

Trade-Offs in Refrigerant Selections: Past, Present, and Future

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ABSTRACT

Recent attention to depletion of stratospheric ozone, by chemicals containing bromine and chlorine, resulted in an international accord to halt their production. The most widely used refrigerants are among them. Chemical and equipment manufacturers mounted aggressive research and development programs to introduce alternative and transition refrigerants, associated lubricants and desiccants, and redesigned equipment. The already difficult criteria became even more complex, with subsequent linkage of chemical emissions from human activities to global climate change. The very successful response to protect the ozone layer has led some regulators and users to assume that ideal substitutes will be found. Such chemicals should be free of all environmental and safety concerns, be chemically and thermally stable, and perform efficiently. The analyses presented in this paper demonstrate that the outlook for discovery or synthesis of ideal refrigerants is extremely unlikely. Trade-offs among desired objectives, therefore, are necessary to achieve balanced solutions. The paper also shows that fragmented regulation of the chemicals involved, to address individual issues, jeopardizes the prospect of solving subsequently addressed problems. The paper reviews the history of refrigerants, their roles in ozone depletion and global climate change, and necessary trade-offs in refrigerant selections.

INTRODUCTION

The air-conditioning and refrigeration industry is in the midst of an unprecedented transition, catalyzed by environmental concerns with the impacts of refrigerant emissions. Compounds containing chlorine and, though less frequently used as refrigerants, bromine are being phased out. Production of chlorofluorocarbons (CFCs) ended in 1995 in developed countries. Attention is now focused on the next issue, global warming, with a view toward reducing greenhouse gas emissions. Chemicals with long atmospheric lifetimes and high fluorine contents are targeted as potent greenhouse gases. Per-

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fluorocarbons (compounds consisting solely of carbon and fluorine) already are perceived as doomed by the technical community, even though specific treaty and regulatory provisions are still being worked out.

Although less visible, a parallel transition toward safer refrigerants, based on both flammability and toxic-

Table 1: Historical introduction of refrigerants

year	refrigerant (/absorbent)	chemical formula or makeup
1830s	caoutchoucine	distillate of india rubber
	sulfuric (ethyl) ether	CH ₃ -CH ₂ -O-CH ₂ -CH ₃
1840s	methyl ether (R-E170)	CH ₃ -O-CH ₃
1850	water / sulfuric acid	H ₂ O / H ₂ SO ₄
1856	ethyl alcohol	CH ₃ -CH ₂ -OH
1859	ammonia / water	NH ₃ / H ₂ O
1866	chymogene	petrol ether and naphtha (hydrocarbons)
	carbon dioxide	CO ₂
1860s	ammonia (R-717)	NH ₃
	methyl amine (R-630)	CH ₃ (NH ₂)
	ethyl amine (R-631)	CH ₃ -CH ₂ (NH ₂)
1870	methyl formate (R-611)	HCOOCH ₃
1875	sulfur dioxide (R-764)	SO ₂
1878	methyl chloride (R-40)	CH ₃ Cl
1870s	ethyl chloride (R-160)	CH ₃ -CH ₂ Cl
1891	blends of sulfuric acid with hydrocarbons	H ₂ SO ₄ , C ₄ H ₁₀ , C ₅ H ₁₂ , (CH ₃) ₂ CH-CH ₃
1900s	ethyl bromide (R-160B1)	CH ₃ -CH ₂ Br
1912	carbon tetrachloride water vapor (R-718)	CCl ₄ H ₂ O
1920s	isobutane (R-600a)	(CH ₃) ₂ CH-CH ₃
	propane (R-290)	CH ₃ -CH ₂ -CH ₃
1922	dielene (R-1130) ^a	CHCl=CHCl
1923	gasoline	hydrocarbons
1925	trielen (R-1120)	CHCl=CCl ₂
1926	methylene chloride (R-30)	CH ₂ Cl ₂

^a blend of *cis*- and *trans*-1,2-dichloroethene isomers

ity, has been underway. Unfortunately, some of the obvious solutions to the environmental concerns raise flammability and/or toxicity concerns; the hydrocarbons and ammonia are examples.

The concept of sequentially eliminating chemicals by class, defined by molecular composition, raises the question of what will be left as successive issues are addressed (Wuebbles and Calm, 1997). The answer begins with examination of the refrigerants now used.

HISTORICAL REFRIGERANTS

Refrigeration goes back to ancient times, using stored ice and a number of evaporative processes; they are outlined by Thévenot (1979). Oliver Evans proposed the use of a volatile fluid in a closed cycle to freeze water into ice (Evans, 1805). He described a system that produced refrigeration by evaporating ether, under a vacuum, and then pumped the vapor to a water-cooled heat exchanger to be condensed for reuse. Although there is no record that he built a working machine, his ideas probably influenced both Jacob Perkins and Richard Trevithick. The latter proposed an air-cycle system for refrigeration in 1828, but he also did not build one.

Actual refrigerants were introduced in the 1830s, with invention of the vapor-compression machine by Perkins. He designed the machine to use *sulfuric* (ethyl) ether as the refrigerant. His patent describes a cycle using a “volatile fluid for the purpose of producing the cooling and freezing ... and yet at the same time condensing such volatile fluids, and bringing them into operation without waste” (Perkins, 1834). The first machine actually used *caoutchoucine*, an industrial solvent that Perkins apparently utilized in his business as a printer. It seems the first trade-off in refrigerants — and one still driving selections — was based on availability.

Table 1 summarizes early refrigerants, namely those

light metals	brittle metals		ductile metals		low melt	nonmetallic		inert gases
							H	
						C	N	O
								F
							S	Cl
								Br
lanthanides (rare earth elements)								
actinides (transuranium elements)								

Figure 1: Periodic table of the elements highlighting Midgley’s selections

predating fluorinated chemicals. Downing (1988), Nagegast (1989 and 1996), and Thévenot (1979) present further details.

The first century of refrigerant use was dominated by innovative efforts with familiar fluids in almost prototypical machines. The goals were to provide refrigeration and, later, durability. Use of blends was attempted where single-compound solutions could not be found (Pictet, 1885).

As production increased following World War I, attention turned to safety and performance as well. Willis H. Carrier, known for his advances in psychrometrics and air conditioning, and R. W. Waterfill initiated one of the first documented systematic searches (Carrier and Waterfill, 1924). They investigated a range of candidate refrigerants for suitability, for both positive displacement and centrifugal compression machines. These analyses closely examined ammonia, ethyl ether, carbon dioxide, carbon tetrachloride, sulfur dioxide, and water. They concluded, for example, that the performance of carbon dioxide would depend on the cycle and amount of liquid subcooling, but that it yielded the lowest predicted performance of the fluids analyzed. They also noted that ammonia and water would require excessive stages of compression for the conditions sought, and that water “gives a low efficiency of performance.” Sulfur dioxide was discarded for safety reasons and carbon tetrachloride because it attacks metals, especially in the presence of water. They finally selected *dielene* (1,2-dichloroethene, R-1130) for the first centrifugal machine, though an international search was needed to find a source for it (Ingels, 1952).

Midgley Elements

Nearly all of the early refrigerants were flammable, toxic, or both, and some also were highly reactive. Accidents were common. For perspective, propane was marketed as *the odorless safety refrigerant* (CLPC, 1922).

The discovery of fluorinated refrigerants began with a phone call to Thomas Midgley, Jr., in 1928. He already had established himself by finding tetraethyl lead, to improve the octane rating of gasoline. The caller stated that “the refrigeration industry needs a new refrigerant if they expect to get anywhere” (Midgley, 1937).

With his associates Albert L. Henne and Robert R. McNary, Midgley scoured property tables to find chemicals with the desired boiling point. They restricted the search to those known to be stable, but not toxic or flammable. An error in the published boiling point for tetrafluoromethane (*carbon tetra-*

fluoride) drew their attention to the organic fluorides; the correct boiling temperature later was found to be much lower. Nevertheless, the incorrect value was in the range sought and suggested consideration of fluorinated chemicals. While fluorine was known to be toxic by itself, Midgley and his collaborators felt that compounds containing it could be nontoxic.

Recognizing the deficiencies of the published literature, Midgley turned to the periodic table of the elements. He quickly eliminated those yielding insufficient volatility. He then eliminated those resulting in unstable and toxic compounds as well as the inert gases, based on their low boiling points. He was left with just eight elements: carbon, nitrogen, oxygen, sulfur, hydrogen, fluorine, chlorine, and bromine. They clustered at an intersecting row and column of the periodic table of the elements, with fluorine at the intersection. They are shown on a modern periodic table in figure 1; see Midgley (1937) for the arrangement then used.

Midgley and his colleagues then made three interesting observations. First, flammability decreases from left to right for the eight elements as shown in figure 1. Second, toxicity generally decreases from the heavy elements at the bottom to the lighter elements at the top. And third, every known refrigerant at the time was made from combinations of those elements. This observation can be verified by comparing the compositions of the historical refrigerants, listed in table 1, to figure 1. The historical fluids actually comprised only seven of the eight Midgley elements, since there appears to be no record of prior use of refrigerants containing fluorine.

The first publication on fluorochemical refrigerants shows how chlorination and fluorination of hydrocarbons can be varied to provide desired boiling points (Midgley, 1930). This paper also shows how the composition influences relative flammability and toxicity. Commercial production of R-12 began in 1931, followed by R-11 in 1932 (Downing, 1966 and 1984).

Other investigators have repeated Midgley's search with newer methods and modern databases, but they have come to similar findings. McLinden and Didion (1987) documented an extensive screening of industrial chemicals. Of the chemicals meeting their criteria, all but two — both highly reactive and toxic — consisted of the Midgley elements.

ENVIRONMENTAL ISSUES

More than forty years passed, during which fluorochemicals became the dominant refrigerants, until they were connected with environmental concerns (Molina and Rowland, 1974). Other fluorochemicals also were introduced in this period, and most of the earlier refrigerants were retired. A notable exception is R-717 (ammonia), which remains the preferred refrigerant in some industrial applications.

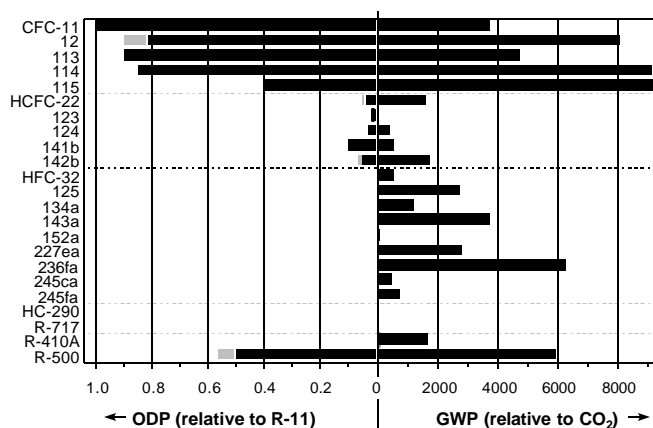


Figure 2: ODP versus GWP for common refrigerants

Stratospheric Ozone Depletion

The first global environmental problem identified was depletion of stratospheric ozone. The problem arises from destruction of ozone molecules in the upper atmosphere, primarily by bromine and chlorine from anthropogenic chemicals. The chlorine and bromine react catalytically to destroy ozone molecules, thereby reducing the natural shield from incoming ultraviolet-B radiation. Mario Molina and F. Sherwood Rowland (1974) identified CFCs as a source for the chlorine in the stratosphere and the potential for more serious ozone depletion, with projected growth in use of these chemicals.

The index used to indicate the relative ability of a refrigerant or other chemical to destroy stratospheric ozone is the ozone depletion potential (ODP) (Wuebbles, 1981). Figure 2 shows the ODPs of common refrigerants and selected candidates for future use. The shaded tips on several of the ODP bars indicate the higher values obtained by semi-empirical determination, as contrasted to the modeled values shown in black (WMO, 1994).

Chlorinated and brominated refrigerants, along with similar solvents, foam blowing agents, aerosol propellants, fire suppressants, and other chemicals are being phased out under the Montreal Protocol, a landmark international treaty to protect the ozone layer (UNEP, 1987 and 1997).

Global Warming

Concerns also have been raised with the prospect of global climate change. The average temperature at the surface of our planet results from an equilibrium, between incoming solar energy and heat radiated back into space. Most of the latter is in the infrared range of emissions. Gases that absorb this infrared energy enhance the greenhouse effect of our atmosphere, leading to warming of the Earth. While this mechanism is ac-

cepted, scientific debate remains on natural feedback mechanisms and both the timing and extent of the resultant warming.

Refrigerants, most notably those with long atmospheric lifetimes and high numbers of carbon-fluorine bonds, have been identified as greenhouse gases. The measure most commonly used to quantify the degree of concern is the global warming potential (GWP). Figure 2 shows GWP values alongside the ODPs for common refrigerants and candidates. The GWPs depicted are relative to the warming effect of a similar mass of carbon dioxide for 100 year time frames. Shorter integration periods emphasize near-term effects, while longer intervals better reflect the total impact of a release. The Intergovernmental Panel on Climate Change assessment (IPCC, 1996) and Wuebbles (1995) discuss the influence of the integration period and present data values.

Carbon dioxide is used as the reference chemical for GWPs because it is the one with the greatest net impact. Other chemicals, including most refrigerants, are more potent as greenhouse gases; the difference comes from the increasing abundance of carbon dioxide in the atmosphere. Most of the change results from increased use of fuels, in combustion processes, to meet our energy needs.

Air conditioners, heat pumps, and refrigeration devices that use refrigerants also use energy. They contribute to global warming both by release of refrigerants and by emission of carbon dioxide and other greenhouse gases, in powering the devices. Detailed studies have shown that energy-related component, commonly dubbed the *indirect effect*, is far greater than the *direct effect* from refrigerant releases for most applications (Calm, 1993)

One expression of the combined effects is the total equivalent warming impact (TEWI). Unlike ODP and GWP values, which can be determined from measurements of the compounds involved and other atmospheric data, TEWI determination also requires application data. Among those needed are the fuel or fuel mix to power the system, the conversion efficiencies, equipment efficiencies, loads, refrigerant release rates (manufacturing, installation, leakage, service, disposal, and other losses), energy uses for heat rejection, related pump or fan energy for distribution systems, and others. Calm (1993) and Fischer et al. (1991 and 1994) discuss these factors and consequent findings.

Figure 3 illustrates the comparative magnitudes of warming impacts from emission of refrigerants and associated energy use for water-cooled chillers. The efficiencies used in this example are the highest commercially available in 1996. Table 2 presents these efficiencies, which were taken from an industry survey (ARI, 1996). The indicators shown are Integrated Part Load Values (IPLVs), expressed both as a coefficient of per-

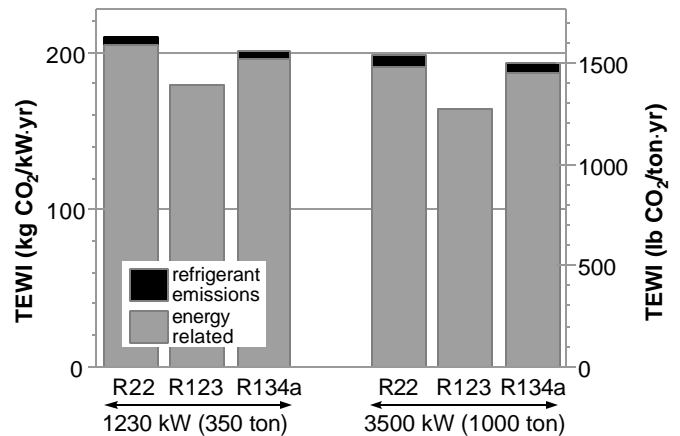


Figure 3: Total equivalent warming impact (TEWI) for the best available chillers

Table 2: Best available efficiency (specific power) for water-cooled chillers in 1996 based on certified integrated part-load values (IPLVs)

compressor refrigerant	1250 kW (350 ton)		3500 kW (1000 ton)	
	kW/kW	kW/ton	kW/kW	kW/ton
<u>centrifugal</u>				
R-22	5.96	0.59	6.51	0.54
R-123	7.03	0.50	7.82	0.45
R-134a	6.28	0.56	6.64	0.53
<u>screw</u>				
R-22	6.39	0.55	5.86	0.60
R-134a	5.96	0.59	NA	NA

NA = not available

formance (COP, kW/kW) and specific power (kW/ton). The survey was restricted to equipment with certified performance ratings, and the submissions were verified.

While the data in table 2 provide an objective comparison of the best chiller offerings then available, three caveats are necessary. First, the fraction of products sold with the highest efficiencies offered is small. Competitive products are available with each of the refrigerants shown at average performance levels, which are approximately 20% lower (~20% higher on a kW/ton basis). Second, additional options are now available; R-410A chillers are now marketed. And third, while the data are less than a year old, improvements have emerged in that time. The best available performance improved by 5%, to 8.18 kW/kW (fallen to 0.43 kW/ton), also for a certified IPLV, in the half year since the survey. Improvements continue, particularly for R-123 and R-134a. Nevertheless, the tabulated data provide a consistent comparison of the highest performance options recently available.

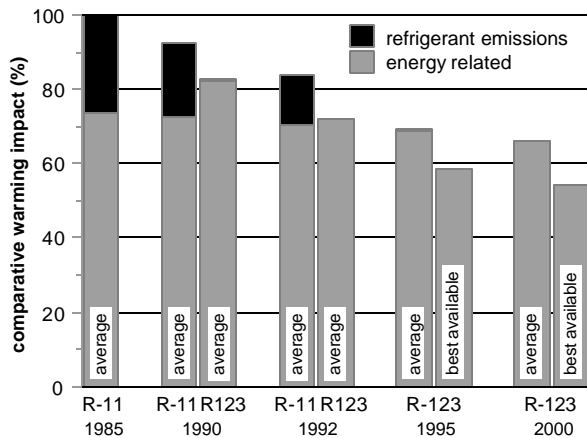


Figure 4: Progression and projection for chiller total equivalent warming impacts (TEWIs)

The calculation method and remaining data used for the analyses summarized in figure 3 are consistent with those in Calm (1993). The refrigerant emission rates and equipment lives were updated to those presented in Calm et al. (1997) and new GWP data (IPCC, 1996) were used. Electricity generation mixes and heat rates were updated to revised projections (NERC, 1995), and load profiles were decreased to correspond to an equivalent-full load level of 1500 hr/yr.

As shown in figure 3, the direct effect of refrigerant emissions amounts to only 2%-4% of the annual total for chillers using R-22, which has the highest GWP of the three refrigerants shown. These fractions drop slightly, to 2%-3%, in chillers with average efficiencies. The direct effect in figure 3 is 2%-3% of the total for R-134a chillers. It is less than 0.2% for R-123, which also offers the lowest energy-related impact, based on the highest available efficiency. From a TEWI perspective, phaseout of the hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) provides only small gain for chillers with low refrigerant releases. There is far greater opportunity by efficiency improvement. The same conclusion holds true for most other air-conditioning and refrigeration products as well. Two exceptions are mobile air conditioners and supermarket refrigeration systems, which still have high loss rates.

Figure 4 summarizes the recent progression in efficiency and reductions in refrigerant releases. The data shown are for 1750 kW (500 ton) R-11 and R-123 chillers. More than half of the centrifugal chillers installed in the years shown used these refrigerant. Similar conclusions can be drawn for R-12 and R-134a for the same time frame, although the TEWIs both start and end at higher levels.

R-11 dominated in centrifugal chillers almost since its introduction. Refrigerant losses were high; they often exceeded 15% of the total charge each year, as shown for 1985. Small efficiency gains appeared by 1990, but more significant gains were introduced in system tight-

ening and improved purge technologies. Figure 4 shows the resultant drop in impacts from emissions. R-123 use also had begun, though the first machines — essentially R-11 designs with materials changes for compatibility — yielded 14%-16% lower efficiency. The direct warming impact of R-123 emissions is barely visible, owing to a 98% lower GWP.

Release reductions continued, both by equipment tightening (e.g., minimization of the number of joints and replacement of mechanical fittings with brazed connections) and improved service practices. By 1992, the last year in which R-11 chillers were manufactured for domestic use in the United States, net emissions for machines of comparable capacities, were half those in 1985 and before. These release reductions offer several benefits beyond reduced global warming. They also lower the impact on ozone depletion. ODP and GWP only characterize chemical releases. Refrigerant that does not escape, and is recovered for reuse or safe disposal, does not harm the environment. Reduced losses also eliminate the need for makeup, thereby saving other resources and lowering costs, improve safety, and avoid performance losses from insufficient refrigerant charge.

Figure 4 also shows the dramatic improvements made in R-123 chiller optimization by 1992, leading to higher practical efficiency than available with the retired R-11 designs. This achievement, and subsequent further gains, are all the more impressive since R-11 holds a theoretical efficiency advantage over R-123, as shown below.

Further improvements in performance followed and are expected to continue, but the pace will slow as gains approach theoretical limits. The best efficiencies available, reflected in figures 3 and 4, are double those for many old machines still in operation. Coupled with emission reductions and R-123's very low GWP, the best chillers in 1995 reduced net global warming impacts by more than 40% compared to typical machines a decade earlier.

While stratospheric ozone depletion and global warming are distinct phenomena, they are linked in several ways. First, the increase in carbon dioxide — a greenhouse gas with the highest net impact — cools the stratosphere. That results in formation of ice crystals, which, in turn, increases the efficiency of bromine and chlorine attack on ozone. Second, ozone itself is a greenhouse gas; reduction of its average equilibrium concentration reduces its warming contribution. Third, efficiency improvement in energy systems is a key option for long-term reduction of greenhouse gas emissions. Eliminating the most efficient refrigerants (for example, R-123), to protect the ozone layer removes one of the most cost-effective options to reduce global warming.

Uncertainties remain in global warming timing, offsets, and therefore magnitude, but it is clear that the

warming issue will be much more difficult to address than ozone depletion. That heightens the need for balanced, rather than fragmented, solutions to global climate change issues. Simplistic elimination based on ODP and GWP alone, without distinction between open and closed uses (highly emissive versus contained applications), defeats this goal. Likewise, any GWP criterion that ignores emissions of associated, energy-related greenhouse gases is likely to exacerbate the problem. And, the possibility of yet unforeseen environmental issues cannot be eliminated. Distinction between short- and long-lived chemicals increases the options to respond to future issues, without a long recovery period from prior releases.

TRADE-OFFS

In addition to having the desired thermodynamic properties, an ideal refrigerant would be nontoxic, nonflammable, completely stable inside a system, environmentally benign even with respect to decomposition products, and abundantly available or easy to manufacture. It also would be self-lubricating (or at least compatible with common lubricants), compatible with other materials used to fabricate and service refrigeration systems, easy to handle and detect, and low in cost. It would not require extreme pressures, either high or low.

There are additional criteria, but no current refrigerants are ideal even based on the partial list. Furthermore, future discovery of ideal refrigerants is extremely unlikely. The discussion that follows illustrates conflicts in desired molecular makeup and properties, which virtually preclude the possibility that ideal refrigerants exist or can be synthesized.

Flammability, Toxicity, and Atmospheric Lifetime

Increasing the hydrogen content of a compound generally decreases its atmospheric lifetime, but increases its flammability; the former is desirable in a refrigerant, while the latter is undesirable. The CFCs, which contain no hydrogen, have long atmospheric lives, but are not flammable. In contrast, the hydrocarbons tend to have short lifetimes, but are highly flammable. HCFCs and HFCs fall in between. Those with high hydrogen content, such as R-152a, tend to be more flammable (Corr et al., 1995). Those with slightly lower hydrogen content, R-141b, R-142b, and R-143a, exhibit lower flammability. Those with low hydrogen content, such as R-22, R-23, R-123, R-124, R-125, and R-134a are not flammable under normal conditions. Refrigerants generally are marginally flammable when the number of hydrogen atoms constitutes half of the total atoms connected to the carbons. Higher fractions become increasingly flammable. This observation can be verified by examination the lower-flammability limits of refriger-

ants (for example, see Richard and Shankland, 1992). The second numerical digit from the right, in standard fluorochemical designations for molecules with one to four carbon atoms (the methane, ethane, propane, and butane series), indicates the hydrogen content. The actual hydrogen count is one less than that digit. Using R-134a as an example, the hydrogen atom count is 3 minus 1 equals 2.

Increasing the chlorine content tends to increase the normal boiling point temperature (McLinden and Didion, 1987). Increasing the fluorine content (indicated by the right-most digit in the fluorochemical designation system) tends to reduce toxicity (Clayton, 1967). Increasing the fluorine by displacement of hydrogen tends to reduce flammability (Dekleva 1994, and Smith and Tufts, 1994), while doing so by displacement of chlorine increases the atmospheric lifetime. Comparison of perchlorinated and perfluorinated chemicals, R-10 (CCl_4) versus R-14 (CF_4) for example, reveals a change from 42 to 50,000 years. Indeed, the perfluorocarbons (R-14, R-116, R-218, R-C318, R-31-10, R-41-12, and others) tend to have exceptionally long lives.

McLinden and Didion (1987) summarized these trade-offs as shown in figure 5, where the top of the triangle represents hydrocarbons (hydrogen and carbon only). The two bottom vertices represent perchlorinated (chlorine and carbon only) and perfluorinated (fluorine and carbon only) chemicals.

ODP versus GWP

There is no way to directly compare the demerits of ozone depletion and global warming, since they are distinct phenomena. As illustrated in figure 6, increasing the chlorine content in refrigerant molecules generally increases the ODP. Compounds that contain no bro-

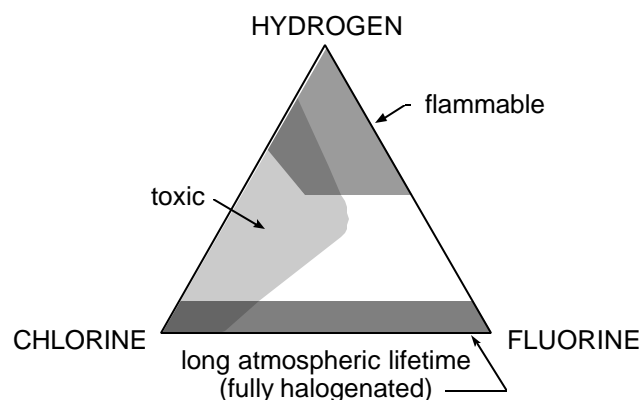


Figure 5: Trade-offs in flammability, toxicity, and atmospheric lifetime with changes in molecular chlorine, fluorine, and hydrogen content in organic refrigerants (McLinden and Didion, 1987)

mine or chlorine have ODPs that are nearly zero. Likewise, increasing the fluorine count generally increases the GWP. In both cases, increasing the hydrogen count tends to shorten the atmospheric lifetime. Compounds with very short lives will have low ODPs, since most emissions will decompose before reaching the stratosphere. They also will have low GWP values, since their atmospheric persistence will be comparatively short in duration.

As was shown in figure 2, CFCs generally have very high ODPs and GWPs. Most HCFCs have low ODP and GWP. HFCs have ODPs of almost zero, but GWPs that range from very low to very high. Relatively few fluorochemicals have both very low, or zero, ODP and very low GWP. Among them are R-123 and R-152a, both of which have short atmospheric lifetimes of 1.4 and 1.5 years, respectively. R-152a, however, is flammable.

Even though ODP and GWP cannot be equated, some conclusions still can be drawn on trade-offs between them for specific compounds. One method requires determination of the chlorine-bromine loading (CBL) contribution. CBL is an indicator of the available chlorine and bromine reaching the tropopause, in turn suggestive of the maximal impact on ozone destruction.

A detailed analysis for R-123 (Calm et al., 1997) shows that its use in chillers, at current emission rates for converted and new equipment, has a negligible impact on the ozone layer. Its peak impact, with phaseout as scheduled under the Montreal Protocol, amounts to approximately 0.002% of the total CBL from all sources, natural and anthropogenic. Continued use of R-123 as a refrigerant would barely increase the 0.002% peak, and the average CBL impact through 2050 would be approximately 0.001%. Moreover, the contribution that coincides with the CBL peak from re-

sidual CFC and halon effects is much smaller. These fractions are considerably lower than the variability in CBL from natural sources.

Conversely, figures 3 and 4 point to a significant opportunity to reduce global warming by use of R-123. As discussed above, its short lifetime suggests a second benefit in the event that additional, but currently unforeseen, atmospheric issues surface. R-123's high theoretical and practical efficiencies also lead to immediate advantages in energy conservation and reduced use of other resources. Trade-off of a negligible impact on ozone depletion for significant warming avoidance, and other benefits, suggests a strong environmental rationale for allowing continued use of R-123.

Importance of Efficiency

As shown in figures 3 and 4 above, there is little opportunity for further TEWI reductions by elimination of the direct effect of refrigerant emissions, particularly for refrigerants with very low GWP. Future decreases, therefore, must come from containment, load reductions, and efficiency improvements. Figure 4 illustrated the substantial progress in equipment tightening for chillers. Table 3 summarizes efficiency limits in theoretical cycles for current and candidate refrigerants.

Two cautions are warranted. First, the differences in efficiency limits for some of the primary candidates are small, and may be distorted by imprecision in the refrigerant properties used. Second, theoretical efficiency limits alone do not govern practical efficiencies. Other properties, such as viscosity and thus heat transfer coefficients, may have significant impacts on overall performance. Likewise, cycle design impacts performance. Increased subcooling may reduce the efficiency distinctions in simple cycles, as seen by examination of the data presented in table 3. Use of multistage compression with economizers also may do so. Table 3 shows an efficiency advantage of 3%-4% for R-123 over R-245fa, depending on the conditions examined. This difference drops to less than 1% with three or four compression stages at typical conditions; this finding parallels that for comparisons of R-123 and R-11.

These analyses indicate only the maximum efficiencies for the conditions, cycles, and refrigerants modeled. Practical efficiencies will be lower, as demonstrated by comparison of the performance levels in tables 2 and 3. Moreover, the ratios between attainable and theoretical or between practical and theoretical efficiencies differ among refrigerants. Atwood and Hughes (1990) urge skepticism for simplistic comparisons. They note that efficiency is not an inherent property of a fluid, but that achieving the highest efficiencies depends on optimization of the system and individual components for the refrigerant. Nevertheless, cycle analyses are useful to prioritize candidates and to discount those resulting in significantly lower performance.

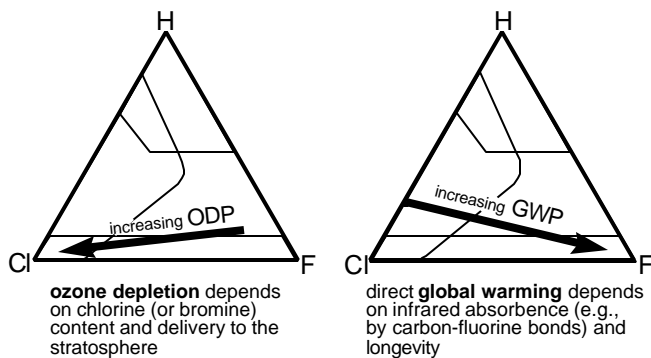


Figure 6: Chlorination and fluorination impacts on ozone depletion and global warming potentials

Table 3. Comparative refrigerant efficiencies at standard chiller rating conditions

conditions	ideal cycle ^{a,b}			typical conditions ^{b,c}		
	(°C)	(%)	(°F)	(°C)	(%)	(°F)
average evaporating temperature	6.7		44.0	5.0		41.0
superheat	0.0		0.0	1.0		1.8
average condensing temperature	29.4		85.0	35.0		95.0
subcooling ^d	0.0		0.0	5.0		9.0
isentropic compressor efficiency		100			80	
motor efficiency		100			95	
control and other power use		0			0	

refrigerant	COP (kW/kW)	specific power (kW/ton)	COP (kW/kW)	specific power (kW/ton)
R-11	11.52	0.31	6.60	0.53
R-12	10.92	0.32	6.26	0.56
R-22	10.85	0.32	6.19	0.57
R-113	11.14	0.32	6.41	0.55
R-114	10.94	0.32	6.30	0.56
R-123	11.38	0.31	6.54	0.54
R-134a	10.89	0.32	6.26	0.56
R-141b	11.25	0.31	6.46	0.55
R-236fa	10.89	0.32	6.28	0.56
R-245ca	11.11	0.32	6.39	0.55
R-245fa	10.97	0.32	6.32	0.56
R-290 (propane)	10.72	0.33	6.16	0.57
R-410A	10.51	0.33	5.99	0.59
R-500	11.27	0.31	6.46	0.55
R-717 (ammonia)	11.17	0.31	6.26	0.56
R-744 (carbon dioxide)	6.44	0.55	e	e

^a Conditions are those for standard chiller ratings in the United States for water-cooled chillers (ARI, 1990).

^b Calculations were made with CYCLE_D version 1.1 (Domanski et al., 1997) for all refrigerants except R-11, for which version 1.0 was used.

^c Conditions approximate those typically encountered on the refrigerant side of water-cooled chillers at standard rating conditions for representative approach temperatures, subcooling, and superheat.

^d Typical subcooling varies by refrigerant for the reasons discussed later in this paper. The level shown is a representative selection for comparisons.

^e Conditions exceed critical point (requires a transcritical cycle).

Of the refrigerants shown in table 3, R-11 stands out as offering the highest potential efficiency. It also offers two important, practical advantages. First, the requirements for pressure vessels generally do not apply, leading to savings in equipment fabrication costs, since R-11 chillers operate at low pressure. Second, its liquid state at room temperature simplifies handling. These advantages are partially offset by the need for a purge

device, due to subatmospheric evaporation, and higher toxicity — specifically its potency for cardiac sensitization — than most alternatives. In balance, R-11 emerged as the most widely used refrigerant in equipment (primarily chillers) with centrifugal compressors. It was not competitive in smaller equipment, using positive displacement compressors, due to its high volume-flow requirement.

With R-11 phaseout, based on its high ODP, R-123 has become the most widely used refrigerant in centrifugal chillers. As shown in tables 2 and 3, R-123 also offers exceptionally high efficiency. Like R-11, it is a low-pressure refrigerant and miscible with mineral oil lubricants. It is safer to use than R-11 by most acute (short term, single exposure) measures (Calm, 1994). Its chronic (long-term, repeat exposure) toxicity is very low, but higher than that of R-11 and most alternatives. R-123 does not qualify as a toxic substance under most federal laws and most building, fire, and mechanical codes in the United States. It nevertheless is classified as a B1 refrigerant, reflecting its chronic toxicity (ASHRAE, 1993). Introduction of R-123 required significant changes in fabrication materials, due to differences in its solvency, but those matters were resolved by 1990.

While long-term alternatives have been identified for most refrigerant needs, the search continues for R-123's replacement. For perspective, R-134a has largely replaced R-12 in appliances, commercial and transport refrigeration, mobile air conditioners, chillers, and other uses. Hydrocarbons and hydrocarbon blends also have gained acceptance in some countries. R-410A and, for limited applications R-407C and R-407E, are leading candidates to replace R-22 in window, unitary, packaged terminal, and water-source air conditioners and heat pumps and in chillers and refrigeration. R-404A and R-507A are the front runners to replace R-502 in low temperature refrigeration; R-407A and several other blends are used in some applications. The replacements cited for R-12, R-22, and R-502 together with R-717 are becoming the norm in all but ultra-low temperature, industrial refrigeration. These uses — and the elusive R-123 replacement — are the plums of the refrigerant market. More than 40 new refrigerants, including blends, have been commercialized since 1989 to compete for the applications discussed and more limited uses. This quantity is doubled if short-term R-12 replacements are counted. Most of them are service fluids for existing equipment; the number of survivors in a decade will be similar to that a decade ago.

Despite all the activity for the plums, niche applications, and service fluids, the important successor to replace R-123 has not emerged. Solutions have been sought by chemical and equipment manufacturers, government laboratories, research organizations, environmental groups, universities, and others.

Among the hoped-for options, the fluoroether R-E245fa1 (2-difluoromethoxy-1,1,1-trifluoroethane) was found to react explosively with glass and to be unstable with fibrous-glass motor materials (Doerr et al., 1993). 1,1,2,2,3-Pentafluoropropane (HFC-245ca) was found to be flammable (Smith et al., 1993) and not suited for CFC-11 and HCFC-123 retrofits (Glamm et al., 1996). Blends that inert its flammability degrade performance.

Sand and Fischer (1994) identified three candidates, by modeling, that might exceed the efficiency of R-123, among them R-143, R-E143, R-152. However, all three are flammable and their toxicities are not well characterized, particularly for R-E143. The blends suggested to address flammability concerns were found unattractive. Tests of R-245fa, fluoroethers, and fluoroether blends are continuing. R-245fa may approach R-123's efficiency, particularly in multistage designs, but will require compliance with pressure vessel restrictions and will not be suited for retrofit of the very large inventory of R-11 and R-123 chillers. And its GWP exceeds that of R-123 by a factor greater than nine.

No viable refrigerant has yet surfaced that offers higher efficiencies than R-11 or R-123. The theoretical advantage of R-123 over current alternatives, namely R-22 and R-134a, is 3%-5%. The difference for the best available equipment is 9%-20%.

POSSIBLE FUTURE REFRIGERANTS

The influences of chemical composition on behavior suggest several insights for future refrigerant candidates. The following discussion is limited to impacts on efficiency.

The critical point and molar heat capacity are among the most important parameters driving thermodynamic performance. Operation close to the critical point results in high volumetric capacity, but low efficiency, since the refrigerating effect is decreased. Operating far from the critical point results in the opposite condition, namely good efficiency but low capacity (McLinden and Didion, 1987). A review of current refrigerant selections for common applications shows that the reduced (normalized to the critical point temperature) condensing temperature typically falls in the range of 0.7-0.9. This finding is similar to that of Angelino and Invernizzi (1988) for complex molecules, considered as refrigerants for high temperature heat pumps.

Figure 7 illustrates an ideal vapor-compression cycle on a temperature-entropy (T-S) diagram. In this context, ideal cycle refers to one having no components (such as subcoolers, liquid-line/suction-line heat exchangers, or expansion turbines) for expansion loss recovery. The area designated as the refrigerating effect represents the heat per unit mass of refrigerant transported from the evaporator to the condenser. Both the capacity and the efficiency depend heavily on maximizing this amount, since a decrease requires that more mass flow be compressed to achieve the same capacity.

Figure 8 shows correlations, for two reduced condensing temperatures, between the fraction of latent heat constituting the refrigerating effect and the liquid heat capacity. The points shown are those for common refrigerants, based on property data from REFPROP (Huber et al., 1996). Comparing the plotted correlations,

the ratio of refrigerating effect to latent heat decreases as condensing temperature approaches the critical temperature and as the liquid heat capacity increases.

McLinden (1990) quantitatively examined the influences of the critical point and molar (ideal gas) heat capacity on refrigerant performance. He showed that operation would be optimized for fluids with heat capacities of 35-70 J/mol·K, depending on the critical point. The cited range corresponds to simple refrigerant molecules, typically those with a single carbon atom. Refrigerants containing two or three carbon atoms have higher heat capacities, up to 250 J/mol·K; they can be optimized only through cycles that recover expansion-side losses.

Domanski et al. (1994) simulated the addition of a 100% effective liquid-line/suction-line heat exchanger to an ideal cycle. The resulting efficiencies were nearly the same for all of the refrigerants examined, essentially those plotted in figure 8.

Wood (1982), Morrison (1994), and others have shown that the molar heat capacity is a strong indicator of the skew in the saturation boundaries for refrigerants on a T-S diagram. More specifically, the slope of the saturated-vapor line increases, and then bends over, as heat capacity increases. This shape change causes two problems. First, it creates the possibility of re-entering the two-phase (“wet”) region during isentropic compression, unless the refrigerant is superheated before compression. In extreme cases, it leads to the possibility of never leaving the two-phase region, forcing destructive and inefficient wet compression. Second, the decreasing slope of the saturated liquid line degrades the refrigerating effect, in similar manner to critical point proximity.

Figure 9 illustrates the increasing skew of the saturation boundaries on T-S diagrams for R-11, R-123, R-245ca, and R-245fa. The first three have very similar pressure-temperature relationships; the fourth also is similar, but has slightly higher pressures. As noted above, R-123 has replaced R-11 as the most common refrigerant in new centrifugal chillers, and R-245ca and R-245fa are candidates to replace R-123. The number of carbon atoms increases from one in R-11, to two in R-123, to three in the R-245 isomers. The increasing number of bonded atoms increases the molar heat capacity and, consequently, the skew of the saturation boundaries. As indicated by the analyses summarized in table 3, the ideal and typical efficiency limits fall in the same progression. Comparison of the efficiency decreases for these fluids between those for ideal and typical cycles (see table 3) shows that subcooling reduces the deterioration for the larger (more complex) molecules. As discussed above, use of multistage cycles with inter-stage economizers also would partially offset the efficiency decreases.

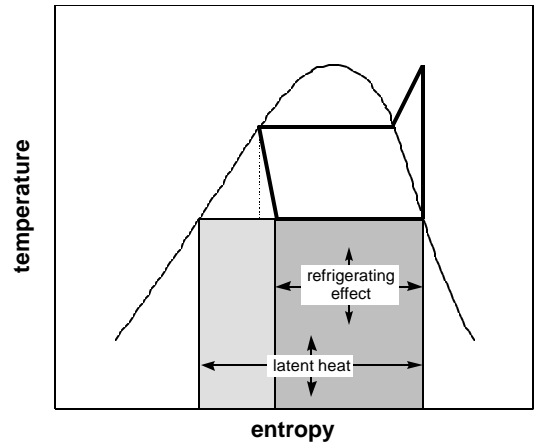


Figure 7: Relationship between the refrigerating effect and latent heat in a vapor-compression cycle

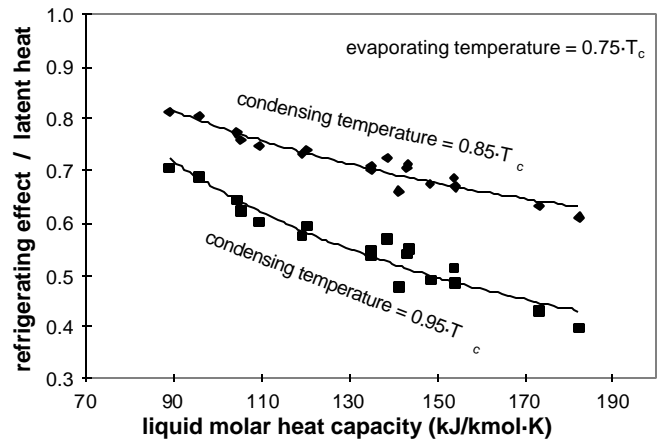


Figure 8. Refrigerating effect degradation (multiply J/mol·K by 1.706 for Btu/kmol·R)

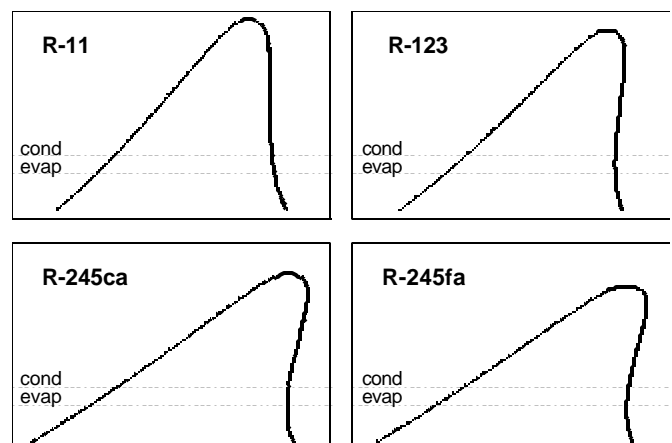


Figure 9: Increasing skew of the saturation boundaries, as seen on T-S diagrams, with increasing molecular complexity and heat capacity

The plots for R-245ca and R-245fa show that more is involved than simple molecular size. The two isomers have the same mass, but the less symmetric isomer, R-245fa, thermodynamically behaves like a more complex molecule (i.e., its T-S saturation boundaries are more skewed than those of R-245ca). It also has a lower critical temperature.

Use of refrigerants with low critical temperatures results in operation at higher reduced temperatures. As an example, the reduced temperature for condensing with R-410A (a 50/50 blend by mass of R-32 and R-125) may reach 0.95 in air-cooled air conditioners. This high reduced temperature suggests that added devices for expansion-side recovery will be needed to achieve maximum capacity and efficiency for this R-22 replacement.

One might conclude that all refrigerants have the potential to achieve similar cycle efficiencies, but they require changes in machinery size and complexity to do so. Furthermore, working fluids with simple molecular structures require simple machines with relatively few components, as has been the case with the CFCs. As we eliminate these simple molecules, we will be forced to consider more complex machines to optimize performance. Whether the conclusion is true in every case is less important than its implications. Specifically, true optimization requires that the refrigerant and the machine be designed together, via mixtures and additional components if needed.

From an engineering perspective, each element of added complexity increases costs, refrigerant charge (amount), the potential for leaks, and thermodynamic irreversibilities. Each addition also reduces the system's reliability. Hence, simple refrigerant molecules have an inherent advantage to reach higher efficiencies at lower costs and with lower system risk of environmental harm. Conversely, elimination of the simple molecules implies higher system costs and higher risks.

One of the lessons, from repeated searches for new refrigerants, is that the number of suitable elements that

can be combined at the molecular level is small. Figure 10 returns to elements identified by Midgley and his cohorts (shaded) as well as subsequent research. Examination of these options suggests that increasing the content of:

- carbon increases the molecule size, generally increasing the normal boiling point and molar heat capacities, making large molecules unsuitable,
- nitrogen makes the resulting compound more reactive, generally increasing toxicity and decreasing stability,
- oxygen reduces the atmospheric stability, and therefore ODP and GWP, but also may increase flammability, reactivity, and toxicity,
- sulfur generally increases toxicity and may decrease stability,
- hydrogen generally decreases atmospheric lifetime, and therefore ODP and GWP, but also increases flammability especially when the number of hydrogen atoms exceeds the number of connected halogen atoms,
- fluorine attached to carbon increases the GWP, particularly in perfluorinated molecules,
- chlorine increases lubricant miscibility, but also the ODP and, generally, the toxicity,
- bromine rapidly increases the ODP, but greatly diminishes flammability, and
- total fraction of attached halogens increases atmospheric lifetime, particularly for perhalogenated compounds, and therefore ODP and GWP.

Corr et al. (1995) note that the toxicities and pungent odors of compounds containing carbon, hydrogen, nitrogen or sulfur, and optionally oxygen strongly reduce their potential as refrigerants. Furthermore, partially fluorinated analogs of these compounds lack stability.

Three other elements have drawn intense scrutiny, namely boron (which falls to the left of carbon in the periodic table of the elements), silicon (which sits below carbon), and iodine (which lies below bromine). Increasing the content of:

- boron makes chemicals highly reactive and, generally, toxic.
- silicon makes analogs to CFCs react with water, sometimes violently, and its more complex compounds have failed either thermodynamic or toxicity screening criteria.
- iodine generally increases reactivity, which shortens the atmospheric lifetime but raises concerns with long-term stability inside refrigeration machines. The one iodochemical tested for cardiac sensitization potential, R-131I, showed an effect at low concentra-

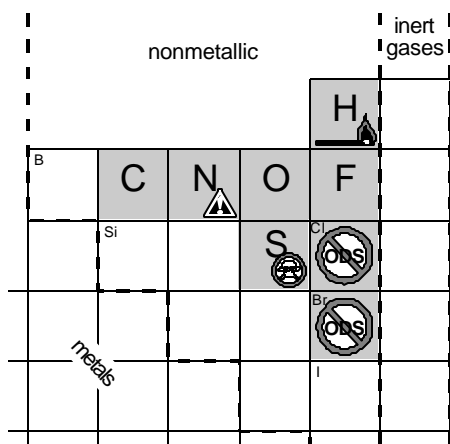


Figure 10: Candidate elements for refrigerants

tions. Some volatile iodides have been rejected for toxicity.

The number of potential chemical combinations of these elements drops quickly as individual elements are removed. Most compounds containing chlorine and bromine, including those used as refrigerants, have been or are being phased out under the Montreal Protocol. Fluorinated compounds are under attack as greenhouse gases. Most chemicals containing nitrogen, and sulfur that are suited as refrigerants raise safety concerns, though one, ammonia, is widely used. Hydrocarbons tend to be good refrigerants, but they are highly flammable. Most exhibit cardiac sensitization potentials and anesthetic effects that are similar to halocarbons, but offer lower toxicity risks upon decomposition. Also, hydrocarbons have been implicated in the generation of tropospheric ozone — an irritant and factor in smog formation — when subjected to solar irradiation, thus reducing air quality in urban areas (Corr et al., 1995). Carbon dioxide introduces high pressures and lowers thermodynamic efficiencies; carbon monoxide is quite toxic.

CONCLUSIONS

The first generation of refrigerants, from the advent of mechanical refrigeration in the 1830s through the next hundred years, was characterized by use of *whatever-worked*. Early inventors tried a variety of familiar, volatile fluids. Systematic screening, to improve performance and safety, did not begin until late in that era.

The second generation began in the 1930s, with discovery of fluorinated refrigerants, and lasted approximately 60 years. The driving factors were safety and durability. For the first time, refrigerants were synthesized to obtain desired properties.

The third generation began in the 1990s, with introduction of alternative refrigerants for environmental protection. The initial concern was depletion of the stratospheric ozone layer, but selections anticipated the need to mitigate greenhouse gas effects as well. One distinction of this era is the advent of service fluids, to enable continued use of the large inventory of existing equipment. Another is introduction of transition compounds, those used — and even newly commercialized — despite anticipated phaseout, while long-term solutions are sought. A third distinction is higher dependence on blends, and zeotropes in particular, in the absence of single-compound options to meet complex criteria.

Rapid introduction of the alternatives created an illusion that more choices can be found for each new set of rules, if simply imposed. Most of the alternative refrigerants of the 1990s had been examined before, but were found less competitive under old criteria. The earlier examinations, and in some cases equipment tests, enabled rapid commercialization when the rules changed.

One hallmark of the progression in refrigerants is that chemical and equipment manufacturers opposed compromises that retrenched on safety and performance.

Interest, or more correctly revived interest, is emerging in chemicals dubbed *natural*. The desirable thermodynamic properties of some hydrocarbons and other refrigerants deemed *natural* were recognized in the 19th century. These refrigerants were largely retired in the 20th century to improve safety rather than performance. Their future — as refrigerants for the 21st century — may depend not only on new selection criteria but also on new technologies to reduce their risks.

Several conclusions are evident. First, the probability of finding an ideal refrigerant, particularly with the exhaustive searches performed to date, is practically zero. Those waiting for a perfect solution will be disappointed. Second, greater attention is needed in addressing both environmental and safety concerns by containment, particularly for compounds with minimal adverse impacts, rather than phaseout. Tremendous progress has been made in the last decade, and further emission reductions are likely. Third, indiscriminate elimination of entire classes of compounds, without regard to offsetting benefits for those of low concern, may force less desirable compromises later. R-123 is a clear example. Its ODP is not zero, but it is so low that use of R-123 in closed systems, such as chillers, yields a negligible effect on ozone depletion. This effect is more than offset by a short atmospheric lifetime, extremely low GWP, and very high thermodynamic efficiency. And fourth, efforts to address stratospheric ozone depletion and reduce greenhouse gas emissions have spawned numerous secondary benefits, in terms of increased safety, higher efficiency, resource conservation, and lowered life-cycle costs.

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