CHLOROFLUOROCARBONS AND THEIR SUBSTITUTES

John T. McMullan
Energy Research Centre, School of the Built Environment, University of Ulster, Coleraine, U.K.

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Summary

The most common thermodynamic cycle used for refrigeration is the reversed Rankine, or *vapor compression* cycle in which a working fluid, called the refrigerant, circulates around the inside of the system, removing heat from the cold refrigerated space and rejecting it to a warmer heat sink such as the outside air. Initially, many different fluids were used as refrigerants, but none of them was entirely satisfactory. In 1932, however, Thomas Midgley and his associates introduced the chlorofluorocarbon (CFC) refrigerants. These seemed to be the answer to all of the problems. They were chemically very stable, and had all of the desirable thermodynamic and physical properties. They rapidly became the fluids of choice and, because the entire range of applications of the industry could be catered for by a small number of fluids, they allowed an unprecedented degree of standardization in the design of refrigeration equipment.

Subsequently, the damage that the emission of chlorinated human-made chemicals to the atmosphere could cause to the stratospheric ozone layer became a matter of concern. This led to the formulation of a series of intergovernmental agreements (notably the Vienna Convention on the Protection of the Ozone Layer (1985) and the Montreal Protocol on Substances that Deplete the Ozone Layer (1987)) that introduced measures to reduce the production and use of materials with high ozone-depletion potentials (ODPs). Since then, there has been an extensive program to find alternatives from the very limited set of possible chemical compounds. This has resulted in the increased use of refrigerant mixtures and natural refrigerants such as propane.

1. Refrigeration, Refrigerants, Ozone Depletion, and Global Warming

The first stage in the development of the modern refrigeration industry began in Australia in 1850, when James Harrison built a commercial ice factory in Sydney. In

1851, he also installed refrigeration plant in a brewery. The subsequent development of large cold stores, and of refrigerated ships and trains, revolutionized the food industry and allowed perishable food products to be carried for long distances without spoilage. The most striking example was the transport of meat from Australia to the British Isles, which laid the foundation for the Australian livestock farming industry and, indeed, for the development of the Australian economy itself.

The most common thermodynamic cycle used for refrigeration is the reversed Rankine, or *vapor compression* cycle shown in Figure 1. In this cycle, a working fluid, called the refrigerant, circulates around the inside of the system, removing heat from the cold refrigerated space and rejecting it to a warmer heat sink such as the outside air. The refrigerant is admitted to the evaporator as a low-pressure boiling liquid. This boils in the evaporator, cooling the refrigerated space, and producing a vapor that is fed to the compressor. In the compressor, the refrigerant vapor is compressed to a high pressure and temperature, after which it gives up its heat in the condenser, where it condenses back to the liquid state. It is then fed back to the evaporator through the expansion valve, which reduces the pressure and temperature to the starting conditions, allowing the cycle to be repeated. Thus, a quantity of heat (Q_c) is absorbed by the refrigerant in the evaporator, mechanical work (W) is added by the compressor to raise the temperature and pressure, and heat ($Q_h = Q_c + W$) is rejected in the condenser. The efficiency of the refrigerator is measured by a quantity called the *coefficient of performance* (COP), which is the amount of cooling achieved per unit of work supplied to the compressor. That is, $\text{COP} = Q_c/W = Q_c/(Q_h - Q_c)$.

Thus, the properties desired for the refrigerant are specified by the temperatures of the heat source and sink. Essentially, the vapor pressures at the evaporating and condensing temperatures should be acceptable for the design and safety of the refrigeration plant itself. The pressure in the evaporator should preferably be higher than one bar, so that in the event of a leak the leakage is out of the system rather than into it—so protecting the plant from air and water ingress. The pressure in the condenser should preferably be less than about 25 bar so that pressure limits on the condenser and the high pressure pipework are not too extreme, and so forth.

Additionally, the refrigerant working fluid should ideally be chemically stable, non-toxic, non-corrosive, non-flammable, and non-explosive. It should have a high latent heat of evaporation and condensation at the appropriate temperatures, its critical point should be significantly higher than the condensing temperature, and it should have a high density so that the compressors and heat exchangers can be smaller, so reducing construction costs.

Initially, many different fluids were used as refrigerants. None of them was entirely satisfactory in terms of the list of properties described above, and the development of the refrigeration industry was hampered to an extent by the lack of standardization imposed by the wide range of properties of the fluids being used.

This changed in 1932, however, when Thomas Midgley and his associates introduced the chlorofluorocarbon (CFC) refrigerants. These were derived from methane and ethane by replacing all of the hydrogens with chlorine or fluorine. The CFCs seemed to be the answer to all of the problems of the industry. They were chemically very stable, and had all of the desirable thermodynamic and physical properties. They rapidly became the fluids of choice for the industry and, because the entire range of applications of the industry could be catered for by a small number of fluids, they allowed an unprecedented degree of standardization to be achieved in the design of refrigeration equipment.

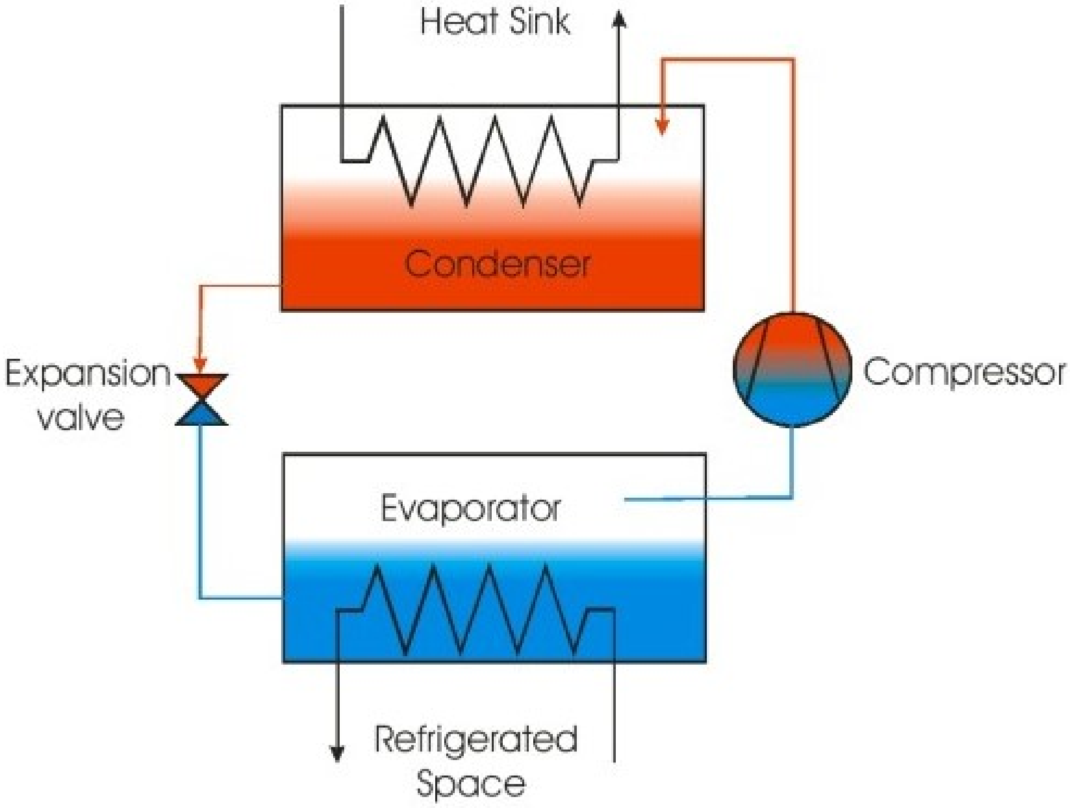

Figure 1. Schematic diagram of vapor compression refrigerator

As a direct result of the standardization and reliability created by the CFCs, refrigeration developed extremely rapidly and, today, global food supplies are highly dependent on reliable refrigerated transport and storage. The industry is now extremely large, and accounts for between 10% and 20% of total world energy demand.

Ironically, the very stability that made the CFCs so attractive has been their downfall. In 1974, Rowland and Molina proposed that the emission of chlorinated human-made chemicals to the atmosphere could damage the stratospheric ozone layer. Subsequently, an extensive worldwide program of stratospheric ozone monitoring confirmed that there is a pattern of depletion that is most pronounced over the Antarctic during springtime. This led to the formulation of a series of intergovernmental agreements (notably the Vienna Convention on the Protection of the Ozone Layer (1985) and the Montreal Protocol on Substances that Deplete the Ozone Layer (1987)) that introduced measures to reduce the production and use of materials with high ozone-depletion potentials (ODPs). First, the halons were banned, then the CFCs, and now there is a push to ban the hydrochlorofluorocarbons (HCFCs).

Officially, halon and CFC production and use have already been phased out in industrialized countries. All production is to cease by the year 2006. In practice, however, CFC production remains well above target levels, and the 2006 phase-out date cannot be achieved. This excess production is being driven by the continued sale of CFC-based systems in developing countries, and the export of used equipment from industrialized to developing countries. These actions are needlessly reinforcing CFC dependency and enhancing demand.

For HCFCs, the official phase-out dates are 2030 for industrialized countries and 2040 for developing countries. The European Union (E.U.) has pushed for an earlier HCFC phase-out date of 2015, but this was defeated following opposition by the United States, Canada, and some developing countries. The E.U. proposal was based on the increasing availability of non-depleting substitutes for HCFCs and on recent evidence that many HCFCs are acutely toxic following regular exposure. Meanwhile, different countries are adopting their own phase-out strategies. For example, Germany banned the use of HCFC-22 in new plant since the beginning of the year 2000.

Following the ozone depletion worries, global warming has appeared as a second major environmental concern affecting the use of refrigerants. Public concern over global warming has created a consensus that has driven large-scale government activity to reduce greenhouse gas emissions. Initially, the emphasis was on carbon dioxide (CO_2) from combustion processes, but the net is now being widened to include other infrared absorbing molecules, including methane and the refrigerants. As most of the compounds being proposed to replace the ozone-depleting CFCs have high infrared absorption coefficients, and consequently high global warming potentials (GWP), the refrigeration industry is now beginning to be influenced by these effects, and concerns on this issue are beginning to complicate our handling of ozone depletion.

2. Refrigerant Numbering

The literature on CFC replacement is littered with refrigerant numbers such as R12 or HFC134a. While these look very complicated, they are actually quite straightforward and describe the molecule accurately according to a simple set of rules. Inorganic refrigerants and refrigerant blends are included in the scheme, but the notation is less helpful.

The inorganic refrigerants are numbered by adding 700 to the molecular weight. Thus ammonia is R717, and water is R718.

Refrigerant blends are numbered serially, the first zeotropic blend being R400 and the first azeotropic blend R500. Each serial number represents mixtures of the same group of molecules, but the numbers do not represent blend properties. Blends of the same components in different compositions are distinguished by capital letters. Thus, all variants of R401 contain the same three compounds (HCFC-22, HFC-152a, and HCFC-124) but in different proportions; the weight percentage composition of R401A is (53/13/34), while that of R401B is (61/11/28).

In the expressions CFC, HCFC, etc., the first “C” is for chlorine, “F” is for fluorine, “H” is for hydrogen, and the final “C” is for carbon. If a “B” is present, as in HBFC, it means that the molecule contains bromine instead of chlorine. Compounds used as refrigerants may be described by using as prefix either “Refrigerant,” “R,” or the name (CFC, etc.). Numbers are then used to identify the specific working fluid.

The methane, ethane, . . . derived refrigerants are numbered using three digits, with alphabetic modifiers providing additional information. The basic number has the form:
Prefix L M N, (1)
where L is one less than the number of carbon atoms in the molecule, M is one more than the number of unsubstituted hydrogen atoms, and N is the number of fluorine atoms. If L = 0, it is omitted. The number of chlorines is then determined by subtracting the number of hydrogens and fluorines from the number of hydrogens in the unsubstituted parent molecule. As a short cut, if 90 is added to the number LMN, then the result directly yields the number of carbons, hydrogens, and fluorines in the molecule.

Thus, for R12, adding 90 converts the index to 102, so there is one carbon (implying a methane derivative, with four bonds), there are no unsubstituted hydrogens and there are two fluorines. The number of chlorines must be two, so R12 is CCl_2F_2 and is a CFC.

Similarly, for R123, adding 90 converts the index to 213, implying an ethane derivative, with six bonds. The full equation is $C_2HCl_2F_3$, making R123 an HCFC.

By contrast, R14, a methane derivative with four fluorines, is the fully fluorine substituted perfluorocarbon (PFC) CF_4.

The other important factor is the isomerism of the molecule. Where appropriate, this is denoted by final lowercase characters. For single-carbon molecules, no isomerism is possible; for two-carbon molecules, the asymmetry is determined by adding the atomic weights of the atoms on each carbon and calculating the difference. Thus, R134 is the symmetrical isomer CHF_2–CHF_2, and R134a is the unsymmetrical CF_3–CH_2F.

For three-carbon molecules, a two-character code is used in which the first character represents the grouping on the middle carbon, and the second is determined as for two-carbon molecules, using the two end carbons. The code for the first letter is given in Table 1 and, as an example, R225ca ($C_3HF_5Cl_2$) is CF_3–CF_2–$CHCl_2$. Higher asymmetry would be denoted by R225cb, etc.

Atoms on middle carbon	Code letter
Cl, Cl	a
Cl, F	b
F, F	c
H, Cl	d
H, F	e
H, H	f

Table 1. Code letters for middle carbon of three-carbon molecules

Finally, if the molecule contains bromine, then the number part of the code is followed by Bn, where n is the number of bromine atoms; the number part of the code is prefixed by C if the molecule is cyclic, or E if it is based on an ether.

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Biographical Sketch

John McMullan is director of the Energy Research Centre of the University of Ulster in Northern Ireland. He has been working in the energy field for over 30 years and his interests center on the environmental impacts of fuel conversion, power generation, and energy use systems. In refrigeration and heat pumps, his research has concentrated on the problems of finding substitutes for the CFCs, and on the associated issues of lubrication and long-term stability and performance of the working fluids. Professor McMullan has acted as an adviser on energy technology and policy to the European Commission, and to different U.K. government departments.