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Thermodynamics of refrigerants: Or why did we ever go with the F-gases?☆

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ABSTRACT

This review considers the evolution of refrigerants and the ever-changing constraints that have driven the need to consider new refrigerant molecules. Recent regulations limit future refrigerant choices, particularly in Europe where the fluorinated refrigerants ("F-gases") will be severely restricted. Here we consider the "why" behind fluorine. What did fluorine bring to the party, and what are the trade-offs in moving away from fluorine? The role of fluorine in reducing flammability is well known. Less appreciated is the ability to "tune" the thermodynamic properties of a fluid by adjusting the fluorine content. Historically, the halogenated fluids came to dominate refrigeration for very good reasons related to safety and performance, and these reasons remain valid. While limiting the halogenated refrigerants would be workable, it would require that systems be designed to match the refrigerant rather than being able to choose a refrigerant to best fit the requirements of the application.

1. Introduction

Refrigeration is central to modern society, ranging from the cold chain that allows the safe distribution of fresh meat and produce, to comfort air conditioning, to cooling of the data centers that power the internet.

The vast majority of refrigeration systems employ the vapor-compression cycle wherein a volatile working fluid (commonly known as a "refrigerant") continuously cycles through the system, evaporating and condensing, thereby moving heat from a lower to a higher temperature. Refrigerants in present systems are predominantly halogenated hydrocarbons, and specifically fluorinated alkanes, known as hydrofluorocarbons or HFCs. More recently a subclass of the HFCs, the fluorinated alkenes, also termed the hydrofluoroolefins or HFOs, have come into widespread use. (Here, we will consider HFCs and HFOs as separate classes.)

The choice of working fluid is a primary parameter in the design of refrigeration equipment, and the dominant fluids in use have changed over the decades since the first demonstration of mechanical refrigeration in the 19th century. This evolution has been driven largely by external constraints and regulations around safety and environmental considerations (Calm, 2008) (McLinden and Huber, 2020) (United Nations Environment Programme, 2016), and to a lesser degree by thermodynamic considerations, including efficiency. There is no single "best" refrigerant, and different refrigerants are optimal for different operating temperature ranges and types of equipment.

In addition to refrigeration accounting for 20 % of global electricity consumption (Baha et al., 2025), the environmental liabilities of the fluorinated refrigerants (i.e., the "F-gases") are increasingly being recognized. Some refrigerants have a high global warming potential (GWP) and some produce the environmentally persistent trifluoroacetic acid (TFA) upon breakdown in the atmosphere. This has led to increasing restrictions on their use, including recent European regulations (European Union, 2024) that place strict GWP limits on most applications and would completely phase out HFCs by 2050. Many advocate for the use of the so-called natural refrigerants comprising simple hydrocarbons, ammonia, and carbon dioxide. (Lorentzen, 1994, 1995)

Here we briefly consider the historical evolution that led to the HFCs and HFOs and the fortuitous intersection of safety characteristics and thermodynamic properties that led to the dominance of the halogenated refrigerants from the 1930s into the 21st century. We examine the "why" behind fluorine. What did fluorine bring to the party, and what are the trade-offs in moving away from fluorine?

2. Background and historical perspective

Calm (2008) has defined the evolution of refrigerants in terms of four generations. He characterized the first generation (up to the 1930s) as "whatever worked." While this period saw the first use of ammonia, carbon dioxide, and propane (to be discussed in Section 5), many of the fluids employed were chosen on the basis of expediency or availability

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combined with the most basic thermodynamic considerations—primarily the normal boiling point temperature. These included methyl chloride (CH_3Cl), sulfur dioxide (SO_2), methyl formate (HCO_2CH_3), and carbon disulphide (S=C=S), fluids that are flammable and toxic. Newspaper headlines of the day reported fatalities from leaking systems; for example: "Ice Machine Gas Kills 15 in Chicago … Coroner's Jury Lay Death of Woman Artist to Methyl Chloride." Advertisements in trade journals touted propane as the "Odorless Safety Refrigerant" (alluding to the strong odors of ammonia and SO_2) and made "No Odors, No Explosions" a selling point for CO_2. (These are reproduced in Supplemental Information.)

Against this backdrop, Charles Kettering (the head of research at General Motors, a manufacturer of early household refrigerators) stated that "the refrigeration industry needs a new refrigerant if they expect to get anywhere" in his charge to Thomas Midgley in 1928 to find a safer refrigerant. (Midgley, 1937) Midgley and his associates Albert Henne and Robert McNary recognized patterns of volatility and toxicity in the periodic table that pointed to fluorine compounds as having suitable volatility and low toxicity. Three days later they synthesized dichlorofluoromethane ($CHCl_2F$ or R-21, a hydrochlorofluorocarbon or HCFC) and demonstrated that it was of low acute toxicity. (Midgley, 1937) A systematic examination of other chloro/fluoro derivatives of methane led to dichlorodifluoromethane (CCl_2F_2 or R-12, a chlorofluorocarbon or CFC), also known by the trade name "Freon 12." In a dramatic demonstration at the 1930 meeting of the American Chemical Society, Midgley inhaled a lungful of R-12 and used it to extinguish a candle. (Downing, 1988) Here was seemingly the perfect refrigerant: nonflammable, low toxicity, and simple and inexpensive to manufacture. That chlorine and fluorine, highly hazardous elements individually, could form a nonflammable, low-toxicity compound was a surprise. (The low toxicity of the CFCs cannot, however, be generalized: some fluorinated chemicals are highly toxic. (Kyzer and Martens, 2021)) Other CFCs and HCFCs followed. Such was the start of the 2nd generation of refrigerants, characterized as "safety and reliability" (Calm, 2008) and which lasted into the 1990s.

Beyond the safety aspects, the thermodynamic properties of the simple CFCs and HCFCs were well matched to the simple vapor-compression cycle as laid out by McLinden (1990). And while this combination of cheap, safe refrigerants with simple equipment may have led to complacency there was little reason to search beyond the CFCs and HCFCs.

So, the initial answer to "Why the F-gases?" is that the refrigerants in use a century ago posed substantial hazards that inhibited the widespread adoption of refrigeration, and the CFCs and HCFCs presented seemingly benign alternatives.

From the 1930s through the 1970s the refrigerant landscape was quite boring: R-12 was dominant in household refrigerators; small air-conditioning systems used R-22 ($CHClF_2$) upon its commercialization in the 1950s; and R-11 (CCl_3F) was common in large central-plant chillers. Of the "first generation" refrigerants, only ammonia saw continued widespread use in large-scale systems, such as large breweries and cold-storage warehouses, because of its good efficiency, high reliability, and low cost.

In 1974, Molina and Rowland (1974) hypothesized that the long life of the CFCs would allow them to diffuse to the stratosphere where ultraviolet radiation would dissociate them, releasing chlorine radicals that would destroy ozone. Further studies followed, and a 1982 summary by the U.S. National Academy of Sciences (National Research Council, 1982) predicted only a 5 % to 7 % reduction in global ozone with continued production of CFC-11 and CFC-12. Three years later, however, Farman et al. (1985) tied decreased ozone in the Antarctic spring (the "ozone hole") to chlorine from CFCs. The next year Solomon et al. (1986) provided the experimental proof of chlorine monoxide reacting with ozone on the surface of polar stratospheric clouds, with that chlorine coming from CFCs.

The "Montreal Protocol on Substances that Deplete the Ozone Layer" (United Nations, 1987) quickly followed. (198 countries are parties to the Protocol, representing every member country of the U.N.) The original 1987 Protocol called only for a 50 % phase-down in the production of the CFCs. Subsequent amendments would call for a complete phase-out of the CFCs and HCFCs. Years earlier HFC-134a had been identified as a replacement for CFC-12 and HCFC-123 for CFC-11 (Orfeo et al., 1977), and the phase-out of the CFCs began with these. A range of additional HFCs were subsequently developed. This period also saw a resurgence of interest in ammonia, propane, and carbon dioxide—the so-called natural refrigerants—spearheaded by Lorentzen (1994, 1995). This was the "third generation" of refrigerants characterized as "ozone protection." (Calm, 2008)

The subsequent answer to "Why the F-gases?" or, rather, "Why (are we still using) the F-gases?" is that HFCs were developed that were near-drop-in replacements for the ozone-depleting CFCs and HCFCs, allowing for a straightforward transition. The technology of an HFC-134a automotive air conditioner, for example, was basically the same as one using CFC-12. To be sure, details of the compressor design, as well as the lubricants and materials for hoses were different, but servicing procedures were similar, and importantly, the changes were not apparent to the consumer.

As the use of the HFCs expanded, concern grew over their relatively high GWP values. This was known in the 1980s, but the urgent need at the time was to replace the ozone-depleting substances, and the GWP of the HFCs was felt to be "low enough." The HFCs have generally much lower GWPs than the CFCs that they replaced. For example, the GWP of the most common refrigerant in automotive systems was reduced by a factor of nearly eight (10200 to 1300) when R-12 was replaced with R-134a. (Myhre et al., 2013) Thus, the Montreal Protocol, which was originally targeted at stratospheric ozone protection, has already significantly reduced the average GWP of refrigerants, as reported by Velders et al. (2007). This was furthered by the 2016 Kigali Amendment to the Montreal Protocol (United Nations, 2016), which calls for a 80 % to 85 % reduction in the GWP-weighted production of 18 regulated HFCs by 2035. This spurred the development of the HFOs; these compounds have a carbon-carbon double bond, which is reactive with hydroxyl radical in the atmosphere, resulting in much lower atmospheric lifetimes and GWP values on the order of 1. Thus, we are currently in the "fourth generation" of refrigerants characterized as "global warming." (Calm, 2008)

We ask again, "Why the F-gases?", and the answer remains that replacements for the high-GWP HFCs (i.e., the HFOs) were found and developed. The HFOs allowed the continued use of familiar technology. But now, the transition is not quite as straightforward. Most of the HFOs have "lower flammability" as defined by industry classification standards, namely ASHRAE Standard 34 (ASHRAE, 2024b) and ISO 817 (ISO, 2024), meaning that such fluids are more difficult to ignite, burn at a slower rate, and release less heat compared to hydrocarbons, but they are, nonetheless, still flammable. Use of flammable refrigerants require lower system charges in equipment and additional safety measures, as spelled out in ASHRAE Standard 15 (ASHRAE, 2022, 2024a) and ISO 5149 (ISO, 2014), among others.

The concerns around the high GWP of the HFCs and the generation of TFA for some of the HFCs and HFOs have led to calls to greatly reduce or eliminate fluorine altogether. The 2024 EU F-gas Regulation (European Union, 2024), for example, prohibits all fluorinated refrigerants (including HFOs) in a number of small systems (i.e., <12 kW refrigeration capacity) with phase-out dates of January 2026 to January 2035. A maximum GWP of 150 (which would allow HFOs) is imposed on most other systems with effective dates ranging up to January 2033 (with intermediate GWP limits in some cases). For many types of systems, exceptions are made "if required to meet safety requirements at the site of operation" and for military equipment. In some cases, the safety exemption would allow GWP < 750, but for other system types there is no specification of the maximum allowed GWP. So even these regulations seem to acknowledge the need for some continued use of

fluorinated gases. The EU Regulation calls for the complete phase out of the HFCs by 2050.

But are there reasons to stay with the traditional vapor-compression cycle and the F-gases?

There is increased interest in solid-state ("caloric") and other alternative refrigeration cycles, which do not use conventional refrigerants at all. The consideration of caloric and other alternative technologies is beyond the scope of this article but consider that most such cycles have been known for decades and remain in the lab or in limited niche applications. Vapor-compression systems remain dominant because the technology is simple (both in terms of the equipment and the required materials), has relatively high efficiency, and scales from small refrigerators to multi-MW systems serving large buildings. While an entrenched technology will always have an advantage, a superior technology can upset the status quo—the example of flat-panel technology almost completely replacing CRT (cathode-ray tube)-based TVs and monitors comes to mind.

Vapor-compression technology can work with a range of fluid types, and the choice of refrigerants is considered in the next three sections.

3. Thermodynamics of the vapor-compression cycle

Refrigeration is the process of moving heat from a lower to a higher temperature, counter to the normal flow. The thermodynamic limit for a refrigeration cycle is the reverse Carnot cycle, consisting of (1) isentropic compression of the working fluid with the input of work, (2) isothermal heat rejection to a high-temperature sink, (3) isentropic expansion with the generation of work, and (4) isothermal heat absorption from a low-temperature source. The cycle is represented on a temperature-entropy diagram in Fig. 1. Energy flows and work correspond to areas on the *T-s* diagram.

The practical cycle that most closely approximates the reverse Carnot cycle is the reverse-Rankine, or vapor-compression (v-c), cycle. The isentropic compression of the Carnot cycle is approached by numerous types of gas compressors. Condensation (i.e., a heat releasing process) of a single-component working fluid at a constant pressure occurs at a constant temperature, replicating the Carnot process. An isentropic expansion could be approximated by some type of expansion engine (which would feed its generated work to the compressor), but this complication is usually replaced by an expansion at constant enthalpy, which represents a loss of efficiency. Finally, evaporation (i.e., a heat absorbing process) at constant pressure replicates the final step of the Carnot cycle.

The Carnot cycle is a rectangle on *T-s* coordinates, and examining the v-c cycle on a *T-s* diagram is useful for understanding the differences between refrigerants. The phase boundary of real fluids does not trace a rectangle on *T-s* coordinates—the phase boundary between the two-phase region and the liquid phase (on the left side of the diagram) and vapor phase (on the right) traces a "two-phase dome", which can take on a range of shapes (Fig. 2), which influence the efficiency and practicality

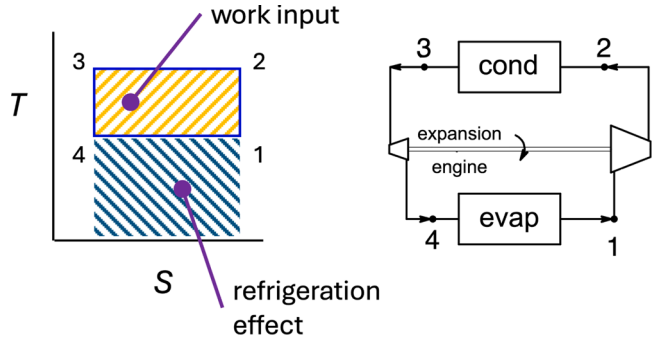

Fig. 1. Representation of the Carnot refrigeration cycle on temperature-entropy coordinates.

of the real cycle. For the present purpose of "Why the F-gases" comparisons based on the simple v-c cycle and focusing on the *T-s* diagram are instructive.

The ideal v-c cycle feeds saturated vapor to the compressor and saturated liquid to the inlet of the expansion device. With an "upright" dome (Fig. 2(a)) the compression process extends into the superheated vapor region, and this "overshoot" in temperature represents excess work that must be input to the compression process. Conversely, a dome that "leans" to the right (Fig. 2(c)) will result in a compression process that enters the two-phase region, and liquid droplets are damaging to many types of compressors. On the liquid side, the difference between an isenthalpic and isentropic process represents lost refrigeration effect, and this effect becomes larger as the dome leans. The result of these trade-offs is an optimal two-phase dome on *T-s* coordinates that has a nearly vertical vapor phase boundary (Fig. 2(b)).

Morrison (1994) showed that the shape of the two-phase dome, and in particular, the slope of the vapor-phase boundary is largely dependent on the heat capacity of the vapor, as represented by the limit of the constant-pressure heat capacity at zero density, C_p^0. Small values of C_p^0 on a molar basis will give an upright dome (Fig. 2(a)) and large values will result in a dome that leans to the right (Fig. 2(c)). Thus, the optimal refrigerant will have an intermediate value of C_p^0. The value of C_p^0 increases with the mass and complexity of the molecule as discussed in Section 4.1.

The position of the cycle relative to the critical point is also important. The dome is wider at lower temperatures, and its liquid and vapor sides meet at the critical point. Thus, for a cycle operating at low temperatures relative to the critical temperature the lost refrigeration effect due to the isenthalpic expansion is a smaller fraction of the total compared to a cycle operating closer to the critical point. The trade-off here is that operating at a low reduced temperature (the ratio T/T_{crit}) also implies a lower working pressure and a lower volumetric capacity (refrigeration effect per unit volume of vapor entering the compressor), and this is associated with larger equipment.

3.1. Beyond thermodynamics

But it's not just thermodynamics. Heat exchange and flow processes are also important, and these are highly dependent on the transport properties of thermal conductivity and viscosity. Domanski et al. (2014) demonstrated a clear efficiency versus capacity trade-off in the ideal vapor-compression cycle. They considered real fluids and also hypothetical fluids modelled in terms of basic thermodynamic parameters (e.g., critical temperature, critical pressure, vapor heat capacity, and acentric factor) arriving at a "Pareto front" that defines the thermodynamic limit of fluid behavior, as shown in Fig. 3(a) for the case of air conditioning with evaporator and condenser temperatures of 10 °C and 40 °C, respectively. (The "ideal" cycle has no pressure drops or temperature differences across the heat exchangers, 100 % compressor efficiency, saturated liquid entering the expansion valve, isenthalpic expansion, and saturated vapor entering the compressor.) However, the picture is different with simulations that included the effects of transport properties on heat transfer and pressure drop, optimized the circuitry in the heat exchangers, maintained the same heat flux in the evaporator, and included a pressure-ratio effect on the compressor isentropic efficiency. (McLinden et al., 2017) With these more realistic simulations there was a broad optimum in COP corresponding to a moderately high refrigeration capacity, as shown in Fig. 3(b). Here the generally superior transport properties of ammonia and the simple hydrocarbons leads to higher COPs for those fluids.

3.2. Cycle modifications

Furthermore, the basic v-c cycle can be modified to accommodate the thermodynamic characteristics of the refrigerant. Numerous varia-

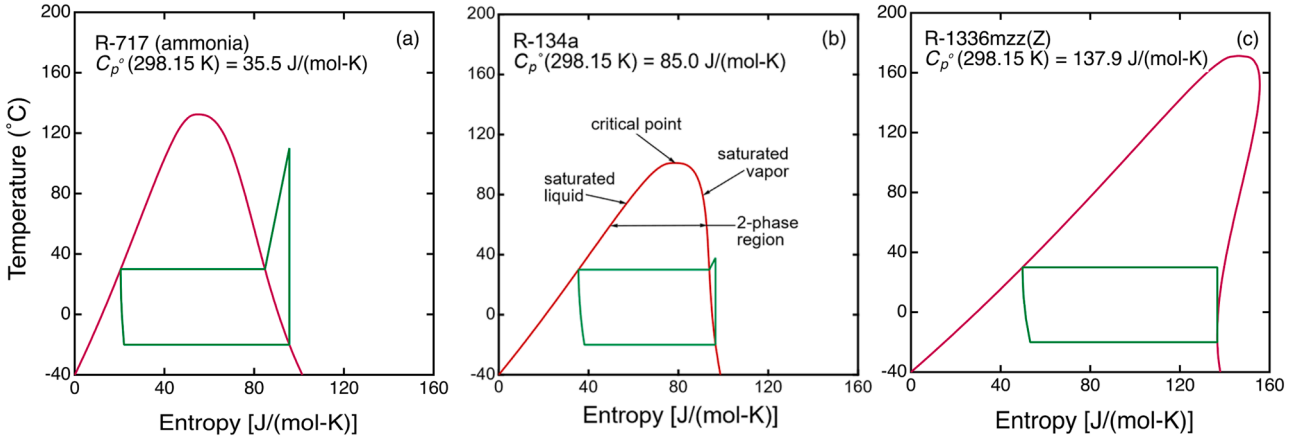

Fig. 2. Representation of the vapor-compression cycle on *T-s* coordinates for a range of fluid behaviors, as characterized by the value of C_p^0.

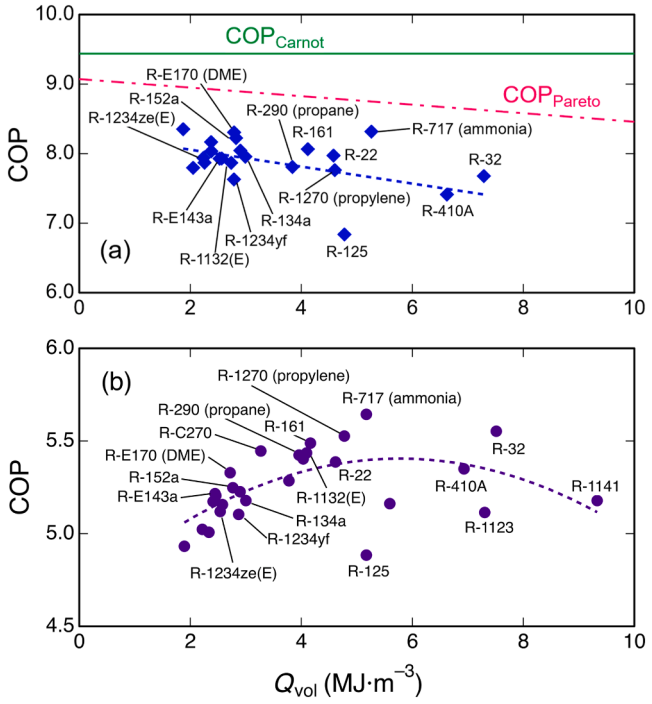

Fig. 3. Coefficient of performance (COP) as a function of volumetric refrigeration capacity (Q_{vol}) for a range of refrigerants and different modeling assumptions; (a) solid line, Carnot limit; dash-dot line, thermodynamic limit of hypothetical refrigerants in an ideal cycle (Domanski et al., 2014); ♦, real refrigerants in an ideal cycle; (b) ● real refrigerants in a cycle including non-ideal effects as discussed in Section 3.1. The dashed lines in (a) and (b) approximate the general trends in COP. Data are from (Domanski et al., 2014) for panel (a) and (McLinden et al., 2017) for panel (b); note that these two sources considered different sets of fluids.

tions on the basic cycle are well known; these include intra-cycle heat exchange (for example, between the liquid line exiting the condenser and the suction line entering the compressor, which is effective for refrigerants with high values of C_p^0); two-stage expansion and compression, also known as the flash-economizer cycle wherein vapor resulting from the first expansion stage bypasses the evaporator and is sent directly to the second stage of compression; and two-stage compression with cooling between the stages, which is helpful for refrigerants with low C_p^0. Further modifications to cycle components to, for example, reduce refrigerant charge can allow the safe use of a wider range of refrigerants (McLinden et al., 2020). Refrigerant selection is thus seen to be a highly complex, multifunction optimization problem.

4. Fluorine and the F-gases

Fluorine is element number 9 and sits at the upper right of the periodic table. It is a halogen, along with chlorine, bromine, iodine, and the radioactive and exceedingly rare astatine. Halogens have one unpaired electron in their outer shell, and thus they form single covalent bonds in molecules. Fluorine is the most electronegative element, meaning that it attracts other electrons in the molecule towards it; this characteristic can result in highly polar compounds. Elemental fluorine is a very strong oxidizer such that some normally nonflammable compounds will "burn" in a fluorine atmosphere. Fluorine is a key element in numerous polymers, including polytetrafluoroethylene (PTFE), and elastomers, such as Viton. It is a component of a significant fraction of drugs and is used in the production of steel and aluminum. It is also, of course, the quintessential element in the F-gases, including many refrigerants.

The carbon-fluorine bond is the strongest single bond in organic chemistry, and this strength gives many fluorine compounds great stability and is directly or indirectly responsible for many of the characteristics of the F-gases.

4.1. Fluorine and thermodynamics

As discussed in Section 3 the shape of the two-phase dome on *T-s* coordinates is a strong function of the vapor heat capacity C_p^0. Each "degree of freedom" in a molecule—meaning each internal vibration, rotation, or bending of bonds—contributes to the value of C_p^0. Based on the group-contribution method of Benson et al. (1969) a –CF_3 group attached to a carbon, for example, contributes 53.2 J·mol^{-1}·K^{-1} to C_p^0 at T= 298.15 K; this compares to 25.9 J·mol^{-1}·K^{-1} for a –CH_3 group. As a result, the C_p^0 of the HFCs and HFOs varies over a wide range; for example C_p^0 (T= 298.15 K) is 42.9 J·mol^{-1}·K^{-1} for R-32 (difluoromethane, CH_2F_2) and 137.9 J·mol^{-1}·K^{-1} for R-1336mzz(Z) (CF_3–CH=CH–CF_3); these compare to 35.5 J·mol^{-1}·K^{-1} for ammonia (NH_3) and 96.6 J·mol^{-1}·K^{-1} for isobutane ($(CH_3)_3CH$).

The normal boiling points for the F-gases also span a wide range, from –128 °C for R-14 (CF_4) to 33 °C for R-1336mzz(Z). The heat of vaporization (on a molar basis) is roughly proportional to boiling-point temperature, as given by Trouton's rule:

$$\Delta H_{vap} \cong 87 \times T_{boil} \quad (1)$$

where ΔH_{vap} is the heat of vaporization in (J·mol^{-1}·K^{-1}) and T_{boil} is the normal boiling point in K.

On a mass basis, this becomes:

$$\Delta h_{vap} \cong 87 \times T_{boil}/\mathrm{MW} \quad (2)$$

where now Δh_{vap} is in units of $(J{\cdot}g^{-1}{\cdot}K^{-1})$ and MW is the molar mass in $(g{\cdot}mol^{-1})$.

A fluorine atom is considerably heavier than hydrogen, so the molar mass of the F-gases is generally higher than the natural refrigerants (e.g., ranging from 52.02 $g{\cdot}mol^{-1}$ for R-32 to 164.06 $g{\cdot}mol^{-1}$ for R-1336mzz(Z) compared to a range of 17.03 $g{\cdot}mol^{-1}$ for ammonia to 58.12 $g{\cdot}mol^{-1}$ for isobutane).The refrigeration capacity is approximately the flow rate times the enthalpy of vaporization (with both on a molar basis); thus, the mass flow rate required for a given refrigeration effect is larger for the (heavier) F-gases compared to ammonia or the hydrocarbons. This affects pressure drops and heat transfer as discussed in Section 3.1

The HFCs and HFOs thus offer a range of thermodynamic characteristics simply because of the large number of permutations and combinations available when fluorinating a base hydrocarbon. This allows the possibility to tailor the refrigerant molecule to obtain properties matched to the application.

4.2. Fluorine and flammability

The flammability of a compound depends on both thermodynamics (i.e., the energetics of the reaction with oxygen) and the kinetics, or speed of the reaction. A reaction is thermodynamically favorable (meaning that it will move to a more stable, lower energy state) if there is a decrease in the Gibbs energy of the products compared to the reactants:

$$\Delta G = (H - TS)_{\mathrm{products}} - (H - TS)_{\mathrm{reactants}} \quad (3)$$

$$\Delta G < 0 : \text{reaction is favored} \quad (4)$$

$$\Delta G > 0 : \text{reaction is not favored} \quad (5)$$

The enthalpy term ($H_{\mathrm{products}} - H_{\mathrm{reactants}}$) is calculated by taking the difference of the enthalpies of formation, $\Delta_f H$, of the reactants and products:

$$\Delta H = \sum_i \Delta_f H_{\mathrm{product},i} - \sum_j \Delta_f H_{\mathrm{reactant},j} \quad (6)$$

where the summations are over the i products and j reactants. The enthalpy of formation is related to the stability of a molecule, with more stable molecules having more negative $\Delta_f H$; fluorinated molecules often have large negative $\Delta_f H$, again stemming from the stability of the C–F bond. Thus, the overall ΔH of the combustion reaction becomes more positive (absorbing heat rather than releasing heat) as the fluorine content increases. This is somewhat counteracted by the entropy change of the reaction, which is typically negative because a large molecule (e.g., a refrigerant) is reacting with oxygen to yield a greater number of smaller molecules. The ΔH term usually dominates over the ΔS term, and the ΔG of the combustion reaction becomes more positive (i.e., less flammable) as the fluorine content increases.

In addition, the kinetics must be sufficiently rapid for the reaction to be self-sustaining. Thus, some hypothetical combustion reactions with a $\Delta G < 0$ do not actually occur under typical conditions (e.g., a refrigerant leaking into the air and encountering an ignition source).

4.3. Fluorine and GWP

Incoming solar radiation peaks in the visible wavelengths of 400 to 700 nm (0.4 to 0.7 μm), where the atmosphere is largely transparent (Fig. 4). The atmosphere is largely opaque to infrared (I-R) radiation emitted by warm objects (e.g., the Earth's surface) except for wavelengths between about 8 and 14 μm, which is termed the "atmospheric window." By Wien's Law, the 15 °C average surface temperature of the Earth corresponds to a peak I-R wavelength of 10 μm. The high GWP of some of the F-gases stems from the stability of the C–F bond, together with its absorptance of infrared radiation at wavelengths of 7 to 10 μm (overlapping the atmospheric window) due to the stretching of that bond. The first characteristic contributes to a long atmospheric lifetime, which in turn, allows the second characteristic to have an influence on climate. The HFOs have an I-R absorptance similar to the HFCs but have very low GWP values because the reactivity of the carbon-carbon double bond to hydroxyl radical in the atmosphere results in a very short atmospheric lifetime.

4.4. Atmospheric breakdown products of the F-gases

The short atmospheric lifetime of the HFO refrigerants transfers environmental concerns from their atmospheric effects (i.e., GWP) to possible effects associated with their atmospheric breakdown products. These are often CO_2 and benign fluoride salts. For some fluids that contain a $-CF_3$ group in the molecule (which includes some HFOs and some HFCs), however, the breakdown products can include trifluoroacetic acid (TFA, $CF_3C{=}OOH$) (Solomon et al., 2016). TFA is toxic, but

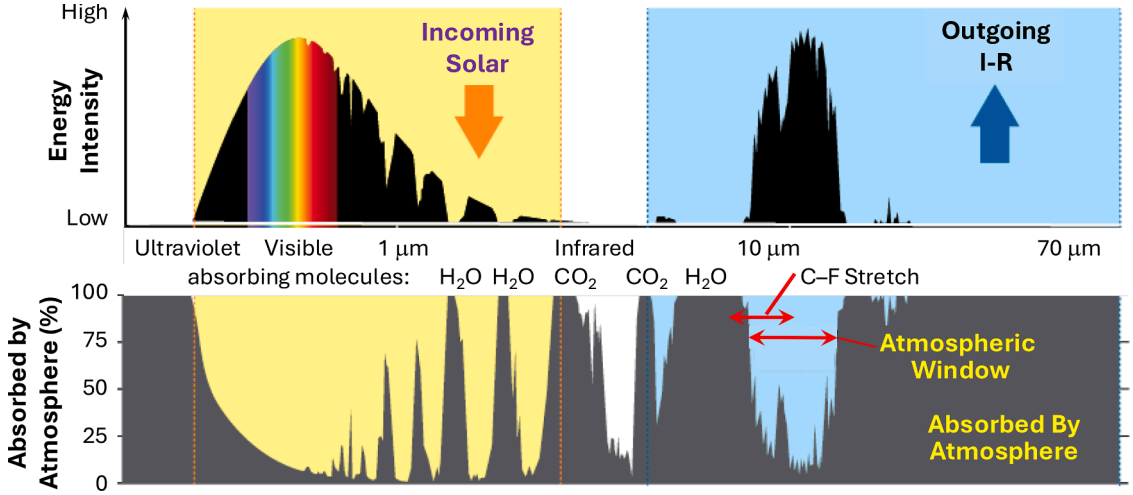

Fig. 4. Incoming solar radiation at ground level and emitted infrared radiation from the upper atmosphere (top panel) and atmospheric absorptance (bottom panel), both as a function of wavelength. Graphic adapted from (National Oceanic and Atmospheric Administration, 2023) [https://www.noaa.gov/jetstream/satellites/absorb].

the issue is whether it is toxic at the extremely low ambient concentrations that would result from the breakdown of F-gases, with the refrigerants being just one of many anthropogenic sources of TFA. The 2022 report of the United Nations Environmental Effects Assessment Panel (EEAP) (UNEP/EEAP, 2022) provides an analysis of the extensive literature, namely that TFA is highly water soluble and is, thus, quickly rained out of the atmosphere and enters the hydrologic cycle, where it is persistent in fresh and ocean waters.

TFA is present in the ocean at remote locations and great depths, suggesting a natural source of TFA. Some argue that there is no plausible natural source of TFA (Joudan et al., 2021). On the other hand, a global mass balance on the industrial production of fluorochemicals between the 1930s and 1999 reveals a mismatch of several orders of magnitude between plausible anthropogenic TFA and that measured in the oceans (Lindley, 2023). The EEAP report concludes that TFA is not toxic at concentrations currently measured or predicted to occur up to the year 2100, although it does recommend periodic monitoring and evaluations because of the uncertainty of potential TFA effects on marine organisms and the expected increase in TFA concentration in the atmosphere due to increased emissions from multiple sources (UNEP/EEAP, 2022).

The very short atmospheric lifetimes of the HFOs complicates the picture with regards to TFA. With HFO lifetimes on the order of days or weeks, any generated TFA would be rained out much more locally, which is to say near or downwind of major population centers, making a global-average TFA concentration an academic number. This is in contrast to TFA production from HFCs: with their much longer lifetimes, the TFA from HFCs would be distributed more-or-less globally, and the TFA production would be spread out over many years. R134a is the largest refrigerant-related source (UNEP/EEAP, 2022) because of its widespread use. But even here there is uncertainty: Vincent et al. (2026) predicts essentially no formation of TFA from R134a due to energy barriers under atmospheric conditions; this casts doubt on the previously proposed mechanism (Wallington et al., 1996), which predicts a 7–20 % molar yield of TFA from R134a.

Many of the F-gases fall under one or more definitions of per- and polyfluoroalkyl substances, or PFAS. These are often referred to as "forever chemicals" because of their persistence in the environment; furthermore, some members of this chemical class are toxic. They are the subject of current and proposed regulations. The EU definition of PFAS is a "substance that contains at least one fully fluorinated methyl (–CF_3) or methylene (–CF_2–) carbon atom (without any H/Cl/Br/I attached to it)" (ECHA, 2023), which includes TFA and many HFCs and HFOs. On the other hand, the definition of PFAS under the U.S. Toxic Substances Control Act (TSCA) (Environmental Protection Agency, 2023) requires one of three specific molecular structures and at least two fluorinated carbons, which would exclude TFA and many of the refrigerants. The inclusion of refrigerants, especially the HFO refrigerants, as PFAS is debated (Singh and Papanastasiou, 2021) because the HFO refrigerants are neither persistent (their atmospheric lifetimes are on the order of days or weeks) nor toxic (almost all have a "lower toxicity" ASHRAE safety classification). However, TFA is included in the EU definition of PFAS, and thus the environmental liability of the HFOs may hinge on the yield of TFA upon atmospheric breakdown, which varies between 0 % and 100 % for different HFOs. The EEAP report (UNEP/EEAP, 2022) summarizes the TFA yield of some of the F-gases. The uncertainty around TFA and PFAS is increasingly a factor considered in the development of new refrigerants.

5. Natural refrigerants

The natural refrigerants are generally considered to comprise ammonia (NH_3, R-717), carbon dioxide (CO_2, R-744) and simple hydrocarbons, in particular propane ($CH_3CH_2CH_3$, R-290) and isobutane ($(CH_3)_3CH$, R-600a). Air and water are also included although air is not suitable for use in v-c equipment, and water operates as such low pressures that radically different equipment is required. Sometimes dimethyl ether (CH_3–O–CH_3, R-E170) is also included in this category, not because it is a naturally occurring fluid but because of its similarities to propane.

Other three- and four-carbon hydrocarbons are unlikely to be good refrigerants. Cyclopropane (–$CH_2CH_2CH_2$–) and cyclopropene (–CH═CH–CH_2–) have properties intermediate between propane and isobutane, but they are difficult to manufacture, and the highly-strained nature of the three-carbon ring raises doubts about their stability. Among the cyclic C4 hydrocarbons, cyclobutane, would operate at even lower pressures than *n*-butane, and cyclobutene (–CH_2–CH═CH–CH_2–) is unstable.

A wide range of heavier hydrocarbons exist, which would, in principle, provide the range of boiling points and C_p^0 seen with the F-gases. However, the molar mass, boiling point, and C_p^0 of the hydrocarbons all generally trend higher together. Hydrocarbons with a normal boiling point above the evaporator temperature would operate at negative pressures relative to atmospheric, meaning that a leak in the evaporator would result in leakage of air into the system, rather than refrigerant leaking out. While systems can tolerate some leakage of refrigerant, the inward leakage of air is more problematic: a noncondensable gas, such as air, will accumulate in the condenser and lower heat transfer coefficients, but more significantly, a large inward leak of air into the evaporator could lead to a compression-ignition in the compressor when the refrigerant-air mixture was subsequently compressed. This limits the hydrocarbons that can be used in practice.

Propane and ammonia generally perform very well. For the cooling case presented in Fig. 3(b), for example, ammonia had the highest COP, and propane and propylene were above the trend line. This is due, in part, to their good transport properties, i.e., lower viscosities and higher thermal conductivities compared to most of the fluorinated fluids. Furthermore, the molar mass of the natural fluids is generally lower, meaning that the mass flow rate needed to meet a given refrigeration load is lower (as discussed in Section 4.1), and this reduces efficiency penalties associated with pressure drops.

Apart from water, carbon dioxide is the only natural fluid that is both nonflammable and low toxicity. Its low critical temperature of 30.98 °C implies operation in a transcritical cycle in many situations, meaning that the evaporator would be below the critical point and would operate in the normal way, but the "condenser" would be above the critical point and operate as a gas cooler, rather than a condenser. Transcritical operation requires more complex cycles and sophisticated control strategies to avoid performance penalties compared to "normal" v-c cycles. Transcritical CO_2 systems also operate at substantially higher pressures than all other sub-critical cycles; while this presents challenges in designing efficient compressors, the main issue is simply the paucity of equipment designed for such pressures, rather than any inherent technical hurdles.

The primary obstacles for the natural refrigerants are related to safety (primarily flammability). Safety standards, such as ASHRAE Standards 15 and 15.2 (ASHRAE, 2022, 2024a) and ISO 5149 (ISO, 2014) spell out the requirements needed to mitigate these concerns. For the flammable hydrocarbons, the maximum charge of refrigerant is limited, making a direct substitution into typical current equipment impossible for all but the smallest systems (e.g., home refrigerators and retail bottle coolers). On the other hand, Schnabel et al. (2023) describe the steps needed to drastically reduce refrigerant charge, including advanced heat exchangers and a "monobloc" design (meaning that all components are housed in a single unit, often located outdoors) and present a "current best solution" for a heat pump having specific charge of <10 g propane per kW of heating capacity, an order of magnitude lower than current systems.

Ammonia is classified as "B2L", meaning "higher toxicity" and "lower flammability" by ASHRAE Standard 34 (ASHRAE, 2024b) and ISO Standard 817 (ISO, 2024). The use of ammonia is governed by standards, e.g. (IIAR, 2021), of the International Institute of All-Natural

Refrigeration (IIAR), which have the practical effect of limiting its use. On the other hand, ammonia is low in cost (an important consideration for large systems with many tonnes of charge); there is long experience with safe operation; and it is tolerant of water and high condenser temperatures. There is increasing interest in "ultra-low-charge" ammonia systems that could expand its use. (Expósito Carrillo et al., 2021; Shanmugam and Mital, 2019)

6. Refrigerant options

The current refrigerant options are the natural refrigerants (e.g., ammonia, CO_2, and the simple hydrocarbons) and the fluorinated alkanes and alkenes (the HFCs and HFOs), collectively termed the F-gases, which might possibly be extended to the fluorinated alkynes (compounds with a carbon-carbon triple bond). (Zhang et al., 2022) Gases such as helium, nitrogen, and argon are used as the working fluid in cryogenic systems but are not suitable for typical v-c systems.

Other chemical classes have been considered. For example, in 1998 Bivens and Minor (1998) reviewed the work of several groups investigating alternative chemistries. These included fluorinated ethers (oxygenated compounds with a C–O–C linkage), amines (derivatives of ammonia, i.e., nitrogen compounds), sulfur compounds, and fluorinated silanes (compounds based on silicon); notably, they did not consider HFOs. They concluded that "none of the next generation candidates appear to have a balance of refrigerant fluid performance, safety/environmental properties, and manufacturing feasibility/costs to challenge HFCs." The assignment of a safety classification in ASHRAE Standard 34 (ASHRAE, 2024b) is an early step for the commercial use of a refrigerant. (While not an actual requirement, building codes reference the refrigerants in Standard 34, so the use of any refrigerant not listed in the Standard would require a variance.) By this measure, the only fluids (apart from the cryogenic gases) outside the "natural" and "F-gas" categories assigned a classification are dimethyl ether (CH_3OCH_3), methyl formate ($HCOOCH_3$), and sulfur dioxide (SO_2); the latter two of these being historical fluids that are no longer used because of their toxicity.

The availability of modern molecular estimation techniques allows the simulation of any molecule that can be imagined. Any new molecule that might be proposed as a refrigerant would, however, face high hurdles to commercialization. Low toxicity is extremely important; no toxic refrigerant is being considered for widespread use (ammonia being the only current exception). Non- or low-flammability would be required to seriously consider any new candidate—otherwise why not use one of the hydrocarbons? Once a promising molecule was identified, the next step would be to synthesize a few grams. If the synthesis is straightforward, it remains a candidate; if the synthesis is difficult (e.g., many steps, low yields, or expensive starting materials) the possibility for commercial production of many tonnes of material seems unlikely, and the candidate could be set aside. Next would be the measurement of some of the key thermodynamic properties (e.g., normal boiling point) on those few grams so that the estimated properties could be verified with data. This would be straightforward, except that one would not know of potential toxicity or instability, so special handling procedures would be required. Next would be testing requiring kg-scale quantities of sample including more comprehensive measurements of the thermophysical properties (to enable accurate cycle simulations) and the key safety properties of flammability and stability; testing for materials compatibility and atmospheric lifetime would also require modest quantities of sample. Continued testing (e.g., for system performance and chronic toxicity) would require large quantities of sample, implying the participation of a chemical manufacturer to develop a process to produce the chemical at pilot-plant scale. If all these tests yielded positive results, the large-scale commercial production of a commodity chemical (which most refrigerants are) would require a capital investment on the order of hundreds of millions of dollars, either for a new plant or the repurposing of an existing plant. (For example, two plants built in the late 2010's to manufacture HFO-1234yf cost USD230 M and USD300 M. (Reisch, 2017)) Thus, the costs rapidly increase and present a very high barrier for any new molecule.

Considering the arguments of the three preceding paragraphs, the possibilities are limited, and Fig. 5 presents a sampling of the options for typical heating, refrigerating, and air-conditioning systems, again on temperature-entropy coordinates. The fluids shown with dashed lines may not be suitable for many applications because of their toxicity, low critical temperatures, or flammable fluids operating at sub-atmospheric pressures.

The F-gases (Fig. 5(a)) offer a wide range of thermodynamic behaviors, although the acceptability of some may be in question due to the generation of TFA. For the natural fluids (Fig. 5(b)), there are simply fewer choices. Note the gap between ethane and propane/propylene; it would be desirable to have a refrigerant in this region for cold-climate heat pumps; otherwise, a modified cycle might be required for good performance. Ammonia is an excellent refrigerant, but it is flammable and toxic. Carbon dioxide is nonflammable and of low toxicity, but it has a low critical temperature. Among the hydrocarbons, ethane (with two carbons) has a low critical temperature, and ethylene ($CH_2{=}CH_2$) has an even lower critical temperature. Propane and propylene (with three carbons) fall in the range of "moderate pressure" refrigerants and have good properties for refrigeration. Propylene, however, is not allowed as a refrigerant in most applications under U.S. regulations because of its high photochemical reactivity in the atmosphere. Among the butanes (four carbons), isobutane is widely used, for example in refrigerators; *n*-butane, however, may operate at sub-ambient pressures.

7. Conclusions

There were valid reasons the refrigeration industry embraced halogenated refrigerants (later limited to fluorinated fluids or F-gases) for nearly a century. The ability of fluorine to suppress flammability was, and still is, the primary advantage of the F-gases. But also, the fluorinated refrigerants have thermodynamic characteristics well-matched to the simple vapor-compression cycle, although the transport properties of thermal conductivity and viscosity are often inferior to those of ammonia and the simple hydrocarbons. Furthermore, by varying the fluorine content of the molecule the thermodynamic characteristics can be tuned to match differing requirements. Due to the high GWP and persistence of atmospheric breakdown products that characterize some (but not all) of the F-gases, refrigerant choices are becoming more limited. A recent EU Regulation calls for a complete phase out of the HFCs by 2050. Such restrictions will limit the ability to choose a refrigerant that best matches the thermodynamic requirements of the application and instead require that equipment be designed to accommodate the thermodynamic and safety characteristics of the remaining available refrigerants. This is certainly possible: the refrigeration industry functioned with just a few refrigerants for much of the 20th Century—notably, CFC-11, CFC-12, HCFC-22, and ammonia. Any new, limited slate of fluids with different properties (whether they are F-gases or natural refrigerants) may require modifications to the basic vapor-compression cycle, more complex heat exchanger designs to reduce refrigerant quantities (to mitigate flammability risks), or different compressor designs to compensate for an inherently less-efficient refrigerant.

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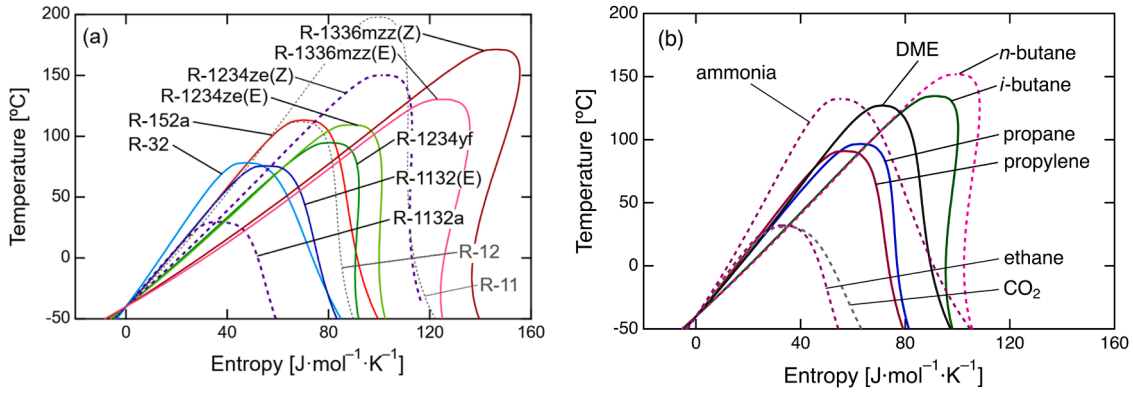

Fig. 5. Representation of the range of fluid behavior on temperature-entropy coordinates; (a) selected F-gases with medium to ultra-low GWP; (b) selected natural refrigerants. The dashed lines represent fluids that may not be suitable for many applications because of their toxicity, low critical temperatures, or flammable fluids operating at sub-atmospheric pressures; R-11 and R-12 are shown in panel (a) as fine dotted lines for historical perspective.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ijrefrig.2026.107033.

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