effectiveness of the absorber as a compressor. The effect is the result of the attraction between the absorbent and refrigerant molecules, a subject which will be discussed in more detail in connection with the discussion of absorbent-refrigerant combinations.

After a given quantity of absorbent has dissolved its quota of vapor, it must be returned to the generator to be reclaimed. Since the generator is at the high side pressure, a pump is required to make the transfer. This pump is not a compressor because the absorber has already accomplished the compression; it is merely a circulating device, and the amount of energy required to drive it is small in comparison to that required to drive a vapor compressor.

The function of the generator is to separate the refrigerant from the absorbent. This is accomplished by vaporizing the refrigerant so that the physical separation of the refrigerant vapor from the absorbent liquid is relatively easy. This process requires the addition of heat, most of which is used to vaporize the refrigerant. The absorbent in concentrated form flows back to the absorber through a flow control, and the refrigerant vapor flows through an unrestricted passage to the condenser.

As indicated in Fig. 17, heat is put into the absorption cycle in two places, i.e., into the generator and into the evaporator. Energy must also be supplied for the solution pump; this is generally very small in comparison to the other heat quantities, and the heat equivalent of the energy used for circulating the solution is simply added to the heat applied to the generator. Heat is dissipated from both the condenser and the absorber.

An absorption cycle may be viewed as the combination of a heat engine and a refrigerating machine; the heat engine converts heat into work which, in turn, drives the refrigerating machine to produce a refrigerating effect. For an ideal, reversible cycle, consider the case in which a quantity of heat Q_g is added to the generator at a temperature of T_g and a quantity of heat Q_c is rejected at temperature T_c. According to the Second Law, the work W produced can be calculated as follows:

$$W = Q_g\left(\frac{T_g - T_c}{T_g}\right) \qquad (15)$$

where

W = work, Btu.
Q_g = heat added to generator, Btu.
T_g = temperature of generator, Rankine degrees.
T_c = temperature of condenser, Rankine degrees.

For a reversible refrigeration cycle taking in a quantity of heat Q_e through an evaporator at temperature T_e and rejecting heat through the absorber at temperature T_a:

$$W = Q_e\left(\frac{T_a - T_e}{T_e}\right) \qquad (16)$$

where

Q_e = heat added to evaporator, Btu.
T_e = temperature of evaporator, Rankine degrees.
T_a = temperature of absorber, Rankine degrees.

Since the work quantity W is common, Equations 15 and 16 may be combined:

$$Q_e\left(\frac{T_a - T_e}{T_e}\right) = Q_g\left(\frac{T_g - T_c}{T_g}\right) \qquad (17)$$

The coefficient of performance (CP) of a refrigerating machine is defined as the ratio of refrigerating effect to heat input; therefore Equation 17 can be rearranged to give

$$\text{(CP)} = \frac{Q_e}{Q_g} = \frac{T_e}{T_g}\left(\frac{T_g - T_c}{T_a - T_e}\right) \qquad (18)$$

It is frequently stated that the CP for an absorption cycle must always be less than one; this is *not* a theoretical limit but rather an artificial limit imposed by conventional design. A study of Equation 18 reveals that there is no finite limit. The value of the factor T_e/T_g must be less than unity for a refrigeration cycle, but the value of the factor $(T_g - T_c)/(T_a - T_e)$ will approach infinity as T_a approaches T_e.

The statement concerning a limit of unity for the CP is based on the concept that if one pound of refrigerant is evaporated from the generator, then only one pound of refrigerant can be available in the evaporator. This artificial limit can be overcome by design, e.g., by using the multiple effect evaporator principle in the generator.

In some cases, the condenser and absorber will have a common heat sink, and T_c will equal T_a; Equation 18 can then be written:

$$\text{(CP)} = \frac{T_e}{T_g}\left(\frac{T_g - T_c}{T_c - T_e}\right) \qquad (19)$$

To show the relation between the sink temperature, the generator temperature, and the ideal coefficient of performance, Equation 19 has been plotted in Fig. 18 for generator temperatures of 200, 300, and 400 F.

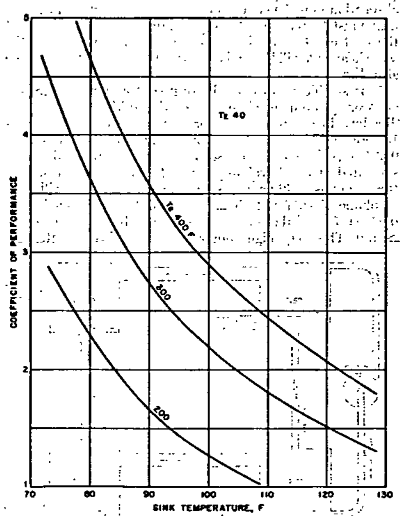

Fig. 18 . . . . Ideal Coefficients of Performance for Reversible Absorption Refrigeration Cycles

Nature of the Absorbent-Refrigerant Combination[24,25]

By definition, the working fluids are liquids; solid materials which, with a suitable refrigerant, can constitute a refrigeration system are called adsorbents, and the systems are called adsorption systems. The liquids, the absorbent, and the refrigerant must, to some degree, meet all of a series of requirements; the more significant requirements are discussed in the following paragraphs.

1. *Affinity.* It is fundamental that the absorbent show a strong affinity for the refrigerant vapor; this is the property which gives the absorber the ability to absorb, i.e., to draw in and compress the refrigerant vapor. This affinity is the result of mild chemical bonding, generally hydrogen bonding.[26] While it is necessary that a strong affinity exist, it is also necessary that the two materials not be so strongly bonded that they cannot be readily separated by the application of heat. The fact that hydrogen bonding is the mechanism yielding satisfactory bonding forces explains why so many of the absorbent-refrigerant combinations utilize molecules containing highly electro-negative atoms, such as oxygen and nitrogen.

In the case of systems using aqueous solutions of hygroscopic salts for the absorption of water vapor, the bonding is generally attributed to solvation.

This affinity is indicated by a large negative deviation from Raoult's Law; the absorbent lowers the vapor pressure of the refrigerant by a far greater amount than would be expected on the basis of ideal solution behavior. The marked evolution of heat when the liquid refrigerant is added to the liquid absorbent is also evidence of the affinity.

2. *Solubility.* It is necessary that the refrigerant and absorbent be mutually soluble over the whole range of operating conditions. If crystallization occurs, the solid particles can make it difficult or impossible for the fluids to circulate properly. Usually, with materials of this nature, the problem is one of solvate formation, and the solution simply goes solid.
3. *Absorbent Volatility.* Ideally, the absorbent should be nonvolatile so that the vapor leaving the generator will be pure refrigerant. If the absorbent is volatile to any appreciable extent, a separation of refrigerant vapor from absorbent vapor is required between the generator and the condenser; this generally necessitates a rectification column which requires energy for operation and thus reduces the CP of the system.
4. *Stability.* In the case of absorption systems, almost absolute stability is required because the fluids will be refluxed together continuously in a hermetically sealed system which is expected to function without trouble for many years.
5. *Corrosion.* It is obvious, because of the long life requirements, that the fluids must not be corrosive to any detectable extent to the materials used in constructing the equipment.
6. *Pressure.* Ideally, the working pressures should be as near to atmospheric as possible, to minimize equipment weight and to minimize leakage into or out of the system. Furthermore, the pressure difference between the high side and the low side should be low, to facilitate circulation of the solution.
7. *Safety.* Low toxicity and noninflammability requirements are generally included in building codes and are quite strict.
8. *Viscosity.* Low viscosity for both fluids is highly desirable, both to promote good heat transfer and to circumvent excessive energy requirements for fluid circulation.
9. A refrigerant with a high latent heat of vaporization is desirable because it holds to a minimum the quantities of fluids to be circulated.

No combinations meeting all these requirements have been found. However, a few absorbent-refrigerant pairs fulfill most of them, and are practical. They are discussed in detail in the next section.

Workable Absorbent-Refrigerant Combinations

Since hydrogen bonding[26] is the primary mechanism creating the attraction between absorbents and refrigerants, the general requirements are that: (1) the molecules be small, (2) at least one of the pair contain a highly electronegative atom such as fluorine, nitrogen or oxygen, and (3) the other molecule of the pair contain hydrogen. Molecules meeting these general requirements include water, the lower alcohols, ammonia, amines, ketones, and ethers. Actually, the list of materials is quite lengthy. However, in most cases where affinity requirements are met, failure to meet some other requirement will eliminate a material from consideration. For example, sulfuric acid would be an ideal absorbent for water vapor, but it is too corrosive to the materials of construction.

Much effort has gone into the search for suitable pairs of materials but, at this time, only two pairs have been found practically useful. These are (1) the ammonia-water combination and (2) the water-aqueous solution of a hygroscopic salt combination, in which lithium bromide has been the only really practical salt. A third combination makes use of dimethoxytetraethylene glycol[27] as the absorbent, and some material such as methylene chloride or Refrigerant 21 as the refrigerant.[28] Lack of stability and a low value for the CP have been the main deterrents to the use of this system.

The ammonia-water combination, in which ammonia serves as the refrigerant and water as the absorbent, is the classical example in absorption refrigeration literature. Both molecules meet the requirements for hydrogen bonding extremely well; both are highly stable, ammonia has a high latent heat of vaporization, and, in general, both are quite compatible with ordinary materials of construction. Even so, the combination is far from perfect, the major difficulties being the volatility of the absorbent and the high condensing pressure. There are other disadvantages, such as the toxicity of ammonia in higher concentrations and the fact that copper and its alloys are not suitable for use in systems containing ammonia. These disadvantages have been successfully handled, with the result that millions of such refrigeration units have been made and used.

The fact that the water (absorbent) is volatile means that the vapor leaving the generator will contain appreciable quantities of water vapor. If allowed to pass to the condenser and flow on to the evaporator, the water would raise the evaporator temperature and carry much unevaporated refrigerant from the evaporator, thus reducing the CP. Therefore, it is necessary to insert a rectifying or distilling column between the generator and condenser. The distilling column requires that a part of the distillate be returned to the top of the column as reflux liquid. This return of condensate to the generator constitutes a loss in refrigerating effect, but this loss is much less than that which would result if the water-rich refrigerant were allowed to pass directly to the evaporator. Fortunately, the relative volatilities of ammonia and water are different enough to make this a relatively easy separation.

The use of water as a refrigerant is quite old. One such system was in use in 1845. A number of strong absorbents for water vapor are well known, e.g., sulfuric acid, phosphoric acid, potassium hydroxide solutions and a series of hygroscopic salt solutions. However, the corrosiveness of many of these, particularly the acids, makes their use impractical, so the aqueous solution of the hydroscopic salts are the only absorbents that have been found useful.

The chlorides, bromides, and iodides of lithium, magnesium, calcium, and zinc are typical of the most useful hygroscopic salts. Of these, lithium bromide is almost exclusively used. It has the advantage over the salts of magnesium, calcium, and zinc that it is soluble in solutions haveng a *pH* higher than 7, and the use of slightly basic solutions makes corrosion much easier to control. The bromide of lithium is also more desirable than the chloride or iodide, in that it has the best solubility-vapor pressure lowering relationship.

The advantages of the water-hygroscopic salt systems are as follows:

1. Water, as a refrigerant, has a very high latent heat of vaporization.
2. The absorbent is nonvolatile.
3. The system operates at low pressures.
4. The materials are nontoxic and nonflammable.

There are certain disadvantages, as follows:

1. Water as a refrigerant is limited to evaporator temperatures above 32 F, its freezing point.