ILLUSTRATION BY RICK STROMOSKI

Green Refrigerants

By Harvey Black

You probably wouldn't guess it, but the warmest spot in the house on a February morning may be the refrigerator. Not the inside of the refrigerator, of course, but the outside—around the back, next to all of those dusty coils. Here, you can feel the heat being expelled. That's the heat from the stored food, removed and pumped out with the help of a special liquid called a refrigerant.

The role of a refrigerant is to take the heat off (see Figure 1). It absorbs the heat from nearby objects, like the food you put in the refrigerator. That absorbed heat is just enough to change a liquid refrigerant into a vapor. The vapor then passes into a compressor, a pump that applies pressure to raise the temperature still more. The warm compressed vapor next goes to a condenser, an array of coils, where the refrigerant cools and returns to a liquid state. Here in the coils at the back of the refrigerator the refrigerant surrenders its heat, and, as the cold liquid returns to the walls of the refrigerator, the whole cycle begins again. Air conditioners operate essentially the same way—removing heat from air which is drawn into the machine and returning the cooler air back to the room or the car in which the air conditioner is located.

For decades, it seemed that CFCs (chlorofluorocarbons) were just about the perfect refrigerants. They appeared to be nontoxic, stable, and ideally suited to the task. And without them, refrigeration probably wouldn't be what it is today. Before chemist Thomas Midgely, Jr., introduced CFCs in 1930, refrigerants—like ammonia and sulfur dioxide—were hardly the sort of chemicals you would want in your kitchen or in your car.

Eric Beckman, professor of chemical engineering at the University of Pittsburgh, remarks that CFCs are still considered to be good refrigerants. Not only are they stable, nontoxic, nonflammable chemicals, but they don't require much energy to do their work. Boiling points, the points at which CFCs vaporize, are close to room temperature. "What you want is to be so close to the boiling point that you can remove the heat from the food and zip it out the back," he says.

But there is a drawback to the use of CFCs, and it is a major one. CFCs, leaking from refrigerators and air conditioners, enter the atmosphere and attack the ozone layer in the Earth's stratosphere. Here, ozone molecules (O_3) form the layer that filters out much of the ultraviolet radiation coming from the Sun—a form of radiation that can, among other things, cause skin cancer in humans.

Chemists F. Sherwood Rowland, Paul Crutzen, and Mario Molina concluded from their Nobel Prize-winning research that it is the chlorine in CFCs that sets off the chain reaction in the stratosphere that depletes ozone. So serious was the concern, that nations meeting in Montreal in 1987 banned the use and manufacture of CFCs as of 1995. With the impending ban of that mainstay refrigerant, chemists began intense efforts to come up with compounds that could keep our food and ourselves cool, without damaging the environment.

Researchers set to work, to come up with replacements for CFCs—chemicals that they hoped would be equally effective while doing no harm to the ozone. Mark McLinden, a chemical engineer with the National Institute of Standards and Technology (NIST) in Boulder, CO, explains that chemists especially had to consider the thermodynamic properties—the heat capacity, as well as the compressibility—of the potential refrigerant. "Those are the factors that determine the performance of a refrigerator or air conditioner. By performance, I mean the *energy efficiency*—how much electricity you have to put into the machine to give it a given amount of cooling, how much heat you remove per unit volume of the refrigerant," he says.

Energy efficiency is a very important but potentially overlooked aspect, agrees Piotr Domanski, a refrigeration engineer with NIST in Gaithersburg, MD. "Low-efficiency refrigerants mean that power plants, most likely fossil fuel power plants, will be working harder, emitting more carbon dioxide, a greenhouse gas," he explains. Greenhouse gases trap infrared radiation, which can, in the view of many scientists, lead to increased global temperatures, which could melt the polar ice caps and raise sea levels.

Refrigerants play almost exactly the same role in the mechanisms of air conditioners as they do in refrigerators. McLinden points out that older automobile air conditioners were major culprits for letting CFCs escape into the atmosphere. "The first auto air conditioners were leaky systems that let CFCs escape through joints, hoses, and seals. Typically, an auto air conditioner would need a new "charge" of CFCs every two or three years. However, it's not uncommon for a home refrigerator to run 20 or 30 or 40 years on its original charge," he says.

Of course, refrigerators and home air conditioners do leak and eventually can run out of refrigerants. A refrigerant designated as 410a serves as a replacement for CFCs in these older appliances. If you buy a car today, it's running on refrigerant 134a. Both 410a and 134a are examples of HFCs—hydrofluorocarbons. HFC molecules contain two hydrogen atoms, two carbon atoms, and four fluorine atoms. Without chlorine, of course, they are no threat to the ozone. The fact that they contain hydrogen is an added advantage. Hydrogen reacts with the hydroxyl radicals (•OH) that are found in the atmosphere. The resulting compounds break down relatively quickly.

The first successful CFC replacement was HCFC, a hydrochlorofluorocarbon compound, marketed as R22. After being tested and used for 20 years, it was phased out because, even though some of the chlorine had been replaced, its use still endangered the stratospheric ozone.

Domanski points out that even HFCs are not without some environmental risks. A buildup of these compounds in the atmosphere increases the amount of greenhouse gases, which can lead to global warming. "They have very significant infrared radiation trapping abilities," he warns.

But Mark Spatz, mechanical engineer with Allied Signal of Buffalo, NY, which makes the compound 410a, notes that the efficiency of this refrigerant means that relatively small amounts can be used. He argues that this actually reduces 410a's impact on global warming.

Designing these replacements can be a complex task that involves more than protect-

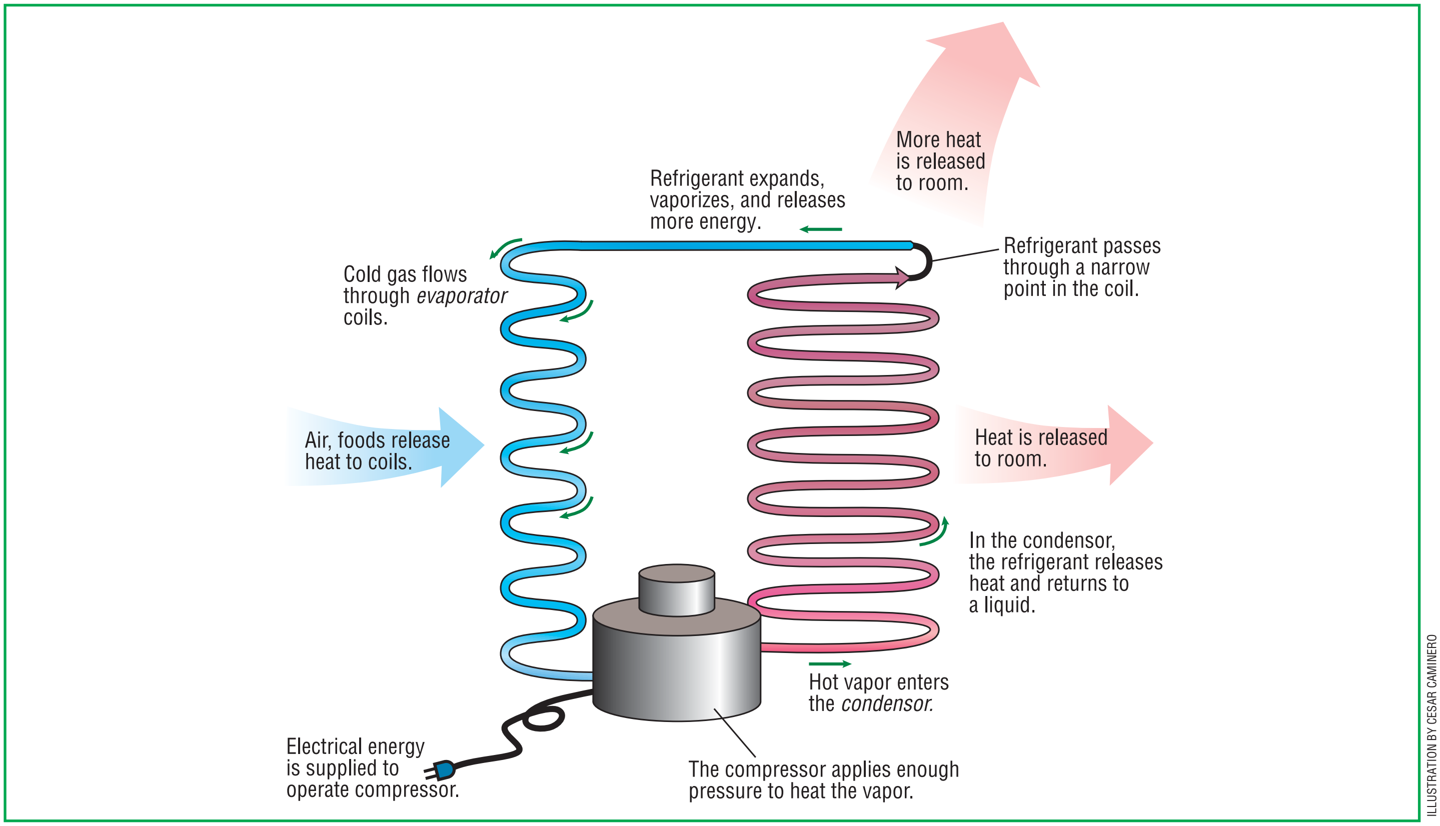

Figure 1. The role of a refrigerant is to take the heat off.

ing stratospheric ozone, as important as that is. “If you come up with a new refrigerant, you have to go to the compressor manufacturers so they can test it out. How does the new refrigerant work with the varnishes on a motor inside a refrigeration system? How does it work with the plastics and metals inside the system?” notes Kevin Joback, a chemical engineer, whose company, Molecular Knowledge Systems in Bedford, NH, searches for chemicals that can substitute for existing ones that are environmentally harmful.

Although much research in the United States seems to focus on modifying fluorocarbons, in Europe scientists and engineers are looking at using hydrocarbons such as propane and butane as possible home refrigerants. Acknowledging that these chemicals can be quite efficient as refrigerants, many experts cite their flammability as a major drawback. For a propane- or butane-based system to work for home refrigeration, the system would be complex and would probably involve a unit placed outside the home.

The search for the ideal refrigerant continues. Among those involved in that effort is Nikalaos Sahinidis, a University of Illinois chemical engineer who uses mathematical models to try and come up with chemicals that are simultaneously effective and friendly to the environment. “It’s not an easy task,” he acknowledges.

Sahinidis hopes to come up with about 100 compounds that are stable, nontoxic, nonflammable, and efficient to be tested for their environmental impact. So far, he has about two dozen whose structures are very different from one another—some with carbon, some without, some with fluorine, some without, some with sulfur, and some without.

Spatz of Allied Signal agrees that the applied effort to develop new refrigerants is demanding. “There’s a lot of chemistry work in terms of the manufacturing process and the compatibility studies with materials that have to be done. Some very challenging halogen exchange chemistry is involved in making these materials. It’s quite a challenge for a chemical engineer to operate and develop new processes for the materials.” One specific challenge, he notes, is to design enough instability into the refrigerant compound, so it degrades in the atmosphere, while still making it stable enough to do its job.

With the Earth’s atmospheric environment hanging in the balance, the search for green refrigerants—those that are both effective and nonpolluting—continues to be a hot topic for researchers.

“The parties to this protocol recognize that worldwide emissions of certain substances can significantly deplete and otherwise modify the ozone layer in a manner that is likely to result in adverse effects on human health and the environment.”

Preamble—The 1987 Montreal Protocol on Substances That Deplete the Ozone Layer

Harvey Black is a freelance science writer living in Madison, WI. His article “Keep the Game Rolling” appeared in the February 1999 issue of *ChemMatters*.

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