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Thermophysical-Property Needs for the Environmentally Acceptable Halocarbon Refrigerants[1]

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The need for and uses of thermodynamic and transport properties in the selection of working fluids for the vapor compression cycle and in equipment design are reviewed. A list of hydrogen-containing halocarbons, as well as their mixtures, is presented as alternatives to the environmentally harmful, fully halogenated chlorofluorocarbons. These fluids range from well-characterized, widely available refrigerants to materials available only by custom synthesis about which very little is known. Data priorities for these fluids are presented; most essential are critical point, vapor pressure, liquid density, ideal-gas heat capacity, and vapor p–V–T data. A critical need exists for these data on a number of candidate working fluids in order not to lose the opportunity to select the best set of future refrigerants.

KEY WORDS: chlorofluorocarbon; refrigerant; thermodynamic properties; thermophysical properties.

1. INTRODUCTION

The chlorofluorocarbons, also called CFCs or halocarbons,[4] are a class of compounds containing the halogens chlorine and/or fluorine on a carbon skeleton. The first such compound to be commercialized, dichlorodifluoromethane or R12, was introduced as a refrigerant in the 1930s. CFCs quickly replaced refrigerants such as ammonia and sulfur dioxide then in

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[4] The term chlorofluorocarbon (CFC) has been used to describe any carbon-based compound containing chlorine and/or fluorine and/or hydrogen; the trend in recent usage is to apply it only to the fully halogenated compounds.

common use and today serve as the working fluid in the vast majority of refrigeration, air-conditioning, and heat-pumping equipment. They are also used extensively as foam-blowing agents and as solvents.

The major CFC refrigerants are characterized by their nonflammability, low toxicity, good thermal properties, and extreme stability. The latter characteristic, long considered an asset, is now seen to be a liability—the fully halogenated CFCs persist for many years once emitted to the atmosphere. This allows them time to diffuse to the upper atmosphere, where the molecule finally breaks down, releasing the chlorine which is responsible for catalyzing the destruction of stratospheric ozone. The fully halogenated CFCs are also major contributors to the greenhouse effect. Because of their long life and strong infrared absorption, the CFCs are responsible for approximately 15–20% of the predicted global warming trend [1] in spite of atmospheric concentrations several orders of magnitude lower than that of carbon dioxide.

Because of their environmental impact, an international protocol to limit the production of certain CFCs was negotiated in 1987. Several countries have announced even more severe restrictions than the eventual 50% reduction called for in the protocol [2]. In addition, the three largest U.S. producers of CFCs have announced the intent to phase out completely production of the fully halogenated compounds. Of the affected compounds, R11 (trichlorofluoromethane) and, especially, R12 are used extensively as refrigerants, with R114 (dichlorotetrafluoroethane) and R115 (chloropentafluoroethane) used in smaller quantities. These impending restrictions have created a new urgency in the search for replacement fluids.

To be acceptable as a refrigerant, a fluid must satisfy a variety of criteria, as indicated in Table I. As examples, the requirements of a nonflammable refrigerant of low toxicity are mandated by safety codes for many applications (e.g., Refs. 3 and 4), while a high vapor dielectric strenght is required by hermetic compressors where the refrigerant is in direct contact with the motor windings. Data for all of the fluid properties outlined in Table I are required to determine the suitability of a fluid for use as a refrigerant and/or for the purposes of equipment design. This paper is limited to the thermophysical properties. The data necessary for preliminary screening, detailed evaluation, and equipment design are presented and prioritized.

2. STATUS OF THE ENVIRONMENTALLY ACCEPTABLE REFRIGERANTS

The compounds that might replace the fully halogenated CFCs are listed, in Table II, in order of normal boiling point. For comparison, the

Table I. Refrigerant Criteria

- Chemical
  - Stable and inert
- Health, safety, and environmental
  - Nontoxic
  - Nonflammable
  - Does not degrade the environment
- Thermophysical properties
  - Critical-point and boiling-point temperature appropriate for the application
  - Low vapor heat capacity
  - Low viscosity
  - High thermal conductivity
- Miscellaneous
  - Soluble in lubricating oil
  - High vapor dielectric strength
  - Low freezing point
  - Compatible with common materials
  - Easy leak detection
  - Low cost

Table II. Fully Halogenated CFC Refrigerants and Environmentally Acceptable Alternatives

Fully halogenated CFC			Alternative refrigerant		
Name	Formula	NBP (°C)	Name	Formula	NBP (°C)
			R141b	CCl_2FCH_3	32
R11	CCl_3F	24	R123/123a	$C_2HCl_2F_3$	27
			R142b	$CClF_2CH_3$	−9
R114	$CClF_2CClF_2$	4	R124	$CHClFCF_3$	−12
			R134	CHF_2CHF_2	−20
R12	CCl_2F_2	−30	R152a	CHF_2CH_3	−25
			R134a	CF_3CH_2F	−27
R115	$CClF_2CF_3$	−39	R22	$CHClF_2$	−41
			R143a	CF_3CH_3	−48
R13	$CClF_3$	−81	R125	CF_3CHF_2	−48
			R32	CH_2F_2	−52
			R23	CHF_3	−82

fully halogenated compounds are also listed. (Among the fully halogenated compounds, R13 does not face restrictions under the international protocol; given its long atmospheric life, this omission is probably a consequence of its limited use.) This tabulation is based on our previous study [5] where it was argued that the hydrogen-containing chlorofluorocarbons were most likely to possess the desired properties. Thermodynamic arguments as well as empirically observed trends for toxicity and flammability further limited the possibilities to the fluorine-rich one- and two-carbon compounds listed. There are some additional possibilities that are briefly discussed later, but the compounds listed in Table II are by far the most likely commercial possibilities in the short to medium term.

Of the hydrogen-containing compounds listed in Table II, at least four are in commercial production. R22 is, of course, a very common and widely available refrigerant. R23 and R152a are specialty refrigerants used in the azeotropic mixtures R503 and R500, respectively. R142b and R152a are currently used as chemical precursors in the production of certain fluorinated polymers.

Three fluids are currently the focus of intense development efforts, by both the chemical producers and refrigeration equipment manufacturers. R134a, the most publicized new refrigerant, shows promise as a replacement for R12, particularly in refrigeration and automotive air-conditioning applications. R123 and R141b are being developed as replacements for R11; much of the effort is directed at foam-blowing applications. The use of R123 as a refrigerant in centrifugal-type compressors appears feasible, while the evaluation of R141b in this application has been seriously hampered by a lack of thermodynamic data. Both R123 and R141b are available in limited quantities, the former as a specialty chemical and the latter as a by-product of the R142b process.

There are several additional compounds that warrant consideration, in terms of both their properties and their prospects for eventual commercial availability. R123a, an isomer of R123, will likely be a minor constituent in commercial-grade R123. Although thermodynamically very similar, there is some indication that R123a is more stable and possibly less toxic than R123. These are desirable attributes for a refrigerant. R123a could be distilled from a R123/R123a mixture for refrigeration use with the R123 used in less critical applications. Depending on the process, R124 and R125 may also be produced as by-products of R123 [6]. Another candidate, R143a, is a by-product of the process to produce R142b; process conditions could be easily changed to increase the yield of R143a if demand warranted [7].

The final two compounds to consider are currently available only on a custom synthesis basis. Difluoromethane, R32, has the highest heat of vaporization (on a mass basis) among the fluids listed in Table II; it also has excellent heat transfer characteristics [8]. R32 was produced many years ago and a quite straightforward synthesis route is known [9]. Finally, at least one study [10] indicates that R134 is thermodynamically superior to its isomer, R134a; this conclusion is based on estimated properties, however, as very few data exist for R134.

There are several reasons to expand the list of considered fluids beyond the R134a, R123, and R22 that are most often discussed. The conversion from the fully halogenated CFCs represents an opportunity to develop the best possible working fluids. Given the long life typical of most types of refrigeration equipment and the great inertia to be overcome in making a change of refrigerant, a less than optimum choice made today will result in long-reaching energy efficiency or other penalties. Fluids such as R134a were targeted for development because of their match with common applications; other, specialized applications may require a refrigerant with different properties. An example is commercial refrigeration systems which currently use R502 (an azeotropic mixture of R22 and R115).

Examining a wider set of fluids lays the groundwork for a backup refrigerant in the event that some unforeseen problem arises with the leading candidates. The hydrogen-containing halocarbons are listed in Table III according to their flammability and chlorine content. If at least limited flammability and chlorine content (i.e., small but nonzero ozone depletion potential) are acceptable, at least a dozen halocarbons are candidates. Toxicity testing is, however, incomplete for several of these compounds; in particular, there are concerns about potential toxicity problems with R123 and R141b. If, however, a nonflammable, chlorine-free (zero-ozone depletion potential) fluid is required, the list is shortened to four. Of these, R23 has a boiling point far too low for most applications.

Table III. Flammability and Chlorine Content of the Hydrogen-Containing Halocarbons

	Flammable	Nonflammable
Chlorine-containing	R141b R142b	R123 R124 R22
Chlorine-free	R152a R143a R32	R134 R134a R125 R23

There are additional possibilities. Ammonia is an excellent refrigerant; but apart from its toxicity, which limits its application, its properties are well established and are not considered here. Likewise, the use of the simple hydrocarbons and other organic compounds such as propane, isobutane, and dimethyl ether is limited by their flammability. Fluorinated propanes and ethers (particularly fluorinated derivatives of dimethyl ether) have been suggested as refrigerants for use in centrifugal compressors. While the greater molecular complexity of these compounds will impose some thermodynamic penalties, they are promising and basic data on them should be collected in the event that the ethane-based alternatives to R11 are not satisfactory.

Mixtures can expand a potentially limited set of pure components. The most obvious example is the combination of flammable and nonflammable pure components to yield a nonflammable mixture. Azeotropic mixtures behave essentially like pure fluids; several are in commercial production. With nonazeotropic mixtures, the compositions of coexisting liquid and vapor differ and condensation and evaporation processes occur over a range of temperature, in contrast to the isothermal phase change seen with pure components or azeotropes. These effects can be exploited to enhance performance but require equipment modifications. An intermediate class of "near-azeotropic" mixtures exhibits such small deviations from azeotropic behavior to be usable in traditional refrigeration equipment without modification. They offer the potential to tailor the properties of the working fluid to a particular application, possibly to the point of obtaining a "drop-in" substitute for use in existing equipment.

3. THERMOPHYSICAL PROPERTIES IN THE VAPOR COMPRESSION CYCLE

The vapor compression refrigeration cycle, the basis for most refrigeration equipment, is represented on pressure–enthalpy coordinates in Fig. 1. The refrigerant is vaporized in the evaporator at low pressure, removing heat from the low-temperature source (e.g., an air-conditionad space). The low-pressure vapor is compressed to a higher pressure by the input of mechanical work; the high-pressure vapor is then condensed, with the heat of condensation being rejected to the high-temperature sink (e.g., outdoor air for an air-conditioning application). Finally, the high-pressure liquid is throttled to the evaporator pressure in an expansion device, completing the process.

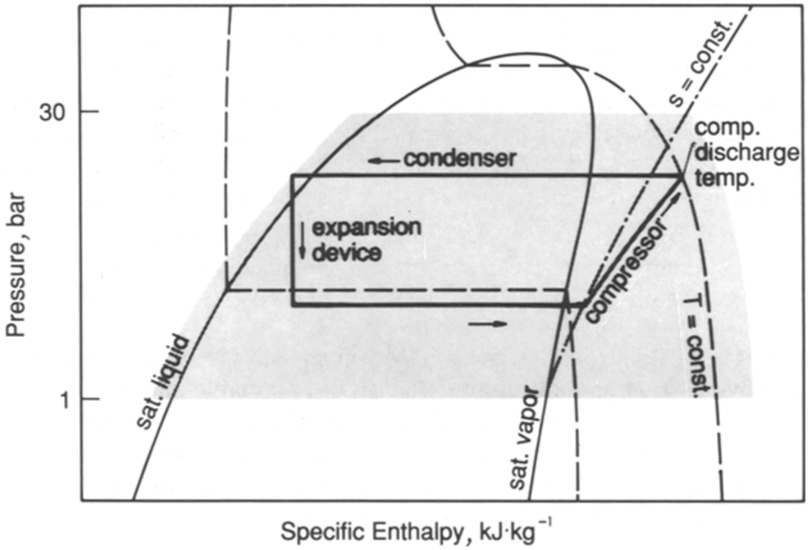

Fig. 1. Vapor compression refrigeration cycle represented on pressure–enthalpy coordinates.

3.1. Thermodynamic Properties

Thermodynamic properties determine the efficiency and capacity of the vapor compression cycle and thus are the key data needed in designing refrigeration equipment and in comparing one refrigerant with another. Of prime importance is the energy involved in the various processes, thus the need for accurate enthalpy values. The ideal compression process is at constant entropy; real compressors are often referenced to the isentropic process. Also important are the operating pressures of the condenser and evaporator; these are largely a function of the vapor pressure. The intersection of the compression process line with the isobar corresponding to the condenser pressure represents the outlet state of the compressor; accurate prediction of this, the highest temperature in the system, is vital in determining the thermal stability of the refrigerant and compressor lubricating oil. For positive displacement (e.g., piston) compressors, the density of the vapor largely determines the mass flow rate through the compressor and thus the refrigeration capacity. For centrifugal-type compressors, the maximum speed of the impellor is limited by the vapor sonic velocity; the pressure rise developed by the compressor is a function of the impellor speed and the refrigerant molecular weight.

Thermodynamic properties are invariably formulated in terms of an equation of state. An equation of state not only correlates directly measured quantities in a thermodynamically consistent way, but also allows the evaluation of derived quantities. For example, enthalpy and entropy are obtained by calculations involving up to second-order derivatives of an equation of state which represents the pressure–volume–temperature data. Pressures and densities in themselves need be known to an accuracy of only a few percent. The importance of the derived quantities places much more stringent requirements on the required accuracy of the *p–V–T* data.

The temperature and pressure ranges of interest are now considered. The vapor compression cycle operates at or near saturation; liquid and vapor are seldom subcooled or superheated by more than 50 or 100 K, respectively. Operation in the critical region is avoided, because of both the high pressures involved and the lower cycle efficiencies. (There is, however, some interest in cycles operating at supercritical pressures.) The practical upper limit on pressure is roughly 25–30 bar. Pressures below atmospheric are also avoided. (The major exception would be large R11 centrifugal chillers which operate at evaporator pressures of roughly 0.5 bar.) The pressures determine the temperature range of interest; for a given application (i.e., specified temperatures for the evaporator and condenser), a refrigerant is chosen such that the vapor pressures are within the desired range. The area where the need for property data is the most critical is indicated as the shaded region in Fig. 1.

3.2. Transport Properties

While the thermodynamic properties of a fluid determine its performance in the vapor compression cycle the transport properties have a major impact on the design of the equipment. Thus the transport properties have a major influence on whether it is economically feasible to build a machine which can actually obtain the theoretical efficiency of the thermodynamic cycle.

Transport properties are particularly important in the design of the heat exchangers (condenser and evaporator). The effectiveness of heat transfer with the refrigerant is expressed in terms of a heat transfer coefficient. For the final optimization of heat exchanger design these heat transfer coefficients are often experimentally determined for the exact combination of refrigerant and surface used. In the screening and preliminary design stages, heat transfer coefficients are estimated via correlations involving thermal conductivity, viscosity, surface tension, density, and heat capacity.

The selection of a refrigerant and the design of refrigeration equipment require knowledge of nearly all of the thermodynamic and transport properties. Indeed, the thermophysical property needs for the working fluid in a refrigeration application are quite extensive, comparable to those for steam in power cycles.

4. DATA PRIORITIES

4.1. Pure Fluids

At present, there is a critical need for at least skeleton data on a variety of potential halocarbon refrigerants (e.g., the listing given in Table II) in order not to lose the opportunity to develop the best set of fluids. Decisions regarding the working fluid to be used in the various applications will be made over the next few years. Retooling for the design changes required of a new refrigerant will be expensive. It would be difficult to commercialize additional refrigerants, even if superior, once industry has made the commitment to convert to a particular substitute for a fully halogenated CFC.

The thermophysical property data needed to allow an assessment of a refrigerant can be categorized and prioritized as follows.

Zero order: Normal boiling point, molecular structure
Group 1: Critical point, saturated liquid density, vapor pressure, ideal-gas heat capacity, vapor p–V–T
Group 2: Viscosity and thermal conductivity for saturated liquid and vapor, surface tension, dielectric strength
Group 3: Liquid heat capacity (or other calorimetric measurements), compressed liquid p–V–T, miscellaneous molecular properties such as dipole moment
Group 4: Supercritical and near-critical p–V–T, more extensive liquid and vapor p–V–T, vapor heat capacity, viscosity and conductivity away from saturation

The zero-order information is the minimum necessary to screen a large number of candidate fluids. This information (along with perhaps the triple point and/or a single liquid density) is also the input required of many property estimation methods, although, in general, the simple methods are not sufficiently precise to determine the best fluid among a set of closely related fluids. This information is available for virtually all of the one- and two-carbon halocarbons but is lacking for many of the "long-shot" fluids such as the fluorinated ethers.

The data in group 1 represent the core thermodynamic information necessary to fit most equations of state, thus allowing an accurate evaluation of the performance of a fluid in refrigeration equipment. Vapor pressure and liquid density data should be taken over as wide a temperature range as practical. Heat capacities at zero pressure (ideal gas) are often evaluated from spectroscopic measurements. This method quickly approaches its limit as molecular complexity increases; even for the substituted ethanes a more direct determination of C_p^0 (via calorimetric or velocity of sound measurements) is desirable.

Group 2 data provide the basic transport properties needed for equipment design. Also included in this group are electrical properties, such as dielectric strength, needed for hermetic compressors. The data in Group 3 allow refinement of the thermodynamic formulation. In particular, knowledge of the liquid heat capacity is important for two reasons. First, the ratio of heat capacity to latent heat determines the amount of liquid which flashes to vapor in the expansion process of the vapor compression cycle. Second, the heat capacity, being a second derivative of the primary p–V–T measurements, is an independent check on the accuracy of equation-of-state formulations. The measurements listed as group 4 provide a much more extensive and complete characterization of a fluid.

The current (August, 1988) status of property measurements for the most promising CFC alternatives is indicated in Table IV. This listing is based primarily on data presented in the open literature. It invariably contains omissions but should, nonetheless, be useful in directing future measurement efforts at the areas of greatest need.

As the top priority, the "group 1" data should be measured and/or gathered, analyzed, and presented as tables, etc., for all of the candidate fluids listed. This would allow a thermodynamic assessment of the fluids. For those fluids which are still promising, the next priority would be the measurements listed in groups 2 and 3. One or two fluids should be developed to reference-fluid status; this would involve collection of extensive data, including "group 4" information. These fluids would then serve as the basis for the development of models into which other polar fluids could be incorporated with more limited data. R22 is already close to this status; R134a is probably the best choice among the ethane series halocarbons.

4.2. Mixtures

Mixture data are needed to allow an assessment of near-azeotropic mixtures as CFC replacements and to aid in the identification of possible azeotropic mixtures. A wide variety of measurements on refrigerant mixtures has been reported in the literature. Unfortunately, most of the mixtures studied contain at least one component which is fully halogenated [11]. Estimation techniques which have been based on these data (e.g.,

Table IV. Availability of Property Data for the Environmentally Acceptable Halocarbons[a]

Fluid	Zero order		Group 1					Group 2		Group 3		Group 4
	Boiling point	Structure	Critical point	Liquid density	Vapor pressure	C_p^0	Vapor p–V–T	Viscosity	Thermal cond.	Liquid C_p	Liquid p–V–T	(combined)
R141b	+	+	(P)	(P)	(P)	–	(P)	0	0	0	0	0
R123	+	+	(P)	(P)	(P)	+	(P)	–	–	0	0	0
R142b	+	+	+	+	+	+	–	–	+	0	0	0
R124	+	+	+	+	–	+	+	0	–	0	+	0
R134	+	+	0	0	0	0	0	0	0	0	0	0
R152a	+	+	+	+	+	+	+	–	–	–	0	–
R134a	+	+	(P)	–(P)	–(P)	+	+(P)	–	–	0	0	0
R22	+	+	*	*	*	*	*	*	*	+	+	+
R143a	+	+	+	–	–	+	–	0	0	0	0	0
R125	+	+	–	–	–	+	–	0	0	0	0	0
R32	+	+	+	+	+	+	+	–	–	0	+	0
R23	+	+	+	+	+	+	+	+	+	+	0	–

[a] 0, no data or only isolated points; –, limited data or of questionable accuracy; +, reliable data available; *, extensive reliable data available; (P), additional work in progress.

Ref. 11) have considerable uncertainty when applied to polar–polar mixtures.

Because of this lack of data, virtually any information for mixtures of the hydrogen-containing (polar) halocarbons would be of great use in extending mixture models. At least a limited amount of mixture data would be only slightly lower in overall priority than the group 1 data for pure fluids outlined above. The most basic and useful data would be bubble-point pressures over a range of composition and temperature. Liquid density and coexisting liquid and vapor compositions would also be desirable. As with the pure fluids, establishing an extensive data set for one or more reference mixtures would be highly useful in developing and verifying mixture models; but otherwise, exhaustive measurements such as pressure–volume–temperature data for the vapor would be justified only for a mixture that has a high probability of being commercialized.

5. DATA FORMAT

To be useful to the design engineer, thermophysical property data must be in the proper format. The bulletins published by ASHRAE [12, 13] and presented in condensed form in Ref. 14 are prime examples; the International Institute of Refrigeration, the Japanese Association of Refrigeration, and others have published similar tabulations. Tables listing properties for the saturated liquid and vapor states at even increments of temperature are the most common and widely used format. As a minimum, these include vapor pressure, liquid and vapor density (or sometimes liquid density and vapor volume), and liquid and vapor enthalpy and entropy. Also desirable is a tabulation of viscosity, thermal conductivity, isochoric and isobaric specific heats, sonic velocity for the saturated liquid and vapor states, sonic velocity for the vapor, and surface tension of the coexisting liquid and vapor, all as a function of temperature. Similar listings at even increments of pressure are particularly useful for nonazeotropic mixtures. The superheated vapor region is usually presented as a set of tables, with properties tabulated over a range of temperature for a number of different pressures.

Thermodynamic diagrams covering a wide range of conditions (typically including the entire two-phase region) are useful in the qualitative analysis of refrigeration cycles, particularly in understanding the effects of using a different refrigerant or in evaluating equipment design changes. The most common presentation is on pressure versus enthalpy coordinates.

Correlations and equations of state constitute the final data format. These are of obvious importance in computer design and simulation models. Indeed, they are essential for producing any sort of tables or diagrams. A wide variety of equations of state has been used for the refrigerants, including the Martin–Hou, virial, Benedict–Webb–Rubin, Carnahan–Starling–DeSantis, and others. A single formulation which encompasses all of the common refrigerants, as well as their mixtures, is desirable. Such a formulation would be particularly useful in evaluating a number of candidate refrigerants.

6. CONCLUSIONS

A set of hydrogen-containing halocarbons and their mixtures has been identified as the most promising fluids to replace the fully halogenated CFC refrigerants. Thermophysical property data on these fluids are critically needed in order not to lose the opportunity to develop the best set of working fluids and to permit the design of efficient refrigeration equipment using them. Priorities for the needed data have been laid out. The fully halogenated CFCs now appear to be doomed as important industrial chemicals, yet the program for the 10th Symposium on Thermophysical Properties [15] in June 1988 indicates that most of the properties work on refrigerants is still concerned with fully halogenated fluids. The fluid properties community would do a great service by turning their attention to the environmentally acceptable working fluids.

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