Refrigerant

The refrigerant is a heat carrying medium which during their cycle (i.e. compression, condensation, expansion and evaporation) in the refrigeration system absorb heat from low temperature system and discards the absorbed heat to a high temperature environment.

Desirable properties of an Ideal Refrigerant

1. The saturation ~~temperature~~ pressure of the refrigerant at a desired low temperature should be above or equal to the atmospheric pressure.
2. The latent heat of evaporation at low temperature should be high.
3. The refrigerant should be chemically stable and should not react with lubricant.
4. It should ~~not~~ be non-flammable, non-explosive.
5. It should be non-toxic.
6. It should have low specific heat of liquid for better heat transfer in condenser.
7. The refrigerant should give high value of COP with low power input per tonne of refrigeration.

(8) Good thermal conductivity for better heat transfer in the condenser and evaporator.

(9) The refrigerant must have freezing point temperature well below the lowest temperature in the cycle.

(10) Low cost.

(11) Low specific volume of ~~volume~~. vapour.

Classification of Refrigerants

It is classified into 2 groups.

(1) Primary refrigerant

(2) Secondary refrigerant

Primary refrigerant – The refrigerant which directly take part in the refrigeration system are called Primary refrigerant.

Secondary refrigerant – The refrigerants which are first cooled by primary refrigerants and then used for cooling purpose.
Ex- Water, Brine

The primary refrigerants are further classified into following groups.

Primary refrigerant –
- Halo-carbon or organic refrigerant
  R-11 (CCl_3F), R-12 (CCl_2F_2)
- Azeotrope refrigerant
  R-500, R-502, R-503
- Inorganic refrigerant
  R-717 (NH_3), R-729 (Air)
- Hydrocarbon refrigerant.
  R-170 (C_2H_6 - Ethane), R-290 (C_3H_8 - Propane)

Designation System for Refrigerant

The refrigerants are internationally designated as 'R'.

A refrigerant followed by a two-digit number indicates that a refrigerant is derived from ~~methane~~ methane base while three-digit number represents ethane base

~~Ax~~ Ex- methane base – R-11, R-12, R-21, R-22

ethane base – R-113, R-115, R-134a, R-123

The numbers assigned to hydro-carbon and halo-carbon refrigerants have a special meaning. The first digit on the right is the number of flourine (F) atoms in the refrigerant. ~~BBA~~ i.e. q

The second digit from the right is one more than the number of hydrogen (H) atoms present. i.e. (n+1)

The third digit from the right is one less than the number of carbon (C) atoms, but ~~the~~ when this digit is zero, it is omitted. i.e. (m-1)

Then, the number of the refrigerant is given by R (m-1)(n+1) q.

The general chemical formula for the refrigerant, either for methane or ethane base, is given as $C_m H_n Cl_p F_q$, in which $n+p+q = 2m+2$

where, m is the number of carbon atoms

n is the number of hydrogen atoms

p is the number of chlorine atoms

q is the number of flourine atoms.

Example - 1

Find the chemical formula and the number of Di chloro- difluro-methane.

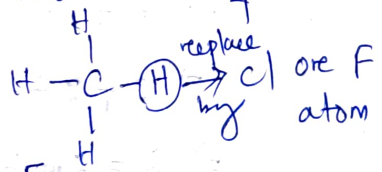
In this refrigerant,

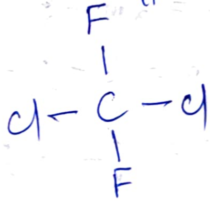
Number of chlorine atoms, $p = 2$

Number of fluorine atoms, $q = 2$

Number of hydrogen atoms, $n = 0$

Methane = CH_4





So, here ~~hydro~~ hydrogen atom is zero. i.e. $n = 0$

$\therefore n + p + q = 2m + 2$

$\Rightarrow 0 + 2 + 2 = 2m + 2$

$\Rightarrow 4 = 2m + 2$

$\Rightarrow 2m = 4 - 2 = 2$

$\Rightarrow m = \frac{2}{2} = 1$

$m = 1$ (Number of carbon atoms)

The general chemical formula is $C_m H_n Cl_p F_q$

i.e. $C_1 H_0 Cl_2 F_2$

$\Rightarrow CCl_2F_2$ (H_0 is omitted)

∴ The chemical formula of Dichloro-difluro-methane is CCl_2F_2.

and the number of refrigerant is

$$R(m-1)(n+1)q = R(1-1)(0+1)2$$

$$= R012 \text{ i.e. } R12$$

Number of refrigerant is R-12.

Example - 2

Find the chemical formula and the number of Dichloro-tetrafluoro-ethane.

In this refrigerant,

Number of chlorine atoms, $p = 2$

Number of fluorine atoms, $q = 4$

Number of hydrogen atoms, $n = 0$

ethane = C_2H_6

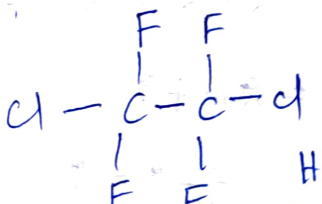
$\therefore n + p + q = 2m + 2$

$\Rightarrow 0 + 2 + 4 = 2m + 2$

$\Rightarrow 6 = 2m + 2$

$\Rightarrow 2m = 6 - 2 = 4$

$\Rightarrow m = \frac{4}{2} = 2$



Hydrogen atom (n) = 0.

$\boxed{m = 2}$ (Number of carbon atoms)

The general chemical formula is $C_m H_n Cl_p F_q$

i.e. $C_2 H_0 Cl_2 F_4 \Rightarrow C_2Cl_2F_4$

Example

Determination of chemical formula from the given number - R22, R113

(i) $R_{22} = R_{022}$

$= R_{(m-1)(n+1)q}$

$m-1=0, \Rightarrow m=1$

$n+1=2 \Rightarrow n=1$

$q=2$

Now, using general equation,

$n+p+q=2m+2$

$\Rightarrow 1+p+2=2\times1+2$

$\Rightarrow p+3=4$

$\Rightarrow p=4-3=1$ $\boxed{p=1}$

So, The general chemical formula

$C_m H_n Cl_p F_q$

$= C_1 H_1 Cl_1 F_2$

$= CHClF_2$

(ii) R-113

$R\text{-}113 = R_{(m-1)(n+1)q}$

$m-1=1 \Rightarrow m=2$

$n+1=1 \Rightarrow n=0$

$q=3$

By using general eqⁿ -

$$n + p + q = 2m + 2$$

$$\Rightarrow 0 + p + 3 = 2 \times 2 + 2$$

$$\Rightarrow p = 6 - 3 = 3$$

$$\therefore p = 3$$

The general chemical formula,

$$C_m H_n Cl_p F_q$$

$$= C_2 H_0 Cl_3 F_3$$

$$= C_2 Cl_3 F_3$$

Case - 2

For Inorganic Refrigerant, (NH_3, Air, CO_2, SO_2, water)

The inorganic refrigerants are designated by 7.

Inorganic refrigerant designation = 700 + molecular weight.

Example - 1

(i) NH_3 (ammonia)

$N = 7 \times 2 = 14$
$H = 3$

The molecular weight or mass of ammonia is = 17

So, designation of NH_3, i.e. R-(700 + 17)

= R - 717

(v) CO_2

Molecular weight of C = 12

Molecular weight of $O_2 = 16 \times 2 = 32$

∴ Molecular weight of $CO_2 = 12 + 32$
$= 44$

Designation of CO_2 i.e. R-(700 + 44)
= R-744

Thermodynamic Properties

Physical Properties

1) Boiling temperature -

The boiling temperature of the refrigerant at atmospheric pressure should be low. If the boiling temp. of the refrigerant is high at atmospheric pressure, the compressure should be operated at high vacuum. The high boiling temp. reduces the capacity of the system.

Refrigerant	Boiling temp at atmospheric pressure
NH_3	$-33.3^\circ C$
R-11	$+23.77^\circ C$
R-12	$-29^\circ C$
R-22	$-41^\circ C$
R-134a	$-26.15^\circ C$
R-744 (CO_2)	$-73.6^\circ C$
R-764 (SO_2)	-10

② Freezing Point / Freezing temperature -

The freezing temperature of a refrigerant should be well below the operating evaporator temperature (-15°C) Since the freezing temp. of most of the refrigerants are below -35°C.

Refrigerant	freezing temp. (°C)
R-12	-157.5
R-22	-160
R-134a	-101
R-744	-56.7
R-764	-75.6
R-113	-35

③ Evaporator and Condenser Pressure -

~~Atm. pressure~~ = 1.01

Both the evaporating and condenser pressure should be above atmospheric pressure. and it should be as near to the atmospheric pressure as possible. The positive pressure are necessary in order to prevent leakage of air and moisture into the refrigerating system.

Atmospheric pressure = 1.01325 bar R-22 → 2.9670 → 12.0340 (Evap. Pres.) (condenser pr.)

④ Critical temperature and Pressure -

The critical temperature of a refrigerant is the highest temperature at which it can be condensed to a liquid. regardless of a higher pressure.

R-11 → 198°C → 0.694

It should be above the highest condensing temperature (+30°c). If the critical temp. of a refrigerant is too near the desired condensing temperature, the excessive power consumption results. R-717 (NH_3) → 133°C → 0.738 KW/TR (power consumption) R-744 (CO_2) → 31°C → 1.372 KW/TR (excess power consumption)

(5) Co-efficient of Performance and power requirement: Power requirement are inversely proportional to the COP. For an ideal refrigerant operating between −15°c evaporator temperature and 30°c condenser temperature, the theoritical co-efficient of performance for the reversed carnot cycle is 5.74.

Critical temp.	Refrigerant	Coefficient of Performance	Power Consumption KW/TR
198°C	R-11	5.09	0.694
	R-22	4.66	0.753
	R-30	4.90	0.716
	R-40	4.90	0.716
	R-113	4.92	0.716
	R-114	4.54	0.792
	R-717	4.76	0.738
Air	R-729	5.74	0.619 → Reversed carnot cycle
31°C	CO_2 R-744	2.56 low COP	1.372 Max^m power consumption
	(H_2S) R-764	4.87	0.724

From the above table, we see that R-11 has the co-efficient of performance equal to 5.09 which is closest to the Carnot cycle value of 5.74. The other refrigerants have also quite high values of COP except R-744 (CO_2) which has the value of COP as 2.56 with a power requirement of 1.372 KW per TR. This is due to its low critical temp. (31°c) and the condensing temp. is very close to it which is 30°C

(6) Latent heat of vaporisation –

A refrigerant should have a high latent heat of vaporisation at the evaporator temperature. The high latent heat results in high refrigeratory affect per kg of refrigerant circulated which reduces the mass of refrigerant.

~~to be~~

Chemical Properties

(1) Flammability –

(i) Hydro-carbon refrigerants such as ethane, methane and propane etc. are highly flammable.

(ii) Ammonia (NH_3) and Methyl chloride (CH_3Cl) are also some what flammable and becomes explosive when mixed with air in the ratio of 16 to 25% of gas by volume.

(iii) The halo-carbon refrigerant are neither flammable nor explosive.

(2) Toxicity –

(i) Some non-toxic refrigerants (i.e. all fluorocarbon refrigerants) when mixed with certain percentage of air become toxic.

(ii) NH_3 and SO_2 are highly toxic and irritating. Therefore these refrigerants are not used in domestic refrigeration and comfort air-conditioning.

The use of toxic refrigerants is only limited cold storage. They are used with indirect cooling methode in which a secondary coolant such as water or brine is used in the system.

(3) Miscibility –

The ability of a refrigerant to mix with oil is called miscibility.

(i) The freon group (halo-carbon) of refrigerants are highly miscible refrigents.

(ii) NH_3, CO_2, SO_2 and CH_3Cl are non-miscible.

The non-miscible refrigerants require larger heat transfer surfaces due to poor heat conduction properties of oil.

④ Effect on perishable materials –

The refrigerants used in cold storage plant and in domestic refrigerators should be such that in case of leakage, it should have no effect on the perishable materials.

Freon group (Chelo-carbon) —no effect→ diary product, meats, vegetable, flowers,
—No change→ colour, taste or texture of the material when exposed to freon.

Methyl chloride —No effect→ furs, flowers, eating foods or drinking beverages.

SO_2 —No effect→ foods
—destroy→ flowers, plants and furs.

NH_3 dissolves easily in water and becomes alkaline in nature. Since most fruits and vegetables are acidic in nature. Therefore NH_3 reacts with these products and spoils the taste.

⑤ Solubility of water –

Water is only slightly soluble in R-12. The solubility of water with R-22 is more than R-12 by a ratio of 3 to 1. If more water is present can be dissolved by the refrigerant, the ice will be formed which chokes the expansion valve used for throttling in the system.

Commonly used Refrigerant

The commonly used refrigerants are R-11, R-12, R-22, R-134a and R-717.

R-11 (CCl_3F)

The chemical name of R-11 is Trichloro-monofluoro-methane. It is a synthetic chemical products which can be used as a refrigerant. The boiling point or temperature at atmospheric pressure is 23.77°c.

Uses:-

(i) It is used in large centrifugal compressor systems.

(ii) It is used as flushing agent for cleaning the internal parts of a refrigerator compressor.

Properties -

It is stable, non-flammable and non-toxic.

evaporator ~~temp.~~ pressure at -15°c	condensing ~~temp.~~ pressure at 30°c	Latent heat at -15°c
0.202 bar	1.2606 bar	195 KJ/kg

R-12 (CCl_2F_2)

The chemical name of R-12 is Dichloro-difluoro methane.

The boiling point at atmospheric pressure is $-29°c$.

Properties:-

It is non-toxic, non-corrosive, non-irritating and non-flammable.

evaporating pressure at $-15°c$	Condensing pressure at $30°c$	Latent heat at $-15°c$
0.82 bar	6.4 bare	159 kJ/kg

Uses:-

It is used in many different types of industrial and commercial applications such as refrigerator, freezers, water coolers, room and window A.C unit.

R-22 ($CHClF_2$)

The chemical name of R-22 refrigerant is Monochloro-difluoro methane.

The R-22 is a man-made refrigerant.

The boiling point of R-22 is $-41°c$ at atmospheric pressure.

The cylinder colour code for R-22 is green.

Properties :-

It is stable, non-toxic, non-corrosive, non-irritating and non-flammable.

Uses :-

It has been successfully used in air conditioning units and in household refrigerators.

evaporator pressure at -15°c	Condensing pressure at 30°c	Latent heat at -15°c
~~10.88 bar~~ 1.92 bar	10.88 bar	216.5 kJ/kg

R-134a (CF_3CH_2F)

The chemical name is Tetrafluoro-ethane.

The R-134a is considered to be the most ~~preff~~ preferred substitute for R-12.

Its boiling point is -26.15°c at atmospheric pressure.

Properties :-

It is not soluble in mineral oil. (Ex- paraffin oil)

Uses :-

(i) It is used in domestic refrigerator.

(ii) Now-a-days, widely used in car-conditioners

R-717 (Ammonia - NH_3)

The chemical name is Ammonia.
It is one of the oldest and most widely used of all the refrigerants.
Its boiling point at atmospheric pressure is −33.3°C.

Properties

(i) It is flammable.
(ii) Melting point from the solid is −78°C

Evaporator Pressure −15°C	Condenser pressure at 30°c	Latent heat at −15°c
—	10.78 bar	1315 kJ/kg

Uses :-

(i) It is used in cold storage, warehouse plant, ice cream manufacture, ice manufacture and food freezing plant.

(ii) It is used in absorption type system.

Substitutes for Chloro-fluoro-Carbon (CFC) Refrigerants

The most commonly used halo-carbon or organic refrigerants are the chloro-fluoro derivatives of methane (CH_4) and ethane (C_2H_6). The fully ~~gen~~ helogenated refrigerants with chlorine (Cl) atom in their molecules are referred to as chloro-fluoro-carbon (CFC) refrigerants. The refrigerants such as R-11, R-12, R-13, R-113, R-114 and R-115 are CFC refrigerants.

The refrigerants which contain hydrogen (H) atoms in their molecule along with chlorine (Cl) and fluorine (F) atoms are referred to as hydro-chloro-fluoro-carbon (HCFC) refrigerants. The refrigerants such as R-22, R-123.

The refrigerants which contain no chlorine atoms in their molecules are referred to as hydro-fluoro carbon (HFC) refrigerants. The refrigerants such as R-134a, R-152a.

The refrigerants which contain no chlorine and fluorine atoms in their molecules are referred to as hydrocarbon (HC) refrigerants. The refrigerants such as R-290, R-600a.

It may be noted that the fluorine (F) atom in the molecule of the refrigerants makes them physiologically more favourable. The chlorine (Cl) atom in the molecule of the refrigerants is considered to be responsible for the depletion of ozone layer in the upper atmosphere which allows harmful ultra-violet rays from the sun to penetrate through the atmosphere and reach the earth's surface causing skin cancer.

The chloro-fluoro-carbon have varying degree of ozone depletion potential (ODP).

The CFC refrigerants such as R-11 and R-12 have the heighest ODP = 1

The HCFC refrigerants have a relatively low ODP i.e. R-22 has ODP = 0.05

R-123 has ODP = 0.02.

The HFC refrigerants do not cause any ozone depletion, R-134a has zero ODP.

According to an international agreement (Montreal Protocal, 1987), the use of halogenated CFC refrigerants that are considered to have high ODP (such as R-11, R-12, R-113, R-114 and R-502) have been passed out. The refrigerant R-22 refrigerant is not covered under the original Montreal Protocol as its ODP is 0.05 of R-11 and R-12. But because of its Global warming potential (GWP) i.e. increase in CO_2 concentration, NO_2 emission, it has to be phased out.

The hydrocarbon (HC) and hydro-fluoro carbon (HFC) refrigerants provide an alternative to fully halogenated CFC refrigerants. Since they contain no chlorine atom at all, ~~they~~ therefore they have zero ODP (i.e. ODP = 0). Even hydro-chloro-fluoro carbon (HCFC) refrigerants which contain some chlorine atoms, but in association with hydrogen atoms, have much reduced ODP. However, the HFCs, because of their hydrogen content, may be slightly flammable.

At present, the following substitutes are available,

1. The HCFC refrigerant R-123 (CF_3CHCl_2) in place of R-11 (CCl_3F).
2. The HFC refrigerant R-134a (CF_3CH_2F) and R-152a (CH_3CHF_2) in place of R-12.

3. The HFC refrigerant R-134a (CH_3CF_3) and R-125 (CHF_2CF_3) in place of R-502 (a mixture of R-22 and R-115)

4. The HC refrigerants ~~are~~. propane. i.e. R-290 (C_3H_8) and R-600a (C_4H_{10}) may also be used in place of R-12.