

## CHAPTER 1

# THERMODYNAMICS AND REFRIGERATION CYCLES

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**T**HERMODYNAMICS is the study of energy, its transformations, and its relation to states of matter. This chapter covers the application of thermodynamics to refrigeration cycles. The first part reviews the first and second laws of thermodynamics and presents methods for calculating thermodynamic properties. The second and third parts address compression and absorption refrigeration cycles, the two most common methods of thermal energy transfer.

## THERMODYNAMICS

A **thermodynamic system** is a region in space or a quantity of matter bounded by a closed surface. The surroundings include everything external to the system, and the system is separated from the surroundings by the system boundaries. These boundaries can be movable or fixed, real or imaginary.

The concepts that operate in any thermodynamic system are **entropy** and **energy**. Entropy measures the molecular disorder of a system. The more mixed a system, the greater its entropy; conversely, an orderly or unmixed configuration is one of low entropy. Energy has the capacity for producing an effect and can be categorized into either stored or transient forms as described in the following sections.

### Stored Energy

**Thermal (internal) energy** is the energy possessed by a system caused by the motion of the molecules and/or intermolecular forces.

**Potential energy** is the energy possessed by a system caused by the attractive forces existing between molecules, or the elevation of the system.

$$PE = mgz \quad (1)$$

where

$m$  = mass

$g$  = local acceleration of gravity

$z$  = elevation above horizontal reference plane

**Kinetic energy** is the energy possessed by a system caused by the velocity of the molecules and is expressed as

$$KE = mV^2/2 \quad (2)$$

where  $V$  is the velocity of a fluid stream crossing the system boundary.

**Chemical energy** is energy possessed by the system caused by the arrangement of atoms composing the molecules.

**Nuclear (atomic) energy** is energy possessed by the system from the cohesive forces holding protons and neutrons together as the atom's nucleus.

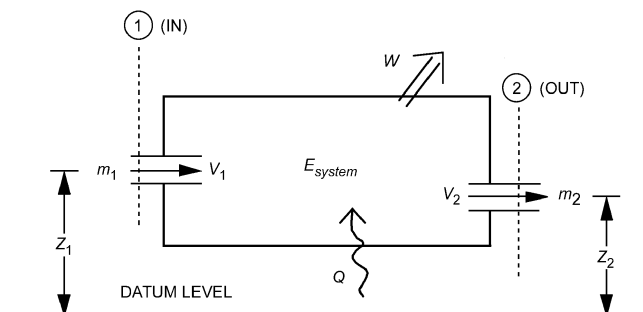
### Energy in Transition

**Heat ( $Q$ )** is the mechanism that transfers energy across the boundary of systems with differing temperatures, always toward the lower temperature. Heat is positive when energy is added to the system (see [Figure 1](#)).

**Work** is the mechanism that transfers energy across the boundary of systems with differing pressures (or force of any kind), always toward the lower pressure. If the total effect produced in the system can be reduced to the raising of a weight, then nothing but work has crossed the boundary. Work is positive when energy is removed from the system (see [Figure 1](#)).

**Mechanical or shaft work ( $W$ )** is the energy delivered or absorbed by a mechanism, such as a turbine, air compressor, or internal combustion engine.

**Flow work** is energy carried into or transmitted across the system boundary because a pumping process occurs somewhere outside the system, causing fluid to enter the system. It can be more easily understood as the work done by the fluid just outside the



**Fig. 1** Energy Flows in General Thermodynamic System

The preparation of the first and second parts of this chapter is assigned to TC 1.1, Thermodynamics and Psychrometrics. The third part is assigned to TC 8.3, Absorption and Heat-Operated Machines.

system on the adjacent fluid entering the system to force or push it into the system. Flow work also occurs as fluid leaves the system.

$$\text{Flow Work (per unit mass)} = pv \quad (3)$$

where  $p$  is the pressure and  $v$  is the specific volume, or the volume displaced per unit mass.

A **property** of a system is any observable characteristic of the system. The **state** of a system is defined by listing its properties. The most common thermodynamic properties are temperature  $T$ , pressure  $p$ , and specific volume  $v$  or density  $\rho$ . Additional thermodynamic properties include entropy, stored forms of energy, and enthalpy.

Frequently, thermodynamic properties combine to form other properties. **Enthalpy** ( $h$ ), a result of combining properties, is defined as

$$h \equiv u + pv \quad (4)$$

where  $u$  is internal energy per unit mass.

Each property in a given state has only one definite value, and any property always has the same value for a given state, regardless of how the substance arrived at that state.

A **process** is a change in state that can be defined as any change in the properties of a system. A process is described by specifying the initial and final equilibrium states, the path (if identifiable), and the interactions that take place across system boundaries during the process.

A **cycle** is a process or a series of processes wherein the initial and final states of the system are identical. Therefore, at the conclusion of a cycle, all the properties have the same value they had at the beginning.

A **pure substance** has a homogeneous and invariable chemical composition. It can exist in more than one phase, but the chemical composition is the same in all phases.

If a substance exists as liquid at the saturation temperature and pressure, it is called **saturated liquid**. If the temperature of the liquid is lower than the saturation temperature for the existing pressure, it is called either a **subcooled liquid** (the temperature is lower than the saturation temperature for the given pressure) or a **compressed liquid** (the pressure is greater than the saturation pressure for the given temperature).

When a substance exists as part liquid and part vapor at the saturation temperature, its quality is defined as the ratio of the mass of vapor to the total mass. Quality has meaning only when the substance is in a saturated state; i.e., at saturation pressure and temperature.

If a substance exists as vapor at the saturation temperature, it is called **saturated vapor**. (Sometimes the term **dry saturated vapor** is used to emphasize that the quality is 100%.) When the vapor is at a temperature greater than the saturation temperature, it is **superheated vapor**. The pressure and temperature of superheated vapor are independent properties, since the temperature can increase while the pressure remains constant. Gases are highly superheated vapors.

## FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is often called the **law of the conservation of energy**. The following form of the first law equation is valid only in the absence of a nuclear or chemical reaction.

Based on the first law or the law of conservation of energy for any system, open or closed, there is an energy balance as

$$\left[ \begin{array}{c} \text{Net Amount of Energy} \\ \text{Added to System} \end{array} \right] = \left[ \begin{array}{c} \text{Net Increase in Stored} \\ \text{Energy of System} \end{array} \right]$$

or

$$\text{Energy In} - \text{Energy Out} = \text{Increase in Energy in System}$$

Figure 1 illustrates energy flows into and out of a thermodynamic system. For the general case of multiple mass flows in and out of the system, the energy balance can be written

$$\begin{aligned} & \sum m_{in} \left( u + pv + \frac{V^2}{2} + gz \right)_{in} \\ & - \sum m_{out} \left( u + pv + \frac{V^2}{2} + gz \right)_{out} + Q - W \\ & = \left[ m_f \left( u + \frac{V^2}{2} + gz \right)_f - m_i \left( u + \frac{V^2}{2} + gz \right)_i \right]_{system} \end{aligned} \quad (5)$$

where subscripts  $i$  and  $f$  refer to the initial and final states, respectively.

The steady-flow process is important in engineering applications. Steady flow signifies that all quantities associated with the system do not vary with time. Consequently,

$$\begin{aligned} & \sum_{\text{all streams leaving}} \dot{m} \left( h + \frac{V^2}{2} + gz \right) \\ & - \sum_{\text{all streams entering}} \dot{m} \left( h + \frac{V^2}{2} + gz \right) + \dot{Q} - \dot{W} = 0 \end{aligned} \quad (6)$$

where  $h = u + pv$  as described in Equation (4).

A second common application is the closed stationary system for which the first law equation reduces to

$$Q - W = [m(u_f - u_i)]_{system} \quad (7)$$

## SECOND LAW OF THERMODYNAMICS

The second law of thermodynamics differentiates and quantifies processes that only proceed in a certain direction (irreversible) from those that are reversible. The second law may be described in several ways. One method uses the concept of entropy flow in an open system and the irreversibility associated with the process. The concept of irreversibility provides added insight into the operation of cycles. For example, the larger the irreversibility in a refrigeration cycle operating with a given refrigeration load between two fixed temperature levels, the larger the amount of work required to operate the cycle. Irreversibilities include pressure drops in lines and heat exchangers, heat transfer between fluids of different temperature, and mechanical friction. Reducing total irreversibility in a cycle improves the cycle performance. In the limit of no irreversibilities, a cycle will attain its maximum ideal efficiency.

In an open system, the second law of thermodynamics can be described in terms of entropy as

$$dS_{system} = \frac{\delta Q}{T} + \delta m_i s_i - \delta m_e s_e + dI \quad (8)$$

where

$dS_{system}$  = total change within system in time  $dt$  during process

$\delta m_i s_i$  = entropy increase caused by mass entering (incoming)

$\delta m_e s_e$  = entropy decrease caused by mass leaving (exiting)

$\delta Q/T$  = entropy change caused by reversible heat transfer between system and surroundings

$dI$  = entropy caused by irreversibilities (always positive)

Equation (8) accounts for all entropy changes in the system. Rearranged, this equation becomes

$$\delta Q = T[(\delta m_e s_e - \delta m_i s_i) + dS_{sys} - dI] \quad (9)$$

In integrated form, if inlet and outlet properties, mass flow, and interactions with the surroundings do not vary with time, the general equation for the second law is

$$(S_f - S_i)_{system} = \int_{rev} \frac{\delta Q}{T} + \sum (ms)_{in} - \sum (ms)_{out} + I \quad (10)$$

In many applications the process can be considered to be operating steadily with no change in time. The change in entropy of the system is therefore zero. The irreversibility rate, which is the rate of entropy production caused by irreversibilities in the process, can be determined by rearranging Equation (10)

$$\dot{I} = \sum (\dot{ms})_{out} - \sum (\dot{ms})_{in} - \int \frac{\dot{Q}}{T_{surr}} \quad (11)$$

Equation (6) can be used to replace the heat transfer quantity. Note that the absolute temperature of the surroundings with which the system is exchanging heat is used in the last term. If the temperature of the surroundings is equal to the temperature of the system, the heat is transferred reversibly and Equation (11) becomes equal to zero.

Equation (11) is commonly applied to a system with one mass flow in, the same mass flow out, no work, and negligible kinetic or potential energy flows. Combining Equations (6) and (11) yields

$$\dot{I} = \dot{m} \left[ (s_{out} - s_{in}) - \frac{h_{out} - h_{in}}{T_{surr}} \right] \quad (12)$$

In a cycle, the reduction of work produced by a power cycle or the increase in work required by a refrigeration cycle is equal to the absolute ambient temperature multiplied by the sum of the irreversibilities in all the processes in the cycle. Thus the difference in the reversible work and the actual work for any refrigeration cycle, theoretical or real, operating under the same conditions becomes

$$\dot{W}_{actual} = \dot{W}_{reversible} + T_0 \sum \dot{I} \quad (13)$$

### THERMODYNAMIC ANALYSIS OF REFRIGERATION CYCLES

Refrigeration cycles transfer thermal energy from a region of low temperature  $T_R$  to one of higher temperature. Usually the higher temperature heat sink is the ambient air or cooling water. This temperature is designated as  $T_0$ , the temperature of the surroundings.

The first and second laws of thermodynamics can be applied to individual components to determine mass and energy balances and the irreversibility of the components. This procedure is illustrated in later sections in this chapter.

Performance of a refrigeration cycle is usually described by a **coefficient of performance**. COP is defined as the benefit of the cycle (amount of heat removed) divided by the required energy input to operate the cycle, or

$$\text{COP} = \frac{\text{Useful refrigerating effect}}{\text{Net energy supplied from external sources}} \quad (14)$$

For a mechanical vapor compression system, the net energy supplied is usually in the form of work, mechanical or electrical, and may include work to the compressor and fans or pumps. Thus

$$\text{COP} = \frac{Q_{evap}}{W_{net}} \quad (15)$$

In an absorption refrigeration cycle, the net energy supplied is usually in the form of heat into the generator and work into the pumps and fans, or

$$\text{COP} = \frac{Q_{evap}}{Q_{gen} + W_{net}} \quad (16)$$

In many cases the work supplied to an absorption system is very small compared to the amount of heat supplied to the generator, so the work term is often neglected.

Application of the second law to an entire refrigeration cycle shows that a completely reversible cycle operating under the same conditions has the maximum possible Coefficient of Performance. A measure of the departure of the actual cycle from an ideal reversible cycle is given by the **refrigerating efficiency**:

$$\eta_R = \frac{\text{COP}}{(\text{COP})_{rev}} \quad (17)$$

The Carnot cycle usually serves as the ideal reversible refrigeration cycle. For multistage cycles, each stage is described by a reversible cycle.

### EQUATIONS OF STATE

The equation of state of a pure substance is a mathematical relation between pressure, specific volume, and temperature. When the system is in thermodynamic equilibrium,

$$f(p, v, T) = 0 \quad (18)$$

The principles of statistical mechanics are used to (1) explore the fundamental properties of matter, (2) predict an equation of state based on the statistical nature of a particular system, or (3) propose a functional form for an equation of state with unknown parameters that are determined by measuring thermodynamic properties of a substance. A fundamental equation with this basis is the **virial equation**. The virial equation is expressed as an expansion in pressure  $p$  or in reciprocal values of volume per unit mass  $v$  as

$$\frac{pv}{RT} = 1 + B'p + C'p^2 + D'p^3 + \dots \quad (19)$$

$$\frac{pv}{RT} = 1 + (B/v) + (C/v^2) + (D/v^3) + \dots \quad (20)$$

where coefficients  $B'$ ,  $C'$ ,  $D'$ , etc., and  $B$ ,  $C$ ,  $D$ , etc., are the virial coefficients.  $B'$  and  $B$  are second virial coefficients;  $C'$  and  $C$  are third virial coefficients, etc. The virial coefficients are functions of temperature only, and values of the respective coefficients in Equations (19) and (20) are related. For example,  $B' = B/RT$  and  $C' = (C - B^2)/(RT)^2$ .

The ideal gas constant  $R$  is defined as

$$R = \lim_{p \rightarrow 0} \frac{(pv)_T}{T_{tp}} \quad (21)$$

where  $(pv)_T$  is the product of the pressure and the volume along an isotherm, and  $T_{tp}$  is the defined temperature of the triple point of water, which is 273.16 K. The current best value of  $R$  is 8314.41 J/(kg mole · K).

The quantity  $pv/RT$  is also called the **compressibility factor**; i.e.,  $Z = pv/RT$  or

$$Z = 1 + (B/v) + (C/v^2) + (D/v^3) + \dots \quad (22)$$

An advantage of the virial form is that statistical mechanics can be used to predict the lower order coefficients and provide physical significance to the virial coefficients. For example, in Equation

(22), the term  $B/v$  is a function of interactions between two molecules,  $C/v^2$  between three molecules, etc. Since the lower order interactions are common, the contributions of the higher order terms are successively less. Thermodynamicists use the partition or distribution function to determine virial coefficients; however, experimental values of the second and third coefficients are preferred. For dense fluids, many higher order terms are necessary that can neither be satisfactorily predicted from theory nor determined from experimental measurements. In general, a truncated virial expansion of four terms is valid for densities of less than one-half the value at the critical point. For higher densities, additional terms can be used and determined empirically.

Digital computers allow the use of very complex equations of state in calculating  $p$ - $v$ - $T$  values, even to high densities. The Benedict-Webb-Rubin (B-W-R) equation of state (Benedict et al. 1940) and the Martin-Hou equation (1955) have had considerable use, but should generally be limited to densities less than the critical value. Strobridge (1962) suggested a modified Benedict-Webb-Rubin relation that gives excellent results at higher densities and can be used for a  $p$ - $v$ - $T$  surface that extends into the liquid phase.

The B-W-R equation has been used extensively for hydrocarbons (Cooper and Goldfrank 1967):

$$P = (RT/v) + (B_o RT - A_o - C_o/T^2)/v^2 + (bRT - a)/v^3 + (a\alpha)/v^6 + [c(1 + \gamma/v^2)e^{(-\gamma/v^2)}]/v^3 T^2 \quad (23)$$

where the constant coefficients are  $A_o, B_o, C_o, a, b, c, \alpha, \gamma$ .

The Martin-Hou equation, developed for fluorinated hydrocarbon properties, has been used to calculate the thermodynamic property tables in [Chapter 20](#) and in ASHRAE *Thermodynamic Properties of Refrigerants* (Stewart et al. 1986). The Martin-Hou equation is as follows:

$$p = \frac{RT}{v-b} + \frac{A_2 + B_2 T + C_2 e^{(-kT/T_c)}}{(v-b)^2} + \frac{A_3 + B_3 T + C_3 e^{(-kT/T_c)}}{(v-b)^3} + \frac{A_4 + B_4 T}{(v-b)^4} + \frac{A_5 + B_5 T + C_5 e^{(-kT/T_c)}}{(v-b)^5} + (A_6 + B_6 T)e^{\alpha v} \quad (24)$$

where the constant coefficients are  $A_i, B_i, C_i, k, b$ , and  $\alpha$ .

Strobridge (1962) suggested an equation of state that was developed for nitrogen properties and used for most cryogenic fluids. This equation combines the B-W-R equation of state with an equation for high density nitrogen suggested by Benedict (1937). These equations have been used successfully for liquid and vapor phases, extending in the liquid phase to the triple-point temperature and the freezing line, and in the vapor phase from 10 to 1000 K, with pressures to 1 GPa. The equation suggested by Strobridge is accurate within the uncertainty of the measured  $p$ - $v$ - $T$  data. This equation, as originally reported by Strobridge, is

$$p = RT\rho + \left[ Rn_1 T + n_2 + \frac{n_3}{T} + \frac{n_4}{T^2} + \frac{n_5}{T^4} \right] \rho^2 + (Rn_6 T + n_7) \rho^3 + n_8 T \rho^4 + \rho^3 \left[ \frac{n_9}{T^2} + \frac{n_{10}}{T^3} + \frac{n_{11}}{T^4} \right] \exp(-n_{16} \rho^2) + \rho^5 \left[ \frac{n_{12}}{T^2} + \frac{n_{13}}{T^3} + \frac{n_{14}}{T^4} \right] \exp(-n_{16} \rho^2) + n_{15} \rho^6 \quad (25)$$

The 15 coefficients of this equation's linear terms are determined by a least-square fit to experimental data. Hust and Stewart (1966) and Hust and McCarty (1967) give further information on methods and techniques for determining equations of state.

In the absence of experimental data, Van der Waals' principle of corresponding states can predict fluid properties. This principle relates properties of similar substances by suitable reducing factors; i.e., the  $p$ - $v$ - $T$  surfaces of similar fluids in a given region are assumed to be of similar shape. The critical point can be used to define reducing parameters to scale the surface of one fluid to the dimensions of another. Modifications of this principle, as suggested by Kamerlingh Onnes, a Dutch cryogenic researcher, have been used to improve correspondence at low pressures. The principle of corresponding states provides useful approximations, and numerous modifications have been reported. More complex treatments for predicting property values, which recognize similarity of fluid properties, are by generalized equations of state. These equations ordinarily allow for adjustment of the  $p$ - $v$ - $T$  surface by introduction of parameters. One example (Hirschfelder et al. 1958) allows for departures from the principle of corresponding states by adding two correlating parameters.

## CALCULATING THERMODYNAMIC PROPERTIES

While equations of state provide  $p$ - $v$ - $T$  relations, a thermodynamic analysis usually requires values for internal energy, enthalpy, and entropy. These properties have been tabulated for many substances, including refrigerants (See [Chapters 6, 20, and 38](#)) and can be extracted from such tables by interpolating manually or with a suitable computer program. This approach is appropriate for hand calculations and for relatively simple computer models; however, for many computer simulations, the overhead in memory or input and output required to use tabulated data can make this approach unacceptable. For large thermal system simulations or complex analyses, it may be more efficient to determine internal energy, enthalpy, and entropy using fundamental thermodynamic relations or curves fit to experimental data. Some of these relations are discussed in the following sections. Also, the thermodynamic relations discussed in those sections are the basis for constructing tables of thermodynamic property data. Further information on the topic may be found in references covering system modeling and thermodynamics (Stoecker 1989, Howell and Buckius 1992).

At least two intensive properties must be known to determine the remaining properties. If two known properties are either  $p$ ,  $v$ , or  $T$  (these are relatively easy to measure and are commonly used in simulations), the third can be determined throughout the range of interest using an equation of state. Furthermore, if the specific heats at zero pressure are known, specific heat can be accurately determined from spectroscopic measurements using statistical mechanics (NASA 1971). Entropy may be considered a function of  $T$  and  $p$ , and from calculus an infinitesimal change in entropy can be written as follows:

$$ds = \left( \frac{\partial s}{\partial T} \right)_p dT + \left( \frac{\partial s}{\partial p} \right)_T dp \quad (26)$$

Likewise, a change in enthalpy can be written as

$$dh = \left( \frac{\partial h}{\partial T} \right)_p dT + \left( \frac{\partial h}{\partial p} \right)_T dp \quad (27)$$

Using the relation  $Tds = dh - vdp$  and the definition of specific heat at constant pressure,  $c_p \equiv (\partial h / \partial T)_p$ , Equation (27) can be rearranged to yield

$$ds = \frac{c_p}{T}dT + \left[ \left( \frac{\partial h}{\partial p} \right)_T - v \right] \frac{dp}{T} \quad (28)$$

Equations (26) and (28) combine to yield  $(\partial s / \partial T)_p = c_p / T$ . Then, using the Maxwell relation  $(\partial s / \partial p)_T = -(\partial v / \partial T)_p$ , Equation (26) may be rewritten as

$$ds = \frac{c_p}{T}dT - \left( \frac{\partial v}{\partial T} \right)_p dp \quad (29)$$

This is an expression for an exact derivative, so it follows that

$$\left( \frac{\partial c_p}{\partial p} \right)_T = -T \left( \frac{\partial^2 v}{\partial T^2} \right)_p \quad (30)$$

Integrating this expression at a fixed temperature yields

$$c_p = c_{p0} - \int_0^p T \left( \frac{\partial^2 v}{\partial T^2} \right)_p dp_T \quad (31)$$

where  $c_{p0}$  is the known zero pressure specific heat, and  $dp_T$  is used to indicate that the integration is performed at a fixed temperature. The second partial derivative of specific volume with respect to temperature can be determined from the equation of state. Thus, Equation (31) can be used to determine the specific heat at any pressure.

Using  $Tds = dh - vdp$ , Equation (29) can be written as

$$dh = c_p dT + \left[ v - T \left( \frac{\partial v}{\partial T} \right)_p \right] dp \quad (32)$$

Equations (28) and (32) may be integrated at constant pressure to obtain

$$s(T_1, p_0) = s(T_0, p_0) + \int_{T_0}^{T_1} \frac{c_p}{T} dT_p \quad (33)$$

$$\text{and } h(T_1, p_0) = h(T_0, p_0) + \int_{T_0}^{T_1} c_p dT \quad (34)$$

Integrating the Maxwell relation  $(\partial s / \partial p)_T = -(\partial v / \partial T)_p$  gives an equation for entropy changes at a constant temperature as

$$s(T_0, p_1) = s(T_0, p_0) - \int_{p_0}^{p_1} \left( \frac{\partial v}{\partial T} \right)_p dp_T \quad (35)$$

Likewise, integrating Equation (32) along an isotherm yields the following equation for enthalpy changes at a constant temperature

$$h(T_0, p_1) = h(T_0, p_0) + \int_{p_0}^{p_1} \left[ v - T \left( \frac{\partial v}{\partial T} \right)_p \right] dp \quad (36)$$

Internal energy can be calculated from  $u = h - pv$ .

Combinations (or variations) of Equations (33) through (36) can be incorporated directly into computer subroutines to calculate properties with improved accuracy and efficiency. However, these equations are restricted to situations where the equation of state is valid and the properties vary continuously. These restrictions are violated by a change of phase such as evaporation and condensation, which are essential processes in air-conditioning and refrigerating devices. Therefore, the Clapeyron equation is of particular value; for evaporation or condensation it gives

$$\left( \frac{dp}{dT} \right)_{sat} = \frac{s_{fg}}{v_{fg}} = \frac{h_{fg}}{Tv_{fg}} \quad (37)$$

where

$s_{fg}$  = entropy of vaporization

$h_{fg}$  = enthalpy of vaporization

$v_{fg}$  = specific volume difference between vapor and liquid phases

If vapor pressure and liquid and vapor density data are known at saturation, and these are relatively easy measurements to obtain, then changes in enthalpy and entropy can be calculated using Equation (37).

### Phase Equilibria for Multicomponent Systems

To understand phase equilibria, consider a container full of a liquid made of two components; the more volatile component is designated  $i$  and the less volatile component  $j$  (Figure 2A). This mixture is all liquid because the temperature is low—but not so low that a solid appears. Heat added at a constant pressure raises the temperature of the mixture, and a sufficient increase causes vapor to form, as shown in Figure 2B. If heat at constant pressure continues to be added, eventually the temperature will become so high that only vapor remains in the container (Figure 2C). A temperature-concentration ( $T$ - $x$ ) diagram is useful for exploring details of this situation.

Figure 3 is a typical  $T$ - $x$  diagram valid at a fixed pressure. The case shown in Figure 2A, a container full of liquid mixture with mole fraction  $x_{i,0}$  at temperature  $T_0$ , is point 0 on the  $T$ - $x$  diagram. When heat is added, the temperature of the mixture increases. The point at which vapor begins to form is the **bubble point**. Starting at point 0, the first bubble will form at temperature  $T_1$ , designated by point 1 on the diagram. The locus of bubble points is the **bubble point curve**, which provides bubble points for various liquid mole fractions  $x_i$ .

When the first bubble begins to form, the vapor in the bubble may not have the  $i$  mole fraction found in the liquid mixture. Rather, the mole fraction of the more volatile species is higher in the vapor than in the liquid. Boiling prefers the more volatile species, and the  $T$ - $x$  diagram shows this behavior. At  $T_1$ , the vapor-forming bubbles have an  $i$  mole fraction of  $y_{i,1}$ . If heat continues to be added, this preferential boiling will deplete the liquid of species

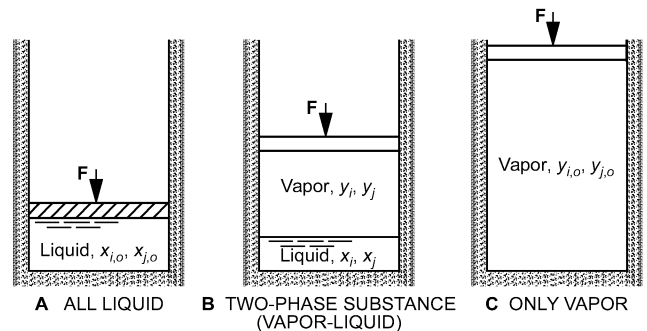


Fig. 2 Mixture of  $i$  and  $j$  Components in Constant Pressure Container

$i$  and the temperature required to continue the process will increase. Again, the  $T$ - $x$  diagram reflects this fact; at point 2 the  $i$  mole fraction in the liquid is reduced to  $x_{i,2}$  and the vapor has a mole fraction of  $y_{i,2}$ . The temperature required to boil the mixture is increased to  $T_2$ . Position 2 on the  $T$ - $x$  diagram could correspond to the physical situation shown in Figure 2B.

If the constant-pressure heating continues, all the liquid eventually becomes vapor at temperature  $T_3$ . At this point the  $i$  mole fraction in the vapor  $y_{i,3}$  equals the starting mole fraction in the all-liquid mixture  $x_{i,1}$ . This equality is required for mass and species conservation. Further addition of heat simply raises the vapor temperature. The final position 4 corresponds to the physical situation shown in Figure 2C.

Starting at position 4 in Figure 3, the removal of heat leads to 3, and further heat removal would cause droplets rich in the less volatile species to form. This point is called the **dew point**, and the locus of dew points is called the **dew-point curve**. The removal of heat will cause the mixture to reverse through points 3, 2, 1, and to starting point 0. Because the composition shifts, the temperature

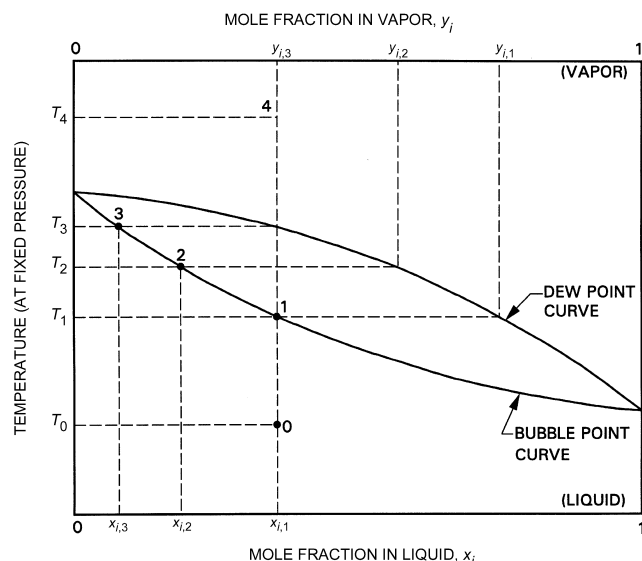


Fig. 3 Temperature-Concentration ( $T$ - $x$ ) Diagram for Zeotropic Mixture

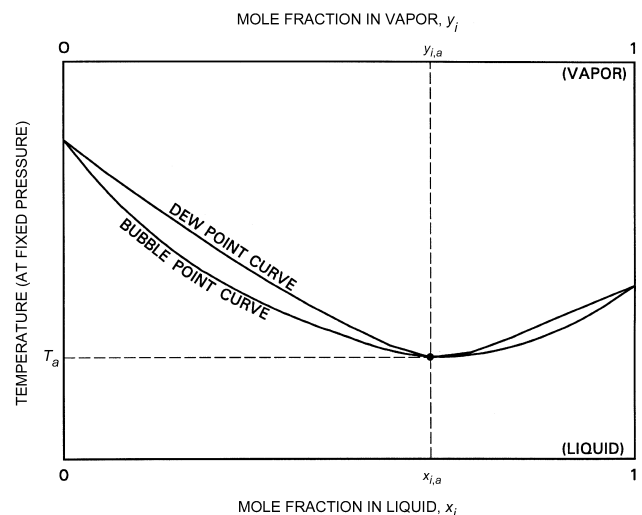


Fig. 4 Azeotropic Behavior Shown on  $T$ - $x$  Diagram

required to boil (or condense) this mixture changes as the process proceeds. This mixture is therefore called **zeotropic**.

Most mixtures have  $T$ - $x$  diagrams that behave as previously described, but some have a markedly different feature. If the dew point and bubble point curves intersect at any point other than at their ends, the mixture exhibits what is called **azeotropic** behavior at that composition. This case is shown as position a in the  $T$ - $x$  diagram of Figure 4. If a container of liquid with a mole fraction  $x_a$  were boiled, vapor would be formed with an identical mole fraction  $y_a$ . The addition of heat at constant pressure would continue with no shift in composition and no temperature glide.

Perfect azeotropic behavior is uncommon, while near azeotropic behavior is fairly common. The azeotropic composition is pressure dependent, so operating pressures should be considered for their impact on mixture behavior. Azeotropic and near-azeotropic refrigerant mixtures find wide application. The properties of an azeotropic mixture are such that they may be conveniently treated as pure substance properties. Zeotropic mixtures, however, require special treatment, using an equation-of-state approach with appropriate mixing rules or using the fugacities with the standard state method (Tassios 1993). Refrigerant and lubricant blends are a zeotropic mixture and can be treated by these methods (see Thome 1995 and Martz et al. 1996a, b).

## COMPRESSION REFRIGERATION CYCLES

### CARNOT CYCLE

The Carnot cycle, which is completely reversible, is a perfect model for a refrigeration cycle operating between two fixed temperatures, or between two fluids at different temperatures and each with infinite heat capacity. Reversible cycles have two important properties: (1) no refrigerating cycle may have a coefficient of performance higher than that for a reversible cycle operated between the same temperature limits, and (2) all reversible cycles, when operated between the same temperature limits, have the same coefficient of performance. Proof of both statements may be found in almost any textbook on elementary engineering thermodynamics.

Figure 5 shows the Carnot cycle on temperature-entropy coordinates. Heat is withdrawn at the constant temperature  $T_R$  from the region to be refrigerated. Heat is rejected at the constant ambient temperature  $T_0$ . The cycle is completed by an isentropic expansion and an isentropic compression. The energy transfers are given by

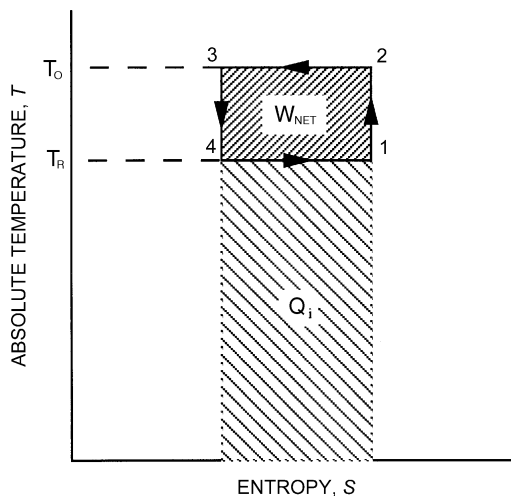


Fig. 5 Carnot Refrigeration Cycle

$$Q_o = T_o(S_2 - S_3)$$

$$Q_i = T_R(S_1 - S_4) = T_R(S_2 - S_3)$$

$$W_{net} = Q_o - Q_i$$

Thus, by Equation (15),

$$\text{COP} = \frac{T_R}{T_o - T_R} \quad (38)$$

**Example 1.** Determine entropy change, work, and coefficient of performance for the cycle shown in Figure 6. Temperature of the refrigerated space  $T_R$  is 250 K and that of the atmosphere  $T_o$  is 300 K. Refrigeration load is 125 kJ.

**Solution:**

$$\Delta S = S_1 - S_4 = Q_i / T_R = 125 / 250 = 0.5 \text{ kJ/K}$$

$$W = \Delta S(T_o - T_R) = 0.5(300 - 250) = 25 \text{ kJ}$$

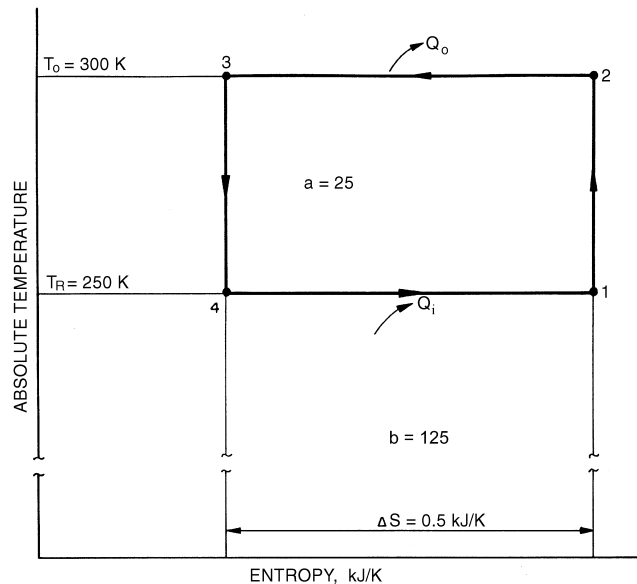
$$\text{COP} = Q_i / (Q_o - Q_i) = Q_i / W = 125 / 25 = 5$$

Flow of energy and its area representation in Figure 6 is:

| Energy | kJ  | Area    |
|--------|-----|---------|
| $Q_i$  | 125 | $b$     |
| $Q_o$  | 150 | $a + b$ |
| $W$    | 25  | $a$     |

The net change of entropy of any refrigerant in any cycle is always zero. In Example 1 the change in entropy of the refrigerated space is  $\Delta S_R = -125/250 = -0.5 \text{ kJ/K}$  and that of the atmosphere is  $\Delta S_o = 125/250 = 0.5 \text{ kJ/K}$ . The net change in entropy of the isolated system is  $\Delta S_{total} = \Delta S_R + \Delta S_o = 0$ .

The Carnot cycle in Figure 7 shows a process in which heat is added and rejected at constant pressure in a two-phase region of a refrigerant. Saturated liquid at state 3 expands isentropically to the low temperature and pressure of the cycle at state d. Heat is added isothermally and isobarically by evaporating the liquid phase refrigerant from state d to state 1. The cold saturated vapor at state 1 is compressed isentropically to the high temperature in the cycle at state b. However the pressure at state b is below the saturation pressure corresponding to the high temperature in the cycle. The



**Fig. 6** Temperature-Entropy Diagram for Carnot Refrigeration Cycle of Example 1

compression process is completed by an isothermal compression process from state b to state c. The cycle is completed by an isothermal and isobaric heat rejection or condensing process from state c to state 3.

Applying the energy equation for a mass of refrigerant  $m$  yields (all work and heat transfer are positive)

$${}_3W_d = m(h_3 - h_d)$$

$${}_1W_b = m(h_b - h_1)$$

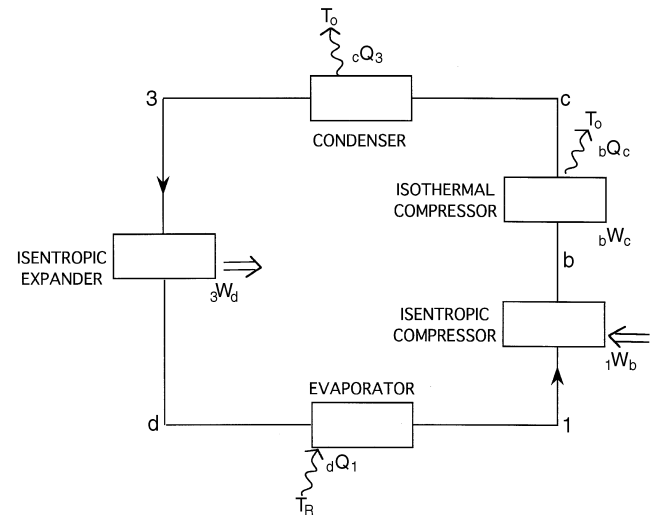
$${}_bW_c = T_o(S_b - S_c) - m(h_b - h_c)$$

$${}_dQ_1 = m(h_1 - h_d) = \text{Area defld}$$

The net work for the cycle is

$$W_{net} = {}_1W_b + {}_bW_c - {}_3W_d = \text{Area d1bc3d}$$

and 
$$\text{COP} = \frac{{}_dQ_1}{W_{net}} = \frac{T_R}{T_o - T_R}$$



**Fig. 7** Carnot Vapor Compression Cycle

### THEORETICAL SINGLE-STAGE CYCLE USING A PURE REFRIGERANT OR AZEOTROPIC MIXTURE

A system designed to approach the ideal model shown in [Figure 7](#) is desirable. A pure refrigerant or an azeotropic mixture can be used to maintain constant temperature during the phase changes by maintaining a constant pressure. Because of such concerns as high initial cost and increased maintenance requirements, a practical machine has one compressor instead of two and the expander (engine or turbine) is replaced by a simple expansion valve. The valve throttles the refrigerant from high pressure to low pressure.

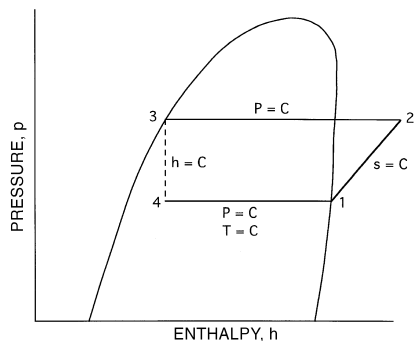
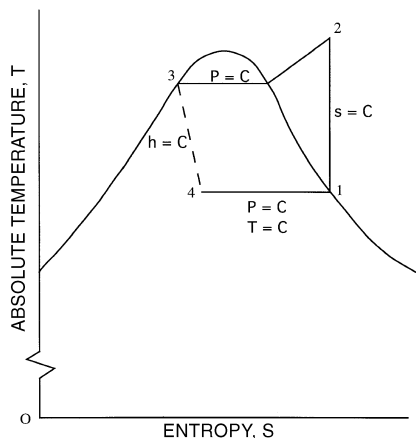
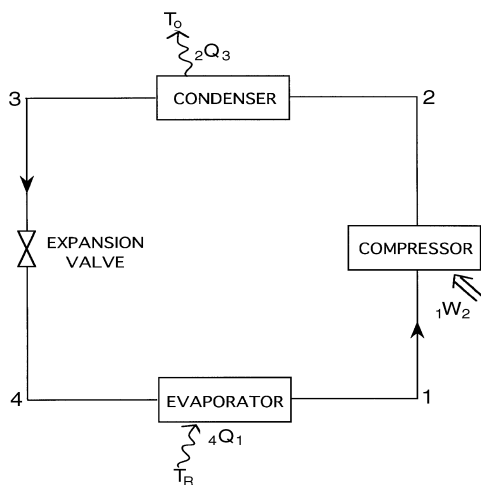


Fig. 8 Theoretical Single-Stage Vapor Compression Refrigeration Cycle

[Figure 8](#) shows the theoretical single-stage cycle used as a model for actual systems.

Applying the energy equation for a mass of refrigerant  $m$  yields

$$\begin{aligned} 4Q_1 &= m(h_1 - h_4) \\ {}_1W_2 &= m(h_2 - h_1) \\ {}_2Q_3 &= m(h_2 - h_3) \\ h_3 &= h_4 \end{aligned} \quad (39)$$

The constant enthalpy throttling process assumes no heat transfer or change in potential or kinetic energy through the expansion valve.

The coefficient of performance is

$$\text{COP} = \frac{{}_4Q_1}{{}_1W_2} = \frac{h_1 - h_4}{h_2 - h_1} \quad (40)$$

The theoretical compressor displacement CD (at 100% volumetric efficiency), is

$$\text{CD} = \dot{m} v_3 \quad (41)$$

which is a measure of the physical size or speed of the compressor required to handle the prescribed refrigeration load.

**Example 2.** A theoretical single-stage cycle using R-134a as the refrigerant operates with a condensing temperature of 30°C and an evaporating temperature of -20°C. The system produces 50 kW of refrigeration. Determine (a) the thermodynamic property values at the four main state points of the cycle, (b) the coefficient of performance of the cycle, (c) the cycle refrigerating efficiency, and (d) rate of refrigerant flow.

**Solution:**

(a) [Figure 9](#) shows a schematic  $p$ - $h$  diagram for the problem with numerical property data. Saturated vapor and saturated liquid properties for states 1 and 3 are obtained from the saturation table for R-134a in Chapter 19 of the 1997 *ASHRAE Handbook—Fundamentals*. Properties for superheated vapor at state 2 are obtained by linear interpolation of the superheat tables for R-134a in Chapter 19 of the 1997 *ASHRAE Handbook—Fundamentals*. Specific volume and specific entropy values for state 4 are obtained by determining the quality of the liquid-vapor mixture from the enthalpy.

$$x_4 = \frac{h_4 - h_f}{h_g - h_f} = \frac{241.65 - 173.82}{386.66 - 173.82} = 0.3187$$

$$\begin{aligned} v_4 &= v_f + x_4(v_g - v_f) = 0.0007374 + 0.3187(0.14744 - 0.0007374) \\ &= 0.04749 \text{ m}^3/\text{kg} \end{aligned}$$

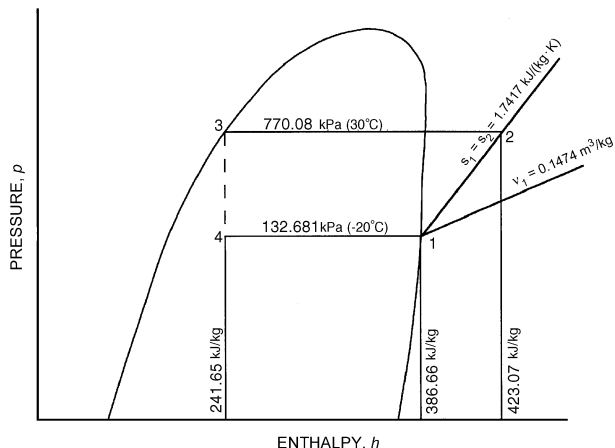


Fig. 9 Schematic  $p$ - $h$  Diagram for Example 2

$$s_4 = s_f + x_4(s_g - s_f) = 0.9009 + 0.3187(1.7417 - 0.9009) = 1.16886 \text{ kJ/(kg} \cdot \text{K)}$$

The property data are tabulated in [Table 1](#).

**Table 1 Thermodynamic Property Data for Example 2**

| State | $t, ^\circ\text{C}$ | $p, \text{kPa}$ | $v, \text{m}^3/\text{kg}$ | $h, \text{kJ/kg}$ | $s, \text{kJ/(kg} \cdot \text{K)}$ |
|-------|---------------------|-----------------|---------------------------|-------------------|------------------------------------|
| 1     | -20.0               | 132.68          | 0.14744                   | 386.66            | 1.7417                             |
| 2     | 37.8                | 770.08          | 0.02798                   | 423.07            | 1.7417                             |
| 3     | 30.0                | 770.08          | 0.00084                   | 241.65            | 1.1432                             |
| 4     | -20.0               | 132.68          | 0.04749                   | 241.65            | 1.1689                             |

(b) By Equation (40)

$$\text{COP} = \frac{386.66 - 241.65}{423.07 - 386.66} = 3.98$$

(c) By Equation (17)

$$\eta_R = \frac{\text{COP}(T_3 - T_1)}{T_1} = \frac{(3.98)(50)}{253.15} = 0.79 \text{ or } 79\%$$

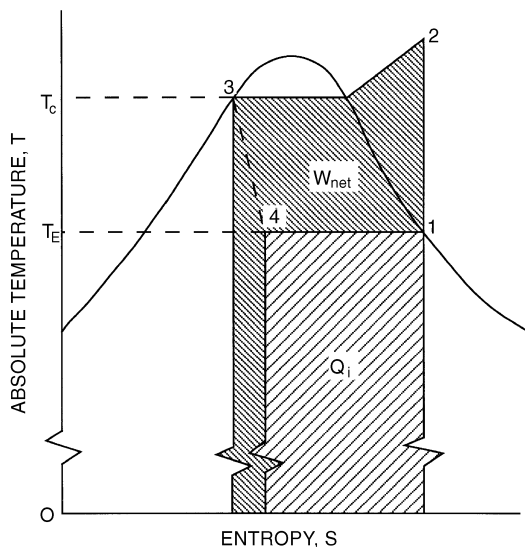
(d) The mass flow of refrigerant is obtained from an energy balance on the evaporator. Thus

$$\dot{m}(h_1 - h_4) = \dot{q}_i = 50 \text{ kW}$$

$$\text{and } \dot{m} = \frac{\dot{Q}_i}{(h_1 - h_4)} = \frac{50}{(386.66 - 241.65)} = 0.345 \text{ kg/s}$$

The saturation temperatures of the single-stage cycle have a strong influence on the magnitude of the coefficient of performance. This influence may be readily appreciated by an area analysis on a temperature-entropy ( $T$ - $s$ ) diagram. The area under a reversible process line on a  $T$ - $s$  diagram is directly proportional to the thermal energy added or removed from the working fluid. This observation follows directly from the definition of entropy [see Equation (8)].

In [Figure 10](#) the area representing  $\dot{Q}_o$  is the total area under the constant pressure curve between states 2 and 3. The area representing the refrigerating capacity  $\dot{Q}_i$  is the area under the constant pressure line connecting states 4 and 1. The net work required  $\dot{W}_{net}$  equals the difference ( $\dot{Q}_o - \dot{Q}_i$ ), which is represented by the shaded area shown on [Figure 10](#).



**Fig. 10 Areas on  $T$ - $s$  Diagram Representing Refrigerating Effect and Work Supplied for Theoretical Single-Stage Cycle**

Because  $\text{COP} = \dot{Q}_i / \dot{W}_{net}$ , the effect on the COP of changes in evaporating temperature and condensing temperature may be observed. For example, a decrease in evaporating temperature  $T_E$  significantly increases  $\dot{W}_{net}$  and slightly decreases  $\dot{Q}_i$ . An increase in condensing temperature  $T_C$  produces the same results but with less effect on  $\dot{W}_{net}$ . Therefore, for maximum coefficient of performance, the cycle should operate at the lowest possible condensing temperature and at the maximum possible evaporating temperature.

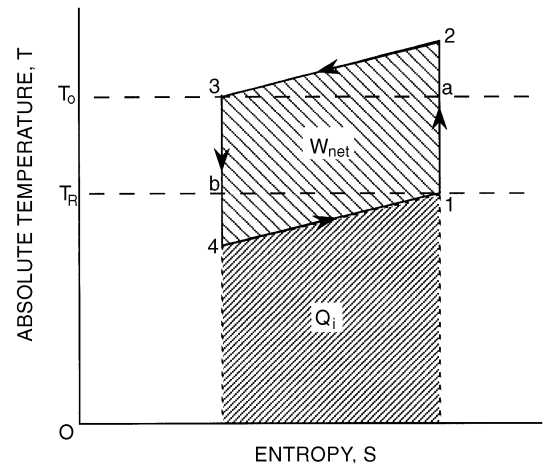
## LORENZ REFRIGERATION CYCLE

The Carnot refrigeration cycle includes two assumptions which make it impractical. The heat transfer capacity of the two external fluids are assumed to be infinitely large so the external fluid temperatures remain fixed at  $T_0$  and  $T_R$  (they become infinitely large thermal reservoirs). The Carnot cycle also has no thermal resistance between the working refrigerant and the external fluids in the two heat exchange processes. As a result, the refrigerant must remain fixed at  $T_0$  in the condenser and at  $T_R$  in the evaporator.

The Lorenz cycle eliminates the first restriction in the Carnot cycle and allows the temperature of the two external fluids to vary during the heat exchange. The second assumption of negligible thermal resistance between the working refrigerant and the two external fluids remains. Therefore the refrigerant temperature must change during the two heat exchange processes to equal the changing temperature of the external fluids. This cycle is completely reversible when operating between two fluids, each of which has a finite but constant heat capacity.

[Figure 11](#) is a schematic of a Lorenz cycle. Note that this cycle does not operate between two fixed temperature limits. Heat is added to the refrigerant from state 4 to state 1. This process is assumed to be linear on  $T$ - $s$  coordinates, which represents a fluid with constant heat capacity. The temperature of the refrigerant is increased in an isentropic compression process from state 1 to state 2. Process 2-3 is a heat rejection process in which the refrigerant temperature decreases linearly with heat transfer. The cycle is concluded with an isentropic expansion process between states 3 and 4.

The heat addition and heat rejection processes are parallel so the entire cycle is drawn as a parallelogram on  $T$ - $s$  coordinates. A Carnot refrigeration cycle operating between  $T_0$  and  $T_R$  would lie between states 1, a, 3, and b. The Lorenz cycle has a smaller refrigerating effect than the Carnot cycle and more work is required. However this cycle is a more practical reference to use than the Carnot cycle when a refrigeration system operates between two single-phase fluids such as air or water.



**Fig. 11 Processes of Lorenz Refrigeration Cycle**

The energy transfers in a Lorenz refrigeration cycle are as follows, where  $\Delta T$  is the temperature change of the refrigerant during each of the two heat exchange processes.

$$Q_0 = (T_0 + \Delta T/2)(S_2 - S_3)$$

$$Q_i = (T_R - \Delta T/2)(S_1 - S_4) = (T_R - \Delta T/2)(S_2 - S_3)$$

$$W_{net} = Q_0 - Q_R$$

Thus by Equation (15),

$$\text{COP} = \frac{T_R - (\Delta T/2)}{T_0 - T_R + \Delta T} \quad (42)$$

**Example 3.** Determine the entropy change, the work required, and the coefficient of performance for the Lorenz cycle shown in Figure 11 when the temperature of the refrigerated space is  $T_R = 250$  K, the ambient temperature is  $T_0 = 300$  K, the  $\Delta T$  of the refrigerant is 5 K and the refrigeration load is 125 kJ.

**Solution:**

$$\Delta S = \int_4^1 \frac{Q_i}{T} = \frac{Q_i}{T_R - (\Delta T/2)} = \frac{125}{247.5} = 0.5051 \text{ kJ/K}$$

$$Q_0 = [T_0 + (\Delta T/2)]\Delta S = (300 + 2.5)0.5051 = 152.78 \text{ kJ}$$

$$W_{net} = Q_0 - Q_R = 152.78 - 125 = 27.78 \text{ kJ}$$

$$\text{COP} = \frac{T_R - (\Delta T/2)}{T_0 - T_R + \Delta T} = \frac{250 - (5/2)}{300 - 250 + 5} = \frac{247.5}{55} = 4.50$$

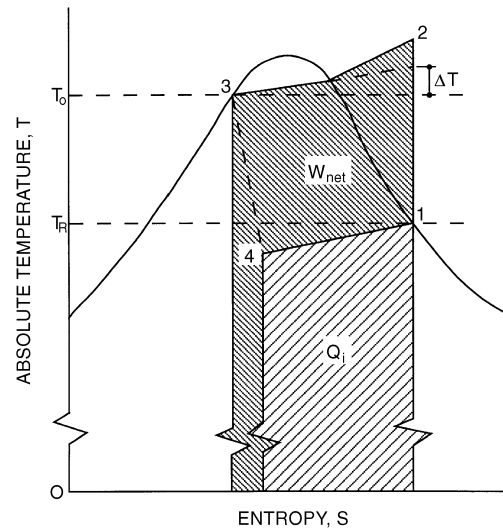
Note that the entropy change for the Lorenz cycle is larger than for the Carnot cycle at the same temperature levels and the same capacity (see Example 1). That is, the heat rejection is larger and the work requirement is also larger for the Lorenz cycle. This difference is caused by the finite temperature difference between the working fluid in the cycle compared to the bounding temperature reservoirs. However, as discussed previously, the assumption of constant temperature heat reservoirs is not necessarily a good representation of an actual refrigeration system because of the temperature changes that occur in the heat exchangers.

### THEORETICAL SINGLE-STAGE CYCLE USING ZEOTROPIC REFRIGERANT MIXTURE

A practical method to approximate the Lorenz refrigeration cycle is to use a fluid mixture as the refrigerant and the four system components shown in Figure 8. When the mixture is not azeotropic and the phase change processes occur at constant pressure, the temperatures change during the evaporation and condensation processes and the theoretical single-stage cycle can be shown on  $T$ - $s$  coordinates as in Figure 12. This can be compared with Figure 10 in which the system is shown operating with a pure simple substance or an azeotropic mixture as the refrigerant. Equations (14), (15), (39), (40), and (41) apply to this cycle and to conventional cycles with constant phase change temperatures. Equation (42) should be used as the reversible cycle COP in Equation (17).

For zeotropic mixtures, the concept of constant saturation temperatures does not exist. For example, in the evaporator, the refrigerant enters at  $T_4$  and exits at a higher temperature  $T_1$ . The temperature of saturated liquid at a given pressure is the **bubble point** and the temperature of saturated vapor at a given pressure is called the **dew point**. The temperature  $T_3$  on Figure 12 is at the bubble point at the condensing pressure and  $T_1$  is at the dew point at the evaporating pressure.

An analysis of areas on a  $T$ - $s$  diagram representing additional work and reduced refrigerating effect from a Lorenz cycle operating



**Fig. 12** Areas on  $T$ - $s$  Diagram Representing Refrigerating Effect and Work Supplied for Theoretical Single-Stage Cycle Using Zeotropic Mixture as Refrigerant

between the same two temperatures  $T_1$  and  $T_3$  with the same value for  $\Delta T$  can be performed. The cycle matches the Lorenz cycle most closely when counterflow heat exchangers are used for both the condenser and the evaporator.

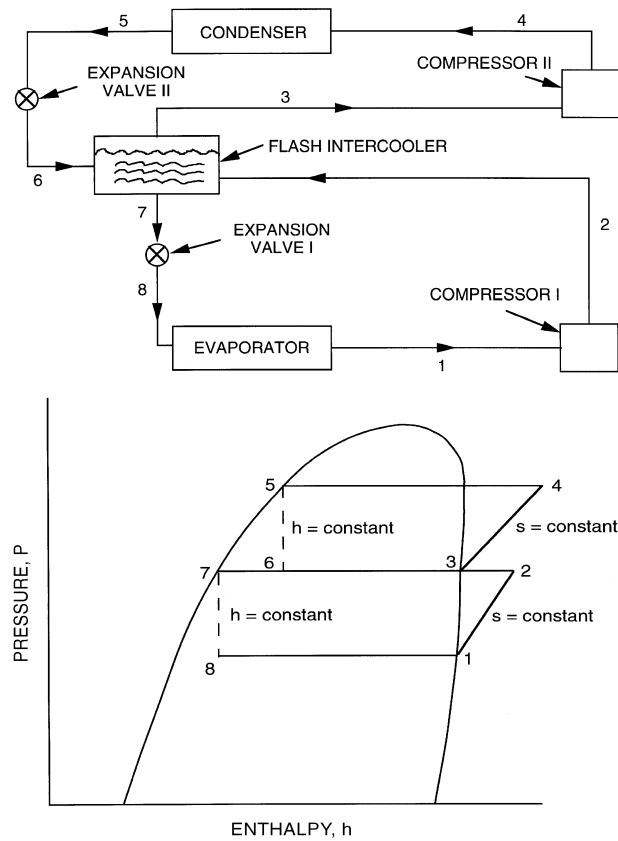
In a cycle that has heat exchangers with finite thermal resistances and finite external fluid capacity rates, Kuehn and Gronseth (1986) showed that a cycle which uses a refrigerant mixture has a higher coefficient of performance than a cycle that uses a simple pure substance as a refrigerant. However, the improvement in COP is usually small. The performance of the cycle that uses a mixture can be improved further by reducing the thermal resistance of the heat exchangers and passing the fluids through them in a counterflow arrangement.

### MULTISTAGE VAPOR COMPRESSION REFRIGERATION CYCLES

Multistage vapor compression refrigeration is used when several evaporators are needed at various temperatures such as in a supermarket or when the temperature of the evaporator becomes very low. Low evaporator temperature indicates low evaporator pressure and low refrigerant density into the compressor. Two small compressors in series have a smaller displacement and usually operate more efficiently than one large compressor that covers the entire pressure range from the evaporator to the condenser. This is especially true in refrigeration systems that use ammonia because of the large amount of superheating that occurs during the compression process.

The thermodynamic analysis of multistage cycles is similar to the analysis of single-stage cycles. The main difference is that the mass flow differs through various components of the system. A careful mass balance and energy balance performed on individual components or groups of components ensures the correct application of the first law of thermodynamics. Care must also be exercised when performing second law calculations. Often the refrigerating load is comprised of more than one evaporator, so the total system capacity is the sum of the loads from all evaporators. Likewise the total energy input is the sum of the work into all compressors. For multistage cycles, the expression for the coefficient of performance given in Equation 15 should be written as

$$\text{COP} = \sum Q_i / W_{net} \quad (43)$$



**Fig. 13 Schematic and Pressure-Enthalpy Diagram for Dual-Compression, Dual-Expansion Cycle of Example 4**

When compressors are connected in series, the vapor between stages should be cooled to bring the vapor to saturated conditions before proceeding to the next stage of compression. Intercooling usually minimizes the displacement of the compressors, reduces the work requirement, and increases the COP of the cycle. If the refrigerant temperature between stages is above ambient, a simple intercooler that removes heat from the refrigerant can be used. If the temperature is below ambient, which is the usual case, the refrigerant itself must be used to cool the vapor. This is accomplished with a flash intercooler. Figure 13 shows a cycle with a flash intercooler installed.

The superheated vapor from compressor I is bubbled through saturated liquid refrigerant at the intermediate pressure of the cycle. Some of this liquid is evaporated when heat is added from the superheated refrigerant. The result is that only saturated vapor at the intermediate pressure is fed to compressor II. A common assumption is to operate the intercooler at about the geometric mean of the evaporating and condensing pressures. This operating point provides the same pressure ratio and nearly equal volumetric efficiencies for the two compressors. Example 4 illustrates the thermodynamic analysis of this cycle.

**Example 4.** Determine the thermodynamic properties of the eight state points shown in Figure 13, the mass flows, and the COP of this theoretical multistage refrigeration cycle when R-134a is the refrigerant. The saturated evaporator temperature is  $-20^{\circ}\text{C}$ , the saturated condensing temperature is  $30^{\circ}\text{C}$ , and the refrigeration load is 50 kW. The saturation temperature of the refrigerant in the intercooler is  $0^{\circ}\text{C}$ , which is nearly at the geometric mean pressure of the cycle.

**Solution:**

Thermodynamic property data are obtained from the saturation and superheat tables for R-134a in Chapter 19 of the 1997 *ASHRAE Handbook—Fundamentals*. States 1, 3, 5, and 7 are obtained directly from the saturation table. State 6 is a mixture of liquid and vapor. The quality is calculated by

**Table 2 Thermodynamic Property Values for Example 4**

| State | Temperature, $^{\circ}\text{C}$ | Pressure, kPa | Specific Volume, $\text{m}^3/\text{kg}$ | Specific Enthalpy, kJ/kg | Specific Entropy, kJ/(kg·K) |
|-------|---------------------------------|---------------|-----------------------------------------|--------------------------|-----------------------------|
| 1     | -20.0                           | 132.68        | 0.14744                                 | 386.66                   | 1.7417                      |
| 2     | 2.8                             | 292.69        | 0.07097                                 | 401.51                   | 1.7417                      |
| 3     | 0.0                             | 292.69        | 0.06935                                 | 398.68                   | 1.7274                      |
| 4     | 33.6                            | 770.08        | 0.02726                                 | 418.68                   | 1.7274                      |
| 5     | 30.0                            | 770.08        | 0.00084                                 | 241.65                   | 1.1432                      |
| 6     | 0.0                             | 292.69        | 0.01515                                 | 241.65                   | 1.1525                      |
| 7     | 0.0                             | 292.69        | 0.00077                                 | 200.00                   | 1.0000                      |
| 8     | -20.0                           | 132.68        | 0.01878                                 | 200.00                   | 1.0043                      |

$$x_6 = \frac{h_6 - h_7}{h_3 - h_7} = \frac{241.65 - 200}{398.68 - 200} = 0.20963$$

Then,

$$\begin{aligned} v_6 &= v_7 + x_6(v_3 - v_7) = 0.000773 + 0.20963(0.06935 - 0.000773) \\ &= 0.01515 \text{ m}^3/\text{kg} \\ s_6 &= s_7 + x_6(s_3 - s_7) = 1.0 + 0.20963(0.7274 - 1.0) \\ &= 1.15248 \text{ kJ}/(\text{kg}\cdot\text{K}) \end{aligned}$$

Similarly for state 8,

$$x_8 = 0.12300, v_8 = 0.01878 \text{ m}^3/\text{kg}, s_8 = 1.0043 \text{ kJ}/(\text{kg}\cdot\text{K})$$

States 2 and 4 are obtained from the superheat tables by linear interpolation. The thermodynamic property data are summarized in Table 2.

The mass flow through the lower circuit of the cycle is determined from an energy balance on the evaporator.

$$\begin{aligned} \dot{m}_1 &= \frac{\dot{Q}_i}{h_1 - h_8} = \frac{50}{386.66 - 200} = 0.2679 \text{ kg/s} \\ \dot{m}_1 &= \dot{m}_2 = \dot{m}_7 = \dot{m}_8 \end{aligned}$$

For the upper circuit of the cycle,

$$\dot{m}_3 = \dot{m}_4 = \dot{m}_5 = \dot{m}_6$$

Assuming the intercooler has perfect external insulation, an energy balance on it is used to compute  $\dot{m}_3$ .

$$\dot{m}_6 h_6 + \dot{m}_2 h_2 = \dot{m}_7 h_7 + \dot{m}_3 h_3$$

Rearranging and solving for  $\dot{m}_3$ ,

$$\dot{m}_3 = \dot{m}_2 \frac{h_7 - h_2}{h_6 - h_3} = 0.2679 \frac{200 - 401.51}{241.65 - 398.68} = 0.3438 \text{ kg/s}$$

$$\begin{aligned} \dot{W}_I &= \dot{m}_1(h_2 - h_1) = 0.2679(401.51 - 386.66) \\ &= 3.978 \text{ kW} \end{aligned}$$

$$\begin{aligned} \dot{W}_{II} &= \dot{m}_3(h_4 - h_3) = 0.3438(418.68 - 398.68) \\ &= 6.876 \text{ kW} \end{aligned}$$

$$\text{COP} = \frac{\dot{Q}_i}{\dot{W}_I + \dot{W}_{II}} = \frac{50}{3.978 + 6.876} = 4.61$$

Examples 2 and 4 have the same refrigeration load and operate with the same evaporating and condensing temperatures. The two-stage cycle in Example 4 has a higher COP and less work input than the single-stage cycle. Also the highest refrigerant temperature leaving the compressor is about  $34^{\circ}\text{C}$  for the two-stage cycle versus about  $38^{\circ}\text{C}$  for the single-stage cycle. These differences are more pronounced for cycles operating at larger pressure ratios.

### ACTUAL REFRIGERATION SYSTEMS

Actual systems operating steadily differ from the ideal cycles considered in the previous sections in many respects. Pressure drops occur everywhere in the system except in the compression process. Heat transfers occur between the refrigerant and its environment in all components. The actual compression process differs substantially from the isentropic compression assumed above. The working fluid is not a pure substance but a mixture of refrigerant and oil. All of these deviations from a theoretical cycle cause irreversibilities within the system. Each irreversibility requires additional power into the compressor. It is useful to understand how these irreversibilities are distributed throughout a real system. Insight is gained that can be useful when design changes are contemplated or operating conditions are modified. Example 5 illustrates how the irreversibilities can be computed in a real system and how they require additional compressor power to overcome. The input data have been rounded off for ease of computation.

**Example 5.** An air-cooled, direct-expansion, single-stage mechanical vapor-compression refrigerator uses R-22 and operates under steady conditions. A schematic drawing of this system is shown in Figure 14. Pressure drops occur in all piping and heat gains or losses occur as indicated. Power input includes compressor power and the power required to operate both fans. The following performance data are obtained:

|                                                           |                                          |
|-----------------------------------------------------------|------------------------------------------|
| Ambient air temperature,                                  | $t_O = 30^\circ\text{C}$                 |
| Refrigerated space temperature, $t_R = -10^\circ\text{C}$ |                                          |
| Refrigeration load,                                       | $\dot{Q}_{\text{evap}} = 7.0 \text{ kW}$ |
| Compressor power input,                                   | $\dot{W}_{\text{comp}} = 2.5 \text{ kW}$ |
| Condenser fan input,                                      | $\dot{W}_{\text{CF}} = 0.15 \text{ kW}$  |
| Evaporator fan input,                                     | $\dot{W}_{\text{EF}} = 0.11 \text{ kW}$  |

Refrigerant pressures and temperatures are measured at the seven locations shown on Figure 14. Table 3 lists the measured and computed thermodynamic properties of the refrigerant neglecting the dissolved oil. A pressure-enthalpy diagram of this cycle is shown in Figure 15 and is compared with a theoretical single-stage cycle operating between the air temperatures  $t_R$  and  $t_O$ .

Compute the energy transfers to the refrigerant in each component of the system and determine the second law irreversibility rate in each component. Show that the total irreversibility rate multiplied by the absolute ambient temperature is equal to the difference between the actual power input and the power required by a Carnot cycle operating between  $t_R$  and  $t_O$  with the same refrigerating load.

**Solution:** The mass flow of refrigerant is the same through all components, so it is only computed once through the evaporator. Each component in the system is analyzed sequentially beginning with the evaporator. Equation (6) is used to perform a first law energy balance on each component and Equation (13) is used for the second law analysis. Note that the temperature used in the second law analysis is the absolute temperature.

*Evaporator:*

Energy balance

$$\dot{Q}_1 = \dot{m}(h_1 - h_7) = 7.0 \text{ kW}$$

$$\dot{m} = \frac{7.0}{(402.08 - 240.13)} = 0.04322 \text{ kg/s}$$

Second law

$$\begin{aligned} \dot{I}_1 &= \dot{m}(s_1 - s_7) - \frac{\dot{Q}_1}{T_R} \\ &= 0.04322(1.7810 - 1.1561) - \frac{7.0}{263.15} \\ &= 0.4074 \text{ W/K} \end{aligned}$$

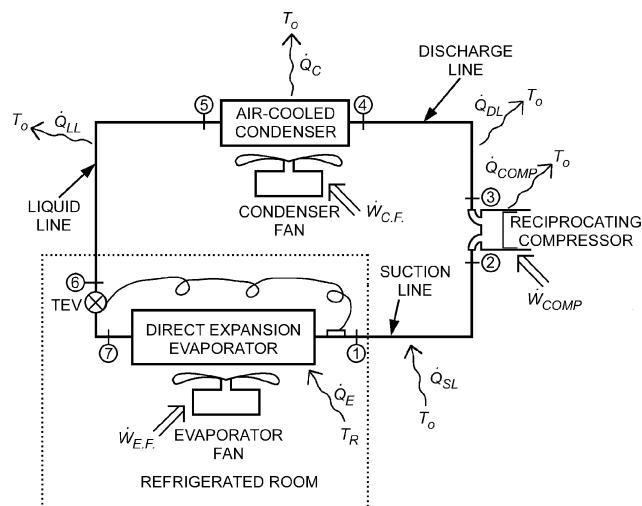
*Suction Line:*

Energy balance

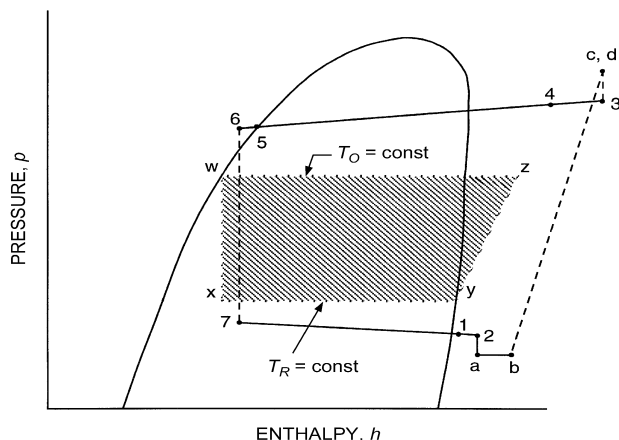
$$\begin{aligned} \dot{Q}_2 &= \dot{m}(h_2 - h_1) \\ &= 0.04322(406.25 - 402.08) = 0.1802 \text{ kW} \end{aligned}$$

**Table 3 Measured and Computed Thermodynamic Properties of Refrigerant 22 for Example 5**

| State | Measured      |                 | Computed                 |                             |                        |
|-------|---------------|-----------------|--------------------------|-----------------------------|------------------------|
|       | Pressure, kPa | Temperature, °C | Specific Enthalpy, kJ/kg | Specific Entropy, kJ/(kg·K) | Specific Volume, m³/kg |
| 1     | 310.0         | -10.0           | 402.08                   | 1.7810                      | 0.07558                |
| 2     | 304.0         | -4.0            | 406.25                   | 1.7984                      | 0.07946                |
| 3     | 1450.0        | 82.0            | 454.20                   | 1.8165                      | 0.02057                |
| 4     | 1435.0        | 70.0            | 444.31                   | 1.7891                      | 0.01970                |
| 5     | 1410.0        | 34.0            | 241.40                   | 1.1400                      | 0.00086                |
| 6     | 1405.0        | 33.0            | 240.13                   | 1.1359                      | 0.00086                |
| 7     | 320.0         | -12.8           | 240.13                   | 1.1561                      | 0.01910                |



**Fig. 14 Schematic of Real, Direct-Expansion, Single-Stage Mechanical Vapor-Compression Refrigeration System**



**Fig. 15 Pressure-Enthalpy Diagram of Actual System and Theoretical Single-Stage System Operating Between Same Inlet Air Temperatures  $T_R$  and  $T_O$**

Second law

$$\begin{aligned} {}_1\dot{I}_2 &= \dot{m}(s_2 - s_1) - \frac{{}_1\dot{Q}_2}{T_o} \\ &= 0.04322(1.7984 - 1.7810) - 0.1802/303.15 \\ &= 0.1575 \text{ W/K} \end{aligned}$$

**Compressor:**

Energy balance

$$\begin{aligned} {}_2\dot{Q}_3 &= \dot{m}(h_3 - h_2) + {}_2\dot{W}_3 \\ &= 0.04322(454.20 - 406.25) - 2.5 \\ &= -0.4276 \text{ kW} \end{aligned}$$

Second law

$$\begin{aligned} {}_2\dot{I}_3 &= \dot{m}(s_3 - s_2) - \frac{{}_2\dot{Q}_3}{T_o} \\ &= 0.04322(1.8165 - 1.7984) - (-0.4276/303.15) \\ &= 2.1928 \text{ kW} \end{aligned}$$

**Discharge Line:**

Energy balance

$$\begin{aligned} {}_3\dot{Q}_4 &= \dot{m}(h_4 - h_3) \\ &= 0.04322(444.31 - 454.20) = -0.4274 \text{ kW} \end{aligned}$$

Second law

$$\begin{aligned} {}_3\dot{I}_4 &= \dot{m}(s_4 - s_3) - \frac{{}_3\dot{Q}_4}{T_o} \\ &= 0.04322(1.7891 - 1.8165) - (-0.4274/303.15) \\ &= 0.2258 \text{ W/K} \end{aligned}$$

**Condenser:**

Energy balance

$$\begin{aligned} {}_4\dot{Q}_5 &= \dot{m}(h_5 - h_4) \\ &= 0.04322(241.4 - 444.31) = -8.7698 \text{ kW} \end{aligned}$$

Second law

$$\begin{aligned} {}_4\dot{I}_5 &= \dot{m}(s_5 - s_4) - \frac{{}_4\dot{Q}_5}{T_o} \\ &= 0.04322(1.1400 - 1.7891) - (-8.7698/303.15) \\ &= 0.8747 \text{ W/K} \end{aligned}$$

**Liquid Line:**

Energy balance

$$\begin{aligned} {}_5\dot{Q}_6 &= \dot{m}(h_6 - h_5) \\ &= 0.04322(240.13 - 241.40) = -0.0549 \text{ kW} \end{aligned}$$

Second law

$$\begin{aligned} {}_5\dot{I}_6 &= \dot{m}(s_6 - s_5) - \frac{{}_5\dot{Q}_6}{T_o} \\ &= 0.04322(1.1359 - 1.1400) - (-0.0549/303.15) \\ &= 0.0039 \text{ W/K} \end{aligned}$$

**Expansion Device:**

Energy balance

$${}_6\dot{Q}_7 = \dot{m}(h_7 - h_6) = 0$$

Second law

$$\begin{aligned} {}_6\dot{I}_7 &= \dot{m}(s_7 - s_6) \\ &= 0.04322(1.1561 - 1.1359) = 0.8730 \text{ W/K} \end{aligned}$$

These results are summarized in [Table 4](#). For the Carnot cycle,

**Table 4** Energy Transfers and Irreversibility Rates for Refrigeration System in Example 5

| Component        | $\dot{Q}$ , kW | $\dot{W}$ , kW | $\dot{I}$ , W/K | $\dot{I}/\dot{I}_{total}$ , % |
|------------------|----------------|----------------|-----------------|-------------------------------|
| Evaporator       | 7.0000         | 0              | 0.4074          | 9                             |
| Suction line     | 0.1802         | 0              | 0.1575          | 3                             |
| Compressor       | -0.4276        | 2.5            | 2.1928          | 46                            |
| Discharge line   | -0.4274        | 0              | 0.2258          | 5                             |
| Condenser        | -8.7698        | 0              | 0.8747          | 18                            |
| Liquid line      | -0.0549        | 0              | 0.0039          | ≈0                            |
| Expansion device | 0              | 0              | 0.8730          | 18                            |
| Totals           | -2.4995        | 2.5            | 4.7351          |                               |

$$\text{COP}_{\text{Carnot}} = \frac{T_R}{T_o - T_R} = \frac{263.15}{40} = 6.579$$

The Carnot power requirement for the 7 kW load is

$$\dot{W}_{\text{Carnot}} = \frac{\dot{Q}_e}{\text{COP}_{\text{Carnot}}} = \frac{7.0}{6.579} = 1.064 \text{ kW}$$

The actual power requirement for the compressor is

$$\begin{aligned} \dot{W}_{\text{comp}} &= \dot{W}_{\text{Carnot}} + \dot{I}_{\text{total}}T_o \\ &= 1.064 + 4.7351(303.15) = 2.4994 \text{ kW} \end{aligned}$$

This result is within computational error of the measured power input to the compressor of 2.5 kW.

The analysis demonstrated in Example 5 can be applied to any actual vapor compression refrigeration system. The only required information for the second law analysis is the refrigerant thermodynamic state points and mass flow rates and the temperatures in which the system is exchanging heat. In this example, the extra compressor power required to overcome the irreversibility in each component is determined. The component with the largest loss is the compressor. This loss is due to motor inefficiency, friction losses, and irreversibilities due to pressure drops, mixing, and heat transfer between the compressor and the surroundings. The unrestrained expansion in the expansion device is also a large loss. This loss could be reduced by using an expander rather than a throttling process. An expander may be economical on large machines.

All heat transfer irreversibilities on both the refrigerant side and the air side of the condenser and evaporator are included in the analysis. The refrigerant pressure drop is also included. The only items not included are the air-side pressure drop irreversibilities of the two heat exchangers. However these are equal to the fan power requirements as all the fan power is dissipated as heat.

An overall second law analysis, such as in Example 5, shows the designer those components with the most losses, and it helps determine which components should be replaced or redesigned to improve performance. However, this type of analysis does not identify the nature of the losses. A more detailed second law analysis in which the actual processes are analyzed in terms of fluid flow and heat transfer is required to identify the nature of the losses (Liang and Kuehn 1991). A detailed analysis will show that most irreversibilities associated with heat exchangers are due to heat transfer, while pressure drop on the air side causes a very small loss and the refrigerant pressure drop causes a negligible loss. This finding indicates that promoting refrigerant heat transfer at the expense of increasing the pressure drop usually improves performance. This analysis does not provide the cost/benefits associated with reducing component irreversibilities. The use of a thermo-economic technique is required.

## ABSORPTION REFRIGERATION CYCLES

An absorption cycle is a heat-activated thermal cycle. It exchanges only thermal energy with its surroundings—no appreciable mechanical energy is exchanged. Furthermore, no appreciable conversion of heat to work or work to heat occurs in the cycle.

Absorption cycles find use in applications where one or more of the heat exchanges with the surroundings is the useful product. This includes refrigeration, air conditioning, and heat pumping. The two great advantages of this type of cycle in comparison to other cycles with similar product are

- No large rotating mechanical equipment is required
- Any source of heat can be used, including low-temperature sources (e.g., waste heat)

### IDEAL THERMAL CYCLE

All absorption cycles include at least three thermal energy exchanges with their surroundings; that is, energy exchange at three different temperatures. The highest temperature and lowest temperature heat flows are in one direction, and the mid-temperature one (or two) is in the opposite direction. In the **forward cycle**, the extreme temperature (hottest and coldest) heat flows are into the cycle. This cycle is also called the heat amplifier, heat pump, conventional cycle, or Type I cycle. When the extreme temperature heat flows are out of the cycle, it is called a **reverse cycle**, heat transformer, temperature amplifier, temperature booster, or Type II cycle. Figure 16 illustrates both types of thermal cycles.

This fundamental constraint of heat flow into or out of the cycle at three or more different temperatures establishes the first limitation on cycle performance. By the first law of thermodynamics (at steady state),

$$Q_{hot} + Q_{cold} = -Q_{mid} \quad (44)$$

(positive heat quantities are into the cycle)

The second law requires that

$$\frac{Q_{hot}}{T_{hot}} + \frac{Q_{cold}}{T_{cold}} + \frac{Q_{mid}}{T_{mid}} \geq 0 \quad (45)$$

with equality holding in the ideal case.

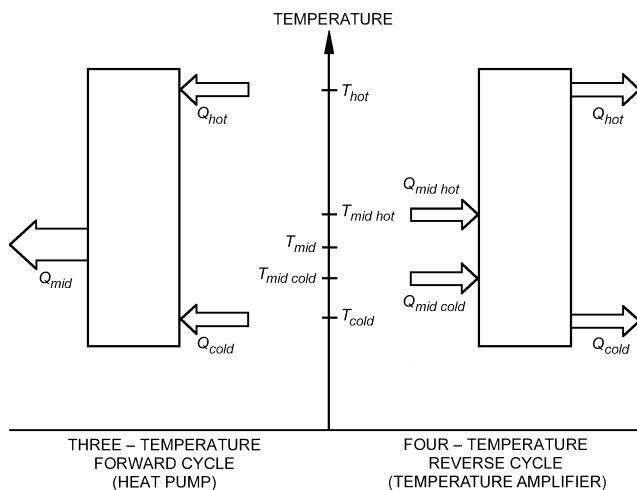


Fig. 16 Thermal Cycles

From these two laws alone (i.e., without invoking any further assumptions) it follows that, for the ideal forward cycle,

$$\text{COP}_{ideal} = \frac{Q_{cold}}{Q_{hot}} = \frac{T_{hot} - T_{mid}}{T_{hot}} \frac{T_{cold}}{T_{mid} - T_{cold}} \quad (46)$$

The heat ratio  $Q_{cold}/Q_{hot}$  is commonly called the **coefficient of performance (COP)**, which is the cooling realized divided by the driving heat supplied.

Heat that is rejected to ambient may be at two different temperatures, creating a **four-temperature cycle**. The ideal COP of the four-temperature cycle is also expressed by Equation (46), with  $T_{mid}$  signifying the entropic mean heat rejection temperature. In that case,  $T_{mid}$  is calculated as follows:

$$T_{mid} = \frac{\frac{Q_{mid hot}}{T_{mid hot}} + \frac{Q_{mid cold}}{T_{mid cold}}}{\frac{Q_{mid hot}}{T_{mid hot}} + \frac{Q_{mid cold}}{T_{mid cold}}} \quad (47)$$

This expression results from assigning all the entropy flow to the single temperature  $T_{mid}$ .

The ideal COP for the four-temperature cycle requires additional assumptions, such as the relationship between the various heat quantities. Under the assumptions that  $Q_{cold} = Q_{mid cold}$  and  $Q_{hot} = Q_{mid hot}$ , the following expression results:

$$\text{COP}_{ideal} = \frac{T_{hot} - T_{mid hot}}{T_{hot}} \frac{T_{cold}}{T_{mid cold}} \frac{T_{cold}}{T_{mid hot}} \quad (48)$$

### WORKING FLUID PHASE CHANGE CONSTRAINTS

Absorption cycles require at least two working substances—a sorbent and a fluid refrigerant; and each substance achieves its cycle function with a phase change. Given this constraint, many combinations are not achievable. The first result of invoking the phase change constraints is that the various heat flows assume known identities. As illustrated in Figure 17, the refrigerant phase changes occur in an evaporator and a condenser, and those of the sorbent in an absorber and a desorber (generator). For the **forward absorption cycle**, the highest temperature heat is always supplied to the generator,

$$Q_{hot} \equiv Q_{gen} \quad (49)$$

and the coldest heat is supplied to the evaporator:

$$Q_{cold} \equiv Q_{evap} \quad (50)$$

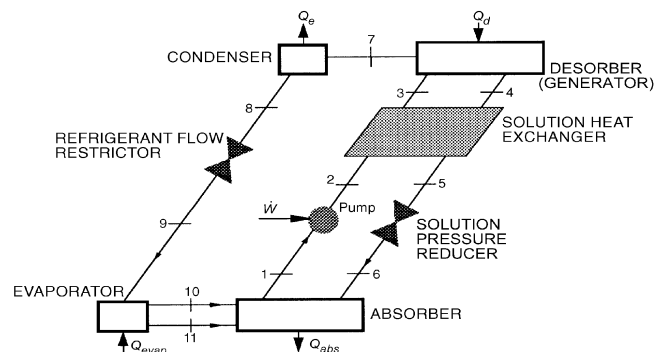


Fig. 17 Single-Effect Absorption Cycle

For the **reverse absorption cycle**, the highest temperature heat is rejected from the absorber, and the lowest temperature heat is rejected from the condenser.

The second result of the phase change constraint is that for all known refrigerants and sorbents over pressure ranges of interest,

$$Q_{evap} \approx Q_{cond} \quad (51)$$

and 
$$Q_{gen} \approx Q_{abs} \quad (52)$$

These two relations are true because the latent heat of phase change (vapor  $\leftrightarrow$  condensed phase) is relatively constant when far removed from the critical point. Thus, each heat input can not be independently adjusted.

The ideal single-effect forward cycle COP expression is

$$COP_{ideal} \leq \frac{T_{gen} - T_{abs}}{T_{gen}} \frac{T_{evap}}{T_{cond} - T_{evap}} \frac{T_{cond}}{T_{abs}} \quad (53)$$

Equality holds only if the heat quantities at each temperature may be adjusted to specific values, which as shown below is not possible.

The third result of invoking the phase change constraint is that only three of the four temperatures  $T_{evap}$ ,  $T_{cond}$ ,  $T_{gen}$ , and  $T_{abs}$  may be independently selected.

Practical liquid absorbents for absorption cycles have a significant negative deviation from behavior predicted by Raoult's law. This has the beneficial effect of reducing the required amount of absorbent recirculation, at the expense of reduced lift and increased sorption duty. The practical effect of the negative deviation is that for most absorbents,

$$\frac{Q_{abs}}{Q_{cond}} \approx 1.2 \text{ to } 1.3 \quad (54)$$

and

$$T_{gen} - T_{abs} \approx 1.2(T_{cond} - T_{evap}) \quad (55)$$

The net result of applying the above approximations and constraints to the ideal cycle COP for the single-effect forward cycle is

$$COP_{ideal} \approx 1.2 \frac{T_{evap} T_{cond}}{T_{gen} T_{abs}} \approx \frac{Q_{cond}}{Q_{abs}} \approx 0.8 \quad (56)$$

In practical terms, the temperature constraint reduces the ideal COP to about 0.9, and the heat quantity constraint further reduces it to about 0.8.

Another useful result is

$$T_{gen \min} = T_{cond} + T_{abs} - T_{evap} \quad (57)$$

where  $T_{gen \min}$  is the minimum generator temperature necessary to achieve a given evaporator temperature.

Alternative approaches are available that lead to nearly the same upper limit on ideal cycle COP. For example, one approach equates the exergy production from a "driving" portion of the cycle to the exergy consumption in a "cooling" portion of the cycle (Tozer et al. 1997). This leads to the expression

$$COP_{ideal} \leq \frac{T_{evap}}{T_{abs}} = \frac{T_{cond}}{T_{gen}} \quad (58)$$

Another approach derives the idealized relationship between the cycle **lift** ( $T_{cond} - T_{evap}$ ) and **drop** ( $T_{gen} - T_{abs}$ ), i.e., between the two temperature differences that define the cycle.

## WORKING FLUIDS

The working fluids for absorption cycles naturally fall into four categories, each requiring a different approach to cycle modeling and thermodynamic analysis. For the liquid absorbents, the important distinction is whether the absorbent is volatile or nonvolatile. In the latter case, the vapor phase is always pure refrigerant (neglecting noncondensables), and analysis is relatively straightforward. For volatile absorbents, wherein vapor concentration is variable, the cycle and component modeling techniques must keep track of vapor concentration as well as liquid concentration.

The sorbent may be either liquid phase or solid phase. For the solid sorbents, the important distinction is whether the solid is a physisorbent (also known as adsorbent) or a chemisorbent. With the physisorbent, the sorbent temperature depends on both pressure and refrigerant loading (bivariance), the same as for the liquid absorbents. In contrast, the chemisorbent temperature does not vary with loading, at least over small ranges, and hence a different modeling approach is required.

Beyond these distinctions, various other characteristics are either necessary or desirable for suitable liquid absorbent-refrigerant pairs, as follows:

**Absence of Solid Phase (Solubility Field).** The refrigerant-absorbent pair should not form a solid over the expected range of composition and temperature. If a solid forms, it will stop flow and cause equipment to shut down. Controls must prevent operation beyond the acceptable solubility range for the pair.

**Relative Volatility.** The refrigerant should be much more volatile than the absorbent so the two can be separated easily. Otherwise, cost and heat requirements may be excessive. Many of the absorbents are effectively nonvolatile.

**Affinity.** The absorbent should have a strong affinity for the refrigerant under conditions in which absorption takes place. Affinity means a negative deviation from Raoult's law and results in an activity coefficient of less than unity for the refrigerant. Strong affinity allows less absorbent to be circulated for the same refrigeration effect, reducing sensible heat losses. A smaller liquid heat exchanger to transfer heat from the absorbent to the pressurized refrigerant-absorption solution is also a benefit of affinity. On the other hand, as affinity increases, extra heat is required in the generators to separate refrigerant from the absorbent, and the COP suffers.

**Pressure.** Operating pressures, established by the thermodynamic properties of the refrigerant, should be moderate. High pressure requires the use of heavy-walled equipment, and significant electrical power may be required to pump the fluids from the low-pressure side to the high-pressure side. Vacuum requires the use of large-volume equipment and special means of reducing pressure drop in the refrigerant vapor paths.

**Stability.** High chemical stability is required because fluids are subjected to severe conditions over many years of service. Instability can cause undesirable formation of gases, solids, or corrosive substances. The purity of all components charged into the system is critical for high performance and corrosion prevention.

**Corrosion.** Most absorption fluids corrode materials used in construction. Therefore, corrosion inhibitors are used.

**Safety.** Precautions as dictated by code are followed in the cases where fluids are toxic, inflammable, or at high pressure. Codes vary according to country and region.

**Transport Properties.** Viscosity, surface tension, thermal diffusivity, and mass diffusivity are important characteristics of the refrigerant-absorbent pair. For example, low viscosity promotes heat and mass transfer and reduces pumping power.

**Latent Heat.** The refrigerant latent heat should be high, so the circulation rate of the refrigerant and absorbent can be minimized.

**Environmental Soundness.** The two parameters of greatest concern are the global warming potential and the ozone depletion potential.

No refrigerant-absorbent pair meets all requirements. Unfortunately, many requirements work at cross-purposes. For example, a greater solubility field goes hand-in-hand with reduced relative volatility. Thus, selection of a working pair is inherently a compromise.

Water-lithium bromide and ammonia-water offer the best compromises of thermodynamic performance and have no known detrimental environmental effect (zero ozone depletion potential and zero global warming potential).

The ammonia-water pair meets most requirements, but its volatility ratio is low and it requires high operating pressures. Ammonia is also a Safety Code Group 2 fluid (ASHRAE *Standard* 15), which restricts its use indoors.

Advantages of the water-lithium bromide pair include high safety, high volatility ratio, high affinity, high stability, and high latent heat. However, this pair tends to form solids and operates at deep vacuum. Because the refrigerant turns to ice at 0°C, the pair cannot be used for low-temperature refrigeration. Lithium bromide (LiBr) crystallizes at moderate concentrations, as would be encountered in air-cooled chillers, which ordinarily limits the pair to applications where the absorber is water-cooled and the concentrations are lower. However, using a combination of salts as the absorbent can reduce this crystallization tendency enough to permit air cooling (Macriss 1968). Other disadvantages of the water-lithium bromide pair include the low operating pressures and high viscosity. This is particularly detrimental to the absorption step; however, alcohols with a high relative molecular mass enhance LiBr absorption. Proper equipment design and additives can overcome these disadvantages.

Other refrigerant-absorbent pairs are listed in [Table 5](#) (Macriss and Zawacki 1989, ISHPC 1999). Several refrigerant-absorbent pairs appear suitable for certain cycles and may solve some problems associated with traditional pairs. However, stability, corrosion, and property information on several is limited. Also, some of the fluids are somewhat hazardous.

**Table 5 Refrigerant-Absorbent Pairs**

| Refrigerant      | Absorbents                     |
|------------------|--------------------------------|
| H <sub>2</sub> O | Salts                          |
|                  | Alkali halides                 |
|                  | LiBr                           |
|                  | LiClO <sub>3</sub>             |
|                  | CaCl <sub>2</sub>              |
|                  | ZnCl <sub>2</sub>              |
|                  | ZnBr                           |
|                  | Alkali nitrates                |
|                  | Alkali thiocyanates            |
|                  | Bases                          |
|                  | Alkali hydroxides              |
|                  | Acids                          |
|                  | H <sub>2</sub> SO <sub>4</sub> |
|                  | H <sub>3</sub> PO <sub>4</sub> |
| NH <sub>3</sub>  | H <sub>2</sub> O               |
|                  | Alkali thiocyanates            |
| TFE<br>(Organic) | NMP                            |
|                  | E181                           |
|                  | DMF                            |
|                  | Pyrrolidone                    |
| SO <sub>2</sub>  | Organic solvents               |

## ABSORPTION CYCLE REPRESENTATIONS

The quantities of interest to absorption cycle designers are temperature, concentration, pressure, and enthalpy. The most useful plots are those with linear scales and in which the key properties plot as straight lines. Some of the following plots are used:

- **Absorption plots** embody the vapor-liquid equilibrium of both the refrigerant and the sorbent. Plots of vapor-liquid equilibrium on linear pressure-temperature coordinates have a logarithmic shape and hence are little used.
- In the **van't Hoff plot** ( $\ln P$  versus  $-1/T$ ), the constant concentration contours plot as nearly straight lines. Thus, it is more readily constructed (e.g., from sparse data) in spite of the awkward coordinates.
- The **Dühring diagram** (solution temperature versus reference temperature) retains the linearity of the van't Hoff plot, while eliminating the complexity of nonlinear coordinates. Thus, it has found extensive use (see [Figure 20](#)). The primary drawback is the need for a reference substance.
- The **Gibbs plot** (solution temperature versus  $T \ln P$ ) retains most of the advantages of the Dühring plot (linear temperature coordinates, concentration contours are straight lines) while eliminating the recourse to a reference substance.
- The **Merkel plot** (enthalpy versus concentration) is used to assist thermodynamic calculations and to solve the distillation problems that arise with volatile absorbents. It has also been used for basic cycle analysis.
- **Temperature-entropy coordinates** are occasionally used to relate absorption cycles to their mechanical vapor compression counterparts.

## CONCEPTUALIZING THE CYCLE

The basic absorption cycle shown in [Figure 17](#) must be altered in many cases to take advantage of the available energy. Examples include the following: (1) the driving heat is much hotter than the minimum required  $T_{gen\ min}$ : a multistage cycle boosts the COP; and (2) the driving heat temperature is below  $T_{gen\ min}$ : a different multistage cycle (half-effect cycle) can reduce the  $T_{gen\ min}$ .

**Multistage** means that one or more of the four basic exchangers (generator, absorber, condenser, evaporator) are present at two or more places in the cycle at different pressures or concentrations. **Multieffect** is a special case of multistaging, signifying the number of times the driving heat is used as it transits the cycle. Thus there are several types of two-stage cycles: the double-effect cycle, the half-effect cycle, and the two-stage, triple-effect cycle.

Two or more single-effect absorption cycles, such as shown in [Figure 17](#), can be combined to form a multistage cycle by coupling any of the components. **Coupling** implies either (1) sharing of component(s) between the cycles to form an integrated single hermetic cycle or (2) alternatively exchanging heat between components belonging to two hermetically separate cycles that operate at (nearly) the same temperature level.

[Figure 18](#) shows a **double-effect absorption cycle** formed by coupling the absorbers and evaporators of two single-effect cycles into an integrated, single hermetic cycle. Heat is transferred between the high-pressure condenser and intermediate-pressure generator. The heat of condensation of the refrigerant (generated in the high-temperature generator) generates additional refrigerant in the lower temperature generator. Thus, the prime energy provided to the high-temperature generator is **cascaded** (used) twice in the cycle, making it a double-effect cycle. With the generation of additional refrigerant from a given heat input, the cycle COP increases. Commercial water-lithium bromide chillers normally use this cycle.

The cycle COP can be further increased by coupling additional components and by increasing the number of cycles that are combined. This way, several different multiple-effect cycles can be

combined by pressure-staging and/or concentration-staging. The double-effect cycle, for example, is formed by pressure-staging two single-effect cycles.

Figure 19 shows twelve generic triple-effect cycles identified by Alefeld and Radermacher (1994). Cycle 5 is a pressure-staged cycle, and Cycle 10 is a concentration-staged cycle. All other cycles are pressure- and concentration-staged. Cycle 1, which is called a dual loop cycle, is the only cycle consisting of two loops that doesn't circulate absorbent in the low-temperature portion of the cycle.

Each of the cycles shown in Figure 19 can be made with one, two, or sometimes three separate **hermetic loops**. Dividing a cycle into separate hermetic loops allows the use of a different working fluid in each loop. Thus, a corrosive and/or high-lift absorbent can be restricted to the loop where it is required, and a conventional additive-enhanced absorbent can be used in other loops to reduce the system cost significantly. As many as 78 hermetic loop configurations can be synthesized from the twelve triple-effect cycles shown in Figure 19. For each hermetic loop configuration, further variations are possible according to the absorbent flow pattern (e.g., series or parallel), the absorption working pairs selected, and various other hardware details. Thus, literally thousands of distinct variations of the triple-effect cycle are possible.

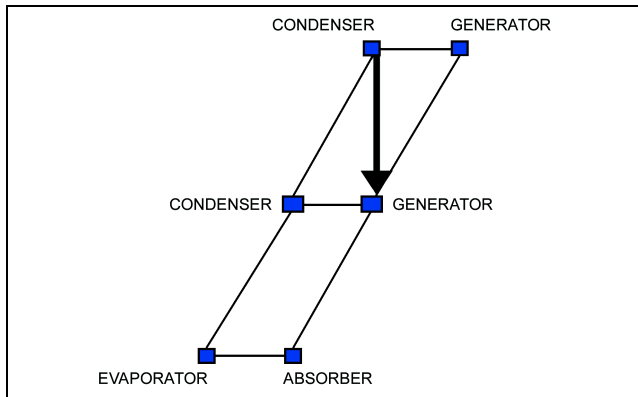


Fig. 18 Double-Effect Absorption Cycle

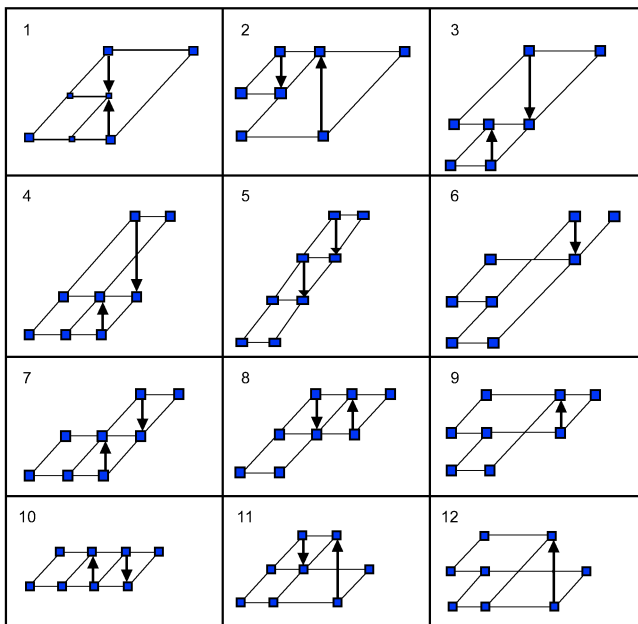


Fig. 19 Generic Triple-Effect Cycles

The ideal analysis can be extended to these multistage cycles (Alefeld and Radermacher 1994). A similar range of cycle variants is possible for situations calling for the half-effect cycle, in which the available heat source temperature is below  $t_{gen\ min}$ .

## ABSORPTION CYCLE MODELING

### Analysis and Performance Simulation

A physical-mathematical model of an absorption cycle consists of four types of thermodynamic equations: mass balances, energy balances, relations describing the heat and mass transfer, and equations for the thermophysical properties of the working fluids.

As an example of simulation, Figure 20 shows a Dühring plot of a single-effect water-lithium bromide absorption chiller. The chiller is hot water driven, rejects waste heat from the absorber and the condenser to a stream of cooling water, and produces chilled water. A simulation of this chiller starts by specifying the assumptions (Table 6) and the design parameters and the operating conditions at the design point (Table 7). Design parameters are the specified  $UA$  values and the flow regime (co/counter/crosscurrent, pool, or film) of all heat exchangers (evaporator, condenser, generator, absorber, solution heat exchanger) and the flow rate of weak solution through the solution pump.

One complete set of input operating parameters could be the design point values of the chilled water and cooling water temperatures  $t_{chill\ in}$ ,  $t_{chill\ out}$ ,  $t_{cool\ in}$ ,  $t_{cool\ out}$ , the hot water flow rate  $\dot{m}_{hot}$ , and the total cooling capacity  $Q_c$ . With this information, a cycle simulation calculates the required hot water temperatures; the cooling water flow rate; and the temperatures, pressures, and concentrations at all internal state points. Some additional assumptions are made that reduce the number of unknown parameters.

Table 6 Assumptions for Single-Effect Water-Lithium Bromide Model (Figure 17)

| Assumptions                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <ul style="list-style-type: none"> <li>Generator and condenser as well as evaporator and absorber are under same pressure</li> <li>Refrigerant vapor leaving the evaporator is saturated pure water</li> <li>Liquid refrigerant leaving the condenser is saturated</li> <li>Strong solution leaving the generator is boiling</li> <li>Refrigerant vapor leaving the generator has the equilibrium temperature of the weak solution at generator pressure</li> <li>Weak solution leaving the absorber is saturated</li> <li>No liquid carryover from evaporator</li> <li>Flow restrictors are adiabatic</li> <li>Pump is isentropic</li> <li>No jacket heat losses</li> <li>The <math>\text{Lmtd}</math> (log mean temperature difference) expression adequately estimates the latent changes</li> </ul> |

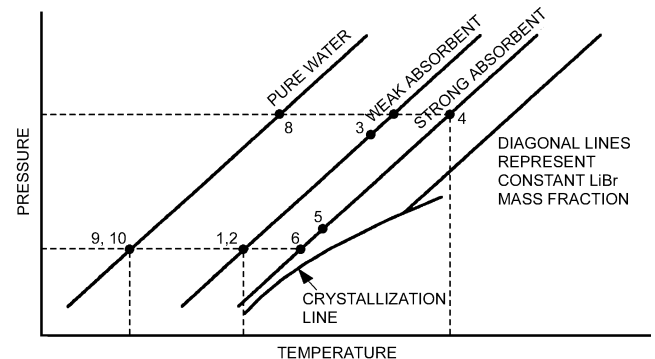


Fig. 20 Single-Effect Water-Lithium Bromide Absorption Cycle Dühring Plot

With these assumptions and the design parameters and operating conditions as specified in [Table 7](#), the cycle simulation can be conducted by solving the following set of equations:

#### Mass Balances

$$\dot{m}_{refr} + \dot{m}_{strong} = \dot{m}_{weak} \quad (59)$$

$$\dot{m}_{strong}\xi_{strong} = \dot{m}_{weak}\xi_{weak} \quad (60)$$

#### Energy Balances

$$\begin{aligned} \dot{Q}_{evap} &= \dot{m}_{refr}(h_{vapor, evap} - h_{liq, cond}) \\ &= \dot{m}_{chill}(h_{chill in} - h_{chill out}) \end{aligned} \quad (61)$$

$$\begin{aligned} \dot{Q}_{evap} &= \dot{m}_{refr}(h_{vapor, gen} - h_{liq, cond}) \\ &= \dot{m}_{cool}(h_{cool out} - h_{cool mean}) \end{aligned} \quad (62)$$

$$\begin{aligned} \dot{Q}_{abs} &= \dot{m}_{refr}h_{vapor, evap} + \dot{m}_{strong}h_{strong, gen} \\ - \dot{m}_{weak}h_{weak, abs} - \dot{Q}_{sol} &= \dot{m}_{cool}(h_{cool mean} - h_{cool in}) \end{aligned} \quad (63)$$

$$\begin{aligned} \dot{Q}_{gen} &= \dot{m}_{refr}h_{vapor, gen} + \dot{m}_{strong}h_{strong, gen} \\ - \dot{m}_{weak}h_{weak, abs} - \dot{Q}_{sol} &= \dot{m}_{hot}(h_{hot in} - h_{hot out}) \end{aligned} \quad (64)$$

**Table 7 Design Parameters and Operating Conditions for Single-Effect Water-Lithium Bromide Absorption Chiller**

|            | Design Parameters                                     | Operating Conditions                                                   |
|------------|-------------------------------------------------------|------------------------------------------------------------------------|
| Evaporator | $UA_{evap} = 319.2$ kW/K, countercurrent film         | $t_{chill in} = 12^\circ\text{C}$<br>$t_{chill out} = 6^\circ\text{C}$ |
| Condenser  | $UA_{cond} = 180.6$ kW/K, countercurrent film         | $t_{cool out} = 35^\circ\text{C}$                                      |
| Absorber   | $UA_{abs} = 186.9$ kW/K, countercurrent film-absorber | $t_{cool in} = 27^\circ\text{C}$                                       |
| Generator  | $UA_{gen} = 143.4$ kW/K, pool-generator               | $\dot{m}_{hot} = 74.4$ kg/s                                            |
| Solution   | $UA_{sol} = 33.8$ kW/K, countercurrent                |                                                                        |
| General    | $\dot{m}_{weak} = 12$ kg/s                            | $\dot{Q}_{evap} = 2148$ kW                                             |

**Table 8 Simulation Results for Single-Effect Water-Lithium Bromide Absorption Chiller**

|            | Internal Parameters                                                                                                                                | Performance Parameters                                                                             |
|------------|----------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|
| Evaporator | $t_{vapor, evap} = 1.8^\circ\text{C}$<br>$p_{sat, evap} = 0.697$ kPa                                                                               | $\dot{Q}_{evap} = 2148$ kW<br>$\dot{m}_{chill} = 85.3$ kg/s                                        |
| Condenser  | $T_{liq, cond} = 46.2^\circ\text{C}$<br>$p_{sat, cond} = 10.2$ kPa                                                                                 | $\dot{Q}_{cond} = 2322$ kW<br>$\dot{m}_{cool} = 158.7$ kg/s                                        |
| Absorber   | $\xi_{weak} = 59.6\%$<br>$t_{weak} = 40.7^\circ\text{C}$<br>$t_{strong, abs} = 49.9^\circ\text{C}$                                                 | $\dot{Q}_{abs} = 2984$ kW<br>$t_{cool, mean} = 31.5^\circ\text{C}$                                 |
| Generator  | $\xi_{strong} = 64.6\%$<br>$t_{strong, gen} = 103.5^\circ\text{C}$<br>$t_{weak, gen} = 92.4^\circ\text{C}$<br>$t_{weak, sol} = 76.1^\circ\text{C}$ | $\dot{Q}_{gen} = 3158$ kW<br>$t_{hot in} = 125^\circ\text{C}$<br>$t_{hot out} = 115^\circ\text{C}$ |
| Solution   | $t_{strong, sol} = 62.4^\circ\text{C}$<br>$t_{weak, sol} = 76.1^\circ\text{C}$                                                                     | $\dot{Q}_{sol} = 825$ kW<br>$\varepsilon = 65.4\%$                                                 |
| General    | $\dot{m}_{vapor} = 0.93$ kg/s<br>$\dot{m}_{strong} = 11.06$ kg/s                                                                                   | COP = 0.68                                                                                         |

$$\begin{aligned} \dot{Q}_{sol} &= \dot{m}_{strong}(h_{strong, gen} - h_{strong, sol}) \\ &= \dot{m}_{weak}(h_{weak, sol} - h_{weak, abs}) \end{aligned} \quad (65)$$

#### Heat Transfer Equations

$$\dot{Q}_{evap} = UA_{evap} \frac{t_{chill in} - t_{chill out}}{\ln\left(\frac{t_{chill in} - t_{vapor, evap}}{t_{chill out} - t_{vapor, evap}}\right)} \quad (66)$$

$$\dot{Q}_{cond} = UA_{cond} \frac{t_{cool out} - t_{cool mean}}{\ln\left(\frac{t_{liq, cond} - t_{cool mean}}{t_{liq, cond} - t_{cool out}}\right)} \quad (67)$$

$$\dot{Q}_{abs} = UA_{abs} \frac{(t_{strong, abs} - t_{cool mean}) - (t_{weak, abs} - t_{cool in})}{\ln\left(\frac{t_{strong, abs} - t_{cool mean}}{t_{weak, abs} - t_{cool in}}\right)} \quad (68)$$

$$\dot{Q}_{gen} = UA_{gen} \frac{(t_{hot in} - t_{strong, gen}) - (t_{hot out} - t_{weak, gen})}{\ln\left(\frac{t_{hot in} - t_{strong, gen}}{t_{hot out} - t_{weak, gen}}\right)} \quad (69)$$

$$\dot{Q}_{sol} = UA_{sol} \frac{(t_{strong, gen} - t_{weak, sol}) - (t_{strong, sol} - t_{weak, abs})}{\ln\left(\frac{t_{strong, gen} - t_{weak, sol}}{t_{strong, sol} - t_{weak, abs}}\right)} \quad (70)$$

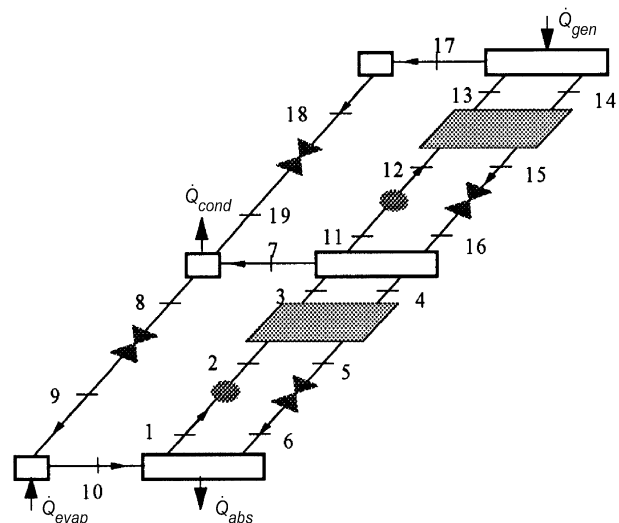
#### Fluid Property Equations at each state point

Thermal Equations of State:  $h_{water}(t, p)$ ,  $h_{so}(t, p, \xi)$   
Two-Phase Equilibrium:  $t_{water, sat}(p)$ ,  $t_{sol, sat}(p, \xi)$

The results are listed in [Table 8](#).

#### Double-Effect Cycle

Double-effect cycle calculations can be performed in a manner similar to that illustrated for the single-effect cycle. Mass and energy balances of the model shown in [Figure 21](#) were calculated using the inputs and assumptions listed in [Table 9](#). The results are shown in [Table 10](#). The COP is quite sensitive to several inputs and



**Fig. 21 Double-Effect Water-Lithium Bromide Absorption Cycle with State Points**

assumptions. In particular, the effectiveness of the solution heat exchangers and the driving temperature difference between the high-temperature condenser and the low-temperature generator influence the COP strongly.

**Table 9 Inputs and Assumptions for Double-Effect Water-Lithium Bromide Model**

| Inputs                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                  |         |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------|---------|
| Capacity                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 | $\dot{Q}_{evap}$ | 1760 kW |
| Evaporator temperature                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | $t_{10}$         | 5.1°C   |
| Desorber solution exit temperature                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | $t_{14}$         | 170.7°C |
| Condenser/absorber low temperature                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | $t_1, t_8$       | 42.4°C  |
| Solution heat exchanger effectiveness                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | $\varepsilon$    | 0.6     |
| Assumptions                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                  |         |
| <ul style="list-style-type: none"> <li>Steady state</li> <li>Refrigerant is pure water</li> <li>No pressure changes except through flow restrictors and pump</li> <li>State points at 1, 4, 8, 11, 14, and 18 are saturated liquid</li> <li>State point 10 is saturated vapor</li> <li>Temperature difference between high-temperature condenser and low-temperature generator is 5 K</li> <li>Parallel flow</li> <li>Both solution heat exchangers have same effectiveness</li> <li>Upper loop solution flow rate is selected such that upper condenser heat exactly matches lower generator heat requirement</li> <li>Flow restrictors are adiabatic</li> <li>Pumps are isentropic</li> <li>No jacket heat losses</li> <li>No liquid carryover from evaporator to absorber</li> <li>Vapor leaving both generators is at equilibrium temperature of entering solution stream</li> </ul> |                  |         |

**Table 10 State Point Data for Double-Effect Water-Lithium Bromide Cycle of Figure 21**

| Point                 | $h$ ,<br>kJ/kg | $\dot{m}$ ,<br>kg/s | $p$ ,<br>kPa | $\dot{Q}$ ,<br>Fraction | $t$ ,<br>°C | $x$ ,<br>% LiBr |
|-----------------------|----------------|---------------------|--------------|-------------------------|-------------|-----------------|
| 1                     | 117.7          | 9.551               | 0.88         | 0.0                     | 42.4        | 59.5            |
| 2                     | 117.7          | 9.551               | 8.36         |                         | 42.4        | 59.5            |
| 3                     | 182.3          | 9.551               | 8.36         |                         | 75.6        | 59.5            |
| 4                     | 247.3          | 8.797               | 8.36         | 0.0                     | 97.8        | 64.6            |
| 5                     | 177.2          | 8.797               | 8.36         |                         | 58.8        | 64.6            |
| 6                     | 177.2          | 8.797               | 0.88         | 0.004                   | 53.2        | 64.6            |
| 7                     | 2661.1         | 0.320               | 8.36         |                         | 85.6        | 0.0             |
| 8                     | 177.4          | 0.754               | 8.36         | 0.0                     | 42.4        | 0.0             |
| 9                     | 177.4          | 0.754               | 0.88         | 0.063                   | 5.0         | 0.0             |
| 10                    | 2510.8         | 0.754               | 0.88         | 1.0                     | 5.0         | 0.0             |
| 11                    | 201.8          | 5.498               | 8.36         | 0.0                     | 85.6        | 59.5            |
| 12                    | 201.8          | 5.498               | 111.8        |                         | 85.6        | 59.5            |
| 13                    | 301.2          | 5.498               | 111.8        |                         | 136.7       | 59.5            |
| 14                    | 378.8          | 5.064               | 111.8        | 0.00                    | 170.7       | 64.6            |
| 15                    | 270.9          | 5.064               | 111.8        |                         | 110.9       | 64.6            |
| 16                    | 270.9          | 5.064               | 8.36         | 0.008                   | 99.1        | 64.6            |
| 17                    | 2787.3         | 0.434               | 111.8        |                         | 155.7       | 0.0             |
| 18                    | 430.6          | 0.434               | 111.8        | 0.0                     | 102.8       | 0.0             |
| 19                    | 430.6          | 0.434               | 8.36         | 0.105                   | 42.4        | 0.0             |
| COP = 1.195           |                |                     |              |                         |             |                 |
|                       |                |                     |              | $q_e$                   | = 1760 kW   |                 |
| $\Delta t = 5$ K      |                |                     |              | $q_g$                   | = 1472 kW   |                 |
| $\varepsilon = 0.600$ |                |                     |              | $q_{shx1}$              | = 617 kW    |                 |
| $q_a = 2328$ kW       |                |                     |              | $q_{shx2}$              | = 546 kW    |                 |
| $q_c = 1023$ kW       |                |                     |              | $\dot{W}_{p1}$          | = 0.043 kW  |                 |
| $q_c = 905$ kW        |                |                     |              | $\dot{W}_{p2}$          | = 0.346 kW  |                 |

## AMMONIA-WATER ABSORPTION CYCLES

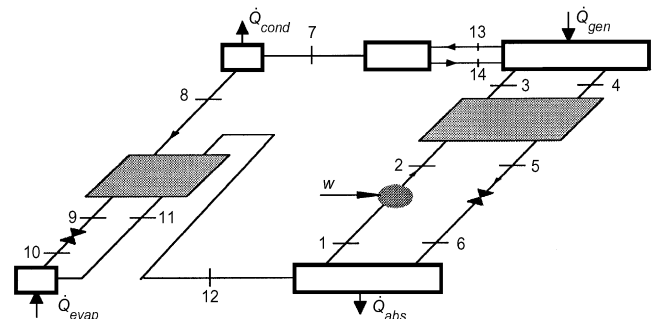
Ammonia-water absorption cycles are similar to the water-lithium bromide cycles, but with some important differences. The differences arise due to the lower latent heat of ammonia compared to water, the volatility of the absorbent, and the different pressure and solubility ranges. The latent heat of ammonia is only about half that of water, so, for the same duty, the refrigerant and absorbent mass circulation rates are roughly double that of water-lithium bromide. As a result, the sensible heat loss associated with heat exchanger approaches is greater. Accordingly, ammonia-water cycles incorporate more techniques to reclaim sensible heat described in Hanna et al. (1995). The refrigerant heat exchanger (RHX), also known as refrigerant subcooler, which improves COP by about 8%, is the most important (Holldorff 1979). Next is the absorber heat exchanger (AHX), accompanied by a generator heat exchanger (GHX) (Phillips 1976). These either replace or supplement the traditional solution heat exchanger (SHX). These components would also benefit the water-lithium bromide cycle, except that the deep vacuum in that cycle makes them impractical there.

The volatility of the water absorbent is also key. It makes the distinction between crosscurrent, cocurrent, and countercurrent mass exchange more important in all of the latent heat exchangers (Briggs 1971). It also requires a distillation column on the high-pressure side. When improperly implemented, this column can impose both cost and COP penalties. Those penalties are avoided by refluxing the column from an internal diabatic section (e.g., solution cooled rectifier [SCR]) rather than with an external reflux pump.

The high-pressure operating regime makes it impractical to achieve multieffect performance via pressure-staging. On the other hand, the exceptionally wide solubility field facilitates concentration-staging. The generator-absorber heat exchange (GAX) cycle is an especially advantageous embodiment of concentration-staging (Modahl and Hayes 1988).

Ammonia-water cycles can equal the performance of water-lithium bromide cycles. The single-effect or basic GAX cycle yields the same performance as a single-effect water-lithium bromide cycle; the branched GAX cycle (Herold et al. 1991) yields the same performance as a water-lithium bromide double-effect cycle; and the VX GAX cycle (Erickson and Rane 1994) yields the same performance as a water-lithium bromide triple-effect cycle. Additional advantages of the ammonia-water cycle include refrigeration capability, air-cooling capability, all mild steel construction, extreme compactness, and capability of direct integration into industrial processes. Between heat-activated refrigerators, gas-fired residential air conditioners, and large industrial refrigeration plants, this technology has accounted for the vast majority of absorption activity over the past century.

Figure 22 shows the diagram of a typical single-effect ammonia-water absorption cycle. The inputs and assumptions in Table 11 are used to calculate a single-cycle solution, which is summarized in Table 12.



**Fig. 22 Single-Effect Ammonia-Water Absorption Cycle**

**Table 11 Inputs and Assumptions for Single-Effect Ammonia/Water Cycle of Figure 22**

| Inputs                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                     |          |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------|----------|
| Capacity                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | $\dot{Q}_{evap}$    | 1760 kW  |
| High-side pressure                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | $p_{high}$          | 1461 kPa |
| Low-side pressure                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | $p_{low}$           | 515 kPa  |
| Absorber exit temperature                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | $t_1$               | 40.6°C   |
| Generator exit temperature                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | $t_4$               | 95°C     |
| Rectifier vapor exit temperature                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | $t_7$               | 55°C     |
| Solution heat exchanger eff.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | $\varepsilon_{shx}$ | 0.692    |
| Refrigerant heat exchanger eff.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | $\varepsilon_{rhx}$ | 0.629    |
| Assumptions                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                     |          |
| <ul style="list-style-type: none"> <li>Steady state</li> <li>No pressure changes except through flow restrictors and pump</li> <li>States at points 1, 4, 8, 11, and 14 are saturated liquid</li> <li>States at point 12 and 13 are saturated vapor</li> <li>Flow restrictors are adiabatic</li> <li>Pump is isentropic</li> <li>No jacket heat losses</li> <li>No liquid carryover from evaporator to absorber</li> <li>Vapor leaving generator is at equilibrium temperature of entering solution stream</li> </ul> |                     |          |

**Table 12 State Point Data for Single-Effect Ammonia/Water Cycle of Figure 22**

| Point                        | $h$ ,<br>kJ/kg | $\dot{m}$ ,<br>kg/s | $p$ ,<br>kPa               | $Q$ ,<br>Fraction | $t$ ,<br>°C | $x$ , Fraction<br>NH <sub>3</sub> |
|------------------------------|----------------|---------------------|----------------------------|-------------------|-------------|-----------------------------------|
| 1                            | -57.2          | 10.65               | 515.0                      | 0.0               | 40.56       | 0.50094                           |
| 2                            | -56.0          | 10.65               | 1461                       |                   | 40.84       | 0.50094                           |
| 3                            | 89.6           | 10.65               | 1461                       |                   | 78.21       | 0.50094                           |
| 4                            | 195.1          | 9.09                | 1461                       | 0.0               | 95.00       | 0.41612                           |
| 5                            | 24.6           | 9.09                | 1461                       |                   | 57.52       | 0.41612                           |
| 6                            | 24.6           | 9.09                | 515.0                      | 0.006             | 55.55       | 0.41612                           |
| 7                            | 1349           | 1.55                | 1461                       | 1.000             | 55.00       | 0.99809                           |
| 8                            | 178.3          | 1.55                | 1461                       | 0.0               | 37.82       | 0.99809                           |
| 9                            | 82.1           | 1.55                | 1461                       |                   | 17.80       | 0.99809                           |
| 10                           | 82.1           | 1.55                | 515.0                      | 0.049             | 5.06        | 0.99809                           |
| 11                           | 1216           | 1.55                | 515.0                      | 0.953             | 6.00        | 0.99809                           |
| 12                           | 1313           | 1.55                | 515.0                      | 1.000             | 30.57       | 0.99809                           |
| 13                           | 1429           | 1.59                | 1461                       | 1.000             | 79.15       | 0.99809                           |
| 14                           | 120.4          | 0.04                | 1461                       | 0.0               | 79.15       | 0.50094                           |
| COP <sub>c</sub> = 0.571     |                |                     | $\dot{Q}_{evap}$ = 1760 kW |                   |             |                                   |
| $\Delta t_{rhx}$ = 7.24 K    |                |                     | $\dot{Q}_{gen}$ = 3083 kW  |                   |             |                                   |
| $\Delta t_{shx}$ = 16.68 K   |                |                     | $\dot{Q}_{rhx}$ = 149 kW   |                   |             |                                   |
| $\varepsilon_{rhx}$ = 0.629  |                |                     | $\dot{Q}_r$ = 170 kW       |                   |             |                                   |
| $\varepsilon_{shx}$ = 0.692  |                |                     | $\dot{Q}_{shw}$ = 1550 kW  |                   |             |                                   |
| $\dot{Q}_{abs}$ = 2869 kW    |                |                     | $\dot{W}$ = 12.4 kW        |                   |             |                                   |
| $\dot{Q}_{cond}$ = 1862.2 kW |                |                     |                            |                   |             |                                   |

## NOMENCLATURE FOR EXAMPLES

|           |                                      |
|-----------|--------------------------------------|
| $c_p$     | = specific heat at constant pressure |
| COP       | = coefficient of performance         |
| $g$       | = local acceleration of gravity      |
| $h$       | = enthalpy, kJ/kg                    |
| $I$       | = irreversibility                    |
| $\dot{I}$ | = irreversibility rate               |
| $m$       | = mass                               |
| $\dot{m}$ | = mass flow, kg/s                    |
| $p$       | = pressure                           |
| $Q$       | = heat energy, kJ                    |
| $\dot{Q}$ | = rate of heat flow, kJ/s            |
| $R$       | = ideal gas constant                 |

|               |                                                        |
|---------------|--------------------------------------------------------|
| $s$           | = entropy, kJ/(kg·K)                                   |
| $S$           | = total entropy                                        |
| $t$           | = temperature, °C                                      |
| $T$           | = absolute temperature, K                              |
| $u$           | = internal energy                                      |
| $W$           | = mechanical or shaft work                             |
| $\dot{W}$     | = rate of work, power                                  |
| $v$           | = specific volume, m <sup>3</sup> /kg                  |
| $V$           | = velocity of fluid                                    |
| $x$           | = mass fraction (of either lithium bromide or ammonia) |
| $x$           | = vapor quality (fraction)                             |
| $z$           | = elevation above horizontal reference plane           |
| $Z$           | = compressibility factor                               |
| $\varepsilon$ | = heat exchanger effectiveness                         |
| $\eta$        | = efficiency                                           |
| $\rho$        | = density, kg/m <sup>3</sup>                           |

## Subscripts

|             |                                          |
|-------------|------------------------------------------|
| <i>abs</i>  | = absorber                               |
| <i>cond</i> | = condenser or cooling mode              |
| <i>cg</i>   | = condenser to generator                 |
| <i>evap</i> | = evaporator                             |
| <i>fg</i>   | = fluid to vapor                         |
| <i>gen</i>  | = generator                              |
| <i>gh</i>   | = high-temperature generator             |
| <i>o, 0</i> | = reference conditions, usually ambient  |
| <i>p</i>    | = pump                                   |
| <i>R</i>    | = refrigerating or evaporator conditions |
| <i>sol</i>  | = solution                               |
| <i>rhx</i>  | = refrigerant heat exchanger             |
| <i>shx</i>  | = solution heat exchanger                |

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