

CHARACTERISTICS OF REFRIGERANTS

By: Dr. Ralph C. Downing
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HISTORY

Modern refrigeration methods, as distinguished from the use of ice and snow, go back to the early part of the 19th century. The following dates and events illustrate the development of the industry and the variety of refrigerants used. Many other gases were studied and some, such as the hydrocarbon group, have found limited use.

1834 - First practical refrigerating machine using the compression cycle was built.

1845 - Air machine developed.

1850 - Absorption machine developed using water and sulfuric acid.

1857 - Ether used quite widely as a refrigerant in the brewing and meat processing industries.

1873 - Ammonia compressor introduced.

1876 - Sulfur dioxide compressor developed.

1881 - The use of carbon dioxide was introduced.

1890 - Demand for small units for home and store use developed.

1900 - Electric motor appeared.

1915 - Sulfur dioxide more generally used.

Commercial introduction of newer refrigerants:

1920 - Methyl chloride

1930 - R-12

1932 - R-11

1933 - R-114

1934 - R-113

1936 - R-22

1945 - R-13

1950 - R-500

1962 - R-502

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GENERAL

The duty of a refrigerant is to carry heat from some area where it is not desired to some other place where it can be disposed of. Small amounts of heat can be transferred by gases (such as air) or even liquids operating between different temperatures. A much larger amount of heat can be absorbed and transferred, however, when a liquid is vaporized to a gas. This method is used in nearly all cooling equipment today, whether the moving force is mechanical as in a compressor or heat as in an absorption system.

In heat pump applications, heat is recovered from the refrigerant as it changes from a gas to a liquid. Although most of the heat comes from condensation of the gas, some heat is also obtained in cooling the hot discharge gas to the condensing temperature. The latter source may amount to 15 to 20 percent of the total under some conditions.

A number of materials have physical and thermodynamic properties suitable for their use as refrigerants. Many different refrigerants have been used in the past and are in use today with good ability to transfer heat from one place to another.

In fact, from the thermodynamic or heat-carrying standpoint, differences among refrigerants with similar boiling points are small. In today's world, other properties of the refrigerant are more important. Safety is perhaps the most important single factor in the selection of a refrigerant. The most reliable way to be safe is to choose a refrigerant that is neither toxic nor flammable. Most of the halogenated refrigerants meet these requirements. Refrigerants for use in homes, theaters, stores, hospitals and other locations where people gather are universally selected from this group. Safety also can be attained by the use of many controls and the constant vigilance of trained operators. For example, hydrocarbon refrigerants, though extremely flammable, are often used in petroleum refineries where techniques for handling such hazardous materials are well developed.

The physical properties of some commonly-used refrigerants are listed in Table 3T34 and briefly discussed below.

Table 3T34

REFRIGERANT PROPERTIES (In The Order of their Boiling Point, °F)						
Name	Chemical Formula	Molecular Weight	Boiling Point, °F	Freezing Point, °F	Toxic	Flammable
Ethylene	C ₂ H ₄	28.03	-155.0	-272	No	Yes
Ethane	C ₂ H ₆	30.04	-127.5	-278	No	Yes
R-13	CClF ₃	104.47	-114.6	-294	No	No
R-502	*	111.6	-50.1	—	No	No
Propane	C ₃ H ₈	44.06	-44.2	-310	No	Yes

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R-22	CHClF ₂	86.48	-41.4	-256	No	No
Ammonia	NH ₃	17.03	-28.0	-108	Yes	Mod.
R-500	**	99.29	-28.0	-254	No	No
R-12	CCl ₂ F ₂	120.93	-21.6	-252	No	No
Methyl Chloride	CH ₃ Cl	50.48	-10.8	-144	Yes	Mod.
Sulfur Dioxide	SO ₂	64.06	14.0	-104	Yes	No
R-114	C ₂ Cl ₂ F ₄	170.93	38.4	-137	No	No
R-11	CCl ₃ F	137.38	74.8	-168	No	No
Methylene Chloride	CH ₂ Cl ₂	84.94	103.6	-142	No	No
R-113	C ₂ Cl ₃ F ₃	187.39	117.6	-31	No	No
Water	H ₂ O	18.02	212	32	No	No

* Azeotropic Mixture of Refrigerants 22 and 115(48.8/51.2% by weight)

** Azeotropic Mixture of Refrigerants 12 and 152a(73.8/26.2% by weight)

R-12 - Dichlorodifluoromethane used in reciprocating and rotary compressors for refrigerators, coolers, freezers, and air conditioning; used in centrifugal compressors for large air conditioning and industrial applications is increasing.

R-22 - Chlorodifluoromethane- used in all types of household and commercial refrigeration and air conditioning applications with reciprocating compressors.

R-11 - Trichlorofluoromethane - used in centrifugal compressors for industrial process cooling and large air conditioning systems - also used as a low temperature brine.

R-717 - (Ammonia) - used in the brewing, ice-making, food-freezing and similar industries in reciprocating compressors also in air conditioning with water in absorption systems .

R-500 - used in reciprocating compressors for air conditioning, and domestic refrigerators

R-502 - used in reciprocating compressors for low temperature freezers, cabinets and display cases.

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Hydrocarbons - used to some extent in process cooling especially in petroleum refineries.

R-113 And R-114 - used in commercial and industrial air conditioning and process cooling with centrifugal compressors especially in small tonnage applications .

R-718 - (Water) - used in air conditioning applications in absorption systems with brine.

R-13 - low-temperature refrigerant used in environmental test boxes, metal hardening and similar applications.

REFRIGERANT PROPERTIES

Molecular Weight

The molecular weight is an indication of the density of the liquid or vapor. Refrigerants with a low molecular weight tend to have low density or high volume.

$$\left(\text{volume, cu ft/lb} = \frac{1}{\text{density, lb/cu ft}} \right)$$

Ammonia and water are exceptions. They both have much higher densities than they should, based on their molecular weights.

Boiling Point

The temperature at which the vapor pressure equals one atmosphere (0 psig) is known as the boiling point. If leaks are present in a system, the boiling point is the dividing line between refrigerant leaking out, at higher temperatures and air and water vapor leaking in, at lower temperatures. With open systems where leaks are sometimes a problem it is desirable to operate with evaporator temperatures above the boiling point of the refrigerant, if possible. With hermetically sealed units, leaks generally are not a problem as far as operating the equipment is concerned. If a leak occurs, especially in small equipment, performance begins to suffer immediately and the leak must be found and repaired.

Vapor Pressure

Figure 3F33 shows the vapor pressure of some refrigerants in common use today. Although most of the curves are quite parallel, some rise faster than others. It is important to remember that the vapor pressure means the pressure of the vapor above the liquid. In order to use the relations between temperature and pressure shown in Figure 3F33, some liquid must be present. For example, the high-side pressure in a refrigeration system is the vapor pressure of the liquid in the condenser (except for a minor pressure drop in the piping). The corresponding temperature found in Figure 3F33 is the condensing temperature even though the temperature may be higher at the point where the pressure measurement is made.

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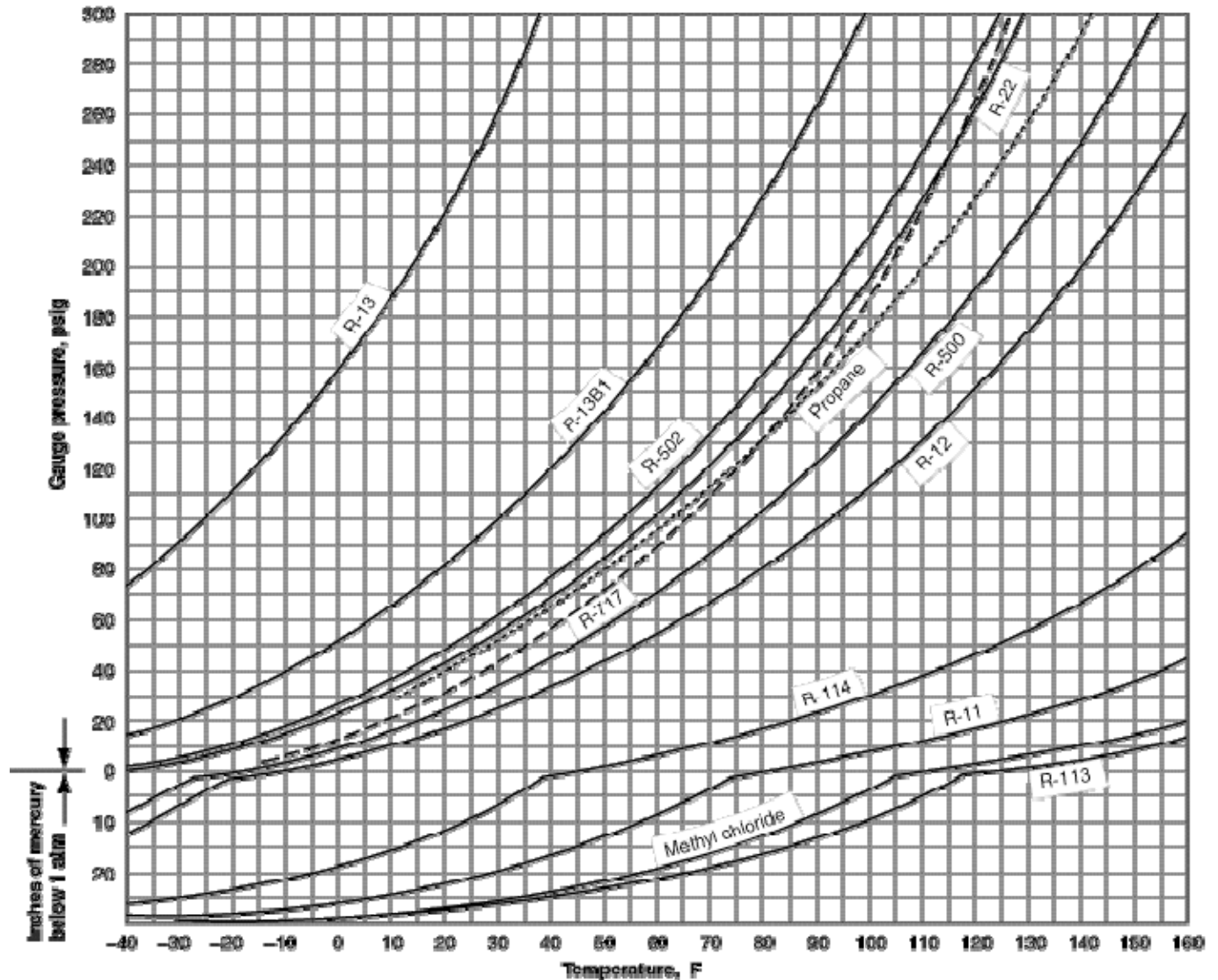


FIGURE 3F33 Pressure-Temperature Relationships of Refrigerants

The measured pressure in the low side of the unit is also the vapor pressure assuming there is some liquid present in the evaporator. The corresponding temperature is that of the boiling liquid even though the gas may be superheated at the point where the pressure is measured. Use of the vapor pressure curve (or tables) with measurements of pressure is generally a much more reliable way of finding the condensing and evaporating temperatures than attempts to measure the temperature directly.

The compression ratio can be determined by dividing the condensing pressure by the evaporating pressure. For this calculation the pressures must be in absolute units (gauge pressure + 14.7).

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Ordinary pressure gages used in refrigeration work give the difference in pressure between the system and the outside atmosphere. The scale on the gage is usually adjusted for an outside pressure of one atmosphere or zero gage. Unless the scale has been changed the gage reading will be high if used at high altitudes where the atmospheric pressure is low. This error amounts to 0.5 psi for every 1,000 feet of elevation. The correction should be subtracted from the gage reading in order to get the true vapor pressure and the corresponding temperature.

Freezing Point

In most applications the freezing points of the refrigerants are so low that they need not be considered. They may be important, however, in some cases when the refrigerant is used as a low temperature brine.

Table 3T34

Name	Chemical formula	Molecular weight	Boiling point, °F	Freezing point, °F	Toxic	Flammable
Ethylene (R-1150)	C ₂ H ₄	28.03	-155.0	-272	No	Yes
Ethane (R-170)	C ₂ H ₆	30.04	-127.5	-278	No	Yes
R-13	CClF ₃	104.47	-114.6	-294	No	No
R-502	*	111.6	-50.1	—	No	No
Propane	C ₃ H ₈	44.06	-44.2	-310	No	Yes
R-22	CHClF ₂	86.48	-41.4	-256	No	No
Ammonia (R-717)	NH ₃	17.03	-28.0	-108	Yes	Mod.
R-500	**	99.29	-28.0	-254	No	No
R-12	CCl ₂ F ₂	120.93	-21.6	-252	No	No
Methyl chloride (R-40)	CH ₃ Cl	50.48	-10.8	-144	Yes	Mod.
Sulfur dioxide (R-764)	SO ₂	64.06	14.0	-104	Yes	No
R-114	C ₂ Cl ₂ F ₄	170.93	74.8	-168	No	No
R-11	CCl ₃ F	137.38	74.8	-168	No	No
Methylene chloride (R-30)	CH ₂ Cl ₂	84.94	103.6	-142	No	No
R-113	C ₂ Cl ₃ F ₃	187.39	117.6	-31	No	No
Water	H ₂ O	18.02	212.0	32	No	No

* Azeotropic mixture of R-22 and R-115 (48.8/51.2% by weight)

** Azeotropic mixture of R-12 and R-152a (73.8/26.2% by weight)

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Toxicity

In Table 3T34 the refrigerants are shown as being either toxic or not toxic. This broad classification distinguishes between products that are quite toxic and those where the hazard is very slight or practically nonexistent. Some differences, however, are recognized among refrigerants of low toxicity. The Safety Code for Mechanical Refrigeration (ASHRAE Standard 15-58 or ASA B9.1-1958) lists the maximum permissible quantity of refrigerant for a direct system located in an area occupied by humans. The quantities are compared in Table 3T35A.

Table 3T35A

MAXIMUM PERMISSIBLE QUANTITY OF REFRIGERANT IN DIRECT SYSTEMS IN HUMANLY OCCUPIED SPACE	
Refrigerant	Maximum Amount of Refrigerant lbs. per 1000 cu. ft. of Space
12	31
22	22
11	35
113	24
114	44
13	27
500	26
Methylene Chloride	6

The data there apply to "... institutional, public assembly, residential and commercial occupancies". Larger amounts are permitted in industrial applications. For complete details, the Standard should be consulted.

No refrigerant or other gas should be present in the air in concentrations large enough to appreciably reduce the amount of oxygen present. Good ventilation should be provided at all times to prevent the build up of foreign gases in the air.

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Flammability

Three classes of flammability are listed in Table 3T34:

Very flammable (yes)

Moderately flammable (Mod.)

Nonflammable (No)

The difference between a very flammable gas and a moderately flammable gas depends on the flammability range of mixtures with air and the lower limit of the range. If the right amount of gas is present, one gas is just as hazardous as the other. For example, the flammable range for propane is about 2 to 9 percent in air, while the range for ammonia is about 15 to 27 percent. Propane is considered more hazardous because a smaller amount can be flammable or explosive. However, ammonia is just as hazardous if enough is present to fall within the flammable range. The flame temperature when ammonia burns in air is over 3000°F and for propane is slightly higher. Of course, flammable gases can be and are used safely but the hazard should be recognized.

Stability

In normal systems that are reasonably clean and dry, the stability of the refrigerant is not ordinarily a factor. Most refrigerants have adequate stability for the applications where they are used. The maximum temperatures recommended for exposure of several halogenated refrigerants are listed in Table 3T35B.

Table 3T35B

THERMAL STABILITY OF REFRIGERANTS	
Refrigerant	Maximum Temperature for continuous exposure in the presence of Oil, Steel and Copper, °F
R-11	225
R-113	225
R-12	250
R-500	250
R-114	250
R-22	275-300
R-502	275-300
R-13	>300

It is assumed that copper, steel and lubricating oil are present in the system. These temperature limits are based on static sealed-tube tests and are probably somewhat conservative. However, they are good guides for the operation of refrigeration equipment. If these limits are not exceeded, systems should operate satisfactorily for many years as far as the refrigerant is concerned. Under abnormal conditions when excessive amounts of water, air, or perhaps other foreign materials may be present, the temperatures listed in Table 3T35B may be too high. However, when this occurs operating problems may develop even at lower temperatures.

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Ammonia and sulfur dioxide are stable refrigerants at ordinary operating conditions even though compressor discharge temperatures usually run higher than those with the halogenated refrigerants.

REFRIGERANTS AND WATER

The presence of water in refrigeration systems is undesirable and special methods and procedures have been designed to dehydrate all parts of the system before charging. Refrigerants and oils are also supplied with very low limits on the amount of water that can be present. Great effort is used to keep water out of refrigeration systems for two reasons.

1. Excess water may freeze at low temperatures and restrict or stop the flow of refrigerants through expansion valves or capillary tubings .
2. Excess water may cause corrosion in the system.

SOLUBILITY OF WATER

The solubility of water in several refrigerants is shown in Table 3T36A.

Table 3T36A

SOLUBILITY OF WATER IN LIQUID REFRIGERANTS						
Temp. °F	Solubility in parts per in parts Million by Weight					
	R-11	R-12	R-22	R-113	R-114	R-502*
100	168	165	1800	168	148	740
80	113	98	1350	113	95	560
60	70	58	970	70	57	440
40	44	32	690	44	33	300
20	26	17	470	26	18	185
0	15	8	308	15	10	120
-20	8	4	195	8	5	70
-40	4	2	120	4	2	40
-60	2	1	68	2	1	20
-80	>1	>1	37	>1	>1	12

* Estimated

With most of these refrigerants the solubility is quite low, especially at low temperatures. If more water is present than will dissolve at temperatures below 32°F, ice will form and may deposit in expansion valves or capillary tubing. When sufficient ice is present, the operation of the system will be impaired or may stop completely. This problem is most serious for R-12 and R-11 and less serious for R-22 and R-502.

Liquid drying agents are sometimes added to refrigeration systems to prevent water from freezing. Their use is not recommended. It is better to remove the water than to risk the addition of other materials which may lead to more corrosion, copper plating or otherwise shorten the operating life of the unit. Standard procedures for dehydrating systems before charging should be followed and permanent liquid line driers used when necessary.

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The solubility of water in hydrocarbon refrigerants is about the same order of magnitude as for R-12.

Ammonia and sulfur dioxide will dissolve any amount of water that might be present so that ice formation is not a problem with these refrigerants.

SOLUBILITY IN WATER

The solubility of a refrigerant in water is of no concern in a refrigeration system since free water should never be present there. However, the question may arise in some applications, such as drinking water coolers, water-cooled condensers and other places where refrigerant might come in contact with water either through equipment failure or, in some cases, by design. In general, the solubility of halogenated or hydrocarbon refrigerants in water is slight. Some information is shown in Table 3T36B.

Table 3T36B

SOLUBILITY OF REFRIGERANTS IN WATER AT 70°F AT SATURATION PRESSURE

Refrigerant	Solubility in Parts Per Million by Weight
R-11	180
R-12	280
R-22	3800
R-113	22

As might be expected, R-22 is considerably more soluble in water than the other refrigerants, although the level of solubility is low.

DISTRIBUTION IN WATER

When refrigerants are stored in cylinders, receivers, condensers, etc., any water present is distributed between the liquid phase of the refrigerant and the vapor phase. With most of the halogenated refrigerants the concentration of water in the vapor phase is higher than it is in the liquid phase. With Refrigerant 22, the situation is reversed. These relationships are shown in Table 3T37A.

Table 3T37A

DISTRIBUTION OF WATER BETWEEN VAPOR AND LIQUID REFRIGERANT

Refrigerant	Ratio: Water in Vapor/Water in Liquid		
	0 °F	40°F	80°F
R-11	63	49	36
R-12	14	10	7
R-22	0.3	0.4	0.4
R-113	138	98	63
R-114	33	24	17

The effect of temperature can also be seen. The ratio of concentrations between the vapor and liquid is higher at low temperatures than at higher temperatures. This distribution of water means, for example,

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that if R-12 vapor is removed from a cylinder, the remaining liquid will become drier. Since a higher concentration of water is removed with the vapor, the refrigerant charged in this way will be wetter than that originally in the cylinder. For this reason, it is desirable to charge through a drier if the refrigerant is removed from the cylinder as a vapor. With R-22 the reverse is true and the remaining liquid becomes wetter as the vapor is removed.

It should be noted that this ratio is in terms of concentration. The total amount of water in a cylinder or other container will be much greater in the liquid phase unless only a very small amount of liquid is present.

CORROSIVE EFFECT OF WATER

Water itself may cause corrosion of the metallic parts of a refrigeration system, especially if some air is also present. Rust and scale may form and migrate to parts of the system where its presence may cause trouble. When water is present in ammonia a strong base is formed which may affect insulation, gasketing and other nonmetallic parts of the system. With sulfur dioxide a strong acid is formed in the presence of water with consequent corrosion of metallic parts.

HYDROLYSIS

Water may cause the hydrolysis of halogenated refrigerants with the formation of acids. These acids may corrode metals and attack insulation and nonmetallic parts of the system. Ordinarily, this hydrolysis is very slow and is most serious when free or undissolved water is present. High operating temperatures will increase the rate of hydrolysis .

From every standpoint, the presence of water in a refrigeration system is undesirable. Every effort should be made to be sure that systems are dry and are kept dry by the use of driers where necessary .

REFRIGERANTS AND OIL

The relationships between refrigerant and oil are important in two ways.

1. Change in the physical properties of the oil when it is diluted by refrigerant.
2. Possible reaction of the oil with halogenated refrigerants at high temperatures.

Although the only function of oils is lubrication of the compressor bearings, some oil is inevitably carried to the low side of the system by the circulating refrigerant. The relationships of refrigerant and oil then are of interest in two different locations, that is, the crankcase and the evaporator. The problems are somewhat different in these two locations.

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SOLUBILITY IN THE CRANKCASE

Some properties of refrigerants and oils are listed in Table 3T37B.

Table 3T37B

SOLUBILITY RELATIONSHIPS OF REFRIGERANTS AND OIL Solutions Containing 10% Oil by Weight

Refrigerant	Solubility	Separation of two Liquid Layers, °F	Position of Oil Layer
R-11	Miscible	<-100	
R-12	Miscible	-90	Top
R-22	Good	16	Top
R-113	Miscible	<-100	
R-114	Good	-26	Top
R-502	Fair	180	Top
Ammonia	Slight	*	Bottom
Sulfur Dioxide	Slight	*	Top

* Not miscible

As can be seen, some refrigerants are completely soluble in oil, some are partly soluble and some are practically insoluble. The examples in Table 3T37B are for "Suniso" 3G oil but the results would be similar for other refrigeration oils.

For refrigerants that are completely soluble in oil, the biggest problem in the crankcase is dilution of the oil and reduction of its lubricating properties while the machine is not operating. Since pressures tend to equalize between the high and low sides of a system when it is not operating, refrigerant tends to accumulate in the crankcase. When the refrigerant dissolves in the oil, the bearings may not get enough lubrication for a brief period when the machine is started. Eventually, this condition may cause excessive wear and bearing failure. Crankcase heaters are often used to prevent this situation by reducing the amount of refrigerant in the oil. If immersion-type heaters are used, some care must be used to be sure that the temperatures are not high enough to carbonize the oil. External heaters are frequently used and have the advantage of giving a more even temperature throughout the whole crankcase.

If the refrigerant is not soluble in the oil, two liquid layers may be formed. With the heavier refrigerants the oil layer will be on top while with lighter refrigerants such as ammonia, the oil layer will be on the bottom. (Table 3T37B) Since the oil does not generally contain much refrigerant, its lubrication properties are not significantly changed. Even though a liquid refrigerant layer may be on the bottom surrounding the bearings, sufficient oil generally remains in the bearings to give adequate lubrication until normal operating conditions are obtained.

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The temperatures at which two liquid layers are formed are different for different refrigerants, as shown in Table 3T37B. The separation temperature also depends on the kind and amount of oil. For example, with "Suniso" 3G oil and R-22 two liquid layers are present at temperatures below 16°F when the mixture contains 10% oil. With mixtures containing 18% oil, the separation temperature is 34°F. At higher oil concentrations the temperature is lowered so that the separation temperature is about -40°F or lower when about 70% or more of oil is present. It is therefore very unlikely that two liquid layers will ever be present in the crankcase with R-22.

SOLUBILITY IN THE EVAPORATOR

In the evaporator, temperatures are, of course, lower than in the crankcase and the concentration of oil present is relatively lower. Under these conditions, the important factor is the viscosity of the oil. It is important because very viscous oil is difficult to remove from the evaporator while more fluid oils are easily swept out of the evaporator by the refrigerant. When refrigerant is dissolved in the oil the viscosity is reduced. Therefore, as a general rule when the refrigerant solubility in the oil is high, the oil tends to be removed from the evaporator more easily. Evaporator design and piping size are also important factors in helping the oil to get out of the evaporator.

STABILITY

Decomposition of oils or reaction of the oil with some halogenated refrigerants may occur at high temperatures at the compressor discharge valve. Varnishes may deposit here or some corrosion or embrittlement of the steel may occur. The stability of commercial refrigeration lubricating oils has been greatly improved in recent years and this problem is not as widespread as it has been in the past.

LEAK DETECTION

Leak detection is a continual problem with the halogenated or hydrocarbon refrigerants but improved methods have helped to make detection easier.

The Halide torch has been used for many years to detect the halogenated refrigerants. Air is drawn through an alcohol or hydrocarbon flame. If a halogenated refrigerant is present a bluish green color develops in the flame. The color is due to the reaction between the decomposed refrigerant and a copper reactor plate, built into the torch. The Halide torch can be used with all of the halogenated refrigerants except those containing a high percentage of fluorine such as R-13 and 14. It is easy and fast to use and will detect very small leaks in the hands of a skilled operator. Since the leak detection depends on visual observation its use depends on how well color changes can be seen by the operator. There is some indication that after long periods of use the eye becomes fatigued and the color change is more difficult to see.

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The electronic type of leak detector is becoming widely used both in field service and in the manufacture and assembly of refrigeration equipment. In this instrument the refrigerant is decomposed at a high temperature by a platinum wire and the change in current due to the ionization of the refrigerant is measured. This type of instrument is very sensitive and some care must be used to be sure that false indications are not observed. It is designed for use with halogenated refrigerants although some other materials, such as alcohol and carbon monoxide may interfere with the test. As with the torch, the electronic leak detector is not recommended for use in atmospheres containing explosive or flammable vapors. The sensitivity of the instrument also depends on the nature of the refrigerant. R-12, R-22 and R-114 can be detected about equally well. Refrigerant- 11 would require a leak about 1-1/4 times as fast as R-12 for the same sensitivity of detection. For Refrigerant 13 the leak would need to be about 35 times as great as that of R-12. With special sensitive equipment and extreme care, leaks of R-14 can also be detected.

The bubble method of leak detection is probably as old as the need for detecting leaks but it still has its place. For hydrocarbon refrigerants it is about the only practical method. Soap solutions brushed over the suspected area will form distinctive bubbles if a leak is present. In some cases entire assemblies are immersed in water or kerosene and observed for bubble formation. In this case a detergent in the liquid is helpful to prevent bubbles from clinging to the object where they cannot easily be seen.

Ammonia can be detected by passing a hydrochloric acid solution or a burning sulfur candle near the suspected area. A white cloud will be formed if ammonia is present.

Sulfur dioxide can be detected by the appearance of the white cloud when an ammonia solution is used.

Leakage can also be determined by evacuating the system or applying pressure and observing the change over a period of time. This is very good practice in testing a system just before charging but is of little help in locating the actual leak.

LEAKAGE RATE OF VARIOUS REFRIGERANTS			
DESIGNATION	CHEMICAL FORMULA	LEAKAGE RATE	
		BY VOLUME	BY WEIGHT
R-12	CCl_2F_2	1	1
R-11	CCl_3F	1.25	0.75
R-13	CClF_3	33	37
R-22	CHClF_2	1	0.75
R-114	$\text{CClF}_2\text{CClF}_2$	1	1.25
R-30	CH_2Cl_2 (Methylene Chloride)	1.25	3.
R-10	CCl_4 (Carbon Tetrachloride)	1	1
R-14	CF_4	Not Reactive	

The above data obtained by using a calibrated leak with a type H1 leak detector.

Table 3T39

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EFFECT ON MATERIALS

The materials used in the construction of refrigeration equipment are not often of direct interest to the service engineer since choices of materials are made by the manufacturer. However, effects of some refrigerants on a few representative elastomers and plastics are shown in Tables 3T40A

Table 3T40A

EFFECT OF LIQUID REFRIGERANTS ON ELASTOMERS AT ROOM TEMPERATURE

Refrigerant	Linear swell, %			
	Buna N	Butyl	Natural Rubber	Neoprene GN
R-12	2	6	6	0
R-22	26	1	6	2
R-11	6	41	23	17
R-113	1	21	17	3
R-114	0	2	2	0
R-13	1	0	1	0
Methylene Chloride	52	23	34	37
Butane	1	20	16	3

and 3T40B,

Table 3T40B

EFFECT OF LIQUID REFRIGERANTS ON PLASTICS AT ROOM TEMPERATURE

Refrigerant	Linear Swell, %							
	Nylon	Cellulose Acetate	Cellulose Nitrate	"Teflon"	"Lucite"	Polyethylene	Polystyrene	Polyvinylidene Chloride
R-12	0	0	0	0	0	0	-0.1	0
R-22	1	-	-	1	*	2	-	-
R-11	0	0	0	0	0	6	*	-0.2
R-113	0	0	0	0	-0.2	2	-0.2	-0.1
R-114	-0.2	0	0	-0.3	-0.2	1	-0.2	0
Methylene Chloride	0	*	*	0	*	5	*	2

- Not tested

* Disintegrated

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as illustrations of the general compatibility. To measure the effect, samples of the material were immersed in the liquid refrigerant and the linear swelling of the test piece observed. Other effects, such as extraction and permanent swelling or shrinkage are also important in determining the compatibility of a refrigerant and elastomer or plastic, but the linear swelling is a good indication. In some instances the presence of lubricating oil will tend to alter the effect of the pure refrigerant.

Most of the common metals are suitable for use with most of the refrigerants. However, there are some exceptions.

Ammonia should not be used with copper, brass, tin or zinc.

Methyl chloride should not be used with aluminum in any form. A highly flammable gas is formed and the explosion hazard is great.

Aluminum containing more than 2% magnesium, magnesium and zinc generally are not recommended for use with halogenated refrigerants, if even a small amount of water can be present.

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REFRIGERANT PERFORMANCE

Some properties of refrigerants are compared in Table 3T41

Table 3T41

REFRIGERANT PERFORMANCE PER TON Based on 5°F Evaporation and 86°F Condensation (1)

Refrigerant	Evaporator Pressure, Gage	Condensing Pressure, Gage	Compression Ratio	Liquid Circulated cu. in./min.	Specific Volume of Suction Gas, cu. ft/lb.	Compressor Displacement, cfm	Horsepower	Temperature of Compressor Discharge, °F
R-502	36.0	175.1	3.75	99.4	0.82	3.61	1.079	99
R-22	28.3	159.8	4.06	68.0	1.25	3.60	1.011	131
Propane	27.2	140.5	3.70	94.0	2.48	4.09	1.030	97
Ammonia	19.6	154.5	4.94	19.6	8.15	3.44	0.989	210
R-500	16.4	113.4	4.12	79.3	1.52	4.97	1.022	105
R-12	11.8	93.3	4.08	85.6	1.46	5.83	1.002	101
Methyl chloride	6.5	80.0	4.48	40.9	4.47	5.95	0.962	172
Sulfur dioxide	5.9*	51.8	5.63	26.6	6.42	9.09	0.968	191
R-114	16.1*	22.0	5.42	89.2	4.34	20.14	1.049	86
R-11	24.0*	3.6	6.24	56.0	12.27	36.32	0.927	113
Methylene chloride	27.6*	9.5*	8.60	30.9	49.90	74.30	0.963	205
R-113	27.9*	13.9*	8.02	66.5	27.04	100.76	0.960	86

* Inches of mercury below one atmosphere.

(1) Saturated suction vapor, except for R-113 and 114. In these cases, enough suction superheat was assumed to give saturated discharge vapor.

for a refrigeration cycle based on 5°F in the evaporator and 86°F in the condenser. The comparisons shown are based on theoretical calculations and some of the properties may be somewhat different in operating machines. For example, it is assumed that there is no superheating of the gas leaving the evaporator and no pressure drop in the connecting lines throughout the system.

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EVAPORATOR PRESSURE

The evaporator pressure is shown in pounds per square inch (psig) or inches of mercury below one atmosphere. Since one atmosphere of pressure is equal to 0 gage, refrigerants with a pressure higher than 0 will operate at higher than atmospheric pressure for this cycle. If a leak should occur, the refrigerant will tend to leak out rather than outside air and water vapor leaking in.

CONDENSING PRESSURE

The condensing pressure is also given in psig. It is the vapor pressure of the liquid at 86°F. The condensing pressure is the high-side pressure from the discharge valve of the compressor to the expansion valve.

COMPRESSION RATIO

The compression ratio is obtained by dividing the condensing pressure by the evaporating pressure.

For this calculation, the pressure must be in pounds per square inch, absolute. (psig + 14.7) .

The compression ratio should be as low as possible. Some of the results of high compression ratios include:

- Higher discharge temperatures
- Higher compression power
- Poorer volumetric efficiency
- Lower capacity

The compression ratio is fixed primarily by the evaporating and condensing temperatures and pressures and is affected by any changes in these conditions. The effect of such changes is shown in Tables 3T41A

Table 3T41A

EFFECT OF CONDENSING TEMPERATURE ON CAPACITY IN BTU PER HOUR At 40°F				
Evaporating Temperature, Compressor Displacement = 2 cu ft./min.				
Refrigerant	Condensing Temperature, °F			
	60	80	100	120
R-12	9260	8540	7810	7050
R-22	14870	13690	12460	11200

and 3T41B.

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Table 3T41B

EFFECT OF EVAPORATING TEMPERATURE ON CAPACITY IN BTU PER HOUR At 120°F Condensing Temperature, Compressor Displacement = 2 cu ft/min.

Refrigerant	Evaporating Temperature, °F			
	-20	0	20	40
R-12	1620	3080	4740	7050
R-22	3180	5000	7590	11200

It can be seen that higher condensing temperatures will increase the compression ratio. Condensing temperatures might be increased by dirty condensers, poor air circulation, high ambient temperatures, water restrictions or warm water if the condenser is water cooled.

If the evaporator temperature is lowered, the compression ratio also will be increased and the capacity reduced. This is shown by the data of Table 3T41B.

Although no rigid rules have been established, it is generally felt that single stage compression ratios for reciprocating machines should not exceed 10 to 12. For rotary compressors maximum is about 5 to 6 and for centrifugal compressors, about 3.

LIQUID CIRCULATED

The amount of liquid circulated throughout the refrigeration system for a ton of refrigeration, (Table 3T41), varies considerably for different refrigerants and depends primarily on the liquid density and the latent heat. The volume of the circulating liquid is important in sizing the expansion valve or capillary tubing and in choosing the proper size line to avoid excessive pressure drops.

VAPOR VOLUME

The specific volume of the refrigerant vapor in the suction line (Table 3T41) is used in calculating compressor performance. It is dependent on the temperature and pressure conditions at the point where the gas enters the compressor cylinder.

COMPRESSOR DISPLACEMENT

The compressor displacement listed in Table 3T41 gives the theoretical cubic feet per minute (cfm) required for one ton of refrigeration. The volumetric efficiency of the compressor would have to be considered in a practical system. In some cases the efficiency may be as low as 40 or 50% of the theoretical discharge rate. It is interesting to note that, even though the specific volume of ammonia vapor is very high, the compressor displacement is similar to that of other refrigerants since the total amount of refrigerant circulated is relatively small.

HORSEPOWER

The theoretical horsepower of compression does not vary widely for the different refrigerants. In small equipment the differences in horsepower are probably negligible. With large equipment the differences may have some importance in relation to the cost of operating the equipment.

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COMPRESSOR DISCHARGE TEMPERATURE

The temperature of the gas as it leaves the compressor should be as low as possible. High temperatures at this point may contribute to oil or refrigerant breakdown and perhaps discharge valve failure. The temperatures shown in Table 3T41 are calculated assuming adiabatic compression. In practice, the discharge temperatures tend to be higher than theoretical. Actually, temperatures may be considerably higher than calculated. On the other hand, in some cases, the discharge temperature may be lower than the theoretical value if some means of removing heat from the compressor is used. This condition might exist when the compressor is cooled with water or where a large amount of radiating surface, such as fins, is present on the compressor. Often, in hermetic compressors, the discharge temperature is close to the calculated value especially when suction line temperatures are in the neighborhood of 65°F.

The discharge temperature is affected by the nature of the refrigerant as can be seen in Table 3T41. Ammonia and sulfur dioxide tend to have high discharge temperatures, Refrigerant-22 and methyl chloride intermediate temperatures, while Refrigerant-12, 502 and others tend to have low discharge temperatures.

Other factors influencing the discharge temperature are compression ratio, the amount of superheat in the suction vapor, the relative velocity of refrigerant through the discharge valve (wire drawing) and other similar effects.

SUBSTITUTION OF REFRIGERANTS

One refrigerant should never be substituted for another one without first consulting the manufacturer of the equipment. Many factors are involved in the use of refrigerants. Some of these factors include power requirements, compatibility with insulation and gasketing, pressure drops and velocity in piping, oil return, operating pressures, etc. Circumstances requiring the substitution of one refrigerant for another are no longer very common. If the need does arise, the change should be given careful study.

DECOMPOSITION OF HALOGENATED REFRIGERANTS

Halogenated refrigerants are defined as products containing a halogen, such as fluorine, chlorine and bromine. Refrigerants of this type include R-11, R-12, R-22 and similar products. When the safety or hazard concerned with the use of this type of refrigerant is considered, the subject should be divided into two parts.

1. The characteristics of the refrigerant itself.
2. The properties of decomposition products that are formed when the refrigerant is exposed to high temperatures, as in a flame or electric resistance heater.

The halogenated refrigerants themselves are for the most part non-hazardous in nature. They have little effect on other materials, they are nonflammable and are practically nontoxic. These qualities have been amply demonstrated during more than 30 years of manufacture and use under widely differing conditions. The safe properties of this class of refrigerants have also been demonstrated by tests at the Underwriters' Laboratories, at the Bureau of Mines and elsewhere. Of course, they can be hazardous in concentrations high enough to significantly reduce the amount of oxygen present in the air.

The conditions under which decomposition may occur and the properties and possible hazards connected with the decomposition products are not as well known. The halogenated refrigerants will decompose when subjected to sufficiently high temperatures. Ordinarily, gas flames, oil flames, electric resistance

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heaters, etc., operate at temperatures over 1000°F and will cause the decomposition of the halogenated refrigerants if they are brought into direct contact. The products of decomposition are halogen acids, phosgene, carbon dioxide and various organic products. Minor quantities of some other products, such as chlorine and carbon monoxide, have also been detected.

Some of these decomposition products are toxic and chemically reactive and their hazardous nature should be understood. While it may be possible for situations to develop where the toxic nature of the decomposed refrigerants might be a threat to humans, the circumstances under which they are formed greatly reduces this possibility. As far as is known, there has been no authenticated case of serious physical harm resulting from the decomposition of the halogenated refrigerants.

The possible effects of decomposition products can be divided into two groups.

1. Physiological effect on humans.
2. Chemical effect on materials.

Hydrochloric acid, hydrofluoric acid and phosgene are the most toxic of the decomposition products. Chlorine and carbon monoxide are also toxic but are formed in such small amounts that their effect is generally negligible. Phosgene is considered to be somewhat more toxic than the halogen acids. However, it is a fairly unstable material and most of it is further decomposed. The halogen acids are nearly always present in larger amounts than phosgene. These acids have a very stringent and irritating effect on the nose so that their presence can easily be detected in amounts considerably below their toxic level. Thus, they serve as warning agents and when their odor is recognized, steps can and should be taken to ventilate the area or evacuate it. It is almost impossible for a person to voluntarily remain in an atmosphere containing toxic amounts of the halogen acids.

The effect of the decomposition products, especially hydrochloric acid, on other materials may be as well recognized as the odor and possible toxic hazard. The halogen acids are strong acids and may damage metals and cotton clothing. Some types of situations where damage has been observed are listed below.

1. A halogenated refrigerant is discharged into the air in a basement where an electric or gas-heated clothes drier is operating. Air containing the refrigerant is drawn across the heated area and decomposed. Cotton clothing present in the drier is greatly affected by hydrochloric acid and may be completely disintegrated or so tenderized that it almost falls apart when handled.
2. A halogenated refrigerant is discharged into the kitchen area while the stove or oven is operating. Some refrigerant is decomposed and parts of the oven may be corroded by the halogen acids.
3. The use of aerosol hair dressing preparations in beauty parlors is increasing rapidly. These products are propelled by halogenated gases. In some areas of the country, small shops of this sort are heated by gas-fired room units.

Halogenated gases passing through the heater are decomposed. The decomposition products are drawn out through the chimney. In some cases, the flue has been severely corroded. In addition to corrosion damage, there is a possible toxic hazard if carbon monoxide in the flue gas is permitted to enter the room through holes formed in the duct work. Air to the burners should be supplied from outside if high concentrations of halogenated propanes are present in the room.

4. Damage to furnace duct work has been observed when halogenated refrigerants have been discharged in basement areas near the furnace.

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Safe working practices would include the following suggestions.

1. If possible, discharge the refrigerant from a unit through a tube or pipe to the outdoors.
2. If this is not practical, discharge the refrigerant into an empty cylinder.
3. If it is necessary to discharge into an enclosed area, be certain that all burners and heaters are not operating.
4. When the characteristic odor of the halogen acids is observed, the ventilation should be improved immediately, or the area should be evacuated.