

Refrigerant Evolution over a Hundred Years

By K Raghavan

Introduction

The Indian HVAC industry started working with and implementing alternate refrigerants in 2003, when the most popular refrigerants of that time (CFCs) R-11 and R-12 were phased-out. Since then, the industry has come a long way, treading carefully, through a lot of discussions on phase-out or phase-down of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs).

Over the last three decades, the alternate refrigerant scenario discussion has attracted a lot of attention on a particular candidate's ozone depletion potential (ODP), global warming potential (GWP) and safety classification. While the zero ODP compliance by the industry was quite swift since Montreal Protocol, the 'near zero' GWP goal has posed a lot of technical challenges. After many years of deliberations, engineering work and field tests by various manufacturers, the industry has recently started witnessing commercial launches of these 'near zero' GWP candidates, even in large capacity centrifugal chillers.

Manufacturers of refrigerants, compressors and HVACR systems have published whitepapers elaborating various design aspects for choosing the appropriate alternate refrigerant candidate. The 'appropriate' chosen candidate by different manufacturers could be different – with strategies in place to adopt it faster at design, production, field installation and field servicing stages – but they all have a common engineering and technology goal of providing a solution to mitigate global warming. This has also been an opportunity for the manufacturers to review system design aspects and to improve system performance and the overall system economy.

This is not the first time the HVACR industry is at this kind of situation, i.e., expected to switch en masse to a new set of refrigerants for certain reasons. Over more than 100 years, this has already happened twice with excellent outcomes. The alternate options being considered today have been developed through a lot of research work by blending different refrigerants like HFCs and hydro-olefins (HFOs) and by further exploring unsaturated organic compounds.

All these new alternate refrigerants and blends are basically hydrocarbon derivatives. This article tries to look back at the evolution of refrigerants in the HVACR industry from natural refrigerants in the 19th century to halogenated methane and ethane based organic compounds dominating

About the Author

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Raghavan was a member of ISHRAE Refrigerants Committee, which came out with a Position Paper on Alternate Refrigerants in 2015-16. He was a HIDECOR trainer during 2002-06, to train SME on implementing CFC transition in the field. He also contributed to updating the Refrigerant chapter of the text book by P.N. Ananthanarayanan, revised and published in 2014.

most part of 20th century to alternate refrigerants scenario like HFCs, HFOs and hydrocarbons (HCs) over the last three decades in different HVACR applications. At appropriate places, we will also discuss different properties of refrigerants, which matter to equipment designers, in various applications. This will help to refresh the readers' memory with the right perspective with which to look at the current new refrigerant scenario and appreciate different efforts of HVACR manufacturers.

Natural Refrigerants

Ammonia, hydrocarbons and carbon-dioxide were the early day 19th century refrigerants used for producing ice even prior to the year 1900. These are natural refrigerants available in plenty and their use was at its peak during 1920-40. These were the times when mechanical, vapor-compression based-refrigeration systems were engineered and were limited to larger systems to start with as shown in *Figure 1*.

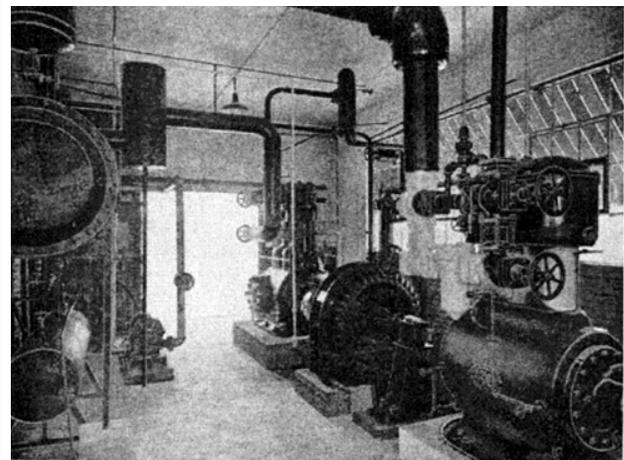


Figure 1: Large mechanical vapor compression ice-making plants of early years using CO₂ and ammonia (Courtesy: Frick, USA archive file picture)

When centrifugal compressor-based chillers were developed in the 1920s, methylene chloride was used as a refrigerant. In large air conditioning applications, methyl chloride and carbon dioxide were extensively used because of their relative safe properties (as understood at that time).

The concept of domestic refrigerator was being proven using Ether as a refrigerant even prior to 1900. In the 1920s, commercially produced domestic refrigerators, using vapor compression systems, predominantly used sulphur dioxide and later switched to methyl chloride as a refrigerant as

Table1: Early years refrigerant properties and their applications

Refrigerants	Chemical symbol	ASRE number designation	Applications #	ASHRAE-34 classification	% by vol. concentration for flammability	Boiling point @ Atmos. Pressure	Molecular weight (g/mol)	Sp vol. vapour ⁽¹⁾	Latent heat at Atm. Pressure	ODP*	GWP*
Methyl Chloride	CH ₃ Cl	R-40	Large AC systems, Domestic and commercial Refrigeration	B2	8.1 – 17.2%	(-23.8°C (-10.8°F)	50.5	4.47 cuf/lb	428.7 / 184.3	0.02	~ 16
Ammonia	NH ₃	R-717	Ice making, Industrial Refrigeration	B2L	16 – 25%	(-33.3°C (-28°F)	17.0	8.15 cuf/lb		0	1
Sulfur dioxide	SO ₂	R-764	Smaller commercial refrigeration	B1	Non-flammable	(-10°C 14°F)	64.0	6.42 cuf/lb	388.6 / 167.1	0	-
Methylene chloride	CH ₂ Cl ₂	R-30	Centrifugal chiller	B2	13 – 23%	40.7°C 105.2°F	84.9	49.9 cuf/lb	312.2 / 134.2	0.001	10
Carbon dioxide	CO ₂	R-744	Ice making, large AC systems	A1	Non-flammable	(-78.5°C (-109.3°F sublim.	44.0	0.27 cuf/lb	572.9 / 246.3	0	1
propane	C ₃ H ₈	R-290	Ice making	A3	3.3 – 7.3%	(-42.3°C (-44.2°F)	44.1	2.48 cuf/lb	425.4 KJ/Kg (182.9 Btu/lb)	0	~ 20

Indicative only; not an exhaustive list.

* ODP, GWP were not known in those times and were not considered by Industry at that time. These columns are added for a comparative understanding.

⁽¹⁾ Specific volume of vapour is at saturated condition at 5°F (-15°C) evaporating temperature

shown in Figure 2.



Figure 2: File photo of 1926 model refrigerator (Courtesy: General Electric)

Smaller size commercial refrigeration units used methyl chloride and sulphur dioxide as refrigerants. Table 1 summarizes the properties of these early years' refrigerants and their applications.

These refrigerants are toxic (sulphur dioxide, ammonia),

moderately flammable (ammonia, methyl chloride), easily flammable (propane and other straight hydrocarbons), corrosive to system components under certain conditions and have issues of oil miscibility.

These were early years with not much understanding or governing national codes in place, educating the industry about toxicity and safety. American Society of Refrigeration Engineers (ASRE#) and other institutions started discussing on the refrigerant safety codes, leading to subsequent development of safety standards. With improving awareness on toxicity and safety and the massive widespread growth of ACR applications, the industry started looking for safer and simple system design refrigerants, which became the prime drivers and led to the development of halogenated refrigerants.

(Note: #ASRE merged with another organization called ASHVE in 1958 to form ASHRAE).

Evolution of Halogenated Refrigerants

HVACR industry started moving to fluorocarbons in the 1930s and 40s, because they were very safe, non-toxic and non-flammable. They had very little hydrolysis (reaction with moisture) and were generally non-corrosive to system components and materials. They had a good miscibility with lubrication oil in the compressor and were compatible with mineral oil. Overall, the fluorocarbons helped to build very safe, reliable and economical systems, compared to early year gases.

Even at that time, with the emergence of halocarbon refrigerants and the options of quite a few candidates – readily available and qualified to be used as refrigerants – the

HVACR industry recognized that there was no ideal refrigerant as such and the choice always depended on the application requirements, safety and economy. A refrigerant approaches 'the ideal' condition, only to the extent that its chemical, physical and thermodynamic properties make it safe and economical.

In the 1930s fluorocarbons like R-12 were commercially produced and introduced. These are halogenated hydrocarbons, using special synthesizing process. Hydrocarbons being the origin for many of the past years and current years fluids, some understanding of how the fluorinated hydrocarbons were derived from base hydrocarbons, will help us understand the subsequent HFC and other alternate refrigerant development.

Hydrocarbons were one of the 'early' natural refrigerants as we discussed. Methane (CH_4), ethane (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}) are hydrocarbons. Elements like chlorine, fluorine and bromine belong to the halogen family. Halogenation is a synthesizing process, in which the hydrogen atoms of methane and ethane are replaced by one of the halogens, resulting in halogenated hydrocarbons. One of the popular and earlier years' Refrigeration textbooks for colleges by Roy J. Dossat, 1961 edition, illustrates this process of halogenation (refer Figure 3) of methane (R-50) molecule first by chlorine, resulting in methyl chloride (R-40), methylene chloride (R-30), chloroform (R-20) and carbon tetra chloride (R-10).

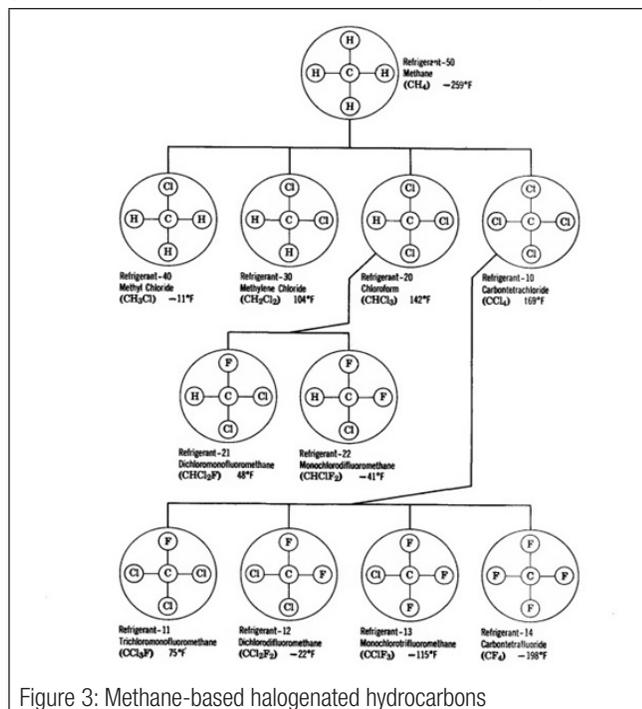


Figure 3: Methane-based halogenated hydrocarbons

The R-10 and R-20 when further fluorinated (replacing each chlorine atom with fluorine atom) results in R-11, 12, 13, 14 and R-21, 22, 23 series refrigerants, respectively. The R-32,

which is one of the currently used and widely considered alternate refrigerants now in light commercial AC application, is a derivative from R-30 and was known to the industry right from those initial years!! ASRE Databook publication of those years included R32.

Note: Referring to Figure 3, readers may notice that R-11, R-12, R-13 and R-14 refrigerants were derived from R-10 (CTC, carbon tetrachloride) and do not have any hydrogen atom in them. These halogenated refrigerants were denoted as 'chlorofluoro carbons' (CFCs). The R-21, R-22, R-23 series have a hydrogen atom in them and were referred as 'Hydrochlorofluoro carbons' (HCFCs). We will have references to CFC and HCFC a little later in this article.

Similarly, referring to Figure 4, Ethane (R-170) when halogenated, results in refrigerants like R-113, R-114 etc. This is how, depending on the base chemical from which it has been derived, the refrigerants are referred as 'methane series' or 'ethane series' halogenated refrigerants. Fluorine being an essential element for the final refrigerant products, in the halogenation process, these refrigerants are also referred as fluorinated hydrocarbons.

These simple illustrations might help a HVACR engineer to understand the origin of some of the popular refrigerants like R-12 and R-22, which dominated the industry for a major part of the 20th century. When we refer to the chemical name of some of the modern-day refrigerants (say R-134a, the chemical name of which is 1,1,1,2 – tetrafluoro ethane), we will be able to understand and appreciate its origin from a specific hydrocarbon family.

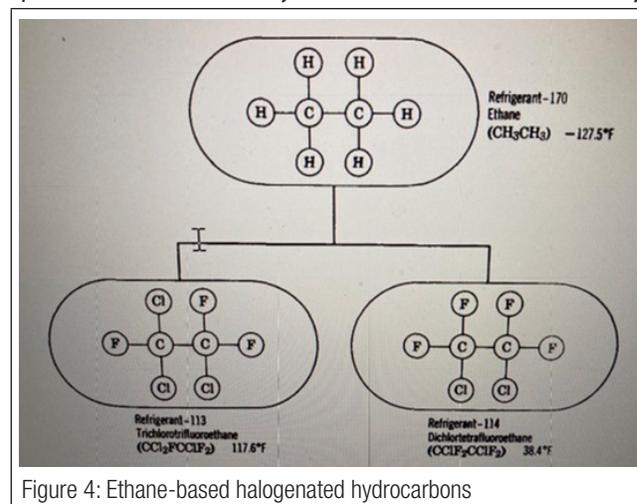


Figure 4: Ethane-based halogenated hydrocarbons

Choice of Suitable Halogenated Refrigerants in Mid-20th Century

Fluorinated hydrocarbon refrigerants offered distinctive advantages of being non-toxic, non-flammable, non-corrosive, having good oil miscibility characteristics and offering refrigeration cycle performance efficiencies nearer to natural refrigerants. It will be interesting to notice here that

Table 2: Comparison of theoretical cycle efficiency of early-years refrigerants and halocarbons

Refrigerant	Ref Number	Pressure [®] 5°F Evp. temp. (Psig)	Pressure [®] 86°F cond. temp. (Psig)	Compr. Ratio (Psia / Psia)	Net Ref. effect [®] 5°F / 86°F (Btu/lb)	Mass flow rate (lb/min)	Discharge gas temperature [®] (°F)	HP per TR	Cycle COP
Methyl Chloride	R-40	6.5	80	4.48	150.2	1.33	172	0.962	4.90
Sulphur Dioxide	R-764	5.9" Hg vac.	51.8	5.63	141.1	1.41	191	0.968	4.87
Dichloro difluoro methane	R-12	11.8	93.2	4.07	51.1	3.92	100	1.002	4.70
Monochloro difluoro methane	R-22	28.3	159.8	4.06	69.3	2.89	131	1.011	4.66

[®] Theoretical discharge gas temp; actual values in a system will be higher because of higher suction gas superheat inside a compressor

the early year refrigerants offered better cycle efficiencies than the R-12 and R-22s. Refer *Table 2*. The driving force for the industry to adopt the fluorinated refrigerants was factors like safety, local code compliance, system reliability, opportunities to review system design and develop simpler, cost-effective systems and easier field installations and service care.

The 'slightly lower' cycle performance of fluorinated refrigerant was more than made up subsequently, with evolving technologies of compressor and motor design, heat exchanger designs, material and design upgrades, improved design concepts etc, over the mid-20th century. (Very similar approach was witnessed subsequently while replacing R22 in 21st century).

Table 3 illustrates the properties of some of the popular fluorocarbon refrigerants and the applications in which they were used predominantly. In each application, one probably would have argued and also evaluated in those years, that options of using a second or third candidate as refrigerant very much existed.

Example

R-22 dominated the air conditioning segment in room AC, ducted, packaged AC, roof top AC, etc. R-12 was also a candidate to be used in air conditioner. Even in India, there were R-12 room ACs sold till the early 1990s, but these were rare and limited instances and R-22, in overall, dominated the AC segment.

The HVACR industry preferred specific refrigerants in each

application, as shown in *Table 3*, due to certain advantages they offered over other refrigerants in terms of system performance, economy and any compliance requirements of that period. It is interesting to note here that R-134a was synthesized and announced in 1936, but R-12 was the preferred choice in domestic and commercial refrigeration segment.

Let us briefly touch upon all the relevant properties of refrigerants for an application and review various application specific requirements, leading to a particular refrigerant candidates' popularity.

Physical and Thermodynamic Properties

(Not an exhaustive list)

1. Lower boiling temperatures at atmospheric pressure: Benefits in positive and higher suction pressures and improved refrigeration system performance.
2. Lower pressures for a given condensing temperature: Comparatively lower condensing pressures helps to improve system performance.
3. Lower specific volume of vapor: High vapor density and low specific volume helps in optimizing compressor displacement, frame size and improved economy.
4. Lower adiabatic compression index: Lower (C_p/C_v) ratio results in lower discharge gas temperatures and enables stable and reliable compressor performance.
5. High latent heat capacity: Refrigerants with high

Table3: Fluorocarbon refrigerant properties and their applications

Refrigerant	Applications [#]	ASHRAE-34 classification	Boiling point [®] Atmos. Pressure	Molecular weight (g/mol)	Sp vol. vapour Cu.ft/lb ⁽¹⁾	ODP*	GWP*
R-11	Centrifugal chillers	A1	23.7°C / 74.7°F	137.4	12.27	1	~ 4,600
R-12	Domestic Refrigerators, commercial refrigeration cabinets	A1	(-)29.8°C / (-)21.6°F	120.9	1.49	1	10,600
R-13	Ultra-low temp lab equipment	A1	(-)81.3°C / (-)114.3°F	104.5	-	1	10,000
R-22	Air conditioners, water chillers	A1	(-)40.8°C / (-)41.5°F	86.5	1.25	0.055	1,900
R-23	Ultra-low temp Lab equipment	A1	(-)82.1°C / (-)115.8°F	70.0	-	0.0004	14,800
R-502	Supermarket Refrigeration	A1	(-)45°C / (-)49°F	111.6	0.881	0.221	6,200

[#] Indicative only; not an exhaustive list.

* ODP, GWP were not known in those times and were not considered by Industry at that time. These columns are added for a comparative understanding.

⁽¹⁾ Specific volume of vapour is at saturated condition at 5°F (-15°C) evaporating temperature – for comparison at same evaporating temp.

latent heat will require lower mass flow rate (i.e. lower compressor displacement and lower cost) to produce desired cooling capacity.

6. Higher specific heat in vapor phase will help to minimize suction superheat.
7. Lower specific heat in liquid phase will help to increase liquid sub-cooling.
8. Higher critical pressure: need to be adequately higher than the maximum system pressures experienced during worst operating condition (pull-down load or worst system demand coupled with maximum ambient conditions).
9. High heat transfers coefficients help improve heat exchanger performance and economy.

Chemical Properties

1. Shall be non-toxic, non-flammable and non-explosive, in pure state as well as when mixed with air in any proportion.
2. Least reaction with moisture. If the refrigerant reacts with moisture and forms acids and corrosive byproducts, the system components will be affected reducing the reliability.
3. Miscibility of refrigerant and lubricating oil in a system is a critical characteristic deserving special attention of designers. Refrigerants which do not chemically react with oil, and which have the ability to mix well and hold oil with itself in a solution, without separation, at all pressures and temperatures experienced in a given system, are the ones preferred, especially in smaller systems.
4. Very high dielectric strength, as most applications use hermetic or semi-hermetic compressors, with 'motor-inside' design.
5. Chemically stable and non-reactive to metals and elastomers used in compressors and other parts of the refrigeration equipment.
6. In case of leak, should not contaminate food items.
7. Non-ODP and low GWP got added to this list after Montreal Protocol.

Let us review the key refrigerant properties, due to which a specific fluorocarbon was preferred over other candidates in the period of 1930s - 1950s and became popular in specific application requirement.

Domestic and Commercial Refrigeration Appliances

R-12 was the popular choice. With its boiling point of -29.8°C , the suction pressure was positive for commercial freezers, coolers and domestic refrigerators. It had a lower condensing pressure with natural draft and forced draft air-cooled condensers. And above all, it had a lower adiabatic compression index (C_p/C_v) resulting in lower discharge temperature and retained the compressor lubrication oil with itself 'in solution' at lower evaporating temperatures.

In comparison with R12, for commercial refrigeration applications, R22 offered following advantages:

- Due to its higher latent heat capacity, R22 could deliver about 40% higher cooling capacity, for a given compressor displacement. (Theoretical calculations indicate still higher capacity).
- With a lower boiling point of -40.8°C , achieving even lower appliance temperature was possible, which is a significant merit in low temperature refrigeration.

But its higher adiabatic compression index, leading to high discharge temperature, higher discharge pressure and its property of refrigerant and oil separating into separate layers at lower evaporating temperatures led to designers opting for R12 in the simple design, smaller sized, fractional HP hermetic compressor-based refrigeration systems.

Compressor manufacturers subsequently came out with semi-hermetic and open type compressors rated for low temperature commercial refrigeration application, but it was with limited operating envelope (restrictions on ambient temperatures) and by including design concepts like liquid injection or cylinder head cooling with water etc. to keep discharge temperature in check. These low temperature systems with R22 also required oil separators in discharge line. Though this kind of R22 in low temperature had some limited success, with the introduction of R502, the low temperature application of R22 further dwindled in supermarket refrigeration and other applications.

Residential and Commercial Air Conditioners

Methyl chloride (R40) is a halogenated methane-based hydrocarbon. It has many desirable thermodynamic properties; but is moderately toxic and is explosive in certain concentration. When safer fluorinated refrigerants became available, R40 gave way to R22.

R22 was the most preferred refrigerant for air conditioners, over R12 and other known refrigerants of that time. R22 delivered approximately 40% higher cooling capacity over R12 for a given compressor displacement, due to its higher latent heat capacity and lower specific volume. The discharge temperature was relatively higher in comparison with R12, but this was still within design limits in air conditioning application, because of higher mass flow rates, lower pressure ratio and less suction superheat, in comparison with R22 parameters in low temperature or medium temperature commercial refrigeration.

R22 system performance, reliability, safety and economy became the benchmark – for future comparison with other refrigerants, in air conditioning applications.

Automobile Air Conditioning

R12 was the choice in this application due to its lower system pressures, lower starting torque requirement and lower discharge gas temperature in comparison with R22.

Industrial Refrigeration

In the 1930s, the early years natural refrigerants like carbon dioxide, propane, methyl chloride, methylene chloride and ethane were making way in different applications, for the newly introduced, non-toxic and non-flammable halogenated Refrigerants. But one natural refrigerant that could not be substituted by halocarbons, which has continued to thrive till date for more than 100 years has been ammonia. Even though ammonia's toxicity and flammability at certain conditions continued to be a concern over the years (in comparison with halocarbons), the beneficial characteristics of ammonia far outweighed these safety distractions. Interested readers may refer to various articles on ammonia published by *ISHRAE ACR Journal* in its earlier issues.

Continuous field education on safe handling of ammonia by International Ammonia Association and Association of Ammonia Refrigeration (AAR) in India and development of specific industry codes to build the system safety requirements in the equipment design itself have strengthened the measures to address these safety concerns.

With zero ODP and zero GWP and introduction of low-charge ammonia chillers in the 21st century, ammonia continues to be the best choice refrigerant in industrial refrigeration applications even today and in foreseeable future.

Water Chillers (Restricted here to AC Applications)

R12 and R22 selections were offered by large open type reciprocating and semi-hermetic compressor manufacturers in the early years. R12 had lower operating pressures and needed lower motor starting torque and its lower discharge temperatures allowed to stretch the application envelope in certain application requirements. But for a given compressor displacement (and compressor block / frame design), R22 delivered about 40% higher capacity than R12 and made more economic sense. With introduction of Screw compressor technology, R22 became a popular refrigerant.

In centrifugal chillers, methylene chloride (R30) gave way to R11, which had near similar characteristics (refer *Table 4*). R30 is a halogenated hydrocarbon of methane series and is non-toxic, non-flammable and non-corrosive even in presence of moisture. R11 was also a high boiling point fluid, requiring negative evaporator pressure and centrifugal compressor for large volume flow handling. However, the

one key benefit offered by R11 was approximately half of the compressor displacement requirement compared to R30. Inversely, for existing compressor blocks, use of R11 helped to double the cooling capacity.

Ultra-Low Temperature Application

Low temperature cabinets with temperature of -60°C, -70°C etc. are required in certain research laboratories and for specific healthcare storage needs. R13 with its very low boiling point of -81.7°C was one of the mostly used refrigerants in these ultra-low temperature cabinets in a cascade system. The compressor and equipment manufacturers (OEMs) reviewed and conducted necessary testing of refrigerant and oil in such cases. Synthetic oils were used in place of mineral oils in such ultra-low temperature applications, as the floc point of compressor lubrication oil need to be much lower than evaporating temperature.

R23 was another ultra-low temperature refrigerant used with necessary approval from compressor manufacturer and with adequate care to control its high discharge temperature. A point of interest is the chemical composition of this refrigerant – Trifluoro methane! Yes, no chlorine atom and the reason for ODP of zero.

Azeotrope and Zeotrope

Azeotropes and zeotropes are compounds of two or more chemicals. The resultant chemical exhibited totally different thermodynamic properties. Azeotropes exhibit phase-change (evaporation and condensing) characteristics, as if it is a homogenous single compound. The glide is so insignificant that the published data have a single boiling and condensing temperature. Azeotropes are very stable in a system and the composition does not change. Hence azeotrope refrigerants could be charged either as a liquid or vapor in a system. Handling azeotropes makes the job of designers and service engineers that much easier.

Zeotropes have different boiling and condensing temperatures of their constituent components. The difference in dew point* and bubble point* in evaporator and condenser is referred to as temperature glide as shown in *Figure 5*. The internal composition is not stable and could change due to system leakage etc. This necessitates zeotrope refrigerant system to be charged only with liquid refrigerant. Zeotrope refrigerant design necessitates that much more attention from designers and field engineers, compared to azeotropes.

Table 4: Theoretical cycle comparison of methylene chloride (R30) and R11 in centrifugal chillers

	Boiling point at Atm. Pre.	Pressure [®] 5°F Evp. temp. (Psig)	Pressure [®] 86°F cond. temp. (Psig)	Compr. Ratio (P _{sia} / P _{sia})	Net Ref. effect ° 5°F / 86°F (Btu/lb)	Mass flow rate (lb/min)	Sp vol. vapour Cu.ft/lb at 5°F evp.	Compressor Displacement CuF/min/TR	Theoretical COP
R30	40.7°C / 105.2°F	27.6"Hg	9.5"Hg	8.6	134.6	1.49	49.9	74.3	4.90
R11	23.7°C / 74.7°F	24"Hg	3.6 psig	6.24	67.5	2.96	12.27	36.32	5.09

R-11 requires ~ 50% of compressor displacement compared to R-30

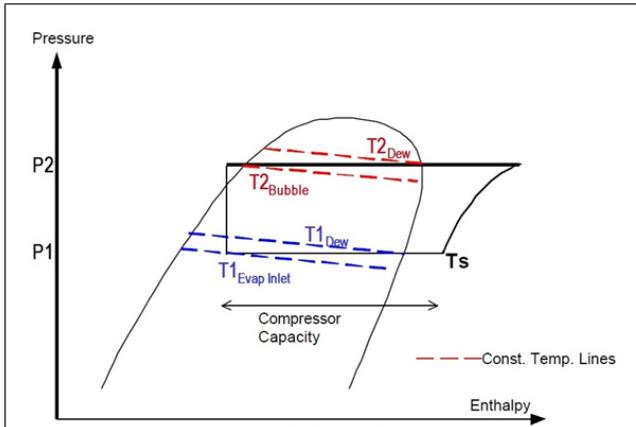


Figure 5: Constant temperature lines of zeotropes – during evaporation and condensation (* dew point refers to saturated vapor point and bubble point refers to saturated liquid point).

A few popular azeotrope refrigerants of yesteryears are described below.

In supermarket refrigeration and similar applications, use of R22 with certain design care in low temperature application was the practice, till R502 was developed and smoothly replaced R22 in supermarket refrigeration systems. R502 offered combined merits of R12 (low discharge temperature, excellent oil miscibility) and R22 (high latent heat, lower specific volume) in low temperature refrigeration application. It is a mixture of R22 and R115 in 48.8%: 51.2% by weight. R502 offered cooling capacity similar to R22, with a lower discharge gas temperature like R12.

R503 was another azeotrope made up of 60% by weight of R13 and 40% of R23 for ultra-low temperature applications. R503 on the low side and R502 on the high side of a cascade system was a popular system for ultra-low temp applications, till the implementation of Montreal protocol.

Refrigerant Nomenclature

In the 1930s, the initial fluorocarbon refrigerants were branded and promoted using different names by refrigerant manufacturers (example: Freon, Genetron, etc.). ASRE refrigerants numbers designation committee came out with a methodology as explained below, using which it became easy to refer to a specific chemical, by its refrigerant number.

Table 5 gives the list of refrigerants and their number designations published in ASRE Databook 1957-58. A quick glance points out that different compounds like halocarbon, organic compound, inorganic compounds etc. have been grouped separately with a different identification number series.

Halocarbons of methane, ethane, propane and cyclobutane based chemicals (0XX, 1XX, 2XX and 3XX series)

Refrigerant standard designation: R (digit₁) (digit₂) (digit₃)

- The 1st numeral (digit₁) = number of carbon atoms present – 1.

Table 5: ASRE Databook 1957-58 archive

ASRE Standard Refrigerant Designation	Chemical Name	Chemical Formula	Molecular Weight	Boiling Point, F	Status ¹
Halocarbon Compounds					
10	Carbontetrachloride	CCl ₄	153.8	170.2	
11	Trichloromonofluoromethane	CCl ₃ F	137.4	74.8	C
12	Dichlorodifluoromethane	CCl ₂ F ₂	120.9	-114.6	C
13	Monochlorotrifluoromethane	CClF ₃	104.5	-114.6	C
13B1	Monobromotrifluoromethane	CBF ₃	148.9	-72.0	S
14	Carbontetrafluoride	CF ₄	88.0	-198.4	S
20	Chloroform	CHCl ₃	119.4	142	
21	Dichloromonofluoromethane	CHCl ₂ F	102.9	48.1	D
22	Monochlorodifluoromethane	CHF ₂ Cl	86.5	-41.4	C
23	Trifluoromethane	CHF ₃	70.0	-119.9	D
30	Methylene chloride	CH ₂ Cl ₂	84.9	105.2	C
31	Monochloromonofluoromethane	CH ₂ ClF	68.5	48.0	
32	Methylene fluoride	CH ₂ F ₂	52.0	-61.4	C
40	Methyl chloride	CH ₃ Cl	50.5	-108.8	C
41	Methyl fluoride	CH ₃ F	34.0	-109	
(50)	Methane	CH ₄	16.0	-259	C*
110	Hexachloroethane	CCl ₂ CCl ₂	236.8	365	
111	Pentachloromonofluoroethane	CCl ₅ CClF	220.3	279	
112	Tetrachlorodifluoroethane	CCl ₄ CCl ₂ F ₂	203.8	199.0	
112a	Tetrachlorodifluoroethane	CCl ₂ CCl ₂ F ₂	203.8	195.8	
113	Trichlorotrifluoroethane	CCl ₃ CClF ₂	187.4	117.6	C
113a	Trichlorotrifluoroethane	CCl ₂ CF ₃	187.4	114.2	
114	Dichlorotetrafluoroethane	CCl ₂ CF ₂ CF ₂	170.9	38.4	C
114a	Dichlorotetrafluoroethane	CCl ₂ CF ₂	170.9	38.5	C
114B2	Dibromotetrafluoroethane	CBR ₂ CF ₂ CF ₂	259.9	117.5	D
115	Monochloropentafluoroethane	CClF ₂ CF ₃	154.5	-37.7	D
116	Hexafluoroethane	CF ₃ CF ₃	138.0	-108.8	
120	Pentachloroethane	CHCl ₂ CCl ₃	202.3	324	
123	Dichlorotrifluoroethane	CHCl ₂ CF ₃	153	83.7	
124	Monochlorotetrafluoroethane	CHClCF ₂ CF ₃	136.5	10.4	
124a	Monochlorotetrafluoroethane	CHClCF ₂	136.5	14	D
125	Pentafluoroethane	CHF ₂ CF ₃	120	-55	
133a	Monochlorotrifluoroethane	CH ₂ ClCF ₃	118.5	43.0	D
140a	Trichloroethane	CH ₃ CCl ₃	133.4	165	
142b	Monochlorodifluoroethane	CH ₂ ClCF ₂	100.5	12.2	S
143a	Trifluoroethane	CH ₃ CF ₃	84	-53.5	
150a	Dichloroethane	CH ₂ CHCl ₂	98.9	140	
152a	Difluoroethane	CH ₂ CHF ₂	66	-12.4	C
160	Ethyl chloride	CH ₃ CH ₂ Cl	64.5	54.0	
(170)	Ethane	CH ₃ CH ₃	30	-127.5	C*
218	Octafluoropropane	C ₃ F ₈	188	-36.4	
(290)	Propane	CH ₃ CH ₂ CH ₃	44	-44.2	C*
Cyclic Organic Compounds					
C316	Dichlorohexafluorocyclobutane	C ₄ Cl ₂ F ₆	233	140	
C317	Monochloroheptafluorocyclobutane	C ₄ ClF ₇	216.5	77	
C318	Octafluorocyclobutane	C ₄ F ₈	200	21.1	D
Azeotropes					
500	Refrigerants-12/152a 73.8/26.2 wt %*	CCl ₂ F ₂ /CH ₂ CHF ₃	99.29	-28.0	C
501	Refrigerants-22/12 75/25 wt %	CHCl ₂ CCl ₂ F ₂	93.1	-42	
502	Refrigerants-11/115 48.8/51.2 wt %	CHCl ₂ CCl ₂ F ₂	112	-50.1	

ASRE Standard Refrigerant Designation	Chemical Name	Chemical Formula	Molecular Weight	Boiling Point, F	Status ¹
Miscellaneous Organic Compounds					
Hydrocarbons					
50	Methane	CH ₄	16.0	-259	C
170	Ethane	CH ₃ CH ₃	30	-127.5	C
290	Propane	CH ₃ CH ₂ CH ₃	44	-44.2	C
600	Butane	CH ₃ CH ₂ CH ₂ CH ₃	58.1	31.3	
601	Isobutane	CH(CH ₃) ₂ CH ₃	58.1	14	
(1150)	Ethylene	CH ₂ =CH ₂	28.0	-155.0	C*
(1270)	Propylene	CH ₂ CH=CH ₂	42.1	-53.7	C*
Oxygen Compounds					
610	Ethyl ether	C ₂ H ₅ OC ₂ H ₅	74.1	94.3	
611	Methyl formate	HCOOCH ₃	60.0	89.2	
Sulfur Compounds					
620					
Nitrogen Compounds					
630	Methyl amine	CH ₃ NH ₂	31.1	20.3	
631	Ethyl amine	C ₂ H ₅ NH ₂	45.1	61.8	
Inorganic Compounds					
717	Ammonia	NH ₃	17	-28.0	C
718	Water	H ₂ O	18	212	
729	Air		29	-318	
744	Carbon dioxide	CO ₂	44	-109	C
744A	Nitrous oxide	N ₂ O	44	(subl.)	
764	Sulfur dioxide	SO ₂	64	-127	C
Unsaturated Organic Compounds					
1112a	Dichlorodifluoroethylene	CCl ₂ -CF ₂	133	67	
1113	Monochlorotrifluoroethylene	CClF=CF ₂	116.5	-18.2	
1114	Tetrafluoroethylene	CF ₂ =CF ₂	100	-105	
1120	Trichloroethylene	CHCl=CCl ₂	131.4	187	
1130	Dichloroethylene	CHCl=CHCl	96.9	118	
1132a	Vinylidene fluoride	CH ₂ =CF ₂	64	-119	
1140	Vinyl chloride	CH ₂ =CHCl	62.5	7.0	
1141	Vinyl fluoride	CH ₂ =CHF	46	-98	
1150	Ethylene	CH ₂ =CH ₂	28.0	-155.0	C
1270	Propylene	CH ₂ CH=CH ₂	42.1	-53.7	C

1. Denotes that as of October 1956, the status of these refrigerants as regards commercial evolution is as follows: C, S, or D. C—Commercial S—Semi-commercial D—Development.
 2. The compounds methane, ethane, and propane appear in the halocarbon section in their proper numerical positions, but in parentheses since these products are not halocarbons.
 3. The compounds ethylene and propylene appear in the hydrocarbon section as parenthetical items in order to indicate that these compounds are hydrocarbons. Ethylene and propylene are properly identified under Unsaturated Organic Compounds.
 From the ASRE Data Book, Design Volume, 1957-58 Edition, Heating, Refrigerating, and Air-Conditioning Engineers.

Inversely this will mean that methane (CH_4) based chemicals will not have the 1st digit (being zero), ethane (C_2H_6) based chemicals will have 1 as the 1st digit and propane (C_3H_8) based chemicals will have 2 as their digit. For R12 and R22, though their actual designation works out to R-012 and R-022, for simplicity the preceding 0 is omitted.

- The 2nd numeral (digit₂) = number of hydrogen atoms present + 1.
- The 3rd numeral (digit₃) indicates the number of fluorine atoms in the chemical.

Zeotropes were assigned 400 series and azeotropes 500 series by the ASRE standards committee. The 2nd and 3rd digits of the number are sequential (ordinal) numbers, in the order the refrigerants were considered by the committee. Zeotropes of 400 series became more pronounced with the development of HFC gases at a later stage (not visible in the 1957-58 Databook).

600 series designate miscellaneous organic compounds and 700 series the inorganic compounds. The molecular weight of inorganic compound is used as the 2nd and 3rd digits of the 700 series. Please refer the molecular weight column in Table 5.

The unsaturated organic compounds are in the 1000' series with digit 1 getting added as a prefix to the subsequent 3 digits indicating the ethene/ ethylene, propene/propylene compounds. These 3 digits respectively indicate the no of carbon, hydrogen and fluorine atoms – as explained above for halogenated compounds.

Other Compounds and Continuous Developments

So far, we were discussing how the halogenated hydrocarbons of methane and ethane series had enabled the HVACR industry in the 1930s and 40s, to offer safer refrigerants in refrigeration equipment. Continuous industrial revolution across the globe, along with innovative and break-through developments in design of compressors, electric motors, flow

control devices, instrumentation and control devices etc. was propelling the growth of HVACR industry in sync with the overall growth of the global economy. Safe refrigerant chemicals played a crucial part in this growth story.

Application of these safe chemicals (of that time) was just not limited to use in HVACR industry as Refrigerants. The chemicals were finding wide-spread use across Industries for different uses, some of which are listed below:

- Laboratory and Industrial solvents and degreasers (example: electronic manufacturing, pharma process, paint stripping)
- Solvents for fat, oil, wax etc.; solvent or cosolvent for fumigation pesticides
- Component for chemical degreasing mixtures
- Aerosol propellant, sometimes used with another chemical
- Foam blowing agent for polystyrene, polyethylene, polyurethane, phenolics etc.
- Dielectric gas in electrical systems
- Diluent for gas mixtures
- Fire suppressant
- Intermediate in production of polymers
- Plasma etchant in metallurgy process
- Inert ingredient for medical sterilant gases
- Coolant in Infrared detector cells
- Inhalation anesthetics
- Fumigant for grains and strawberries
- Extraction solvent for spice oleoresins, hops and caffeine from coffee
- Veterinary pharmaceutical
- Rubber vulcanizing accelerator
- Retarding agent in fermentation
- Constituent in explosives, pyrotechnics and smoke devices
- Additive to raise the flash point of solvents
- Aerating agent for foamed and sprayed food products and as a food additive for vapor depression

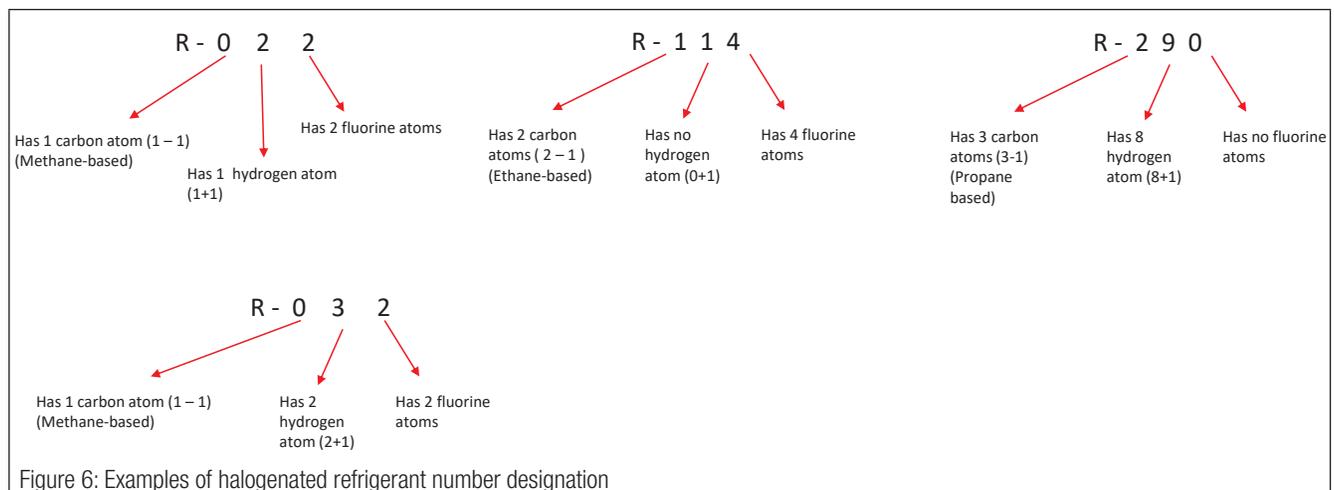


Figure 6: Examples of halogenated refrigerant number designation

- Blend component of adhesives, cosmetics, perfumes, insecticides, and rubber cement and coating formulations.

This context could be easily understood and appreciated by readers, by referring to *Table 5*, which gives a screenshot of ASRE 1956-57 list of refrigerant chemical compounds. Only handful refrigerants were used in ACR equipment. Many of the other chemicals like R10, R115, R133a, R142b, R1113, R1132a etc. were finding use in a variety of applications other than ACR. This enormous amount of work and efforts of chemical manufacturers and scientists, also facilitated them finding any solution for specific requirements of ACR industry, including mixing of available compounds and deriving certain needed outcomes.

Refrigerant Qualification

Introduction of any new refrigerants in ACR industry has been an elaborate and long-drawn process, with lots of qualification testing with respect to performance, safety, refrigerant-oil relationship, chemical stability and many other key parameters.

These tests are initially conducted by the chemical (refrigerant) manufacturers and subsequently pursued by them with compressor manufacturers and equipment manufacturers for testing and necessary approvals. The OEMs usually invest huge sums of money in evaluation, prototype building, performance evaluation, accelerated life tests for reliability assessment, field evaluation etc. This process of

introducing new refrigerant ACR equipment in the market has more or less remained the same since the time of fluorinated hydrocarbons. Advancement in technology, simulation software, reliability assessment tools and techniques etc. have made the whole process more robust and has relatively shortened the new equipment / new refrigerant introduction lead time.

New Findings and Changed Scenario in 90s

All the above deliberations might help us to understand how the refrigerants and ACR industry evolved over the last many decades. Refrigerants like R11, R12, R22, R502 remained dominant till the 1980s and '90s in many of the above applications and set a benchmark for comparison – for any potential future refrigerants. The findings of scientists on the thinning of ozone layer and effects of global warming, brought the limelight back on refrigerants.

References

1. <https://www.ashrae.org/about/mission-and-vision/ashrae-industry-history/air-conditioning-and-refrigeration-timeline>
2. ARTI refrigerant database data summaries, volume 1 and 2
3. 'Principles of Refrigeration', textbook by Roy J. Dossat, 1961 edition.
4. Different ASHRAE and ISHRAE position documents and publications on Refrigerants.

