Quest for alternatives

A molecular approach demonstrates tradeoffs and limitations are inevitable in seeking refrigerants

By Dr. Mark O. McLinden and Dr. David A. Didion, P.E.

THE ADVENT of an international agreement limiting production of certain refrigerants because of their detrimental effects on the atmosphere has caused a sudden and intense concern in the refrigeration and air conditioning industry. With a decision now made as to which refrigerants will be affected and how much production will be cut, it appears that substitutes for trichlorofluoromethane (R-11) and dichlorodifluoromethane (R-12) will have to be developed.

Although there is little doubt that such a development will be possible, there is no doubt that the substitutes will compromise some of the qualities or properties possessed by the current refrigerants. The type and extent of these tradeoffs can have great influence on the form of solution the industry and public take. For example, a substitute that has a property variation sufficient to require a hardware change of any sort in R-12 systems can have enormous impact on the service and supply sectors of the industry. Therefore, it is essential that there be full knowledge of the properties of these new refrigerants and the impact their different properties will have on systems in the field.

Tradeoffs and limitations inevitable

Just as tradeoffs are inevitable so are limitations. With all the advances that have been made in this and other industries over the years, it is easy to delude one's self into thinking that anything is possible if only enough research and development effort is applied. This is *not* true. There are very definite limitations on the number and type of fluids that can reasonably act as refrigerants. This has been known since the development of the first chlorofluorocarbon (CFC)[1] refrigerant some 60 years ago, and all of the research on the subject since then has not altered that opinion except for very special applications of limited use.

During this past year, much attention has been paid to several new compounds that may serve as alternatives. But information concerning these new refrigerants is somewhat fragmentary. In particular, the underlying, fundamental reasons why a specific compound is presented as a replacement for R-11 or R-12 are missing. One is left wondering what other possibilities remain undiscussed. This leads to uncertainty on the part of equipment manufacturers contemplating the substantial capital investment involved in redesigning products to use a different refrigerant. While they may be willing to make such an investment once, they would want some assurance that the chosen alternative will not itself be replaced in a few years.

[1] For the purposes of this article "CFC" will refer to a carbon-based compound to which chlorine, fluorine and/or hydrogen are attached. By this definition, some CFCs contain no chlorine and others no fluorine. All numerical designations will be prefixed by "R" (for refrigerant) in accordance with ANSI/ASHRAE Standard 34-78, avoiding the varied nomenclature (e.g., CFC-11, FC-134a) which is now appearing.

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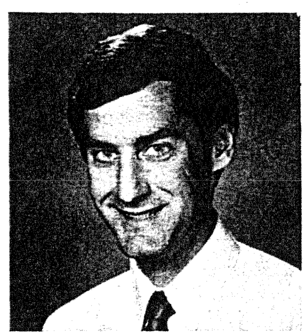

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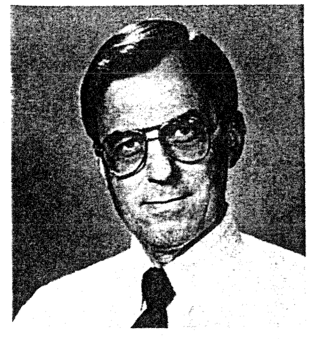

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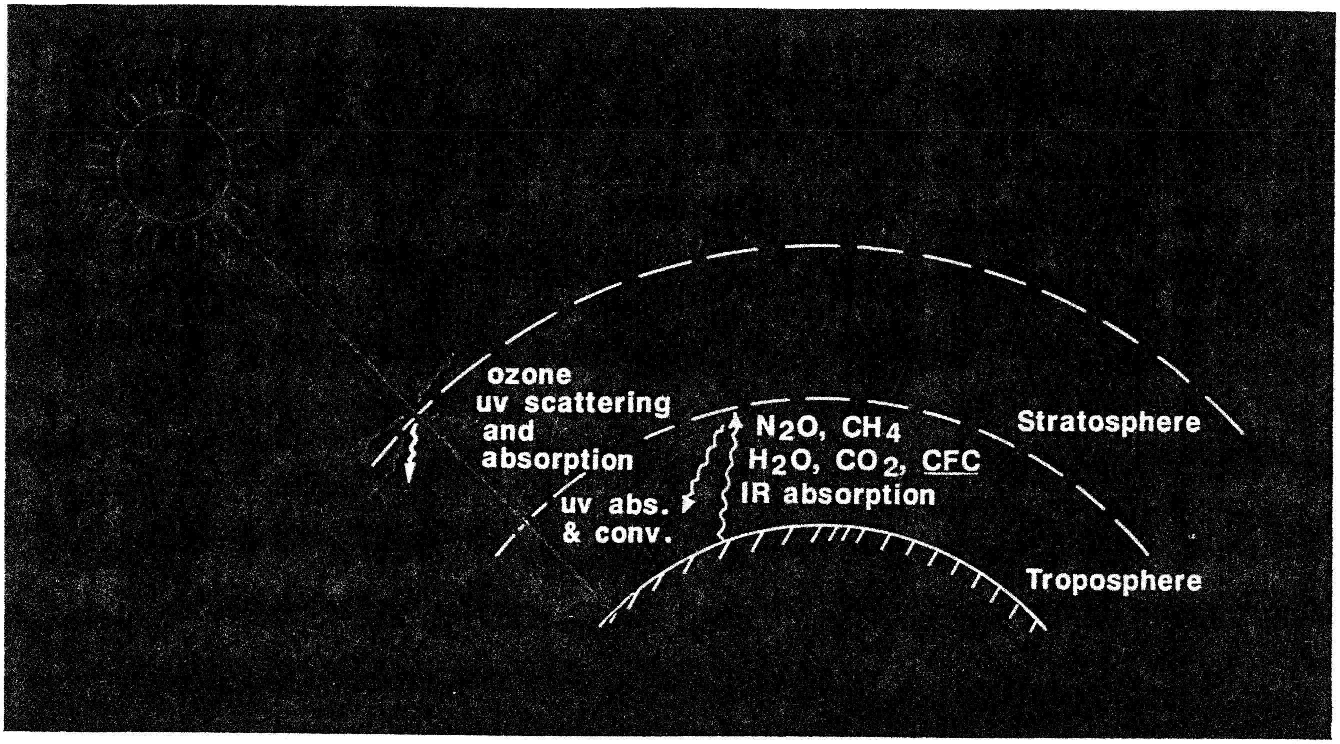

The objectives of this article are to present the criteria required of a refrigerant, discuss the reasons why CFCs were originally investigated as refrigerants (reasons which also make them the most promising in the search for alternatives) and finally to demonstrate that the inevitable tradeoffs among the various alternatives can be treated in a systematic way.

The CFC/atmospheric problem

Much has been written on the subjects of ozone depletion and greenhouse warming and only a very brief overview is given here. The interested reader is referred to the extensive compendium of research compiled by NASA (1) or the excellent summary presented in reference 2.

The so-called "ozone layer" actually consists of ozone present at very low concentrations in the stratosphere between 7 and 28 miles in altitude. Ozone, or O_3, is formed by the interaction of ultraviolet (UV) radiation from the sun with molecular oxygen (O_2). Harmful UV radiation is absorbed during this formation process and also directly by the O_3 once it is formed. Ozone is unstable and eventually will revert back to O_2. The presence of chlorine in the upper atmosphere will, through a complicated series of chemical reactions, catalyze the destruction of ozone and thus upset the balance between its continuous creation and destruction.

The chlorine-containing CFC refrigerants are one source of chlorine but only if they survive in the troposphere (lower atmosphere) intact for the many years necessary for a gas emitted at the earth's surface to be transported to the stratosphere. Compounds that are broken down quickly in the lower troposphere are washed out by rain. Thus, the ozone depletion potential of a refrigerant is related not only to its chlorine content but also to its atmospheric lifetime which has been shown to be a function of its hydrogen content.

The problem of global warming due to the greenhouse effect has received far less attention recently than that of ozone depletion, but is felt by many to be equally important (1, 2).

The greenhouse effect refers to the trapping by the atmosphere of infrared radiation emitted at the surface and the subsequent warming of the earth's climate. While the greenhouse effect is often associated with carbon dioxide from the combustion of fossil fuels, it is now estimated that other trace gases including nitrous oxide, methane and CFCs have a combined greenhouse effect equal to or slightly greater than CO_2. Although the atmospheric concentrations of CFCs are several orders of magnitude smaller than carbon dioxide, they absorb strongly in the infrared, particularly in the wavelengths between 7 and 13 μm where the atmosphere is otherwise largely transparent. This absorption is due to the carbon-chlorine and carbon-fluorine bonds present in CFCs and will take place as long as the molecule is intact.

Just as the problems of ozone depletion and greenhouse warming associated with CFCs can be traced to their molecular structure so too can the solution. Throughout this article a fundamental approach based on molecular structure will be taken in the search for alternative refrigerants.

Requirements of a refrigerant

The working fluid in a vapor compression refrigeration system must satisfy a number of requirements as discussed by Threlkeld (3) and ASHRAE (4) and summarized in *Table 1*. The most essential characteristic is chemical stability within the refrigeration system—all the other properties would be meaningless if the material decomposed or reacted to form something else. Stability can be a double-edged sword; once emitted to the atmosphere a refrigerant should not be so stable that it persists indefinitely. The ideal refrigerant would be totally stable in use but decompose within a few years in the atmosphere due to conditions (such as ultraviolet radiation or reactive chemical species) not present in the sealed system.

The next most important characteristics relate to health and safety. As specified in the ASHRAE Safety Code for Mechanical Refrigeration (5), in residential and most commercial applications a refrigerant must be nonflammable and of a very low order of toxicity. These can be compromised in some industrial applications as evidenced by the use of hydrocarbons and ammonia. The toxicity and flammability classification of refrigerants is dealt with in ASHRAE Standard 34 (6); the proposed revision of this standard (7) defines toxicity in terms of the threshold limit value (TLV®) as set by the American Conference of Governmental and Industrial Hygienists (8). The new environmental requirement must now be added to the traditional health and safety criteria. A refrigerant should not contribute to ozone depletion, low level smog formation or greenhouse warming.

The thermodynamic and transport properties determine the performance of a refrigeration system. We will demonstrate below that the critical or boiling point temperatures and the heat capacity of the vapor are the most significant thermodynamic criteria. These two fundamental criteria account for all the desirable properties usually presented, such as high latent heat of vaporization, positive evaporator pressure, etc. By considering only the most fundamental thermodynamic criteria it is possible to establish a link between bulk properties and molecular structure; this will yield insight into the type of molecule most likely to be a good refrigerant.

A number of other more practical criteria are also necessary or, at least, desirable. High oil solubility and high vapor dielectric strength are most important for hermetic compressors. A freezing point below the lowest expected system temperature is necessary. Finally, compatibility with common materials of construction, easy leak detection and low cost are obviously desirable.

Finding a new refrigerant is thus seen to be no small task. For a refrigerant to be used as a direct substitute in existing equipment virtually all of the above criteria must be satisfied. At most, some compromise in thermal properties could be tolerated at the expense of performance. For an alternate refrigerant for a newly designed system the situation is not as critical since equipment could be adapted for the different pressures and capacity that would accompany a change to a refrigerant with a different boiling point; heat exchangers could be adjusted for different transport properties; and the system could be constructed of different materials. Even in this case, however, it seems unlikely that compromises could be tolerated in the areas of chemical stability and health and safety.

Historical development of refrigerants

In the early years of refrigeration the available refrigerants were less than satisfactory; all were either flammable or toxic or both. In 1928, Thomas Midgley, a research engineer with a subsidiary of General Motors, was asked to see if he could develop a nontoxic, nonflammable refrigerant that would function well as a working fluid for the home refrigerator. As it was put to him, ". . .the refrigeration industry needs a new refrigerant if it is ever to get anywhere" (9). His initial reaction was that no single compound could satisfy these requirements but that a mixture of a nontoxic but flammable material with one that was nonflammable but toxic might yield a nonflammable mixture of moderate toxicity.

Midgley, along with his associate Albert Henne, turned to the periodic table of the elements to find a solution. When arranged according to the number of vacancies in the outer shell of electrons (*Figure 1*) it became apparent to them that those elements to the left and lower portions of the periodic table were metals in their elemental form and formed nonvolatile ionically-bonded compounds when combined with other elements. Only those elements in the upper right portion of the table formed compounds that were sufficiently volatile to be considered. But among these, many could be eliminated because they formed toxic and unstable compounds. The elements in the right-most column, the noble gases, are so stable that they have a very restricted chemistry (i.e., they do not form compounds) and by themselves have normal boiling points that are much too low.

This left Midgley and Henne with just eight elements: carbon, nitrogen, oxygen, sulfur, hydrogen, and the halogens fluorine, chlorine and bromine. They further noticed general trends of flammability decreasing from left to right and toxicity decreasing from bottom to top. These trends, along with an erroneous entry for the normal boiling point of carbontetrafluoride (R-14) in the International Critical Tables, led them to consider fluorine compounds. The high stability of the carbon-fluorine bond further restricted their search to carbon-based compounds. They suspected that the listed boiling point for carbontetrafluoride was in error and also dismissed it as too difficult to make. Instead they decided to try dichlorofluoromethane (R-21). Going against the common wisdom of the day they had a hunch that such a compound might be nontoxic.

Indeed, within three days of receiving their assignment Midgley and Henne had synthesized a small quantity of R-21 (based on a method developed in the 1890's by Swarts) and demonstrated that it was of low acute toxicity.[2] What followed was a very methodical evaluation of a large number of chlorofluorocarbons culminated by a dramatic introduction of R-12 at a meeting of the American Chemical Society in 1930: Midgley inhaled a lung-full of the new refrigerant and then used it to extinguish a candle (10).

This was the beginning of the modern refrigerants as we know them today. All of them are composed of the same eight elements identified by Midgley. If we apply the new environmental criteria we can shorten the list to seven because bromine is considerably more reactive with ozone than even chlorine.

Database search

Taking a completely different approach from that of Midgley, in an unrelated project for the National Aeronautics and Space Administration (NASA), we, at National Bureau of Standards (NBS), have searched a proprietary database of 860 industrially important fluids. In this project the goal was to identify the best fluid for use in a two-phase heat transport system to be installed in space stations. The initial screening criteria are, however, equally applicable for a refrigerant in a vapor-compression system:

1) freezing temperature < -40 F (-40 C)
2) critical temperature > 122 F (50 C)
3) vapor pressure @176 F < 735 psia (5.0 MPa)
4) latent heat $\times$ vapor density > 27.8 Btu/ft^3 (1.0 kJ/ℓ)

The first two criteria insure that the fluid can exist in the two-phase region in the temperature range of interest. The third criterion eliminates fluids that would require excessively heavy construction. The final criterion is an approximate measure of the capacity in a refrigeration system. The numerical value was chosen to be within an order of magnitude of currently used refrigerants; for comparison the values for R-22 and ammonia are 222 and 247 Btu/ft^3 (8.0 and 8.9 kJ/ℓ) respectively.

Of the 860 fluids contained in the database, 51 passed the screening. They include 15 hydrocarbons (e.g., propane and butane), five oxygen compounds (e.g., dimethylether and formaldehyde), five nitrogen compounds (e.g., ammonia and

[2]Later tests would reveal that R-21 causes extensive organ damage upon long-term exposure.

TABLE 1
Refrigerant Criteria

Chemical:
- Stable and inert

Health, Safety and Environmental:
- Nontoxic
- Nonflammable
- Does not degrade the atmosphere

Thermal (Thermodynamic and Transport):
- Critical point and boiling point temperatures appropriate for the application
- Low vapor heat capacity
- Low viscosity
- High thermal conductivity

Miscellaneous:
- Satisfactory oil solubility
- High dielectric strength of vapor
- Low freezing point
- Reasonable containment materials
- Easy leak detection
- Low cost

methylamine), three sulfur compounds (e.g., sulfur dioxide), four miscellaneous compounds and, finally, 19 halocarbons (a group of compounds which includes the CFCs as well as bromine containing compounds) including R-22, R-12, R-11, R-114, R-13B1, R-142b and R-152a. Of these, all of the fluids outside of the halocarbons are either flammable or toxic or both. While some of the halocarbons are also toxic and/or flammable, only this group contains compounds that are both nonflammable and of low toxicity.

There are, of course, other nontoxic, nonflammable materials which can be used as refrigerants, but these are generally useful only at much lower or higher temperatures than the typical refrigeration or air conditioning application. Examples would be helium, nitrogen, carbon dioxide and sulfur hexafluoride for low temperatures and steam at high temperatures. Some of these fluids might also be used at intermediate temperatures but in cycles other than the traditional vapor compression cycle.

It is also interesting to note that, with two exceptions, all of the 51 fluids which passed the screening contain no elements other than carbon, nitrogen, oxygen, sulfur, hydrogen and the halogens fluorine, chlorine and bromine. These are exactly the elements selected by Midgley. The exceptions were the highly reactive and toxic boron trichloride and hydrogen iodide.

Because our database was not exhaustive, compounds of hydrogen and the halogens with elements other than carbon were considered (11). From within Midgley's list of candidate elements the compounds of sulfur and nitrogen which satisfy thermodynamic criteria tend to be toxic and chemically reactive. Midgley did not include compounds of silicon in his list (much of what is known about silicon chemistry post-dates his work). None of the dozen silicon compounds included in our database passed the screening but, because of some similarities between silicon and carbon chemistry, and because silicon-based materials (e.g., the silicones) are used as substitutes for hydrocarbons in certain applications, the silicon compounds were explicitly considered. The most volatile silicone (hexamethyldisiloxane) has a normal boiling point of 211 F (99.6 C); this is much too high for most applications. All the silicon analogs of the CFCs react (sometimes violently) in the presence of water. Indeed all silicon compounds with sufficiently low normal boiling points [e.g., Si_2H_6: T_{boil} = 6 F (−14.5 C)] are water sensitive. A major group of silicon compounds that are chemically stable and nontoxic are the tetraalkylsilanes. The most volatile of these, tetramethylsilane, $(CH_3)_4Si$, has a boiling point of 80 F (26.5 C); this is very similar to that of R-11 but this compound fails other thermodynamic criteria.

The theoretical approach of Midgley and our own empirical database search both point to the chlorofluorocarbons as the most promising in the search for new refrigerants. There would seem to be little justification for expending significant time or money searching for alternative refrigerants outside the CFC family, except perhaps as a minor component in a mixture of compounds.

Thermodynamic criteria

Let's now consider in detail the fundamental thermodynamic requirements of a refrigerant. While Midgley's analysis greatly restricted the elements from which one might construct a refrigerant molecule, a huge number of compounds can be synthesized from these few elements. Even restricting the search to the chlorofluorocarbons, one could start with any of the hundreds of known hydrocarbons and substitute fluorine and/or chlorine for one or more of the hydrogens. However, thermodynamic considerations will immediately limit the multitude of possibilities that must be considered.

A study at NBS (12) has revealed that the refrigerant critical temperature and vapor heat capacity are the key thermodynamic criteria in determining the performance of the theoretical vapor compression cycle. The study was carried out for a hypothetical refrigerant; by varying the critical temperature and vapor heat capacity of this characteristic refrigerant the entire family of CFC compounds could be represented. The effects of varying refrig-

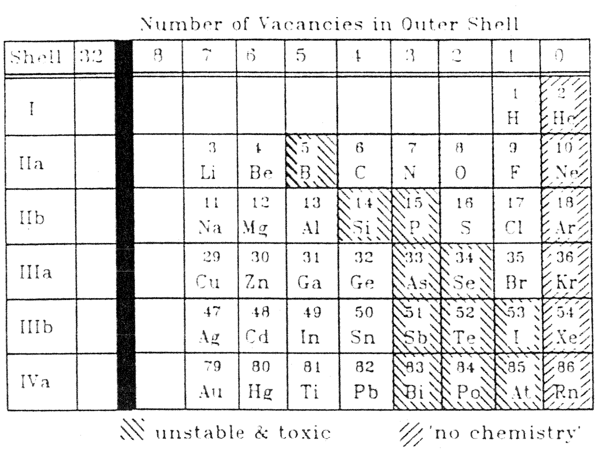

Figure 1—A portion of the periodic table of elements arranged according to the number of vacancies in the outer-most election shell. Only those elements indicated by horizontal hatching form compounds that are suitable for refrigerants.

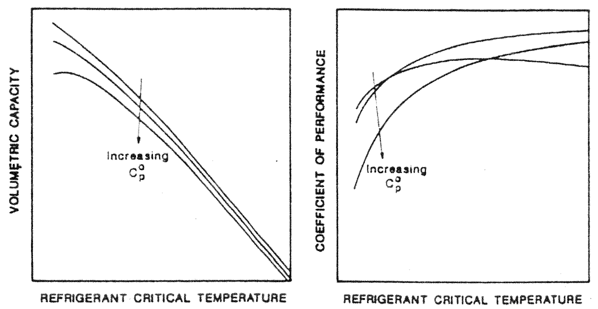

Figure 2—Effect of refrigerant critical temperature and vapor heat capacity (C_p^o) on volumetric capacity and coefficent of performance of the vapor compression cycle.

erant critical temperature for a fixed set of condenser and evaporator temperatures are shown in *Figure 2.*

As the critical temperature is increased the volumetric heating or refrigerating capacity[3] decreases. This is due to the lower vapor pressure and thus lower vapor densities (at a given evaporator temperature) for refrigerants with higher critical temperatures. The coefficient of performance (COP), however, is increased for refrigerants with higher critical temperatures. Or equivalently, the COP drops as the temperature of the condenser approaches the critical temperature of the refrigerant, due to excessive compressor superheat and flash gas losses. This points out the fundamental tradeoff between high capacity and high efficiency one must face in choosing a refrigerant.

A property related to critical temperature is the normal boiling point, the temperature at which the vapor pressure equals one atmosphere. This will be used in most of this article rather than the critical temperature because of the greater familiarity and availability of data for the normal boiling point. It is also an excellent thermodynamic index. Since most fluids (and certainly CFCs) have nearly parallel vapor pressure curves when plotted as a function of temperature, the normal boiling point is a good indicator of vapor pressure at all temperatures and thus the operating pressures in a system.

[3]The volumetric capacity is defined as the capacity per unit volume of refrigerant vapor entering the compressor.

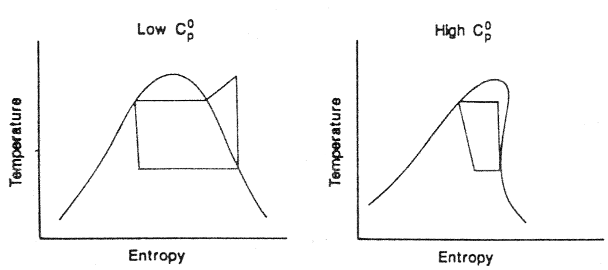

Figure 3—Effect of vapor heat capacity on the shape of the two-phase region on temperature-entropy coordinates.

The normal boiling point is also a good indicator of the critical temperature since the ratio of T_{boil} to T_{crit} is 0.6-0.7 for most fluids. The conclusion is that in order to have a similar capacity, efficiency and operating pressures, a replacement refrigerant will have to have a similar boiling point temperature.

The heat capacity of the vapor, C_p^o, has a lesser effect on performance than the critical temperature but is still significant, as seen in *Figure 2.* (The heat capacity used in this analysis is evaluated in the limit of zero pressure at the critical temperature.) High volumetric capacities are associated with low values of C_p^o. For maximum COP, however, there is an optimum value of C_p^o. The heat capacity affects the performance of the vapor compression cycle primarily through its influence on the shape of the two-phase region or "vapor dome" on a temperature-entropy diagram as shown in *Figure 3.* (This figure also shows a typical vapor compression cycle.)

Low values of C_p^o give a vapor dome such that a compression process starting on the saturated vapor line terminated in the superheated vapor region; excessive superheat reduces efficiency. With a high value of C_p^o, however, the vapor dome is "undercut" so that a compression process terminates in the two-phase region. Such a "wet" compression must be avoided for most types of compressors. The liquid and vapor sides of the two-

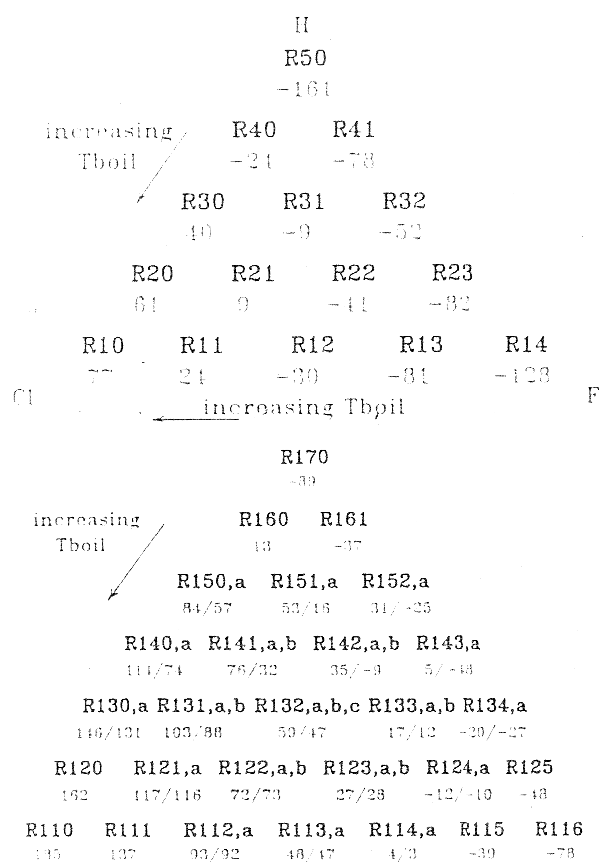

Figure 4—Normal boiling points (°C) for the CFC refrigerants arranged according to molecular structure a) methane series (one-carbon) b) enthane series (two-carbon).

phase region are interconnected and thus high values of C_p^o also result in greater flash losses in the expansion device. The result of these offsetting effects is an optimum value for C_p^o lying between 9.6 and 24 Btu/lb mol R (40 and 100 J/mol K) depending on the critical temperature of the refrigerant. The optimum value of C_p^o results in a vapor dome that gives a small superheat; this is the behavior obtained with most common refrigerants.

To a first approximation, each chemical bond within a molecule makes a discrete contribution to C_p^o ranging from roughly 2.6 Btu/lb mol R (11 J/mol K) for a carbon-hydrogen bond to 5.0 Btu/lb mol R (21 J/mol K) for a carbon-fluorine bond to 6.0 Btu/lb mol R (25 J/mol K) for a carbon-chlorine bond (13). Thus the optimum value of C_p^o would be obtained with small molecules such as CFCs having one or two carbon atoms as a skeleton. But to be useful as a refrigerant, a fluid must have a critical temperature appropriate for the application as well. For a condenser temperature of 95 F (35 C) (typical of many air conditioning, heat pumping and refrigerating applications) a refrigerant critical temperature in the range 149-455 F (65-235 C) is desired. Most of the one- and two-carbon CFCs indeed have critical temperatures in this range.

By contrast, most of the CFCs with three or more carbons have high values of C_p^o and thus vapor domes which imply a 'wet' compression process. Also, they are, in general, much more difficult to manufacture than the smaller molecules and tend to have critical temperatures that are too high for most applications. The few CFCs in this category that have values of C_p^o low enough to avoid a 'wet' compression are flammable. Thus we can restrict our search to the one- and two-carbon CFCs.

Evaluation of alternative CFCs

There is little evidence to indicate that the alternative refrigerants will come from other than the CFC family. This class of compounds should not be discarded because of environmental problems with the fully halogenated CFCs. The task facing the HVAC and refrigeration industry is to identify an environmentally benign CFC or CFC mixture that retains as many of the attributes of R-11 and R-12 as possible.

There are 15 possible one-carbon and (including the different isomeric forms) 55 possible two-carbon CFCs.[4] A means of systematizing the key properties is needed, otherwise one is faced with a seemingly random collection of data and would be frustrated by missing information. We have chosen to arrange the compounds in a triangular pattern according to their molecular structure. The base hydrocarbon (e.g., methane, CH_4 or R-50 shown in *Figure 4a*) is at the top and for each lower row one hydrogen is replaced by a chlorine or fluorine atom down to the fully chlorinated compound (e.g., carbon tetrachloride, CCl_4 or R-10) at the lower left corner and the fully fluorinated molecule (e.g., CF_4 or R-14) at the lower right corner. The bottom row contains the fully halogenated CFCs—all of the hydrogens have been replaced by the halogens chlorine and/or fluorine.

The first property to consider is boiling point. Among the methane (one-carbon) series of CFCs (*Figure 4a*) there is a regular pattern of increase in boiling point towards the lower left corner of the diagram. The same pattern is seen for the ethane (two-carbon) series (*Figure 4b*) although it is confused somewhat by the different isomeric forms. (Isomers contain the same number and kind of atoms but in a different arrangement and are designated by a suffix of a, b or c. In *Figures 4a and 4b* the range of boiling temperatures is given for the different isomeric forms.) *Figure 4* indicates the wide range of boiling points available among the CFC family. For example, there are six compounds with a boiling point within 18 F (10 C) of R-12: namely, R-40, R-161, R-152a, R-134, R-134a and R-115. But boiling point is not the only criterion that must be satisfied.

Evaluating flammability and toxicity

The next property to consider is flammability. Here we will consider the flammability in air at normal atmospheric pressure; at other pressures or in the presence of other gases, the flammability characteristics may differ. For the methane series (*Figure 5a*) a very clear pattern emerges; the compounds in the top half of the diagram are flammable while those in the bottom half (i.e., those with more than half of the hydrogens replaced by halogens) are nonflammable. The same pattern is seen with the ethane series (*Figure 5b*). This latter diagram indicates the usefulness of systematizing properties in this way; because of the clear pattern that has emerged, it is possible to infer properties for compounds for which no data is available. For example, although we could not locate flammability data for R-121 it is almost certainly nonflammable based on its low hydrogen content and the nonflammability of other compounds around it.

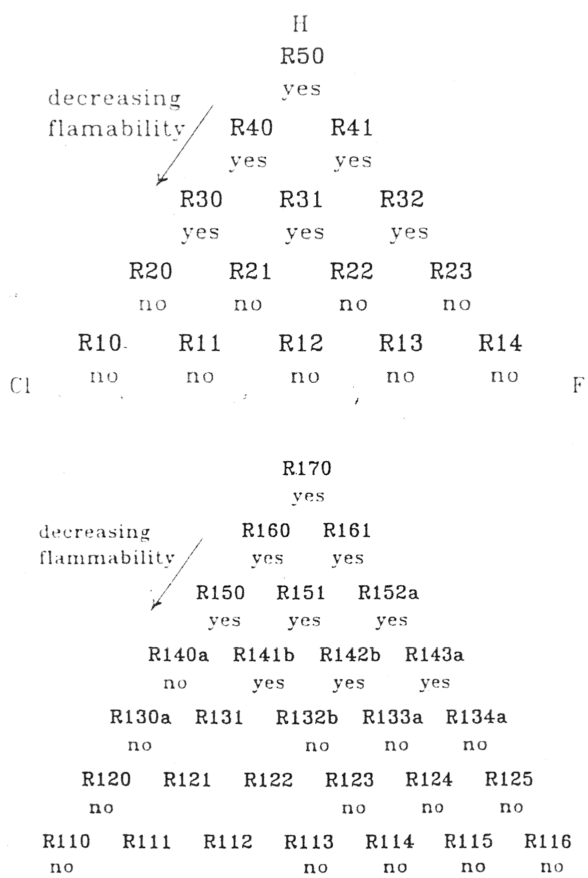

Figure 5—Flammability in air for the CFC refrigerants a) methane series b) ethane series.

[4]The CFC compounds containing a carbon-carbon double bond are not considered because of their lower stability. The bromine containing compounds are not considered because of the much greater ozone depletion potential of bromine relative to chlorine.

Toxicity is the property that is least amendable to a simple systematization scheme. Rather than being a simple physical property, toxicity pertains to the interaction of a chemical substance with a living organism. The situation is further confused by the different types of toxic effects such as acute effects from a single but massive exposure versus chronic effects from low-level but repeated exposures. The toxicity of the CFCs is indicated as simply low, moderate or high and, while this is a gross oversimplification to a rather complex subject, it suits our present purpose. A compound listed as "low" in toxicity would have only slight effects for both a high acute dose and for long-term exposure. A compound of "high" toxicity would produce serious injury at low levels of exposure. The classification of "moderate" toxicity would indicate either an intermediate level of acute effect or a toxic effect only upon long-term exposure.

Despite these complicating factors, there is a pattern for the toxicity of the methane series of CFCs (*Figure 6a*). The compounds in the lower left (chlorine-containing) region of the diagram are more toxic than those towards the right-hand side or upper (fluorine- or hydrogen-containing) regions. The same general trend is seen with the ethane series (*Figure 6b*) although here there are several compounds such as R-133a and R-161 that go against the pattern. This emphasizes that, while generalizations are useful for preliminary screenings, they cannot replace the extensive toxicity studies that must be done to establish the safety of a compound.

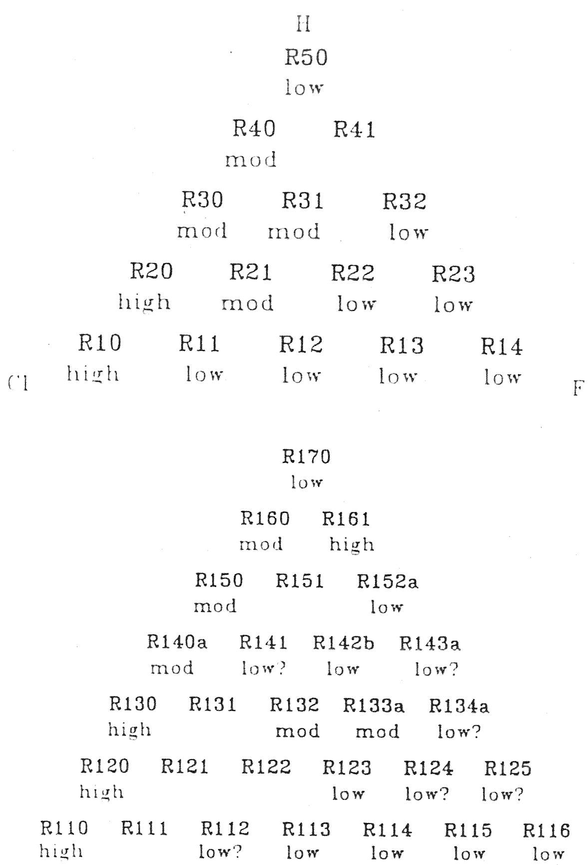

Figure 6—Toxicity for the CFC refrigerants a) methane series b) ethane series ("?" indicates testing incomplete).

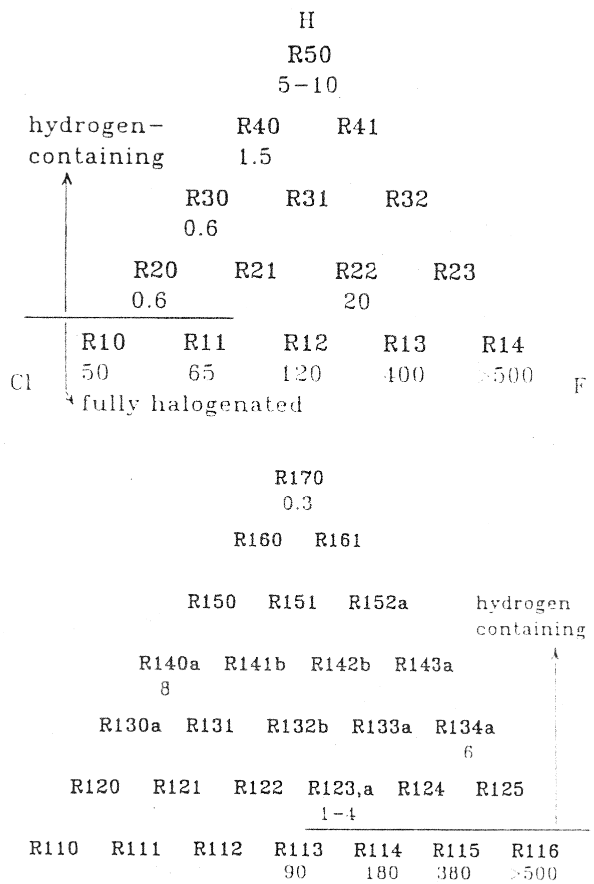

Figure 7—Atmospheric life (years) for the CFC refrigerants a) methane series b) ethane series

The final property to consider is atmospheric lifetime. We have chosen this over an "ozone depletion potential" or similar index because of the importance of atmospheric lifetime in both ozone depletion and the greenhouse effect. For the methane series (*Figure 7a*) the bottom row of compounds—those which are fully halogenated—have very long lifetimes. Furthermore, it increases with a higher percentage of fluorine, reflecting the great stability of the carbon-fluorine bond. On the other hand, the hydrogen-containing compounds have atmospheric lifetimes that are lower by up to three orders of magnitude, due to the reaction of hydrogen in the molecule with compounds present in the lower atmosphere. For the ethane series (*Figure 7b*) the data are sparse but again the same pattern appears. Thus, the presence of a hydrogen atom in the molecule is seen to be the key for environmental acceptability.

A limited area for alternatives

We have demonstrated that the properties of the CFC family of compounds can be dealt with in a systematic fashion based on molecular structure. The tradeoffs are summarized in *Figure*

8. Although there are a large number of compounds in the CFC family, only a limited region in the triangular diagram contains compounds that are simultaneously nonflammable, environmentally acceptable and of low toxicity. It is interesting to note that the new CFCs such as R-134a and R-123 which are receiving much attention lately (as well as R-22) do indeed lie within this region. When the additional constraint of acceptable boiling point range is applied, one is left with very few alternatives for any given application. As an example, although six CFCs had normal boiling points within 18 F (10 C) of R-12 only R-134 and R-134a are hydrogen-containing and nonflammable; toxicity testing on R-134a is incomplete but promising.

Mixtures of refrigerants offer a way to "tailor" the properties of refrigerant and thus to increase the applicability of what may be a very limited set of acceptable pure refrigerants. Because they offer a way to mitigate an undesirable property of an otherwise acceptable compound, mixtures can expand the list of candidate compounds. For example, R-152a is by itself moderately flammable but forms a nonflammable azeotrope (R-500) when mixed with R-12.

In contrast to the azeotropic mixtures (e.g., R-500, R-502) which behave essentially like a pure refrigerant, nonazeotropic mixtures display characteristics (e.g., variable temperature and compositions upon condensation or evaporation) that are unique to mixtures. These characteristics can be exploited to improve performance but generally require hardware modifications. An intermediate class of mixtures (which we have dubbed "near azeotropes") do not form azeotropes but behave sufficiently similar to pure refrigerants to allow their use in ordinary refrigeration equipment. Most importantly, the "near azeotropes" would, by definition, behave such that when a moderate leak would occur, the refrigerant composition would not change enough to cause a significant performance change upon recharging with the original composition.

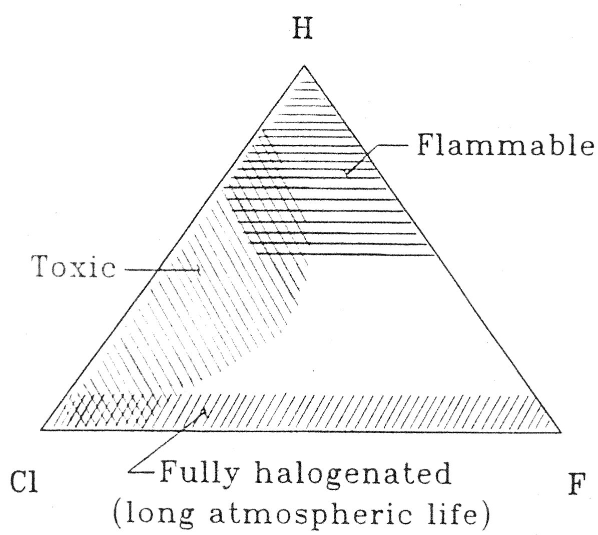

Figure 8—A summary of the tradeoffs among the properties of the CFC refrigerants.

Summary and conclusions

In the search for alternatives to the fully halogenated CFC refrigerants there are not a limitless number of compounds from which to choose. Rather, it has been demonstrated by both theoretical and empirical reasoning that this same class of compounds—the chlorofluorocarbons—remains the clear choice by virtue of their stability, excellent thermodynamic and health and safety characteristics, and familiarity to both manufacturers and users. However, some of the previously acceptable CFC compounds are no longer acceptable because of environmental considerations.

By approaching the problem from the molecular structure, the properties of the various CFC compounds could be treated in a systematic way. This approach revealed a range of CFC compounds (indicated by the blank region in *Figure 8*) that should be environmentally acceptable as well as retaining the other attributes of the fully halogenated CFC refrigerants. The initial research efforts should be directed towards CFC compounds from this region or mixtures where the major component is from this region.

The prudent course of action would seem to be to pursue the development of the newer, environmentally acceptable CFC refrigerants (including refrigerant mixtures) along with the necessary equipment modifications as well as efforts to conserve and recycle refrigerants. In as much as some compromise with the traditional criteria (e.g., capacity, efficiency, flammability, etc.) is inevitable some flexibility for compromise with the environmental criteria would also seem to be in order. Radical proposals such as the elimination of R-22 (which has only five percent of the ozone depletion potential of R-11) should be avoided. Over 30 years of research and development were required to arrive at and maintain the family of refrigerants we have today. A system so much an integral part of our society requires careful scientific and technological planning to effect a significant change. If not, the new 'solution' may bring with it more problems than it solves.

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