Ammonia, methyl chloride, carbon dioxide, propane and other hydrocarbons can serve as refrigerants. Halogenated hydrocarbons came into common use as refrigerants in the 1930s. Most common were the fully halogenated chlorofluorocarbons, CCl_3F (trichlorofluoromethane or CFC-11)[3] and CCl_2F_2 (dichlorodifluoromethane or CFC-12). These stable molecules persist in the atmosphere for hundreds of years, causing severe ozone depletion. Their production has mostly ended. Replacements are certain hydrochlorofluorocarbons, less than fully halogenated hydrocarbons which cause relatively little ozone depletion, and hydrofluorocarbons, which contain no chlorine and cause no ozone depletion. Examples are $CHCl_2CF_3$ (dichlorotrifluoroethane or HCFC-123), CF_3CH_2F (tetrafluoroethane or HFC-134a), and CHF_2CF_3 (pentafluoroethane or HFC-125). A pressure/enthalpy diagram for tetrafluoroethane (HFC-134a) is shown in Fig. G.2; Table 9.1 provides saturation data for the same refrigerant. Tables and diagrams for a variety of other refrigerants are readily available.[4]

Limits placed on the operating pressures of the evaporator and condenser of a refrigeration system also limit the temperature difference $T_H - T_C$ over which a simple vapor-compression cycle can operate. With T_H fixed by the temperature of the surroundings, a lower limit is placed on the temperature level of refrigeration. This can be overcome by the operation of two or more refrigeration cycles employing different refrigerants in a *cascade*. A two-stage cascade is shown in Fig. 9.3.

Here, the two cycles operate so that the heat absorbed in the interchanger by the refrigerant of the higher-temperature cycle 2 serves to condense the refrigerant in the lower-temperature cycle 1. The two refrigerants are so chosen that at the required temperature levels each cycle operates at reasonable pressures. For example, assume the following operating temperatures (Fig. 9.3):

$$T_H = 86(^\circ\text{F}) \qquad T'_C = 0(^\circ\text{F}) \qquad T'_H = 10(^\circ\text{F}) \qquad T_C = -50(^\circ\text{F})$$

If tetrafluoroethane (HFC-134a) is the refrigerant in cycle 2, then the intake and discharge pressures for the compressor are about 21(psia) and 112(psia), and the pressure ratio is about 5.3. If propylene is the refrigerant in cycle 1, these pressures are about 16(psia) and 58(psia), and the pressure ratio is about 3.6. These are all reasonable values. On the other hand, for a single cycle operating between $-50(^\circ\text{F})$ and $86(^\circ\text{F})$ with HFC-134a as refrigerant, the intake pressure to the condenser is about 5.6(psia), well below atmospheric pressure. Moreover, for a discharge pressure of about 112(psia) the pressure ratio is 20, too high a value for a single-stage compressor.

9.4 ABSORPTION REFRIGERATION

In vapor-compression refrigeration the work of compression is usually supplied by an electric motor. But the source of the electric energy for the motor is probably a heat engine (central

[3]The abbreviated designation is nomenclature of the American Society of Heating, Refrigerating, and Air-Conditioning Engineers.

[4]*ASHRAE Handbook: Fundamentals*, Chap. 17, 1989; R. H. Perry and D. Green, *Perry's Chemical Engineers' Handbook*, 7th ed., Sec. 2, 1997. Extensive data for ammonia are given by L. Haar and J. S. Gallagher, *J. Phys. Chem. Ref. Data*, vol. 7, pp. 635–792, 1978.

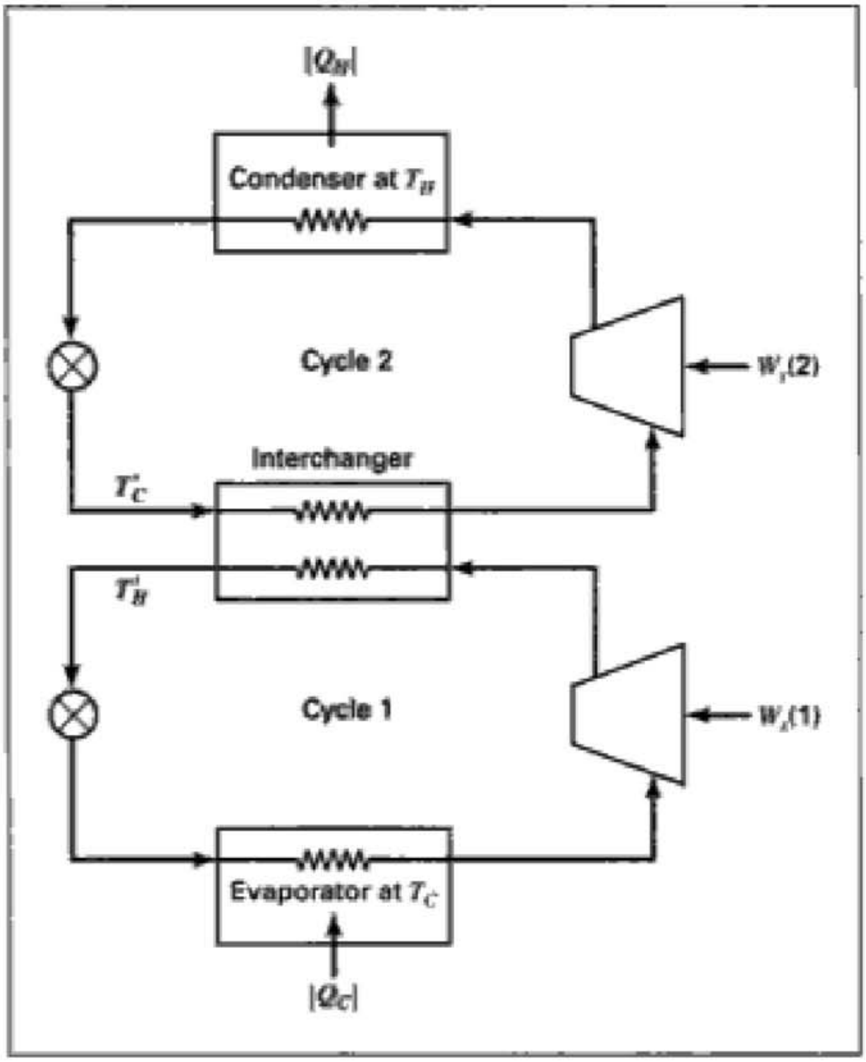

Figure 9.3: A two-stage cascade refrigeration system.

power plant) used to drive a generator. Thus the work for refrigeration comes ultimately from heat at a high temperature level. This suggests the direct use of heat as the energy source for refrigeration. The absorption-refrigeration machine is based on this idea.

The work required by a Carnot refrigerator absorbing heat at temperature T_C and rejecting heat at the temperature of the surroundings, here designated T_S, follows from Eqs. (9.2) and (9.3):

$$W = \frac{T_S - T_C}{T_C}|Q_C|$$

where $|Q_C|$ is the heat absorbed. If a source of heat is available at a temperature above that of the surroundings, say at T_H, then work can be obtained from a Carnot engine operating between this temperature and the surroundings temperature T_S. The heat required $|Q_H|$ for the production of work $|W|$ is found from Eq. (5.8):

$$\eta = \frac{|W|}{|Q_H|} = 1 - \frac{T_S}{T_H} \qquad \text{and} \qquad |Q_H| = |W|\frac{T_H}{T_H - T_S}$$

Elimination of $|W|$ gives:
$$|Q_H| = |Q_C|\frac{T_H}{T_H - T_S}\frac{T_S - T_C}{T_C} \tag{9.6}$$

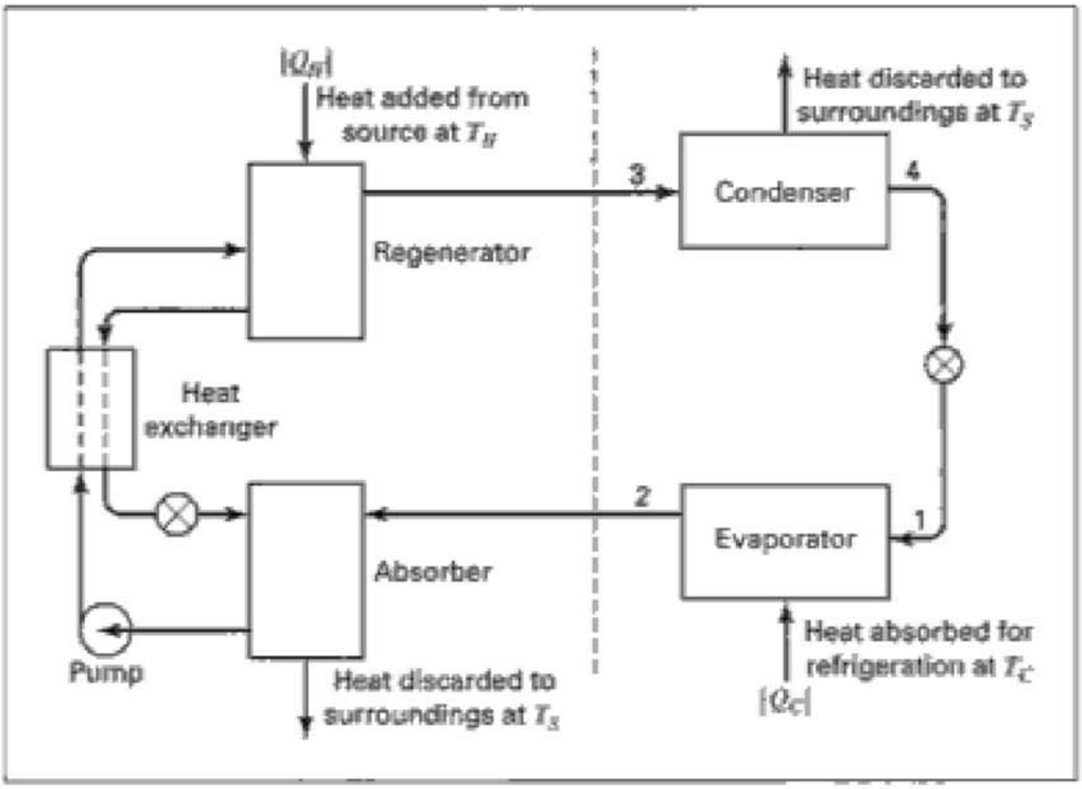

Figure 9.4: Schematic diagram of an absorption-refrigeration unit.

The value of $|Q_H|/|Q_C|$ given by this equation is of course a minimum, because Carnot cycles cannot be achieved in practice.

A schematic diagram for a typical absorption refrigerator is shown in Fig. 9.4. The essential difference between a vapor-compression and an absorption refrigerator is in the different means employed for compression. The section of the absorption unit to the right of the dashed line in Fig. 9.4 is the same as in a vapor-compression refrigerator, but the section to the left accomplishes compression by what amounts to a heat engine. Refrigerant as vapor from the evaporator is absorbed in a relatively nonvolatile liquid solvent at the pressure of the evaporator and at relatively low temperature. The heat given off in the process is discarded to the surroundings at T_S. This is the lower temperature level of the heat engine. The liquid solution from the absorber, which contains a relatively high concentration of refrigerant, passes to a pump, which raises the pressure of the liquid to that of the condenser. Heat from the higher temperature source at T_H is transferred to the compressed liquid solution, raising its temperature and evaporating the refrigerant from the solvent. Vapor passes from the regenerator to the condenser, and solvent, which now contains a relatively low concentration of refrigerant, returns to the absorber by way of a heat exchanger, which serves to conserve energy and adjust stream temperatures toward optimum values. Low-pressure steam is the usual source of heat for the regenerator.

The most commonly used absorption-refrigeration system operates with water as the refrigerant and a lithium bromide solution as the absorbent. This system is obviously limited to refrigeration temperatures above the freezing point of water. It is treated in detail by Perry and Green.[5] For lower temperatures ammonia can serve as refrigerant with water as the solvent. An alternative system uses methanol as refrigerant and polyglycolethers as absorbent.

Consider refrigeration at a temperature level of $-10°C$ ($T_C = 263.15$ K) with a heat source of condensing steam at atmospheric pressure ($T_H = 373.15$ K). For a surroundings temperature of 30°C ($T_S = 303.15$ K), the minimum possible value of $|Q_H|/|Q_C|$ is found from Eq. (9.6):

$$\frac{|Q_H|}{|Q_C|} = \left(\frac{373.15}{373.15 - 303.15}\right)\left(\frac{303.15 - 263.15}{263.15}\right) = 0.81$$

For an actual absorption refrigerator, the value would be on the order of three times this result.

9.5 THE HEAT PUMP

The heat pump, a reversed heat engine, is a device for heating houses and commercial buildings during the winter and cooling them during the summer. In the winter it operates so as to absorb heat from the surroundings and reject heat into the building. Refrigerant evaporates in coils placed underground or in the outside air; vapor compression is followed by condensation, heat being transferred to air or water, which is used to heat the building. Compression must be to a pressure such that the condensation temperature of the refrigerant is higher than the required temperature level of the building. The operating cost of the installation is the cost of electric power to run the compressor. If the unit has a coefficient of performance, $|Q_C|/W = 4$, the heat available to heat the house $|Q_H|$ is equal to five times the energy input to the compressor. Any economic advantage of the heat pump as a heating device depends on the cost of electricity in comparison with the cost of fuels such as oil and natural gas.

The heat pump also serves for air conditioning during the summer. The flow of refrigerant is simply reversed, and heat is absorbed from the building and rejected through underground coils or to the outside air.

Example 9.2

A house has a winter heating requirement of 30 kJ s^{-1} and a summer cooling requirement of 60 kJ s^{-1}. Consider a heat-pump installation to maintain the house temperature at 20°C in winter and 25°C in summer. This requires circulation of the refrigerant through interior exchanger coils at 30°C in winter and 5°C in summer. Underground coils provide the heat source in winter and the heat sink in summer. For a year-round ground temperature of 15°C, the heat-transfer characteristics of the coils necessitate refrigerant temperatures of 10°C in winter and 25°C in summer. What are the minimum power requirements for winter heating and summer cooling?

[5] R. H. Perry and D. Green, *op. cit.*, pp. 11-88–11-89.