressure should be positive that is above atmosphere so that the leakage of the air and water can be prevented into the system.

(ii) **Low freezing point**

It sold be appreciably below the operating temperature of evaporator so as to avoid its freezing and clogging the pipes.

(iii) **High Latent heat of Evaporation**

The latent heat of evaporation should be as large as possible. Evaporation of liquid produces the cooling effect. Also the mass of refrigerant to be circulated in the system will be less if latent heat is high.

Properties of Refrigerants

(iv) **Low Specific Volume**

Low specific volume reduces the size of compressor.

(v) **High Critical Temperature**

It should be high enough as compared to the condensing temperature

(vi) **Low Boiling Point at Atmosphere Pressure**

Low boiling temperature at atmospheric pressure is required for an efficient refrigerant. At atmosphere pressure, specific volume is low so size of the compressor is reduced. Substances with their NBM in the range of -500C to +500C are considered suitable for use as refrigerants.

(vii) **Low Value of Ratio of Two Specific**

Isentropic work of compression is reduced if Cp/Cv is low because heats=

If is low, W is also low.

Chemical Properties

- **(i) Non-Flammability**

It should not catch fire when mixed with air in any concentration. To avoid fire hazard during high compression and over heated conditions, the refrigerant should be non-flammable.

- **(ii) Non-Toxicity and Non-Irritability**

A toxic and irritant refrigerant injuries the human being when mixed with small percentage of air.

- **(iii) Inertness and Stability**

The refrigerant should not react with the metals and should not form harmful compounds in presence of harmful compounds in presence of water and oil. It should remain stable or should not change its chemical composition . Ammonia reacts with copper, brass and other copperous alloys in presence of water. Ammonia uses iron and steel.

- **(iv) Heat Transfer Characteristics**

To reduce the heat exchanger size, the heat transfer coefficients should be high. So properties of refrigerants should be such that heat transfer coefficients are high.

- **(v) No Effect on Perishable Materials**

The refrigerants used in cold storage plant and domestic refrigerators should be such that in case of leakage, it should have no effect on perishable materials. The Freon group refrigerants have no effect on dairy products, meat, vegetables etc.

Physical properties

- **(i).Easy leakage Detection**

The tendency of a refrigerant to leak should be as low as possible and its leakage deduction as simple as possible. Ammonia leakage is easily deducted due to its odour.

- **(ii) Low viscosity and High Thermal Conductivity**

To reduce viscous losses, viscosity should be low. Coefficient of thermal conductivity

Should be high for high heat transfer by conduction.

- **(iii) Non-Solubility with Oil**

The refrigerant should not react with oil otherwise it will loose lubricating property.

- **(iv) Cheap**

The refrigerant should be as cheap as possible. Ammonia refrigerant is the cheapest, R12 more expensive and R22 most expensive.

Refrigerants in Use After 2000

- After the finding that CFCs, and to lesser extend HCFCs deplete the ozone layer, over 100 countries adopted Montreal Protocol (MP) of 1987 to phase out CFCs in the year 2000, and HCFCs by the year 2030.
- HFCs and HCs do not deplete the ozone layer. They can be used even after 2030. Their production and use is not regulated Bt the MP. These refrigerants include R32, R125, R134a,R407C, and R410A. HFCs have some global warning potential though some governments may consider regulate their use too.
- Out of refrigerants being used prior to 2000 AD, all CFCs R11, R12, R113 R114 and the Azeotropes mixture R502 have already been phased out.

Replacement of all important R12, R11, R22, and R502 to date to be used till 2030 are under-mentioned.

1. Replacement of R12

The replacement of R12 has been the easiest. For all practical purposes, replacement of R12 has taken over completely by R134a. R134a is an HFC, its use will continue beyond 2030 unless another more suitable refrigerant is not found. HFCs, R152a can also replace R12. HCs R600a and R290 can also be used in place of R12

Refrigerants in Use After 2000

2. Replacement of R11

R123 has been chosen as most efficient option for R11 in centrifugal chillers. R123 is an HCFC. Its use has to be phased out by 2030.

3. Replacement of R22

As R22 is an HCFC, its use is permitted till 2030. Since it is currently the most favored refrigerant in package units and chillers, its use continues. 70% of commercial refrigeration systems still use R22. Only in food refrigeration, its use not being favored. In food refrigeration, R22 is being replaced by ammonia. Ammonia is environment friendly and has COP. Some industries are using R410A as a replacement for R22. R410A is 50/50 percent R32/R125 blend.

4. Replacement of R502

Presently, R404A has found an application in place of R502

Ozone Depletion Potential and Global Warning Potential of CHC Refrigerants

- The earth's ozone layer in the upper atmosphere called stratosphere is needed for the absorption of harmful ultraviolet rays from the sun. in 1985, the world was shocked to find a gaping hole above Antarctic in the ozone layer that protects the earth from ultra-violet rays. These rays can cause skin cancer. CFCs have been linked to the depletion of the ozone layer. They have varying degrees of ozone depletion potential(ODP). In addition, they act as a greenhouse effect. Hence they have global warming-potential(GWP) as week. According to an international agreement called Montreal Protocol, the use of fully halogenated CFCs (having no hydrogen in the molecule), like R11,R12, R113, R114 and R502, that have high ODP, have been phased out from the year 2000. HCFCs have much lower ODP but some GWP. They have to be phased out by 2030. R22 is an HCFC. Its ODP is 0.05 and that of F12 is 1. So ODP of R22 is only 5% of that of R12. It will be phased out by the year 2030. R22 is widely used as a popular refrigerant.
- Even with the measures taken so farm in 2008, a 2.7 million square kilometers ozone layer hole was detected above Antarctic.
- Chlorine in CFCs molecules depletion of ozone. As CFCs molecules reach stratosphere, they are dissociated by the sun light into active chlorine compounds which, in turn, attack ozone, generating chain reaction. One molecule of CFC is thus sufficient to destroy many hundreds of ozone molecules. The table2.1 shows the relative ozone depletion potential and global warming potential for different

Ozone Depletion Potential and Global Warning Potential of CHC Refrigerants

S.No.	Refrigerant	ODF/RODP	GWP
1	CFC-11	1.00	1.00
2	CFC-12	1.00	3.05
3	CFC-113	0.80	1.3
4	CFC-114	1.00	4.15
5	CFC-115	0.60	9.60
6	CFC-502	0.30	5.10
7	HCFC-22	0.05	0.37
8	HCFC-123	0.02	0.02
9	HFC-134a	0	0.29
10	HFC-125	0	0.58
11	HFC-152a	0	0.10

Introduction to Eco Friendly Refrigerants

- **Hydrocarbons, HCs, and hydro fluorocarbons, HFCs, provide an alternative to fully halogenated CFC refrigerants. They contain no chlorine atom at all, and, therefore have zero ODP. Even hydro-chlorofluorocarbons, HCFCs like R22 and R123 do contain chlorine atom/s, but in association with H-atoms, have much reduced ODP. HCFCs have a lower lever of ODP in addition to GWP. Hence, they have to be phase out ultimately from 2030 onward. Presently, they can be used as a transitional refrigerants.**
- **The HFCs, on the other hand, because of their H-content may be flammable to some extent. The degree of flammability depends on the number of H-atoms in the molecule. Pure HCs are highly flammable.**
- **The two other most commonly used refrigerants having very high ODP are R11 and R12. Refrigerants R113, R114 and R502 have also high ODP. These have been replaced by appropriate substitutes.**
- **R22, which is an HCFC, has only 5% ODP as compared to ODP of R11 or R12. hence, it can continue to be used for some time. However, all HCFCs have GWP. Because of this, even R22 will have to be ultimately phased out by the year 2030.**
- **The list of refrigerants currently being used and those which have potential to be used in future are under mentioned.**

1. Methane Series

(i) HCFC, R22, $CHClF_2$, Monochloro difluoro hethane

(ii) HFC, R32, CH_2Cl_2, Difluoro methane

Introduction to Eco Friendly Refrigerants

2. Ethane Series

(i) HFC, R134a, $CH_2F\text{-}CF_3$, Tetrafluoro ethane

(ii) HFC, R143a, $CH_3\text{-}CF_3$, Trifluoro ethane

(iii) HCFC, R123, $CHCl_2\text{-}CF_3$, Dichloro trifluoro ethane

(iv) HFC, R152a, $CH_3\text{-}CHF_2$, Difluoro ethane

3. Propane Series

(i) HC, R290, C_3H_8, Propane

(ii) HFC, R245fa, $C_3H_3F_3$, Pentafluoro prpane

4. Butane Series

(i)HC, R600a, $C_4H_{10,}$ Isobutane

5. Zeotropic Blends

(i) HFC, R404A {R125/R143a/134a(44/52/4)}

Introduction to Eco Friendly Refrigerants

(ii) HFC, R407C {R32/R125/134a(23/25/52)}

(iii) HFC, R410A {R32/R125(50/52/50)}

6. Azeotropic Blends

(i) HFC, R507A{R125/143a(50/50)}

7. Inorganic Refrigerants

(i) R717,NH_3, Ammonia

It possesses most of the desirable properties of an refrigerant. It has high enthalpy of vaporization, high COP, high refrigeration efficiency , large range of operating temperatures, low cost, available in abundance and leakage detection is very easy. But it is toxic, flammable and has high compression temperature.

(ii) R718, H_2O, Water

Water is a excellent refrigerant for substitute of CFCs. It also possesses most of the desirable properties of a refrigerant. It ha high enthalpy of vaporization, high COP, high coefficient of heat transfer hence reduced construction cost, non-toxic, non-flammable, thermally

Thank You