Section **4**

Heat

BY

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4.1 THERMODYNAMICS
by Peter E. Liley

NOTE: References are placed throughout the text for the reader's convenience. (No material is presented relating to the calibration of thermometers at fixed points, etc. Specific details of the measurement of temperature, pressure, etc. are found in Benedict, ''Fundamentals of Temperature, Pressure and Flow Measurements,'' 3d ed. Measurement of other properties is reviewed in Maglic et al., ''Compendium of Thermophysical Property Measurement Methods,'' vol. 1, Plenum Press. The periodical *Metrologia* presents latest developments, particularly for work of a definitive caliber.)

Thermodynamic properties of a variety of other specific materials are listed also in Secs. 4.2, 6.1, and 9.8.

THERMOMETER SCALES

Let F and C denote the readings on the Fahrenheit and Celsius (or centigrade) scales, respectively, for the same temperature. Then

$$C = \frac{5}{9}(F - 32) \qquad F = \frac{9}{5}C + 32$$

If the pressure readings of a constant-volume hydrogen thermometer are extrapolated to zero pressure, it is found that the corresponding temperature is $-273.15°C$, or $-459.67°F$. An **absolute temperature scale** was formerly used on which zero corresponding with zero pressure on the hydrogen thermometer. The basis now used is to define and give a numerical value to the temperature at a single point, the triple point of water, defined as $0.01°C$. The scales are:

Kelvins (K) = degrees Celsius + 273.15
Degrees Rankine (°R) = degrees Fahrenheit + 459.67

EXPANSION OF BODIES BY HEAT

Coefficients of Expansion The **coefficient of linear expansion** a' of a solid is defined as the increment of length in a unit of length for a rise in temperature of 1 deg. Likewise, the **coefficient of cubical expansion** a''' of a solid, liquid, or gas is the increment of volume of a unit volume for a rise of temperature of 1 deg. Denoting these coefficients by a' and a''', respectively, we have

$$a' = \frac{1}{l}\frac{dl}{dt} \qquad a''' = \frac{1}{V}\frac{dV}{dt}$$

in which l denotes length, V volume, and t temperature. For homogeneous solids $a''' = 3a'$, and the **coefficient of area expansion** $a'' = 2a'$.

The coefficients of expansion are, in general, dependent upon the temperature, but for ordinary ranges of temperature, constant mean values may be taken. If lengths, areas, and volumes at $32°F$ ($0°C$) are taken as standard, then these magnitudes at other temperatures t_1 and t_2 are related as follows:

$$\frac{l_1}{l_2} = \frac{1 + a't_1}{1 + a't_2} \qquad \frac{A_1}{A_2} = \frac{1 + a''t_1}{1 + a''t_2} \qquad \frac{V_1}{V_2} = \frac{1 + a'''t_1}{1 + a'''t_2}$$

Since for solids and liquids the expansion is small, the preceding formulas for these bodies become approximately

$$l_2 - l_1 = a'l_1(t_2 - t_1)$$
$$A_2 - A_1 = a''A_1(t_2 - t_1)$$
$$V_2 - V_1 = a'''V_1(t_2 - t_1)$$

The coefficients of cubical expansion for different gases at ordinary temperatures are about the same. From 0 to $212°F$ and at atmospheric pressure, the values multiplied by 1,000 are as follows: for NH_3, 2.11; CO, 2.04; CO_2, 2.07; H_2, 2.03; NO, 2.07. For an ideal gas, the coeffi-

cient at any temperature is the reciprocal of the (absolute) temperature. (See also Table 6.1.10.)

UNITS OF FORCE AND MASS

Force mass, length, and time are related by Newton's second law of motion, which may be expressed as

$$F \sim ma$$

In order to write this as an equality, a constant must be introduced which has magnitude and dimensions. For convenience, in the fps system, the constant may be designated as $1/g_c$. Thus,

$$F = \frac{ma}{g_c}$$

Since this equation must be homogeneous insofar as the dimensions are concerned, the units for g_c are $mL/(t^2F)$. Consider a 1-lb mass, lbm, in the earth's gravitational field, where the acceleration is 32.1740 ft/s². The force exerted on the pound mass will be defined as the pound force, lbf. This system of units gives for g_c the following magnitude and dimensions:

$$1 \text{ lbf} = \frac{(1 \text{ lbm})(32.174 \text{ ft/s}^2)}{g_c}$$

hence

$$g_c = 32.174 \text{ lbm} \cdot \text{ft}/(\text{lbf} \cdot \text{s}^2)$$

Note that g_c may be used with other units, in which case the numerical value changes. The numerical value of g_c for four systems of units is

$$g_c = 32.174 \frac{\text{lbm} \cdot \text{ft}}{\text{lbf} \cdot \text{s}^2} = 1 \frac{\text{slug} \cdot \text{ft}}{\text{lbf} \cdot \text{s}^2} = 1 \frac{\text{lbm} \cdot \text{ft}}{\text{pdl} \cdot \text{s}^2} = 1 \frac{\text{g} \cdot \text{cm}}{\text{dyn} \cdot \text{s}^2}$$

In SI, the constant is chosen to be unity and $F(\text{N}) = m(\text{kg})a(\text{m/s}^2)$. There are four possible constants, and all have been used. (See Blackman, ''SI Units in Engineering,'' Macmillan.)

Consider now the relationship which involves weight, a gravitational force, and mass by applying the basic equation for a body of fixed mass acted upon by a gravitational force g and no other forces. The acceleration of the mass caused by the gravitational force is the acceleration due to gravity g.

Substituting gives the relationship between weight and mass

$$w = \frac{mg}{g_c}$$

If the gravitational acceleration is constant, the weight and mass are in a fixed proportion to each other; hence for accounting purposes in mass balances they can be used interchangeably. This is not possible if g is a variable.

We may now write the relation between mass m and weight w as

$$w = m\frac{g}{g_c}$$

The constant g_c is used throughout the following paragraphs. (An extensive table of conversion factors from customary units to SI units is found in Sec. 1.)

The SI unit of pressure is the newton per square metre. It is a very small pressure, as normal atmospheric pressure is 1.01325×10^5 N/m². While some use has been made of the pressure expressed in kN/m² or kPa (1 Pa = 1 N/m²) and in MN/m² or MPa, the general techni-

cal usage now seems to favor the bar = 10^5 N/m^2 = 10^5 Pa so that 1 atm = 1.01325 bar. For many approximate calculations the atmosphere and the bar can be equated.

Many representative accounts of the measurement of low and high pressure have appeared. (See, for example, Lawrance, *Chem. Eng. Progr.,* **50,** 1954, p. 155; Leck, ''Pressure Measurement in Vacuum Systems,'' Inst. Phys., London, 1957; Peggs, ''High Pressure Measurement Techniques,'' Appl. Sci. Publishers, Barking, Essex.)

MEASUREMENT OF HEAT

Units of Heat   Many units of heat have been dependent on the experimentally determined properties of some substance. To eliminate experimental variations, the unit of heat may be defined in terms of fundamental units. The International Steam Table Conference (London, 1929) defines the Steam Table (IT) calorie as 1/860 of a watthour. One British thermal unit (Btu) is defined as 251.996 IT cal, 778.26 ft · lb.

Previously, the Btu was defined as the heat necessary to raise one pound of water one degree Fahrenheit at some arbitrarily chosen temperature level. Similarly, the calorie was defined as the heat required to heat one gram of water one degree Celsius at 15°C (or at 17.5°C). These units are roughly the same in value as those mentioned above. In SI, the **joule** is the heat unit, and the newton-metre the work unit of energy. The two are equal, so that 1 J = 1 N · m; that is, in SI, the mechanical equivalent of heat is unity.

Heat Capacity and Specific Heat   The **heat capacity** of a material is the amount of heat transferred to raise a unit mass of a material 1 deg in temperature. The ratio of the amount of heat transferred to raise unit mass of a material 1 deg to that required to raise unit mass of water 1 deg at some specified temperature is the **specific heat** of the material. For most engineering purposes, heat capacities may be assumed numerically equal to specific heats. Two heat capacities are generally used, that at constant pressure c_p and that at constant volume c_v. For unit mass, the instantaneous heat capacities are defined as

$$\left(\frac{\partial h}{\partial t}\right)_p = c_p \qquad \left(\frac{\partial u}{\partial t}\right)_v = c_v$$

Over a range in temperature, the mean heat capacities are given by

$$c_{pm} = \frac{1}{t_2 - t_1} \int_{t1}^{t2} c_p \, dt \qquad c_{vm} = \frac{1}{t_2 - t_1} \int_{t1}^{t2} c_v \, dt$$

Denoting by c the heat capacity, the heat required to raise the temperature of w lb of a substance from t_1 to t_2 is $Q = mc(t_2 - t_1)$, provided c is a constant.

In general, c varies with the temperature, though for moderate temperature ranges a constant mean value may be taken. If, however, c is taken as variable, $Q = m \int_{t1}^{t2} c \, dt$. The *mean* heat capacity from 0 to t deg is given by $c_m = \frac{1}{t} \int_0^t c \, dt$. If $c = a_1 + a_2 t + a_3 t^2 + \cdots$

$$c_m = a_1 + \tfrac{1}{2} a_2 t + \tfrac{1}{3} a_3 t^2 + \cdots$$

Data for the specific heat of some solids, liquids, and gases are found in Tables 4.2.22 and 4.2.27.

Specific Heat of Solids   For elements near room temperature, the specific heat may be approximated by the rule of Dulong and Petit, that the specific heat at constant volume approaches $3R$. At lower temperatures, Debye's theory leads to the equation

$$\frac{C_v}{R} = 3 \left(\frac{T}{\Theta}\right) \int_0^{\Theta_{\max} T} \left(\frac{\Theta}{T}\right)^4 \frac{\exp (\Theta/T)}{[\exp (\Theta/T) - 1]^2} \, d\left(\frac{\Theta}{T}\right)$$

commonly known as Debye's function. Figure 4.1.1 shows the variation of c_v/R with T/Θ, as predicted from the equation above. The principal difficulties in using the Debye equation arise from (1) the difficulty in finding unique values of Θ for any given material and (2) the need to consider other contributions to the specific heat. For further references on the Debye equation, see Harrison and Neighbours, *U.S. Naval Post-*

graduate Lab. Rept. 49, Dec. 1964; Overton and Hancock, *Naval Research Lab. Rept. 5502,* 1960; Hilsenrath and Zeigler, *NBS Monograph 49,* 1962. For a thorough discussion of electronic, lattice, and magnetic contributions to specific heat, see Gopal, ''Specific Heats at Low Temperatures,'' Plenum Press, New York. See also Table 6.1.11.
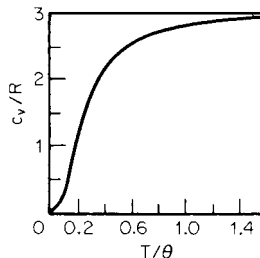
Fig. 4.1.1

For solid compounds at about room temperature, Kopp's approximation is often useful. This states that the specific heat of a solid compound at room temperature is equal to the sum of the specific heats of the atoms forming the compound.

SPECIFIC HEAT OF LIQUIDS

No general theory of any simple practical utility seems to exist for the specific heat of liquids. In ''Thermophysical Properties of Refrigerants,'' ASHRAE, Atlanta, 1976, the interpolation device was a polynomial in temperature, usually up to T^3.

SPECIFIC HEAT OF GASES

The following table summarizes results of kinetic theory for specific heats of gases:

Gas type	c_p/R	c_v/R	c_p/c_v
Monatomic	5/2	3/2	5/3
Diatomic	7/2	5/2	7/5
n degrees of freedom	$(n + 2)/2$	$n/2$	$1 + 2/n$

Determination of the effective number of degrees of freedom limits extending this method to more comlex gases.

Properties of gases are, usually, most readily correlated on the mol basis. A **pound mol** is the mass in pounds equal to the molecular weight. Thus 1 pound mol of oxygen is 32 lb. At the same pressure and temperature, the volume of 1 mol is the same for all perfect gases, i.e., following the gas laws. Experimental findings led Avogadro (1776–1856) to formulate the microscopic hypothesis now known as **Avogadro's principle,** which states that 1 mol of any perfect gas contains the same number of molecules. The number is known as the **Avogadro number** and is equal to

$$N = 6.02214 \times 10^{26} \text{ molecules/(kg · mol)}$$
$$= 2.73160 \times 10^{26} \text{ molecules/(lb · mol)}$$

For perfect gases, $Mc_p - Mc_v = MR = 1.987$.

$$c_i = R/(k - 1) \qquad c_p = Rk(k - 1)$$

Passut and Danner [*Ind. Eng. Chem. Process Design & Dev.* (**11,** 1972, p. 543)] developed a set of thermodynamically consistent polynomials for estimating ideal gas enthalpy, entropy, and heat capacity, fittings being given for 89 compounds. The same journal reported 2 years later an extension of the work to another 57 compounds, by Huang and Daubert. Fittings of a cubic-in-temperature polynomial for 408 hydrocarbons and related compounds in the ideal gas state were reported by Thinh et al. in *Hydrocarbon Processing,* Jan. 1971, pp. 98–104. On p. 153 of a later issue (Aug. 1976), they claimed that the function $C_p = A + B \exp (- c/T^n)$ fitted for 221 hydrocarbons: graphite

and hydrogen gave a more accurate fit. A cubic polynomial in temperature was also fitted for more than 700 compounds from 273 to 1,000 K by Seres et al. in *Acta Phys. Chem.,* Univ. Szegediensis (Hungary), **23,** 1977, pp. 433–468. A 1975 formula of Wilhoit was fitted for 62 substances by A. Harmens in *Proc. Conf. Chemical Thermodynamic Data on Fluids,* IPC Sci. Tech. Press, Guildford, U.K., pp. 112–120. A cubic polynomial fitting for 435 substances appeared in *J. Chem. Eng., Peking* (**2,** 1979, pp. 109–132). The reader is reminded that specific heat at constant pressure values can readily be calculated from tabulated enthalpy-temperature tables, for any physical state. Table 4.2.22 gives values for liquids and gases, while Tables 4.2.27 to 4.2.29 provide similar information for selected solids.

SPECIFIC HEAT OF MIXTURES

If w_1 lb of a substance at temperature t_1 and with specific heat c_1 is mixed with w_2 lb of a second substance at temperature t_2 and with specific heat c_2, provided chemical reaction, heat evolution, or heat absorption does not occur, the specific heat of the mixture is

$$c_m = (w_1 c_1 + w_2 c_2)/(w_1 + w_2)$$

and the temperature of the mixture is

$$t_m = (w_1 c_1 t_1 + w_2 c_2 t_2)/(w_1 c_1 + w_2 c_2)$$

In general, $t_m = \Sigma wct/\Sigma wc$.

To raise the temperature of w_1 lb of a substance having a specific heat c_1 from t_1 to t_m, the weight w_2 of a second substance required is

$$w_2 = w_1 c_1 (t_m - t_1)/c_2 (t_2 - t_m)$$

SPECIFIC HEAT OF SOLUTIONS

For aqueous solutions of salts, the specific heat may be estimated by assuming the specific heat of the solution equal to that of the water alone. Thus, for a 20 percent by weight solution of sodium chloride in water, the specific heat would be approximately 0.8.

Although approximate calculations of mixture properties often consist simply of multiplying the mole fraction of each constituent by the property of each constituent, more accurate calculations are possible. (See ''Technical Data Book—Petroleum Refining'' API, Washington, DC, 1984; Daubert, ''Chemical Engineering Thermodynamics,'' McGraw-Hill; ''The Properties of Gases and Liquids,'' 3d ed., McGraw-Hill; Perry, ''Chemical Engineers Handbook,'' McGraw-Hill; Walas, ''Phase Equilibria in Chemical Engineering,'' Butterworth.)

LATENT HEAT

For pure substances, the heat effects accompanying changes in state at constant pressure are known as latent effects, because no temperature change is evident. Heat of fusion, vaporization, sublimation, and change in crystal form are examples.

The values for the heat of fusion and latent heat of vaporization are presented in Tables 4.2.21 and 4.2.28.

GENERAL PRINCIPLES OF THERMODYNAMICS

Notation

B = availability (by definition, $B = H - T_o S$)
c_p = specific heat at constant pressure
c_v = specific heat at constant volume
E, e = total energy associated with system
g = local acceleration of gravity, ft/s^2
g_c = a dimensional constant
H, h = enthalpy, Btu (by definition $h = u + p_v$)
J = mechanical equivalent of heat = 778.26 ft·lb/Btu = 4.1861 J/cal
$k = c_p/c_v$
m = mass of substance under consideration, lbm

M = molecular weight
p = absolute pressure, lb/ft^2
Q, q = quantity of heat absorbed by system from surroundings, Btu
R = ideal gas constant
R_u = universal gas constant
S, s = entropy
t = temperature, °F
$T = t + 459.69$ = absolute temperature = °R
T_0 = sink or discard temperature
U, u = internal energy
$\bar{v}$ = linear velocity
v = volume
V = total volume
w = weight of substance under consideration, lb
W = external work performed on surroundings during change of state, ft·lb
$Y = \left(\dfrac{p_1}{p_2}\right)^{(k-1)k} - 1$
z = distance above or below chosen datum
g = free energy (by definition, $g = h - Ts$)
f = Helmholtz free energy (by definition, $f = u - Ts$)

In thermodynamics, unless otherwise noted, the convention followed is that the change in any property $\psi = \Delta\psi$ = final value − initial value = $\psi_2 - \psi_1$.

In this notation, small letters usually denote magnitudes referred to a unit mass of the substance, capital letters corresponding magnitudes referred to m units of mass. Thus, v denotes the volume of 1 lb, and $V = mv$, the volume of m lb. Similarly, $U = mu$, $S = ms$, etc. Subscripts are used to indicate different states; thus, p_1, v_1, T_1, u_1, s_1 refer to state 1; p_2, v_2, T_2, u_2, s_2 refer to state 2; Q_{12} is used to denote the heat transferred during the change from state 1 to state 2, and W_{12} denotes the external work done during the same change.

Thermodynamics is the study which deals with energy, the various concepts and laws describing the conversion of one form of energy to another, and the various systems employed to effect the conversions. Thermodynamics deals in general with systems in equilibrium. By means of its fundamental concepts and basic laws, the behavior of an engineering system may be described when the various variables are altered. Thermodynamics covers a very broad field and includes many systems, for example, those dealing with chemical, thermal, mechanical, and electrical force fields and potentials. The quantity of matter within a prescribed boundary under consideration is called the **system,** and everything external to the system is spoken of as the **surroundings.** With a **closed system** there is no interchange of matter between system and surroundings; with an **open system** there is such an interchange. Any change that the system may undergo is known as a **process.** Any process or series of processes in which the system returns to its original condition or state is called a **cycle.**

Heat is energy **in transit** from one mass to another because of a temperature difference between the two. Whenever a force of any kind acts through a distance, **work** is done. Like heat, work is also energy in transit. Work is to be differentiated from the capacity of a quantity of energy to do work.

The two fundamental and general laws of thermodynamics are: (1) energy may be neither created nor destroyed, (2) it is impossible to bring about any change or series of changes the sole net result of which is transfer of energy as heat from a low to a high temperature; in other words, heat will not of itself flow from low to high temperatures.

The **first law of thermodynamics,** one of the very important laws of nature, is the law of conservation of energy. Although the law has been stated in a variety of ways, all have essentially the same meaning. The following are examples of typical statements: Whenever energy is transformed from one form to another, energy is always conserved; energy can neither be created nor destroyed; the sum total of all energy remains constant. The energy conservation hypothesis was stated by a number of investigators; however, experimental evidence was not available until the famous work of J. P. Joule. Transformation of matter

into energy ($E = mc^2$), as in nuclear reactions, is ignored; within the realm of thermodynamics discussed here, mass is conserved.

It has long been the custom to designate the law of conservation of energy, the first law of thermodynamics, when it is used in the analysis of engineering systems involving heat transfer and work. Statements of the first law may be written as follows: Heat and work are mutually convertible; or, since energy can neither be created nor destroyed, the total energy associated with an energy conversion remains constant.

Before the first law may be applied to the analysis of engineering systems, it is necessary to express it in some form of expression. Thus it may be stated for an **open system** as

$$
\left[\begin{array}{c}\text{Net amount of}\\\text{energy added to}\\\text{system as heat}\\\text{and all forms}\\\text{of work}\end{array}\right] + \left[\begin{array}{c}\text{stored}\\\text{energy}\\\text{of mass}\\\text{entering}\\\text{system}\end{array}\right] - \left[\begin{array}{c}\text{stored}\\\text{energy}\\\text{of mass}\\\text{leaving}\\\text{system}\end{array}\right] = \left[\begin{array}{c}\text{net in-}\\\text{crease}\\\text{in stored}\\\text{energy of}\\\text{system}\end{array}\right]
$$

For an open system with fluid entering only at section 1 and leaving only at section 2 and with no electrical, magnetic, or surface-tension effects, this equation may be written as

$$
Q + W + \int \left(h_1 + \frac{v_1^2}{2g_c} + \frac{gz_1}{g_c} \right) \delta m_1
$$
$$
- \int \left(h_2 + \frac{v_2^2}{2g_c} + \frac{gz_2}{g_c} \right) \delta m_2 = U_f - U_i
$$
$$
+ \frac{m_f v_f^2 - m_i v_i^2}{2g_c} + \frac{g}{g_c} (m_f z_f - m_i z_i)
$$

Note that the same sign is given to both heat and work transfers. Heat and work added to the system are given a positive sign; heat lost and work output are given a negative sign. The subscripts i and f refer to entire systems before and after the process occurs, and δm refers to a differential quantity of matter.

It must be remembered that all terms in the first-law equation must be expressed in the same units.

For a **closed stationary system,** the first-law expression reduces to

$$
Q + W = U_2 - U_1
$$

For an **open system** fixed in position but undergoing **steady flow,** e.g., a turbine or reciprocating steam engine, for a mass flow rate of m is

$$
Q + W = m \left[(h_2 - h_1) + \frac{v_2^2 - v_1^2}{2g_c} + \frac{g}{g_c} (z_2 - z_1) \right]
$$

In a **steady-flow** process, the mass rate of flow into the apparatus is equal to the mass rate of flow out; in addition, at any point in the apparatus, the conditions are unchanging with time.

This condition is usually called the **continuity equation** and is written as

$$
\dot{m} = \frac{dm}{dt} = \frac{A\bar{v}}{v} = \frac{A_1 \bar{v}}{v_1} = \frac{A_2 \bar{v}_2}{v_2}
$$

where mass flow rate $\dot{m}$ is related to volume flow rate $\dot{V}$ by $\dot{V} = \dot{m}v$ and A is the cross-sectional area.

Since for many processes the last two terms are often negligible, they will be omitted for simplicity except when such omission would introduce appreciable error.

Work done in overcoming a fluid pressure is measured by $W = -\int p\,dv$, where p is the pressure *effectively* applied to the surroundings for doing work and dv represents the change in volume of the system.

Reversible and Irreversible Processes   A **reversible** process is one in which both the system and the surroundings may be returned to their original states. After an **irreversible** process, this is not possible. No process involving friction or an unbalanced potential can be reversible. No loss in ability to do work is suffered because of a reversible process,

but there is always a loss in ability to do work because of an irreversible process. All actual processes are irreversible. Any series of reversible processes that starts and finishes with the system in the same state is called a **reversible cycle.**

Steady-Flow Processes   With **steady flow,** the conditions at any point in an apparatus through which a fluid is flowing do not change progressively with time. Steady-flow processes involving only mechanical effects are equivalent to similar nonflow processes occurring between two weightless frictionless diaphragms or pistons moving at constant pressure with the system as a whole in motion. Under these circumstances, the total work done by or on a unit amount of fluid is made up of that done on the two diaphragms $p_2 v_2 - p_1 v_1$ and that done on the rest of the surroundings $-\int p\,dv - p_2 v_2 + p_1 v_1$. Differentiating, $-p\,dv - d(p)v = v\,dp$. The net, useful flow work done on the surroundings is $\int v\,dp$. This is often called the shaft work. The net, useful or shaft work differs from the total work by $p_2 v_2 - p_1 v_1$. The first-law equation may be written to indicate this result for a unit mass flow rate as

$$
q + W_{\text{net}} = u_2 - u_1 + p_2 v_2 - p_1 v_1 + \frac{1}{2g_c} (\bar{v}_2^2 - \bar{v}_1^2) + \frac{g}{g_c} (z_2 - z_1)
$$

or, since by definition

$$
u + pv = h
$$
$$
q + W_{\text{net}} = h_2 - h_1 + \frac{1}{2g_c} (\bar{v}_2^2 - \bar{v}_1^2) + \frac{g}{g_c} (z_2 - z_1)
$$

If all net work effects are mechanical,

$$
q + \int v\,dp = h_2 - h_1 + \frac{1}{2g_c} (\bar{v}_2^2 - \bar{v}_1^2) + \frac{g}{g_c} (z_2 - z_1)
$$

Since in evaluating $\int v\,dp$ the pressure is that *effectively* applied to the surroundings, the integration cannot usually be performed except for reversible processes.

If a fluid is passed adiabatically through a conduit (i.e., without heat exchange with the conduit), without doing any net or useful work, and if velocity and potential effects are negligible, $h_2 = h_1$. A process of the kind indicated is the Joule-Thomson flow, and the ratio $(\partial T/\partial p)_h$ for such a flow is the Joule-Thomson coefficient.

If a fluid is passed through a nonadiabatic conduit without doing any net or useful work and if velocity and potential effects are negligible, $q = h_2 - h_1$. This equation is important in the calculation of heat balances on flow apparatus, e.g., condensers, heat exchangers, and coolers.

In many engineering processes the movement of materials is not independent of time; hence the steady-flow equations do not apply. For example, the process of oxygen discharging from a storage bottle represents a transient condition. The pressure within the bottle changes as the amount of oxygen in the tank decreases. The analysis of some transient processes is very complex; however, in order to show the general approach, a simple case will be considered.

The quantity of material flowing into and out of the engineering system in Fig. 4.1.2 varies with time. The amount of work and the heat transfer crossing the system boundary are likewise dependent upon time. According to the law of conservation of mass, the rate of change of mass within the system is equal to the rate of mass flow into and out
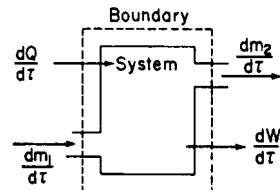

Fig. 4.1.2   Variable-flow system.

of the system. Hence, in terms of mass flow rates,

$$\frac{dm_s}{d\tau} = \frac{dm_1}{d\tau} - \frac{dm_2}{d\tau}$$

For a finite period of time, this relation may be expressed as

$$\Delta m_s = \Delta m_1 - \Delta m_2$$

The first law may be written as follows:

$$\frac{dU_s}{d\tau} = \frac{dQ}{d\tau} + \frac{dW}{d\tau} + \left(h_1 + \frac{\bar{v}_1^2}{2g_c} + \frac{g}{g_c} z_1 \right) \frac{dm_1}{d\tau}$$
$$- \left(h_2 + \frac{\bar{v}_2^2}{2g_c} + \frac{g}{g_c} z_2 \right) \frac{dm_2}{d\tau}$$

Under non-steady-flow conditions the variables h, $\bar{v}$, z may change with time as well as flow rate, in which case the solution is very involved.

If steady-flow conditions prevail, then ΔU_s is equal to 0 and the integrands are independent of time, in which case the above equation reduces to the familiar steady-flow relation.

The **second law of thermodynamics** is a statement that conversion of heat to work is limited by the temperature at which conversion occurs. It may be shown that:

1. No cycle can be more efficient than a reversible cycle operating between given temperature limits.

2. The efficiency of all reversible cycles absorbing heat only at a single constant higher temperature T_1 and rejecting heat only at a single constant lower temperature T_2 must be the same.

3. For all such cycles, the efficiency is

$$\eta = \frac{W}{Q_1} = \frac{T_1 - T_2}{T_1}$$

This is usually called the **Carnot cycle efficiency**. By the first law $W = Q_1 - Q_2$,

$$(Q_1 - Q_2)/Q_1 = (T_1 - T_2)/T_1$$

By algebraic rearrangement,

$$Q_1/T_1 = Q_2/T_2$$

Clapeyron Equation

$$\frac{dp}{dT} = \frac{Q}{TV_{12}}$$

This important relation is useful in calculations relating to constant-pressure evaporation of pure substances. In that case the equation may be written

$$v_{fg} = \frac{h_{fg}}{T\,(dp/dT)}$$

ENTROPY

For reversible cyclical processes in which the temperature varies during heat absorption and rejection, i.e., for any *reversible cycle,* $\int (dQ/T) = 0$. Consequently, for any *reversible process,* $\int (dQ/T)$ is not a function of the particular *reversible path* followed. This integral is called the entropy change, or $\int_1^2 (dQ_{rev}/T) = S_2 - S_1 = S_{12}$. The entropy of a substance is dependent only on its state or condition. Mathematically, dS is a complete or perfect differential and S is a point function in contrast with Q and W which are path functions. For any reversible process, the change in entropy of the system and surroundings is zero, whereas for any irreversible process, the net entropy change is positive.

All actual processes are irreversible and therefore occur with a decrease in the amount of energy available for doing work, i.e., with an increase in unavailable energy. The increase in unavailable energy is the

product of two factors, T_0 the lowest available temperature for heat discard (practically always the temperature of the atmosphere) and the net change in entropy. The increase in unavailable energy is $T_0\,\Delta S_{net}$. Any process that occurs of itself (any spontaneous process) will proceed in such a direction as to result in a net increase in entropy. This is an important concept in the application of thermodynamics to chemical processes.

Three important potentials used in the Maxwell relations are:

1. The familiar potential, known as enthalpy,

$$h = u + pv$$

2. The free energy or the Helmholtz function is defined by the following relation:

$$f = u - Ts$$

3. The free enthalpy or the Gibbs function is defined by

$$g = h - Ts = f + pv = u + pv - Ts$$

The names used for these potentials have not gained universal acceptance. In particular, the name **free energy** is used for g in many textbooks on chemical thermodynamics. One should be very cautious when referring to different books or technical papers and should verify by definition, rather than rely on the name of the potential.

Availability of a system or quantity of energy is defined as $g = h - T_0 s$. In this equation, all quantities except T_0 refer to the system irrespective of the state of the surroundings. T_0 is the lowest temperature available for heat discard. The preceding definition assumes the absence of velocity, potential, and similar effects. When these are not negligible, proper allowance must be made, for example, $g = h - T_0 s + v^2/(2g_c) + (g/g_c)z$. By substitution of $Q = T_0(S_2 - S_1)$ in the appropriate first-law expressions, it may be shown that for any steady-flow process, or for any constant-pressure nonflow process, decrease in availability is equal to the maximum possible (reversible) net work effect with sink for heat discard at T_0.

The availability function g is of particular value in the thermodynamic analysis of changes occurring in the stages of a turbine and is of general utility in determining thermodynamic efficiencies, i.e., the ratio of actual work performed during a process to that which theoretically should have been performed.

Limitations of space preclude a discussion of **availability** or **exergy analysis** which, while basically simple, requires careful evaluation in some processes such as combustion. Refer to the following sources, typical of the many publications of relatively recent date: Krakow, *ASHRAE Trans. Res.,* **97,** no. 1, 1991, pp. 328–336 (dead state analysis); Szargut et al., ''Exergy Analysis of Thermal, Chemical and Metallurgical Processes,'' Hemisphere (262 references); Kotas, *Chem. Eng. Res. Des.,* **64,** May 1986, pp. 212–230, and ''The Exergy Method of Plant Analysis,'' Butterworth; O'Toole, *Proc. Inst. Mech. Eng.,* **204C,** 1990, pp. 329–340; Gallo and Milanez, *Energy,* **15,** no. 2, 1990, pp. 113–121; Horlock and Haywood (*Proc. Inst. Mech. Engrs.,* **199C,** 1985, pp. 11–17) analyze availability in a combined heat and power plant.

The Gibbs function is of particular importance in processes where chemical changes occur. For reversible isothermal steady-flow processes, or for reversible constant-pressure isothermal nonflow processes, change in free energy is equal to net work.

Helmholtz free energy, $f = u - Ts$, is equal to the work during a constant-volume isothermal reversible nonflow process.

All these functions g and f are point functions, and like E, h, and s their differentials are complete or perfect.

PERFECT DIFFERENTIALS. MAXWELL RELATIONS

If z is some function of x and y, in general

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy$$

Substituting M for $(\partial z/\partial x)_y$ and N for $(\partial z/\partial y)_x$,

$$dz = M\,dx + N\,dy$$

But $\dfrac{\partial}{\partial y}\left(\dfrac{\partial z}{\partial x}\right) = \dfrac{\partial}{\partial x}\left(\dfrac{\partial z}{\partial y}\right)$ or $\dfrac{\partial M}{\partial y} = \dfrac{\partial N}{\partial x}$. This is Euler's criterion for integrability. A perfect differential has the characteristics of dz stated above. Many important thermodynamic relations may be derived from the appropriate point function by the use of this relation; see Table 4.1.1.

From the third column of the bottom half of the table, by equating various of the terms which are equal, one may obtain

$$\left(\frac{\partial u}{\partial s}\right)_v = \left(\frac{\partial h}{\partial s}\right)_p \qquad \left(\frac{\partial u}{\partial v}\right)_s = \left(\frac{\partial f}{\partial v}\right)_T$$

$$\left(\frac{\partial h}{\partial p}\right)_s = \left(\frac{\partial g}{\partial p}\right)_T \qquad \left(\frac{\partial g}{\partial T}\right)_p = \left(\frac{\partial f}{\partial T}\right)_v$$

By mathematical manipulation of equations previously given, the following important relations may be formulated:

$$c_v = \left(\frac{\partial q}{\partial T}\right)_v = T\left(\frac{\partial s}{\partial T}\right)_v = \left(\frac{\partial u}{\partial T}\right)_v$$

$$c_p = \left(\frac{\partial q}{\partial T}\right)_p = T\left(\frac{\partial s}{\partial T}\right)_p = \left(\frac{\partial h}{\partial T}\right)_p$$

$$c_p - c_v = T\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_v$$

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

Relations involving q, u, h, and s:

$$dq = c_v\,dT + T\left(\frac{\partial p}{\partial T}\right)_v dv = c_p\,dT - T\left(\frac{\partial v}{\partial T}\right)_p dp$$

$$du = c_v\,dT + \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right]dv$$

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

$$ds = c_v\frac{dT}{T} + \left(\frac{\partial p}{\partial T}\right)_v dv = c_p\frac{dT}{T} - \left(\frac{v}{\partial T}\right)_p dp$$

Since $q + W = du$ and $h = u + pv$, for reversible processes,

$$du = T\,ds - p\,dv \qquad \text{and} \qquad dh = du + p\,dv + v\,dp$$

it follows that

$$v = T\left(\frac{\partial s}{\partial p}\right)_T + \left(\frac{\partial h}{\partial p}\right)_T$$

But from the Maxwell relations,

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T$$

Therefore,

$$\left(\frac{\partial h}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p$$

Similarly,

$$\left(\frac{\partial u}{\partial v}\right)_T = -\left[p - T\left(\frac{\partial p}{\partial T}\right)_v\right]$$

These last two equations give in terms of p, v, and T the necessary relations that must hold for any system, however complex. An equation in p, v, and T for the properties of a substance is called an equation of state. These two equations applicable to any substance or system are known as **thermodynamic equations of state**.

Table 4.1.1 Maxwell Relations

Function	Differential	Maxwell relation
$\Delta u = q + W$	$du = T\,ds - p\,dv$	$\left(\dfrac{\partial T}{\partial v}\right)_s = -\left(\dfrac{\partial p}{\partial s}\right)_v$
$h = u + pv$	$dh = T\,ds + v\,dp$	$\left(\dfrac{\partial T}{\partial p}\right)_s = \left(\dfrac{\partial v}{\partial s}\right)_p$
$f = u - Ts$	$df = -s\,dT - p\,dv$	$\left(\dfrac{\partial s}{\partial v}\right)_T = \left(\dfrac{\partial p}{\partial T}\right)_v$
$g = h - Ts$	$dg = -s\,dT + v\,dp$	$\left(\dfrac{\partial s}{\partial p}\right)_T = -\left(\dfrac{\partial v}{\partial T}\right)_p$

By holding certain variables constant, a second set of relations is obtained:

Differential	Independent variable held constant	Relation
$du = T\,ds - p\,dv$	s	$\left(\dfrac{\partial u}{\partial v}\right)_s = -p$
	v	$\left(\dfrac{\partial u}{\partial s}\right)_v = T$
$dh = T\,ds + v\,dp$	s	$\left(\dfrac{\partial h}{\partial p}\right)_s = v$
	p	$\left(\dfrac{\partial h}{\partial s}\right)_p = T$
$df = -s\,dT - p\,dv$	T	$\left(\dfrac{\partial f}{\partial v}\right)_T = -p$
	v	$\left(\dfrac{\partial f}{\partial T}\right)_v = -s$
$dg = -s\,dT + v\,dp$	T	$\left(\dfrac{\partial g}{\partial p}\right)_T = v$
	p	$\left(\dfrac{\partial g}{\partial T}\right)_p = -s$

Presentation of Thermal Properties Before the laws of thermodynamics can be applied and quantitative results obtained in the analysis of an engineering system, it is necessary to have available the properties of the system, some of which are temperature, pressure, internal energy entropy, and enthalpy. In general, the property of a pure substance under equilibrium conditions may be expressed as a function of two other properties. This is based on the assumption that certain effects, such as gravitational and magnetic, are not important for the condition under investigation. The various properties of a pure substance under equilibrium conditions may be expressed by an equation of state, which in general form follows:

$$p = f(T, v)$$

In this relation the pressure is shown to be a function of both the temperature and the specific volume. Many special forms of equations of state are used in the analysis of engineering systems. Plots of the properties of various pure substances are very useful in studies dealing with thermodynamics. Two-dimensional plots, such as $p - v$, $p - h$, $p - T$, $T - s$, etc., show phase relations and are important in the analysis of cycles.

The constants in the equations of state are usually based on experimental data. The properties may be presented in many different ways, some of which are:

1. As equations of state, e.g., the perfect gas laws and the van der Waals equation.
2. As charts or graphs.
3. As tables.
4. As approximations which may be useful when more reliable data are not available.

IDEAL GAS LAWS

At low pressures and high enough temperatures, in the absence of chemical reaction, all gases approach a condition such that their P-V-T properties may be expressed by the simple relation

$$pv = RT$$

If v is expressed as volume per unit weight, the value of the constant R will be different for different gases. If v is expressed as the volume of one molecular weight of gas, then R_u is the same for all gases in any chosen system of units. Hence $R = R_u/M$.

In general, for any amount of gas, the ideal gas equation becomes

$$pV = nMRT = nR_uT = \frac{m}{M}R_uT$$

where V is now the total gas volume, n is the number of moles of gas in the volume V, M is the molecular weight, and $R_u = MR$ the universal gas constant. An alternative ideal gas equation of state is $pv = R_uT/M$. It is different from the preceding in the use of specific volume v rather than total volume V.

For all ideal gases, $R_u = MR$ in lb·ft is 1,546. One pound mol of any perfect gas occupies a volume of 359 ft³ at 32°F and 1 atm.

For many engineering purposes, use of the gas laws is permissible up to pressures of 100 to 200 lb/in² if the absolute temperatures are at least twice the critical temperatures. Below the critical temperature, errors introduced by use of the gas laws may usually be neglected up to 15 lb/in² pressure although errors of 5 percent are often met when dealing with saturated vapors.

The **van der Waals equation of state**, $p = BT/(v - b) - a/v^2$, is a modification of the ideal gas law which is sometimes useful at high pressures. The quantities B, a, and b are constants.

Many empirical or semiempirical equations of state have been proposed to represent the real variation of pressure with volume and temperature. The Benedict-Webb-Rubin equation is among them; see Perry, ''Chemical Engineers Handbook,'' 6th ed., McGraw-Hill. Computer programs have been devised for the purpose; see Deutsch, ''Microcomputer Programs for Chemical Engineers,'' McGraw-Hill. For computer programs and output for steam and other fluids, including air tables, see Irvine and Liley, ''Steam and Gas Tables with Computer Programs,'' Academic Press.

Approximate *P-V-T* Relations   For many gases, P-V-T data are not available. An approximation useful under such circumstances is based on the observation of van der Waals that in terms of reduced properties most gases approximate a common **reduced equation of state**. The reduced quantities are the actual ones divided by the corresponding critical quantities, e.g., the reduced temperature $T_R = T_{actual}/T_{critical}$, the reduced volume $v_R = v_{actual}/v_{critical}$, the reduced pressure $p_R = p_{actual}/p_{critical}$. The gas laws may be made to apply to any nonperfect gas by the introduction of a correction factor

$$pV = ZNR_uT$$

When the gas laws apply, $Z = 1$ and on a molal basis $Z = pV/(R_uT)$. If on a plot of Z versus p_R lines of constant T_R are drawn, for different substances these are found to fall in narrow bands. Single T_R lines may be drawn to represent approximately the various bands. This has been done in Fig. 4.1.3. To use the chart, only the critical pressure and temperature of the gas need be known.

EXAMPLE.   Find the volume of 1 lb of steam at 5,500 psia and 1200°F (by steam tables, $v = 0.1516$ ft³/lb).

For water, critical temperature = 705.4°F; critical pressure = 3,206.4 psia; reduced temp = 1660/1165 = 1.43; reduced pressure = 5,500/3,206.4 = 1.72; μ (see Fig. 4.1.3) = 0.83, $v = 0.83 (1,546)(1,660)/(18)(5,500)(144) = 0.149$ ft³. Error = 100(0.152 − 0.149)/0.152 = 1.7 percent. If the gas laws had been used, the error would have been 17 percent.

No entirely satisfactory method for calculation for gaseous mixtures has been developed, but the use of average critical constants as proposed by Kay (*Ind. Eng. Chem.*, **28,** 1936, p. 1014) is easy and gives satisfactory results under conditions considerably removed from the critical. He assumes the gaseous mixture can be treated as if it were a single pure gas with a pseudocritical pressure and temperature estimated by a method of molar averaging.

$$(T_c)_{mixture} = (T_c)_a y_a + (T_c)_b y_b + (T_c)_c y_c + \cdots$$
$$(p_c)_{mixture} = (p_c)_a y_a + (p_c)_b y_b + (p_c)_c y_c + \cdots$$

where $(T_c)_a$ is the critical temperature of pure a, etc.; $(p_c)_a$ is the critical pressure of pure a, etc.; and y_a is the mole fraction of a, etc. For a gaseous mixture made up of gases, a, b, c, etc., the pseudocritical constants having been determined, the gaseous mixture is handled on the μ charts as if it were a single pure gas.

IDEAL GAS MIXTURES

Many of the fluids involved in engineering systems are physical mixtures of the permanent gases or one or more of these with superheated or saturated vapors. For example, normal atmospheric air is a mixture of oxygen and nitrogen with traces of other gases, plus superheated or saturated water vapor, or at times saturated vapor and liquid. If the properties of each constituent of a mixture would have to be considered individually during an analysis of a system, the procedures would be
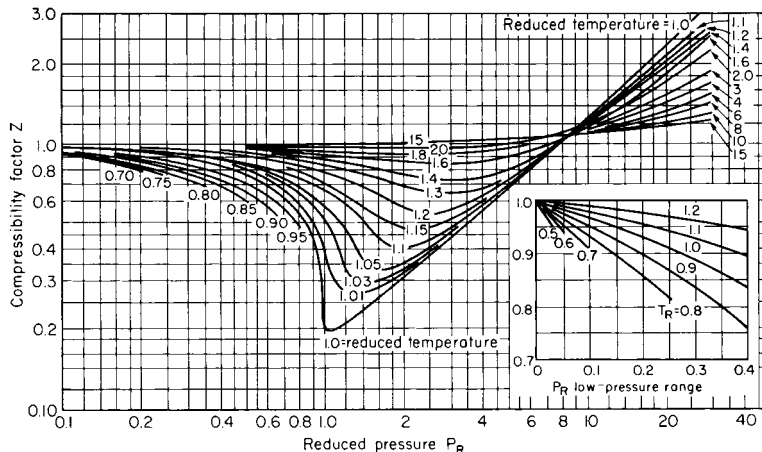
Fig. 4.1.3   Compressibility factors for gases and vapors. (*From Hougen and Watson, ''Chemical Process Principles,''* Wiley.)

very complex. Experience has demonstrated that a mixture of gases may be regarded as an equivalent gas, the properties of which depend upon the kind and proportion of each of the constituents. The general relations applicable to a mixture of perfect gases will be presented. Let V denote the total volume of the mixture, $m_1, m_2, m_3, \ldots$ the masses of the constituent gases, $R_1, R_2, R_3, \ldots$ the corresponding gas constants, and R_m the constant for the mixture. The **partial pressures** of the constituents, i.e., the pressures that the constituents would have if occupying the total volume V, are $p_1 = m_1 R_1 T/V$, $p_2 = m_2 R_2 T/V$, etc.

According to Dalton's law, the **total pressure p of the mixture** is the sum of the partial pressures; i.e., $p = p_1 + p_2 + p_3 + \cdots$. Let $m = m_1 + m_2 + m_3 + \cdots$ denote the total mass of the mixture; then $pV = mR_m T$ and $R_m = \Sigma(m_i R_i)/m$. Also $p_1/p = m_1 R_1/(mR_m)$, $p_2/p = m_2 R_2/(mR_m)$, etc.

Let $V_1, V_2, V_3 + \ldots$ denote the volumes that would be occupied by the constituents at pressure p and temperature T (these are given by the volume composition of the gas). Then $V = V_1 + V_2 + V_3 + \cdots$ and the apparent molecular weight m_m of the mixture is $m_m = \Sigma(m_i V_i)/V$. Then $R_m = 1{,}546/m_m$. The subscript i denotes an individual constituent.

Volume of 1 lb at 32°F and atm pressure $= 359/m_m$.
Mass of 1 ft^3 at 32°F and atm pressure $= 0.002788 m_m$.

The specific **heats of the mixture** are, respectively,

$$c_p = \Sigma(m_i c_{pi})/m \qquad c_v = \Sigma(m_i c_{vi})/m$$

Internal Energy, Enthalpy, and Entropy of an Ideal Gas   If an ideal gas with constant specific heats changes from an initial state p_1, V_1, T_1 to a final state p_2, V_2, T_2, the following equations hold:

$$u_2 - u_1 = mc_v(T_2 - T_1) = (p_2 v_2 - p_1 v_1)(k - 1)$$

$$h_2 - h_1 = mc_p(T_2 - T_1) = k\frac{(p_2 v_2 - p_1 v_1)}{k - 1}$$

$$s_2 - s_1 = m\left(c_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}\right)$$

$$= m\left(c_p \ln \frac{T_2}{T_1} - R \ln \frac{p_2}{p_1}\right) = m\left(c_p \ln \frac{v_2}{v_1} + c_v \ln \frac{p_2}{p_1}\right)$$

In general, the energy per unit mass is $u = c_v T + u_0$, the enthalpy is $h = c_p T + h_0$, and the entropy is $s = c_v \ln T + R \ln v + s_0 = c_p \ln T - R \ln p + s_0' = c_p \ln v + c_p \ln p = s_0''$.

The two fundamental equations for ideal gases are

$$dq = c_v \, dT + p \, dv \qquad dq = c_p \, dT - v \, dp$$

SPECIAL CHANGES OF STATE FOR IDEAL GASES

(Specific heats assumed constant)

In the following formulas, the subscripts 1 and 2 refer to the initial and final states, respectively.

1. *Constant volume:* $p_2/p_1 = T_2/T_1$.

$$Q_{12} = U_2 - U_1 = mc_v(t_2 - t_1) = V(p_2 - p_1)/(k - 1)$$
$$W_{12} = 0 \qquad s_2 - s_1 = mc_v \ln (T_2/T_1)$$

2. *Constant pressure:* $V_2/V_1 = T_2/T_1$.

$$W_{12} = -p(V_2 - V_1) = -mR(t_2 - t_1)$$
$$Q_{12} = mc_p(t_2 - t_1) = kW_{12}/(k - 1)$$
$$s_2 - s_1 = mc_p \ln(T_2/T_1)$$

3. *Isothermal (constant temperature):* $p_2/p_1 = V_1/V_2$.

$$U_2 - U_1 = 0 \qquad W_{12} = -mRT \ln (V_2/V_1) = -p_1 V_1 \ln (V_2/V_1)$$
$$Q_{12} = -W_{12} \qquad s_2 - s_1 = Q_{12}/T = mR \ln (V_2/V_1)$$

4. *Reversible adiabatic, isentropic:* $p_1 V_1^k = p_2 V_2^k$.

$$T_2/T_1 = (V_1/V_2)^{k-1} = (p_2/p_1)^{(k-1)/k}$$
$$W_{12} = U_1 - U_2 = mc_v(t_1 - t_2)$$
$$Q_{12} = 0 \qquad s_2 - s_1 = 0$$
$$W_{12} = (p_2 V_2 - p_1 V_1)/(k - 1)$$
$$= -p_1 V_1 [(p_2/p_1)^{(k-1)/k} - 1]/(k - 1)$$

5. *Polytropic:* This name is given to the change of state which is represented by the equation $pV^n = \text{const}$. A polytropic curve usually represents actual expansion and compression curves in motors and air compressors for pressures up to a few hundred pounds. By giving n different values and assuming specific heats constant, the preceding changes may be made special cases of the polytropic change, thus,

For $n = 1$,	pv $= \text{const}$	isothermal
$n = k$,	$pv^k = \text{const}$	isentropic
$n = 0$,	p $= \text{const}$	constant pressure
$n = \infty$,	v $= \text{const}$	constant volume

For a polytropic change of an ideal gas (for which c_v is constant), the specific heat is given by the relation $c_n = c_v(n - k)(n - 1)$; hence for $1 < n < k$, c_n is negative. This is approximately the case in air compression up to a few hundred pounds pressure. The following are the principal formulas:

$$p_1 V_1^n = p_2 V_2^n$$
$$T_2/T_1 = (V_1/V_2)^{n-1} = (p_2/p_1)^{(n-1)/n}$$
$$W_{12} = (p_2 V_2 - p_1 V_1)/(n - 1)$$
$$= -p_1 V_1 [(p_2/p_1)^{(n-1)/n} - 1]/(n - 1)$$
$$Q_{12} = mc_n(t_2 - t_1)$$
$$W_{12} : U_2 - U_1 : Q_{12} = k - 1 : 1 - n : k - n$$

The quantity $(p_2/p_1)^{(k-1)/k} - 1$ occurs frequently in calculations for perfect gases.

Determination of Exponent n   If two representative points $(p_1, V_1$ and $p_2, V_2)$ be chosen, then

$$n = (\log p_1 - \log p_2)/(\log V_2 - \log V_1)$$

Several pairs of points should be used to test the constancy of n.

Changes of State with Variable Specific Heat   In case of a considerable range of temperature, the assumption of constant specific heat is not permissible, and the equations referring to changes of state must be suitably modified. (This statement does not apply to inert or monatomic gases.) Experiments on the specific heat of various gases show that the specific heat may sometimes be taken as a linear function of the temperature: thus, $c_v = a + bT$; $c_p = a' + b'T$. In that case, the following expressions apply for the change of internal energy and entropy, respectively:

$$U_2 - U_1 = m[a(T_2 - T_1) + 0.5b(T_2^2 - T_1^2)]$$
$$S_2 - S_1 = m[a \ln (T_2/T_1) + b(T_2 - T_1) + R \ln (V_2/V_1)]$$

and for an isentropic change,

$$W_{12} = U_2 - U_1$$
$$R \ln (V_1/V_2) = a \ln (T_2/T_1) + b(T_2 - T_1)$$

GRAPHICAL REPRESENTATION

The change of state of a substance may be shown graphically by taking any two of the six variables p, V, T, S, U, H as independent coordinates and drawing a curve to represent the successive values of these two variables as the change proceeds. While any pair may be chosen, there are three systems of graphical representation that are specially useful.

1. p and V.   The curve (Fig. 4.1.4) represents the simultaneous values of p and V during the change (reversible) from state 1 to state
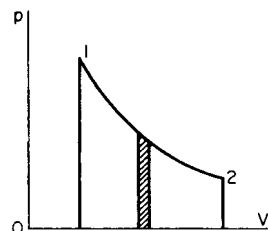
Fig. 4.1.4

2. The area between the curve and the axis OV is given by the integral $\int_{v_1}^{v_2} p\, dV$ and therefore represents the external work W_{12} done by the gas during the change. The area included by a closed cycle represents the work of the cycle (as in the indicator diagram of the steam engine).

2. T and S (Fig. 4.1.5). The absolute temperature T is taken as the ordinate, the entropy S as the abscissa. The area between the curve of change of state and the S axis is given by the integral $\int_{S_1}^{S_2} T\, dS$, and it therefore represents the heat Q_{12} absorbed by the substance from external sources provided there are no irreversible effects. On the T-S diagram, an isothermal is a straight line, as AB, parallel to the S axis; a *reversible* adiabatic is a straight line, as CD, parallel to the T axis.
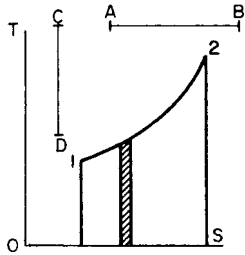
Fig. 4.1.5

In the case of internal generation of heat through friction, as in steam turbines, the increase of entropy is given by $\int_{T_1}^{T_2} (dQ'/T)$ and the area under the curve represents the heat Q' thus generated. In this case, an adiabatic is *not* a straight line parallel to the T axis.

3. H and S. In the system of representation devised by Dr. Mollier, the enthalpy H is taken as the ordinate and the entropy S as the abscissa. If on this diagram (Fig. 4.1.6) a line of constant pressure, as 12, be drawn, the heat absorbed during the change at constant pressure is given by $Q_{12} = H_2 - H_1$, and this is represented by the line segment 23. The **Mollier diagram** is specially useful in problems that involve the flow of fluids, throttling, and the action of steam in turbines.
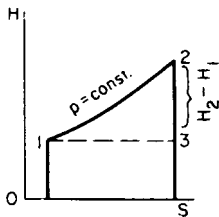
Fig. 4.1.6

IDEAL CYCLES WITH PERFECT GASES

Gases are used as heat mediums in several important types of machines. In air compressors, air engines, and air refrigerating machines, atmospheric air is the medium. In the internal-combustion engine, the medium is a mixture of products of combustion. Engines using gases are operated in certain well-defined cycles, which are described below. In the analyses given, ideal conditions that cannot be attained by actual motors are assumed. However, conclusions derived from such analyses are usually approximately valid for the modified actual cycle.

In the following, the subscripts 1, 2, 3, etc., refer to corresponding points shown in the figures. The work of the cycle is denoted by W and the net heat absorbed by Q.

Carnot Cycle The Carnot cycle (Fig. 4.1.7) is of historic interest. It consists of two isothermals and two isentropics. The heat absorbed
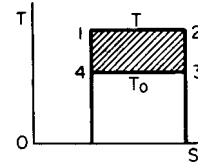
Fig. 4.1.7 Carnot cycle.

along the upper isothermal 12 is $Q_{12} = mRT \ln (V_2/V_1)$, and the heat transformed into work, represented by the cycle area, is $W = Q_{12}(1 - T_0/T)$.

$$W = -mR(T - T_0) \ln \left(\frac{V_2}{V_1} \right)$$

If the cycle is traversed in the reverse sense, $Q_{43} = mRT_0 \ln (V_3/V_4)$ is the heat absorbed from the cold body (brine), and the ratio $Q_{43}:(W) = T_0:(T - T_0)$ is the **coefficient of performance** of the refrigerating machine.

Leff (*Amer. J. Phys.,* **55,** no. 7, 1987, pp. 602–610) showed that the **thermal efficiency** of a heat engine producing the maximum possible work per cycle consistent with its operating temperature range resulted in efficiencies equal to or well approximated by $\eta = 1 - \sqrt{T_c/T_h}$, where c = cold and h = hot, as found by Curzon and Ahlborn (*Amer. J. Phys.,* **43,** no. 1, 1975, pp. 22–24) for maximum power output. If the work output per cycle is kept fixed, the thermal efficiency can be increased by operating the heat engine at less than maximum work output per cycle, the limit being an engine of infinite size having a Carnot efficiency. Leff's paper considers Otto, Brayton-Joule, Diesel, and Atkinson cycles. Figure 4.1.8 illustrates the difference between maximum power and maximum efficiency. Detailed discussion of **finite time thermodynamics** appears in Sieniutcyz and Salamon, ''Finite Time Thermodynamics and Thermoeconomics,'' *Advan. Thermo.,* **4,** 306 pp., 1990, Taylor & Francis, London.
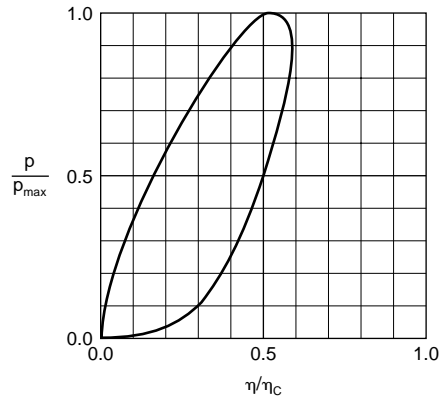
Fig. 4.1.8 Ratio of actual power to maximum power as a function of ratio of actual thermal efficiency to Carnot efficiency.

Finite time thermodynamics is a term applied to the consideration that, for any finite energy transfer, a finite time must occur. A common statement in the literature is that the analysis started from the work of

Curzon and Ahlborn (*Amer. J. Phys., **43,*** 1975, pp. 22–24). According to Bejan (*Amer. J. Phys., **62,*** no. 1, Jan. 1994, pp. 11–12), this statement is not true, and the original analysis was by Novikov (*At. Energy,* **3,** 1957, p. 409, and *Nucl. Energy,* pt. II, **7,** 1958, pp. 125–148). Wu (*Energy Convsn. Mgmt., **34,*** no. 12, 1993, pp. 1239–1247) discusses the *endoreversible Carnot heat engine* being one in which all the losses are associated with the transfer of heat to and from the engine, there being no internal losses within the engine itself and refers to Wu and Kiang (*Trans. J. Eng. Gas Turbines & Power,* **113,** 1991, p. 501) for a detailed literature survey.

Otto and Diesel Cycles   The ideal cycles usually employed for internal-combustion engines may be classified in two groups: (1) explosive—Otto (the fluid is introduced in gaseous form), (2) nonexplosive—Diesel, Joule (the fluid is introduced in liquid form).

Otto Cycle   (Fig. 4.1.9 for pressure-volume plane, Fig. 4.1.10 for temperature-entropy plane)   Isentropic compression 12 is followed by ignition and rapid heating at constant volume 23. This is followed by isentropic expansion, 34. Assuming constant specific heats the following relations hold:

$$\frac{T_2}{T_1} = \frac{T_3}{T_4} = \left(\frac{p_2}{p_1}\right)^{k-1/k} = \left(\frac{p_3}{p_4}\right)^{k-1/k} = \left(\frac{V_1}{V_2}\right)^{k-1}$$

$$Q_{23} = mc_v(T_1 - T_2)$$
$$W = Q_{23}[1 - (T_1/T_2)] = mc_v(T_3 - T_4 - T_2 + T_1)$$

$$\text{Efficiency} = 1 - \frac{T_1}{T_2} = 1 - \left(\frac{V_2}{V_1}\right)^{k-1} = 1 - \left(\frac{p_1}{p_2}\right)^{(k-1)/k}$$

Fig. 4.1.9   Otto cycle.

Fig. 4.1.10   Otto cycle.

If the compression and expansion curves are polytropics with the same value of n, replace k by n in the first relation above. In this case,

$$W = [(p_3V_3 - p_4V_4) - (p_2V_2 - p_1V_1)]/(n - 1)$$
$$= mR(T_3 - T_4 - T_2 + T_1)/(n - 1)$$

The **mean effective pressure** of the diagram is given by

$$p_m = ap_1(p_3/p_2 - 1)$$

where a has the values given in the following table.

$p_2/p_1 = 3$	4	5	6	8	10	12	14	16
($n = 1.4$) $a = 1.70$	1.94	2.13	2.31	2.62	2.88	3.10	3.31	3.50
($n = 1.3$) $a = 1.69$	1.92	2.11	2.28	2.57	2.81	3.03	3.22	3.39
($n = 1.2$) $a = 1.68$	1.90	2.08	2.25	2.51	2.74	2.94	3.12	3.27

A later paper by Wu and Blank (*Energy Convsn. Mgmt., **34,*** no. 12, 1993, pp. 1255–1269) considered optimization of the endoreversible Otto cycle with respect to both power and mean effective pressure.

Diesel Cycle   In the diesel oil engine, air is compressed to a high pressure. Fuel is then injected into the air, which is at a temperature above the ignition point, and it burns at nearly constant pressure (23, in Fig. 4.1.11). Isentropic expansion of the products of combustion is followed by exhaust and suction of fresh air, as in the Otto cycle.

Fig. 4.1.11   Diesel cycle.

The work obtained is

$$W = m[c_p(T_3 - T_2) - c_v(T_4 - T_1)]$$

and the efficiency of the ideal cycle is

$$1 - [(T_4 - T_1)/k(T_3 - T_2)]$$

The **Joule cycle,** also called the **Brayton cycle** (Fig. 4.1.12), consists of two isentropics and two constant-pressure lines. The following relations hold:

$$V_3/V_2 = V_4/V_1 = T_3/T_2 = T_4/T_1$$

$$\frac{T_2}{T_1} = \frac{T_3}{T_4} = \left(\frac{V_1}{V_2}\right)^{k-1} = \left(\frac{V_4}{V_3}\right)^{k-1} = \left(\frac{p_2}{p_1}\right)^{k-1/k}$$

$$W = mc_p(T_3 - T_2 - T_4 + T_1)$$
$$\text{Efficiency} = W/Q_{23} = 1 - T_1/T_2$$

The Joule cycle has assumed renewed importance as a basis for analysis of gas turbine operation.

For additional information on internal combustion engines, see Campbell, ''Thermodynamic Analysis of Internal Combustion Engines,'' Wiley; Taylor, ''The Internal Combustion Engine in Theory and Practice,'' MIT Press. New designs for internal-combustion engines were reviewed by Wallace (*Sci. Progr., Oxford,* **75,** 1991, pp. 15–32).

Fig. 4.1.12   Joule or Brayton cycle.
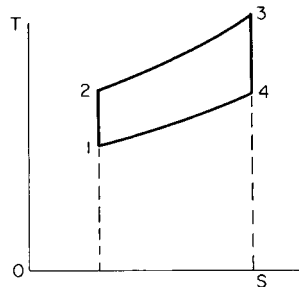
Stirling Cycle The Stirling engine may be visualized as a cylinder with a piston at each end. Between the pistons is a regenerator. The cylinder is assumed to be insulated except for a contact with a hot reservoir at one end and a contact with a cold reservoir at the other end.

Starting with state 1, Fig. 4.1.13, heat from the hot reservoir is added to the gas at T_H (or $T_H - dT$). During the reversible isothermal process, the left piston moves outward, doing work as the system volume increases and the pressure falls. Both pistons are then moved to the right at the same rate to keep the system volume constant (process 2–3). No
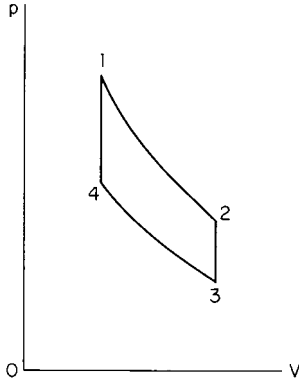
Fig. 4.1.13 Stirling cycle.

heat transfer occurs with either reservoir. As the gas passes through the regenerator, heat is transferred from the gas to the regenerator, causing the gas temperature to fall to T_L by the time the gas leaves the right end of the regenerator. For this heat-transfer process to be reversible, the temperature of the regenerator at each point must equal the gas temperature at that point. Hence there is a temperature gradient through the regenerator from T_H at the left end to T_L at the right end. No work is accomplished during this process. During the path 3–4, heat is removed from the gas at T_L (or $T_L + dT$) to the reservoir at T_L. To hold the gas temperature constant, the right piston is moved inward—doing work on the gas with a resulting increase in pressure. During process 4–1, both pistons are moved to the left at the same rate to keep the system volume constant. The pistons are closer together during this process than they were during process 2–3, since $V_4 = V_1 < V_2 = V_3$. No heat is transferred to either reservoir. As the gas passes back through the regenerator, the energy stored in the regenerator during 2–3 is returned to the gas. The gas emerges from the left end of the regenerator at the temperature T_H. No work is performed during this process since the

Fig. 4.1.14 Two main types of Stirling engine: (1) left, double-cylinder two piston; (2) right, single-cylinder, piston plus displacer. Each has two variable-volume working spaces filled with the working fluid—one for expansion and one for compression of the gas. Spaces are at different temperatures—the extreme temperatures of the working cycle—and are connected by a duct, which holds the regenerators and heat exchangers. (*Intl. Science and Technology,* May 1962.)

volume remains constant. Thus the cycle is completed and is externally reversible. The system exchanges a net amount of heat with only the two energy reservoirs T_H and T_L. Two types of Stirling engines are shown in Fig. 4.1.14. Extensive research-and-development effort has been devoted to the Stirling engines for future use as prime movers in space power systems operating on solar energy. (See also Sec. 9.6.)

More information can be found in Meijer, *De Ingenieur,* **81,** nos. 18 and 19, 1969; Reader and Hooper, ''Stirling Engines,'' Spon, London; Sternlicht, *Chem. Tech.,* **13,** 1983, pp. 28–36; Walker, ''Stirling Engines,'' Oxford Univ. Press.

AIR COMPRESSION

It is assumed that the compressor works under ideal reversible conditions without clearance and without friction losses and that the changes are over ranges where the gas laws are applicable. Where the gas laws cannot be used, analysis in terms of Z charts is convenient. If the compression from p_1 to p_2 (Fig. 4.1.15) follows the law $pV^n = $ const, the work represented by the indicator diagram is

$$W = n(p_2V_2 - p_1V_1)/(n - 1)$$
$$= np_1V_1[(p_2/p_1)^{(n-1)/n} - 1]/(n - 1)$$

The temperature at the end of compression is given by $T_2/T_1 = (p_2/p_1)^{(n-1)/n}$. The work W is smaller the smaller the value on n, and the purpose of the water jackets is to reduce n from the isentropic value 1.4. Under usual working conditions, n is about 1.3.

Fig. 4.1.15 Air compressor cycle.

When the pressure p_2 is high, it is advantageous to divide the process into two or more stages and cool the air between the cylinders. The saving effected is best shown on the T-S plane (Fig. 4.1.16). With single-stage compression, 12 represents the compression from p_1 to p_2, and if the constant-pressure line 23 is drawn cutting the isothermal through point 1 in point 3, the area $1'1233'$ represents the work W. When two stages are used, 14 represents the compression from p_1 to an intermediate pressure p', 45 cooling at constant pressure in the inter-

Fig. 4.1.16 Air compressor cycle.

cooler between the cylinders, and 56 the compression in the second stage. The area under 14563 represents the work of the two stages and the area 2456 the saving effected by compounding. This saving is a maximum when $T_4 = T_6$, and this is the case when the intermediate pressure p' is given by $p' = \sqrt{p_1p_2}$ (see Sec. 14.3).

The total work in two-stage compression is

$$np_1V_1[(p'/p_1)^{(n-1)/n} + (p_2/p')^{(n-1)/n} - 2]/(n - 1)$$

Gas Turbine   The Brayton cycle, also called the Joule or constant pressure cycle, employs an air engine, a compressor, and a combustion chamber. Air enters the compressor wherein the pressure is increased. Fuel burning in the combustion chamber raises the temperature of the compressed air under constant-pressure conditions. The resulting high-temperature gases are then introduced to the engine where they expand and perform work. The excess work of the engine over that required to compress the air is available for operating other devices, such as a generator.

Basically, the simple gas-turbine cycle is the same as the Brayton cycle, except that the air compressor and engine are replaced by an axial flow compressor and gas turbine. Air is compressed in the compressor, after which it enters a combustion chamber where the temperature is increased while the pressure remain constant. The resulting high-temperature air then enters the turbine, thereby performing work.

Boyce (''Gas Turbine Engineering Handbook,'' Gulf) gives numerous examples of ideal and actual gas-turbine cycles. The graphs in this source as well as in a review by Dharmadhikari (*Chemical Engineer (London),* Feb. 1989, pp. 16–20) show the same relation between work output and thermal efficiency as the general graph of Gordon (*Amer. J. Phys.,* **59,** no. 6, 1991, pp. 551–555). MacDonald (ASME Paper 89-GT-103, Toronto Gas Turbine Exposition, 1989) describes the increasing use of heat exchangers in gas-turbine plants and reviews the use of recuperators (i.e., regenerators) (in *Heat Recovery Systs. & CHP.* **10,** no. 1, 1990, pp. 1–30). Gas turbines as the topping cycle with steam in the bottoming cycle were described by Huang (ASME Paper 91-GT-186 and *J. Eng. Gas Turbines & Power,* **112,** Jan. 1990, pp. 117–121) and by Cerri (*Trans. ASME,* **109,** Jan. 1987, pp. 46–54). The use of steam injection in gas-turbine cycles has received renewed attention; see, e.g., Consonni (45th Congr. Nat. Assoc. Termotecnica Ital., **IIID,** 1990, pp. 49–60), Ediss (City Univ. London Conf. Paper, Nov. 1991), Lundberg (*ASME Cogen-Turbo IGTI,* **6,** 1991, pp. 9–18). Fraize and Kinney (*J. Eng. Power,* **101,** 1979, pp. 217–227), and Larson and Williams (*J. Eng. Gas Turbines & Power,* **109,** Jan. 1987, pp. 55–63).

Analysis of closed-cycle gas-turbine plant for maximum and zero power output and for maximum efficiency was made by Woods et al. (*Proc. Inst. Mech. Eng.,* **205A,** 1991, pp. 59–66). See also pp. 287–291 and ibid., **206A,** 1992, pp. 283–288. A series of papers by Najjar appeared in *Int. J. M. E. Educ.* (**15,** no. 4, 1987, pp. 267–286); *High Temp. Technol.* (**8,** no. 4, 1990, pp. 283–289); *Heat Recovery Systems & CHP* (**6,** no. 4, 1986, pp. 323–334). For more detailed information regarding the actual gas-turbine cycles see Sec. 9.

VAPORS

General Characteristics of Vapors   Let a gas be compressed at constant temperature; then, provided this temperature does not exceed a certain critical value, the gas begins to liquefy at a definite pressure, which depends upon the temperature. At the beginning of liquefaction, a unit mass of gas will also have a definite volume v_g, depending on the temperature. In Fig. 4.1.17, *AB* represents the compression and the point *B* gives the **saturation** pressure and volume. If the compression is continued, the pressure remains constant with the temperature, as indicated by *BC*, until at *C* the substance is in the liquid state with the volume v_f.

The curves v_f and v_g giving the volumes for various temperatures at the end and beginning of liquefaction, respectively, may be called the **limit curves.** A point *B* on curve v_g represents the state of **saturated vapor;** a point *C* on the curve v_f represents the saturated liquid state; and a point *M* between *B* and *C* represents a mixture of vapor and liquid of which the part $x = MC/BC$ is vapor and the part $1 - x = BM/BC$ is liquid. The ratio *x* is called the **quality of the mixture**. The region between the curves v_f and v_g is thus the region of liquid and vapor mixtures. The region to the right of curve v_g is the region of **superheated vapor**. The curve v_g dividing these regions represents the so-called **saturated vapor**.

For saturated vapor, saturated liquid, or a mixture of vapor and liquid, the pressure is a function of the temperature only, and the volume of the mixture depends upon the temperature and quality *x*. That is, $p = f(t)$, $v = F(t, x)$.

For the vapor in the superheated state, the volume depends on pressure and temperature [$v = F(p, t)$], and these may be varied independently.

Critical State   If the temperature of the gas lies above a definite temperature t_c called the **critical temperature,** the gas cannot be liquefied by compression alone. The saturation pressure corresponding to t_c is the **critical pressure** and is denoted by p_c. At the critical states, the limit curves v_f and v_g merge; hence for temperatures above t_c, it is impossible to have a mixture of vapor and liquid. Table 4.2.21 gives the critical data for various gases; also the boiling temperature t_b corresponding to atmospheric pressure. Study of the critical region is becoming a specialized topic. NBS Misc. Publ. 273, 1966, contains 33 papers on phenomena near critical points. The ASME symposia on thermophysical properties proceedings contain numerous papers on the subject.

Vapor Pressures   At a specified temperature, a pure liquid can exist in equilibrium contact with its vapor at but one pressure, its vapor pressure. A plot of these pressures against the corresponding temperatures is known as a vapor pressure curve. As noted by Martin, ''Thermodynamic and Transport Properties of Gases, Liquids and Solids,'' ASME, New York, p. 112, the true shape of a log vapor pressure versus reciprocal absolute temperature curve is an S shape. But if the curvature (often slight) is neglected, the equation of the curve becomes $\ln P = A + B/T$. In terms of any two pairs of values (P_1, T_1), (P_2, T_2), $A = (T_2 \ln P_2 - T_1 \ln P_1)/(T_2 - T_1)$ and $B = T_1 T_2/(T_2 - T_1) \ln (P_1/P_2)$. (Note that *B* is always negative.) Once the values of *A* and *B* have been determined, the equation can be used to determine P_3 at $T = T_3$ or T_3 at $P = P_3$. Algebraically, *A* and *B* can be eliminated to yield $\ln (P_3/P_1) = [T_2(T_3 - T_1)/T_3(T_2 - T_1)] \ln (P_2/P_1)$, and at any temperature *T* the slope of the vapor pressure curve is $dP/dT = (1/T^2)[T_1 T_2/(T_1 - T_2)] \ln (P_2/P_1)$.

A classic survey of equations for estimating vapor pressures was given by Miller in *Ind. Eng. Chem.,* **56,** 1964, pp. 46–57. The comprehensive tables of Stull in *Ind. Eng. Chem.,* **39,** 1947 pp. 517–550, are useful though slightly dated. Table 4.2.24 gives *T*(K) for various *P*(bar) for 50 substances; *P*(bar) tables for various *T*(K) for 16 elements are given in Table 4.2.29. Boublik et al., ''The Vapor Pressure of Pure Substances,'' Elsevier, presents an extensive collection of data.
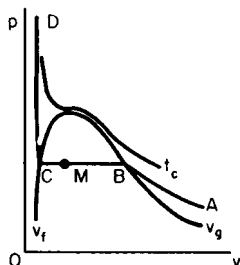
THERMAL PROPERTIES OF SATURATED VAPORS AND OF VAPOR AND LIQUID MIXTURES

Notation

v_f, v_g = specific volume of 1 lb of saturated liquid and vapor, respectively

c_f, c_g = specific heat of saturated liquid and vapor, respectively

h_f, h_g = specific enthalpy of saturated liquid and vapor, respectively

u_f, u_g = specific internal energy of saturated liquid and vapor, respectively

Fig. 4.1.17

$s_f, s_g =$ specific entropy of saturated liquid and vapor, respectively

$v_{fg} = vg - v_f =$ increase of volume during vaporization

$h_{fg} = h_g - h_f =$ heat of vaporization, or heat required to vaporize a unit mass of liquid at constant pressure and temperature

And r may be used for h_{fg} when several heats of vaporization (as r_1, r_2, r_3, etc.) are under consideration.

$u_{fh} = u_g - u_f =$ increase of internal energy during vaporization

$s_{fg} = s_g - s_f = h_{fg}/T =$ increase of entropy during vaporization

$pv_{fg} =$ work performed during vaporization

The energy equation applied to the vaporization process is

$$h_{fg} = u_{fg} + pv_{fg}$$

The properties of a unit mass of a mixture of liquid and vapor of quality x are given by the following expressions:

$$v = v_f + xv_{fg}$$
$$h = h_f + xh_{fg}$$
$$u = u_f + xu_{fg}$$
$$s = s_f + xs_{fg}$$

Any property ψ can be expressed as a function of the property of the saturated liquid, ψ_f, that of the saturated vapor, ψ_g, and the quality x by three entirely equivalent equations:

$$\psi = (1 - x)\psi_f + x\psi_g$$
$$= \psi_f + x\psi_{fg}$$
$$= \psi_g - (1 - x)\psi_{fg}$$

where $\psi_{fg} = \psi_g - \psi_f$. Tables of superheated vapor usually give values of v, h, and s per unit mass. If not tabulated, the internal energy u per unit mass can be found from the equation

$$u = h - pv$$

CHARTS FOR SATURATED AND SUPERHEATED VAPORS

Certain properties of vapor mixtures and superheated vapors may be shown graphically by means of charts. Such charts show the behavior of vapors and have a practical application in the solution of certain problems.

Temperature-Entropy Chart   Figures 4.2.10 and 4.2.11 show the temperature-entropy chart for water vapor. The liquid curve is obtained by plotting corresponding values of T and s_f, and the saturation curve by plotting values of T and s_g. The values are taken from Tables 4.2.17 to 4.2.20. The two curves merge into each other at the critical temperature $T = 1,165.4°R$ (647 K). Between these two curves, constant pressure lines are also lines of constant temperature; but at the saturation curve the constant pressure lines show a sharp break with rising temperature. The constant quality lines $x = 0.2, 0.4$, etc., are equally spaced between the liquid and saturation curves.

Figure 4.2.1 is a temperature-entropy chart for air.

Enthalpy-Entropy Chart (Mollier Chart)   In this chart, the enthalpy h is taken as the ordinate and the entropy s as the abscissa.

Enthalpy–Log Pressure Chart   Previously, a chart with coordinates of enthalpy and pressure was termed a pressure-enthalpy chart. In this edition these charts are called enthalpy–log pressure charts, to more correctly identify the scale plotted for pressure. This follows modern usage. Charts with pressure per se as a coordinate have a greatly different scale and appearance.

For examples of the enthalpy–log-pressure chart, see Sec. 4.2. For enthalpy–log-pressure charts for various fluids, see ''Engineering Data Book,'' 9th ed., Gas Processors Suppliers Assoc., Tulsa, OK; Reynolds, ''Thermodynamic Properties in SI,'' Mech. Eng. Stanford Univ. Publication.

The energy-temperature diagram reported by Bucher (*Amer. J. Phys.,* **54,** 1986, pp. 850–851) for reversible cycles and by Wallingford (*Amer. J. Phys.,* **57,** 1989, pp. 379–381) for irreversible cycles was claimed by Bejan (*Amer. J. Phys.,* **62,** no. 1, Jan. 1994, pp. 11–12) to have been first reported at an earlier date (Bejan, *Mech. Eng. News,* May 1977, pp. 26–28).

CHANGES OF STATE. SUPERHEATED VAPORS AND MIXTURES OF LIQUID AND VAPOR

Isothermal   In the only important cases, the fluid is a mixture of liquid and vapor in both initial and final states.

$$t = \text{const} \qquad p = \text{const}$$
$$x_1, x_2 = \text{initial and final qualities}$$
$$Q_{12} = mh_{fg}(x_2 - x_1)$$
$$W_{12} = mpv_{fg}(x_2 - x_1)$$
$$U_2 - U_1 = mu_{fg}(x_2 - x_1)$$
$$S_2 - S_1 = Q_{12}/T$$

Constant Pressure   If the fluid is a mixture at the beginning and end of the change, the constant pressure change is also isothermal. If the initial state is in the mixture region and the final state is that of a superheated vapor, the following are the equations for Q_{12}, etc. Let h_2, u_2, v_2, and s_2 be the properties of 1 lb of superheated vapor in the final state 2; then

$$Q_{12} = m(h_2 - h_1)$$
$$U_2 - U_1 = m(u_2 - u_1)$$
$$S_2 - S_1 = m(s_2 - s_1)$$
$$W_{12} = - mp(v_2 - v_1)$$
$$h_1 = h_{f1} + x_1 h_{fg1}$$
$$u_1 = u_{f1} + x_1 u_{fg1}$$
$$s = s_{f1} + x_1 s_{fg1}$$
$$v_1 = v_{f1} + x_1 v_{fg1}$$

Constant Volume   Since v_f the liquid volume is nearly constant,

$$x_1 v_{fg1} = x_2 v_{fg2}$$
$$x_2 = x_1 v_{fg1}/v_{fg2} \quad \text{or} \quad x_2 = x_1 v_{g1}/v_{g2} \quad \text{approx}$$
$$Q_{12} = U_2 - U_1 = m(u_2 - u_1) \qquad W_{12} = 0$$

Isentropic $s = \text{const}$.   If the fluid is a mixture in the initial and final states,

$$s_{f1} + x_1 s_{fg1} = s_{f2} + x_2 s_{fg2}$$

If the initial state is that of superheated vapor,

$$s_1 = s_{f2} + x_2 s_{fg2}$$

in which s_1 is read from the table of superheated vapor. The final value x_1 is determined from one of these equations, and the final internal energy u_2 is then

$$u_{f2} + x_2 u_{fg2} \qquad Q_{12} = 0 \qquad W_{12} = U_2 - U_1 = m(u_2 - u_1)$$

For water vapor, the relation between p and v during an isentropic change may be represented approximately by the equation $pv^n = \text{constant}$. The exponent n is not constant, but varies with the initial quality and initial pressure, as shown in Table 4.1.2.

The isentropic expansion of superheated steam is fairly represented by $pv^n = \text{const}$, with $n = 1.315$.

The volume at the end of expansion (or compression) is $V_2 = V_1(p_1/p_2)^{1/n}$, and the external work is

$$W_{12} = (p_2 V_2 - p_1 V_1)/(n - 1)$$
$$= - p_1 V_1[1 - (p_2/p_1)^{(n-1)/n}]/(n - 1)$$

If the initial state is in the region of superheat and final state in the mixture region, two values of n must be used: $n = 1.315$ for the expansion to the state of saturation, and the appropriate value from the first row of Table 4.1.2 for the expansion of the mixture.

Table 4.1.2   Values of n (Water Vapor)

Initial quality	Initial pressure, psia											
	20	40	60	80	100	120	140	160	180	200	220	240
1.00	1.131	1.132	1.133	1.134	1.136	1.137	1.138	1.139	1.141	1.142	1.143	1.145
0.95	1.127	1.128	1.129	1.130	1.131	1.131	1.132	1.133	1.134	1.135	1.136	1.137
0.90	1.123	1.123	1.124	1.124	1.125	1.125	1.126	1.126	1.127	1.127	1.128	1.129
0.85	1.119	1.119	1.119	1.119	1.120	1.120	1.120	1.120	1.120	1.120	1.120	1.121
0.80	1.115	1.115	1.114	1.114	1.114	1.114	1.113	1.113	1.113	1.113	1.112	1.112
0.75	1.111	1.110	1.110	1.109	1.109	1.108	1.107	1.106	1.106	1.105	1.104	1.104

MIXTURES OF AIR AND WATER VAPOR

Atmospheric Humidity   The atmosphere is a mixture of air and water vapor. Dalton's law of partial pressures (for the mixture) and the ideal gas law (for each constituent) may safely be assumed to apply. The **total pressure** p_t (barometric pressure) is the sum of the **vapor pressure** p_v and the **air pressure** p_a.

The temperature of the atmosphere, as indicated by an ordinary thermometer, is the **dry-bulb temperature** t_d. If the atmosphere is cooled under constant total pressure, the partial pressures remain constant until a temperature is reached at which condensation of vapor begins. This temperature is the **dew point** t_c (condensation temperature) and is the saturation temperature, or boiling point, corresponding to the actual vapor pressure p_v. If a thermometer bulb is covered with absorbent material, e.g., linen, wet with distilled water and exposed to the atmosphere, evaporation will cool the water and the thermometer bulb to the **wet-bulb temperature** t_w. This is the temperature given by a psychrometer. The wet-bulb temperature lies between the dry-bulb temperature and the dew point. These three temperatures are distinct except for a saturated atmosphere, for which they are identical. For each of these temperatures, there is a corresponding vapor pressure. The actual vapor pressure p_v corresponds with the dew point t_c. The vapor pressures p_d and p_w, corresponding with t_d and t_w, do not represent pressures actually appearing in the atmosphere but are used in computations.

Relative humidity r is the ratio of the actual vapor pressure to the pressure of saturated vapor at the prevailing dry-bulb temperature $r = p_v/p_d$. Within the limits of usual accuracy, this equals the ratio of actual vapor density to the density of saturated vapor at dry-bulb temperature, $r = p_v/p_d$. It is to be noted that relative humidity is a property of the vapor alone; it has nothing to do with the fact that the vapor is mixed with air. It is a method of expressing the departure of the vapor from saturation. (See ''ASHRAE Handbook'' for information on industrial applications of relative humidity.)

Molal humidity f is the mass of water vapor in mols per 1 mol of air. The laws of Dalton and Avogadro state that the molal composition of a mixture is proportional to the distribution of partial pressures, or $f = p_v/p_a = p_v/(p_t - p_v)$.

Specific humidity (humidity ratio) W is the mass of water vapor (pounds or grains) per pound of dry air. Mass in pounds equals mass in moles multiplied by the molecular weight. The molecular weight of water is 18, and the equivalent molecular weight of air is 28.97. The ratio $28.97/18 = 1.608$, or 1.61 with ample accuracy. Thus $W = f/1.61$.

Air density ρ_a is the pounds of air in one cubic foot. **Vapor density** ρ_v is the pounds of vapor in one cubic foot. **Mixture density** ρ_m is the sum of these, i.e., the pounds of air plus vapor in one cubic foot.

Notation   The subscripts $a, v, m,$ and f apply to air, vapor, mixture, and liquid water, respectively. The subscripts d and w apply to conditions pertaining to the dry- and wet-bulb temperature, respectively.

HUMIDITY MEASUREMENTS

Many methods are in use: (1) the **dew point** method measures the temperature at which condensation begins; water-vapor pressure can then be found from steam tables. Dew point apparatus can either cool a surface or compress and expand moist air. (2) **Hygrometers** measure relative humidity, often by using the change in dimensions of a hygroscopic material such as human hair, wood, or paper; these instruments are simple and inexpensive but require frequent calibration. The electrical resistance of an electrolytic film can also be used as an indication of relative humidity. (3) The wet- and dry-bulb **psychrometer** is widely used. Humidity measurements of air flowing in ducts can be made with psychrometers that use mercury-in-glass thermometers, thermocouples, or resistance thermometers. Humidity measurements of still air can be made with sling psychrometers as aspiration psychrometers. Psychrometric wet-bulb temperatures must be corrected to obtain thermodynamic wet-bulb temperatures, or there must be adequate air motion past the wet-bulb thermometer, 800 to 900 ft/min (with duct walls at air temperature), to ensure a proper balance between radiation and convection. (4) **Chemical analysis** by the use of desiccants such as sulfuric acid, phosphorus pentoxide, lithium chloride, or silica gel can be used as primary standards of humidity measurement.

The following equations give various properties in terms of pressure in inches Hg and temperature in degrees Fahrenheit.

Relative humidity: $r = p_v/p_d$
Specific humidity: $W = p_v/1.61(p_t - p_v)$ lb/lb dry air

Volume of mixture per pound of dry air:

$$v_a = \frac{1}{\rho_a} = 0.754(t_d + 460)/(p_t - rp_d)   \text{ft}^3$$

Volume of mixture per pound of mixture:

$$v_m = \frac{1}{\rho m} = v_a/(1 + W)   \text{ft}^3$$

The **enthalpy** of a mixture of dry air and steam, when each constituent is assumed to be an ideal gas, in Btu per pound of dry air, is the sum of the enthalpy of 1 lb of dry air and the enthalpy of the W lb of steam mixed with that air. The specific enthalpy of dry air (above 0°F) is $h_a = 0.240t_d$ (up to 130°F, the specific heat of dry air is 0.240; at higher temperatures, it is larger). The specific enthalpy of low-pressure steam (saturated or superheated) is nearly independent of the vapor pressure and depends only on t_d. An empirical equation for the specific enthalpy of low-pressure steam for the range of temperatures from -40 to 250°F is

$$h_v = 1,062 + 0.44t_d   \text{Btu/lb}$$

The enthalpy of a mixture of air and steam is

$$h_m = 0.240t_d + W(1,062 + 0.44t_d)$$

The specific heat of a mixture of dry air and steam per pound of dry air may be called **humid specific heat** and is $0.240 + 0.44W$ Btu/lb dry air. For a steady-flow process without change of specific humidity, heat transfers per pound of dry air may be computed as the product of humid specific heat and change in dry-bulb temperature.

Thermodynamic Wet-Bulb Temperature (Temperature of Adiabatic Saturation)   The thermodynamic wet-bulb temperature t^* is an important property of state of mixtures of dry air and superheated steam; it is

the temperature at which water (or ice), by evaporating into a mixture of air and steam, will bring the mixture to saturation at the same temperature in a steady-flow process in the absence of external heat transfer. For a mixture of dry air and saturated steam only, $t^* = t_d$; where $r < 1$, $t^* < t_d$. By writing energy and mass balances for the process of adiabatic saturation with water supplied at t^*, the following equation may be derived:

$$W = W^* - \frac{(0.240 + 0.44W^*)(t_d - t^*)}{1{,}094 + 0.44t_d - t^*}$$

where $W^* =$ specific humidity for saturation at the total pressure of p_t.

The enthalpy of a mixture of dry air and **saturated** steam at the total pressure p_t and thermodynamic wet-bulb temperature t^* exceeds the enthalpy of a mixture of dry air and **superheated** steam at the same p_t and t^* for

$$h_m^* = h_m + (W^* - W)h_f^*$$

A property of the mixture that remains constant for constant p_t and t^* has been called the Σ **function,** for

$$\Sigma^* = h_m^* - W^*h_f^* = \Sigma = h_m - Wh_f^*$$

EXAMPLE.   A mixture of dry air and **saturated** steam; $p_t = 24$ inHg; $t_d = 76°$F. Partial pressure of water vapor from tables:

$$p_v = p_d = 0.905 \text{ inHg}$$

Partial pressure of dry air: $p_a = p_t - p_v = 23.095$ inHg.
Specific humidity:

$$W = 0.905/1.61(23.095) = 0.0243 \text{ lb/lb dry air}$$

Volume of mixture per pound of dry air:

$$v_a = 0.754(536)/23.095 = 17.5 \text{ ft}^3$$

Volume of mixture per pound of mixture:

$$v_m = 17.5/1.0243 = 17.1 \text{ ft}^3$$

Enthalpy of mixture:

$$h_m = 0.240(76) + 0.0243(1{,}095) = 44.85 \text{ Btu/lb dry air}$$

EXAMPLE.   A mixture of dry air and **superheated** steam; $p_t = 24$ inHg; $t_d = 76°$F; $t_w = t^* = 62°$F.
Pressure of saturated steam at $t^* = 0.560$ inHg (from tables):

$$W^* = 0.560/1.61(23.44) = 0.01484 \text{ lb/lb dry air}$$

Specific humidity:

$$W = 0.01484 - \frac{0.2465(14)}{1{,}065.4} = 0.0116 \text{ lb/lb dry air}$$

Partial pressure of water vapor:

$$0.0116 = p_v/[1.61(24 - p_v)] \quad \text{and} \quad p_v = 0.44 \text{ inHg}$$

Relative humidity: $r = 0.44/0.905 = 0.486$.
Volume of mixture per pound of dry air:

$$v_a = 0.754(536)/23.56 = 17.2 \text{ ft}^3$$

Volume of mixture per pound of mixture:

$$v_m = 17.2/1.0116 = 17.0 \text{ ft}^3$$

Enthalpy of mixture:

$$h_m = 0.240(76) + 0.0116(1{,}095) = 30.95 \text{ Btu/lb dry air}$$

PSYCHROMETRIC CHARTS

For occasional use, algebraic equations are less confusing and more reliable; for frequent use, a **psychrometric chart** may be preferable. A disadvantage of charts is that each applies for only one value of barometric pressure, usually 760 mm or 30 inHg. Correction to other barometric readings is not simple. The equations have the advantage that the actual barometric pressure is taken into account. The equations are often more convenient for equal accuracy or more accurate for equal convenience.

Psychrometric charts are usually plotted, as indicated by Fig. 4.1.18,

with dry-bulb temperature as abscissa and specific humidity as ordinate. Since the specific humidity is determined by the vapor pressure and the barometric pressure (which is constant for a given chart), and is nearly proportional to the vapor pressure, a second ordinate scale, departing slightly from uniform graduations, will give the vapor pressure. The
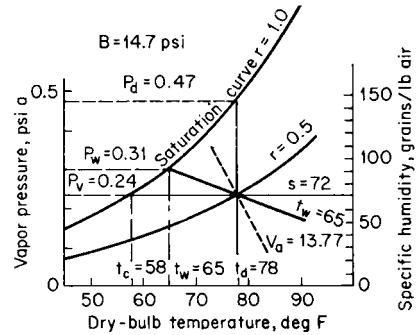
Fig. 4.1.18   Skeleton humidity chart.

saturation curve ($r = 1.0$) gives the specific humidity and vapor pressure for a mixture of air and saturated vapor. Similar curves below it give results for various values of relative humidity. Inclined lines of one set carry fixed values of the wet-bulb temperature, and those of another set carry fixed values of v_a, cubic feet per pound of air. Many charts carry additional scales of enthalpy or Σ function.

Any two values will locate the point representing the state of the atmosphere, and the desired values can be read directly.

Psychrometric charts at different temperatures and barometric pressures are useful in solving problems that fall outside the normal range indicated in Fig. 4.1.18. A collection (''trial set'') of 17 different psychrometric charts in both USCS and SI units, for low, normal, and high temperatures, at sea level and at four elevations above sea level, is available from the Carrier Corp., Syracuse, NY.

AIR CONDITIONING

Air-conditioning processes alter the temperature and specific humidity of the atmosphere. The weight of dry air remains constant and consequently computations are best based upon 1 lb of dry air.

Liquid water may enter or leave the apparatus. Its weight m_f lb of air is often merely the difference between the specific humidities of the entering and leaving atmospheres. Its specific enthalpy at the observed or assumed temperature of supply or removal t_f is

$$h_f = t_f - 32 \text{ Btu/lb of liquid}$$

Because most air conditioning involves steady-flow processes, thermal results are computed by the steady flow equation, written for 1 lb of air. Using subscript 1 for entering atmosphere and liquid water, and for heat supplied; and 2 for departing atmosphere and water, and for heat abstracted; the equation becomes (in the absence of work)

$$h_{m1} + m_{f1}h_{f1} + q_1 = h_{m2} + m_{f2}h_{f2} + q_2 \qquad \text{Btu/lb air}$$

Either or both values of m_f or q may be zero.
In terms of the sigma function, the steady-flow equation becomes

$$\Sigma_1 + W_1(t_{w1} + 32) + m_{f1}h_{f1} + q_1 = \Sigma_2 + W_2(t_{w2} - 32) \\ + m_{f2}h_{f2} + q_2 \qquad \text{Btu/lb air}$$

Unit processes involved in air conditioning include heating and cooling an atmosphere above its dew point, cooling below the dew point, adiabatic saturation, and mixing of two atmospheres. These, in various sequences, make it possible to start with any given atmosphere and produce an atmosphere of any required characteristics.

Heating and cooling above the dew point entail no condensation of

vapor. Barometric pressure and composition being unaltered, partial pressures remain constant. The process is represented in Fig. 4.1.19.

EXAMPLE.   Initial conditions: $p_t = 28$ inHg; $t_a = 60°F$; $t_w = 50°F$; $p_v = 0.26$ inHg; $V = 1,200$ ft³.
Final conditions: $t_d = 82°F$.
Initial computed values: $r = 0.50$; $W = 0.0058$ lb vapor/lb air; $\rho_a = 0.0707$ lb air/ft³; $m_a = V \times \rho_a = 1,200 \times 0.0707 = 84.9$ lb air; $h_m = 20.7$ Btu/lb air.
Final computed values: p_v, W, and m_a unaltered; $r = 0.24$; $\rho_a = 0.0679$ lb air/ft³; $V = m_a/\rho_a = 84.9/0.0679 = 1,250$ ft³; $h_m = 26.1$ Btu/lb air.
Heat added: $q = h_{m2} - h_{m1} = 26.1 - 20.7 = 5.4$ Btu/lb air; $Q = q \times m_a = 5.4 \times 84.9 = 458$ Btu.
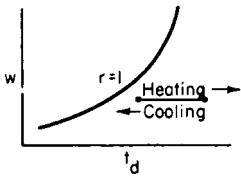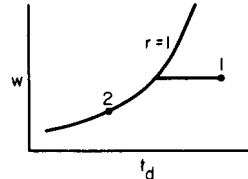
Fig. 4.1.19   Fig. 4.1.20

Cooling below the dew point, and **dehumidification,** entails condensation of vapor; the final atmosphere will be saturated, liquid will appear (see Fig. 4.1.20).

EXAMPLE.   Initial conditions: $p_t = 29$ inHg; $t_d = 75°F$; $t_w = 65°F$; $V = 1,500$ ft³.
Final condition: $t_d = 45°F$.
Initial computed values: $W = 0.0113$ lb vapor/lb air; $\rho_a = 0.0706$ lb air/ft³; $m_a = 1,500 \times 0.0706 = 106.0$ lb air; $h_m = 30.4$ Btu/lb air; $t_c = 60°F$.
Final computed values: $t_d = 45°F$; $p_v = 0.30$ inHg; $r = 1.0$; $W = 0.0065$ lb vapor/lb air; $\rho_a = 0.0754$ lb air/ft³; $V = 106.0/0.0754 = 1,406$ ft³; $h_m = 17.8$ Btu/lb air.
Liquid formed: $m_f = W_1 - W_2 = 0.0113 - 0.0065 = 0.0048$ lb liquid/lb air; $h_f = 50 - 32 = 18$ Btu/lb liquid (assuming that the liquid is drained out at an average temperature $t_f = 50°F$).
Heat abstracted: $q = h_{m1} - h_{m2} - m_1 h_f = 30.4 - 17.8 - 0.0048 \times 18 = 12.5$ Btu/lb air; $Q = q \times m_a = 12.5 \times 106.0 = 1,325$ Btu.

Dehumidification may be accomplished in a **surface cooler,** in which the air passes over tubes cooled by brine or refrigerant flowing through them. The solution of this type of problem is most easily handled on the chart (see Fig. 4.1.21). Locate the point representing the state of the entering atmosphere, and draw a straight line to a point on the saturation curve ($r = 1.0$) at the temperature of the cooling surface. The final state of the issuing atmosphere is approximated by a point on this line whose position on the line is determined by the heat abstracted by the cooling medium. This depends upon the extent of surface and the coefficient of heat transfer.
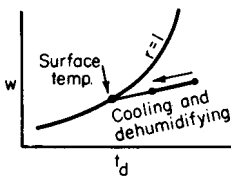
Fig. 4.1.21

Adiabatic saturation (humidification) may be conducted in a spray chamber through which atmosphere flows. A large excess of water is recirculated through spray nozzles, and evaporation is made up by a suitable water supply. After the process has been operating for some time, the water in the spray chamber will have been cooled to the temperature of adiabatic saturation, which differs from the wet-bulb temperature only because of radiation and velocity errors that affect the wet-bulb thermometer. No heat is added or abstracted; the process is adiabatic. The heat of vaporization for the water that is evaporated is supplied by the cooling of the air passing through the chamber. The

wet-bulb temperature of the atmosphere is constant throughout the chamber (Fig. 4.1.22). If the chamber is sufficiently large, the issuing atmosphere will be saturated at the wet-bulb temperature of the entering atmosphere; i.e., as the atmosphere passes through the chamber, t_w remains constant, t_d is reduced from its initial value to t_w. In a chamber of
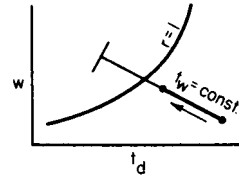
Fig. 4.1.22

commercial size, the action may terminate somewhat short of this, the precise end point being determined by the duration and effectiveness of contact between air and spray water. In any case, the weight of water evaporated equals the increase in the specific humidity of the atmosphere.

EXAMPLE.   Initial conditions $p_t = 30$ inHg; $t_d = 78°F$; $t_w = 55°F$; $r = 0.20$; $W = 28$ grains vapor/lb air.
Final conditions: $t_d = t_w = 55°F$; $r = 1.0$; $W = 64$ grains vapor/lb air.
Water evaporated: $W_2 - W_1 = 64 - 28 = 36$ grains water/lb air

The design of the spray chamber to produce this result is necessarily based upon experience with like apparatus previously built.

In practice, the spray chamber is preceded and followed by heating coils, the first to warm the entering atmosphere to the desired value of t_w, determined by the prescribed final specific humidity, the second to warm the issuing atmosphere to the desired temperature, and simultaneously to reduce its relative humidity to the desired value.

The **spray chamber** that is used for adiabatic saturation (humidification) in winter may be used for dehumidification in summer by supplying the spray nozzles with refrigerated water instead of recirculated water. In this case, the issuing atmosphere will be saturated at the temperature of the spray water, which will be held at the desired dew point. Subsequent heating of the atmosphere to an acceptable temperature will simultaneously reduce the relative humidity to the desired value.

Mixing Two Atmospheres   In recirculating ventilation systems, two atmospheres (1 and 2) are mixed to form a third (3). The state of the final atmosphere is readily found graphically on the psychrometric chart (see Fig. 4.1.23). Locate the points 1 and 2 representing the states of the initial atmospheres. Connect these points by a straight line. Locate a point that divides this line into segments inversely proportional to the weights of air in the respective atmospheres. The division point represents the state of the final mixture, so long as it falls below the saturation curve ($r = 1$). If the final point falls above the saturation curve, as in Fig. 4.1.24, condensation will ensue, and the true final point 4 is found
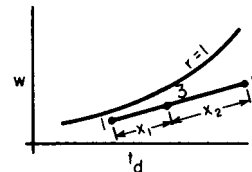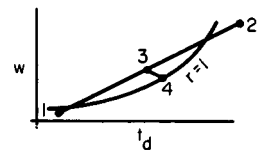
Fig. 4.1.23   Fig. 4.1.24

by drawing a line from the apparent point 3, parallel to the lines of constant wet-bulb temperature, to its intersection with the saturation curve. From all the points involved, readings of specific humidity may be taken, including point 3 when it falls above the saturation curve, and in this case the difference between W_3 and W_4 will be the weight of condensate, pounds per pounds air.

If the chart is sectional and the two points do not fall in the same section, or in any case in which it is preferred, the same method may be carried out arithmetically.

For adiabatic mixing in a steady-flow process of two masses of ''moist'' air, each at the total pressure of p_t,

$$m_{a3} = m_{a1} + m_{a2}$$

In the absence of condensation,

and
$$m_{a3}W_3 = m_{a1}W_1 + m_{a2}W_2$$
$$m_{a3}h_{m3} = m_{a1}h_{m1} + m_{a2}h_{m2}$$

When condensation occurs, assume that the condensate is removed at the final temperature t_4 and that the final mixture consists of dry air and saturated water vapor at this same temperature. The weight of condensate is

$$m_c = m_{a1}W_1 + m_{a2}W_2 - m_{a3}W_4$$

where W_4 is the specific humidity for saturation at temperature t_4 and total pressure p_t. Also

$$m_{a1}h_{m1} + m_{a2}h_{m2} = m_{a2}h_{m4} + m_ch_{f4}$$

In the case of condensation, a trial solution is necessary to find the temperature t_4 that will satisfy these relations.

EXAMPLE.   Two thousand ft^3 of air per min at $t_{d1} = 80°F$ and $t_{w1} = 65°F$ are mixed in an adiabatic, steady-flow process with 1,000 ft^3 of air per min at $t_{d2} = 95°F$ and $t_{w2} = 75°F$; the total pressure of each mixture is 29 inHg.
By computation, $m_{a1} = 140$ lb dry air/min; $W_1 = 0.010$ lb/lb dry air; $m_{a2} = 67.6$ lb dry air/min; $W_2 = 0.0146$ lb/lb dry air.
$\quad m_{a3} = 207.6$ lb dry air/min.
$\quad W_3 = 0.0116$ lb/lb dry air.
$\quad h_{m1} = 30.3$ Btu/lb dry air and $h_{m2} = 38.9$ Btu/lb dry air.
$\quad h_{m3} = 33.1$ Btu/lb dry air.
$\quad t_{d3} = 84.9°F$.

EXAMPLE.   Fifteen hundred ft^3 of air per min at $t_{d1} = 0°F$ and $r_1 = 0.8$ are mixed in an adiabatic, steady-flow process with 1,000 ft^3 of air per min at $t_{d2} = 100°F$ and $r_2 = 0.9$; the total pressure of each mixture is 30 inHg.
By computation, $m_{a1} = 129.6$ lb of dry air/min; $W_1 = 0.000626$ lb/lb dry air; $m_{a2} = 66.9$ lb of dry air/min; $W_2 = 0.03824$ lb/lb dry air; $h_{m1} = 0.09$ Btu/lb dry air; $h_{m2} = 66.29$ Btu/lb dry air.
The three equations that must be satisfied by a choice of the terminal temperature, $t_4 = t_{d4} = t_{w4}$, are

$$m_c = 2.64 - 196.5W_4$$
$$4551 = 196.5h_{m4} + m_ch_{f4}$$
$$W_4 = p_{v4}/1.61(30 - p_{v4}) \quad \text{for } r_4 = 1$$

The value of t_4 that satisfies these equations is 55°F; condensation amounts to 0.84 lb/min.

The **cooling tower** is a chamber in which outdoor atmosphere flows through a spray of entering hot water, which is to be cooled. The temperature of the water is reduced in part by the warming of the air, and in greater part by the evaporation of a portion of the water. The atmosphere enters at given conditions and emerges at a higher temperature and usually saturated ($r = 1$). It is commonly possible to cool the water below the temperature of the entering air, often to about halfway between t_d and t_w. The volume of atmosphere per pound of entering water and the weight of water evaporated are to be computed.

EXAMPLE.   A cooling tower is to receive water at 120°F and atmosphere at $t_d = 90$, $t_w = 80$, whence $p_v = 0.92$, $W = 0.0196$ lb vapor/lb air, $\rho_a = 0.0702$ lb air/ft^3, and $h_m = 43.2$. The water is to be cooled to 85°F. What volume of atmosphere must be passed through the tower, and what weight of water will be lost by evaporation?
The issuing atmosphere will be assumed to be saturated at 115°F. Then $t_d = 115°F$, $p_v = 3.0$ inHg, $W = 0.0690$ lb vapor/lb air, $\rho_a = 0.0623$ lb air/ft^3, and $h_m = 104.4$ Btu/lb air.
The two unknowns are the weight of air to be passed through the tower and the weight of water to be evaporated. The two equations are the water-weight balance and the enthalpy balance (the steady-flow equation for zero heat transfer to or from outside). Assume that 1 lb water enters, of which x lb are evaporated. The water-weight balance $1 + m_aW_1 = 1 - x + m_aW_2$ becomes $x = m_a(W_2 - W_1) = m_a(0.0690 - 0.0196) = 0.0494m_a$. The enthalpy balance $1 \times (120 - 32) + m_ah_{m1} = (1 - x)(85 - 32) + m_ah_{m2}$ becomes $88 + 43.2m_a = 53(1 - x) + 104.4m_a$; whence $53x = 53 - 88 + m_a(104.4 - 43.2) = -35 + 61.2m_a$.
Solving these simultaneous equations, $x = 0.0295$ lb water evaporated per pound of water entering and $m_a = 0.597$ lb air per pound water entering.

In an **evaporative condenser,** vapor is condensed within tubes that are cooled by the evaporation of water flowing over the outside of the tubes; the water evaporates into the atmosphere. The computation of results is similar to that for the cooling tower.

REFRIGERATION

Vapor Compression Machines   The essential parts of a vapor-compression system are the same as in the system using air, except that the expansion cylinder is replaced by an expansion value through which the liquefied medium flows from the high-pressure condensing coils to the low-pressure brine coils. The cycle of operation is best shown on the T-S plane (Fig. 4.1.25). The point B represents the state of the refrigerating medium leaving the brine coils and entering the compressor. Usually in this state the fluid is nearly dry saturated vapor; i.e., point B is near the saturation curve S_g. BC represents the assumed reversible adiabatic compression, during which the fluid is usually superheated. In the state C, the superheated vapor passes into the cooling coils and is cooled at constant pressure, as indicated by CD, and then condensed at temper-
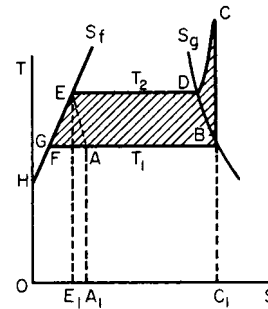
Fig. 4.1.25   Vapor compression refrigeration cycle.

ature T_2, as shown by DE. The liquid now flows through the expansion valve into the brine coils. This is a throttling process, and the final-state point A is located on the T_1-line in such a position as to make the enthalpy for state A ($=$ area $OHGAA_1$) equal to the enthalpy at E ($=$ area $OHEE_1$). The mixture of liquid and vapor now absorbs heat from the brine and vaporizes, as indicated by AB.
The **heat absorbed from the brine,** represented by area A_1ABC_1, is

$$Q_1 = h_b - h_a = h_b - h_e$$

The **heat rejected to the cooling water,** represented by area C_1CDEE_1, is

$$Q_2 = h_c - h_e = c_p(T_c - T_d) + r_2 \quad \text{approx}$$

where r_2 denotes the enthalpy of vaporization at the upper temperature T_2, and c_p the specific heat of the superheated vapor. The **work that must be supplied per pound of fluid circulated** is $W = Q_2 - Q_1 = h_c - h_b$. The ratio $Q_1/W = (h_b - h_e)/(h_c - h_b)$ is sometimes called the **coefficient of performance.**
If Q denotes the heat to be absorbed from the brine per hour, then the **quantity of fluid circulated per hour** is $m = Q/(h_b - h_a)$; or, if B is taken on the saturation curve, $m = Q/(h_{g1} - h_{f2})$.
The work per hour is $W = m(h_c - h_{g1}) = Q(h_c - h_{g1})/(h_{g1} - h_{f2})$ ft$\cdot$lb, and the **horsepower required** is $H = Q(h_c - h_{g1})/2544(h_{g1} - h_{f2})$. The (U.S.) ton of refrigeration represents a cooling rate of 200 Btu/min, which is closely equivalent to that of 50 kcal/min, 210 kJ/min, or 3.5 kW. (Extensive tables of refrigerant properties are found in the ''ASHRAE Handbook.'')
If v_{g1} is the volume of the saturated vapor at the temperature T_1 in the brine coils, and n the number of working strokes per minute, the **displacement volume** of the **compressor cylinder** is $V = mv_{g1}/(60n)$.
The work necessary for operating a refrigerator, although usually supplied through the compressor, may be supplied in other ways. Thus in **absorption refrigerators** (see Secs. 12 and 19) an absorbent, usually water, absorbs the refrigerant, usually ammonia. The water, by its affinity for the ammonia, has, in a thermodynamic sense, ability to do work.

Having absorbed the ammonia and thereby lost its ability to do work, the water may have its work capacity restored by passing the ammonia-water solution through a rectifying column from which water and ammonia emerge. With operation under a suitable pressure, the ammonia is condensed to a liquid. This, in turn, may be evaporated, yielding refrigeration, the ammonia vapors being once again absorbed in the water. Thermodynamically the analysis for these absorption cycles is similar to that for compression cycles. See Wood, ''Applications of Thermodynamics,'' 2d ed., Addison-Wesley, for an in-depth discussion of the absorption refrigeration cycle.

Other papers on absorption refrigeration or **heat pump systems** include Chen, *Heat Recovery Systs. & CHP,* **30,** 1988, pp. 37–51; Narodoslawsky et al., *Heat Recovery Systs. & CHP,* **8,** no. 5, 1988, pp. 459–468, and **8,** no. 3, 1988, pp. 221–233; Egrican, **8,** no. 6, 1988, pp. 549–558; and for the aqua ammonia system, Ataer and Goguy, *Int. J. Refrig.,* **14,** Mar. 1991, pp. 86–92. Kalina (*J. Eng. Gas Turbines & Power,* **106,** 1984, pp. 737–742) proposed a new cycle using an ammonia-water solution as a bottoming cycle system. The proper selection of the composition and parameters of the working fluid was stated to be critical in the cycle design. Absorption replaces condensation of the working fluid after expansion in the turbine. Special care is also needed to regulate pressure drops between turbine stages. Chuang et al. [*AES (A.S.M.E.),* **10,** no. 3, 1989, pp. 73–77] evaluated exergy changes in the cycle while Kouremenos and Rogdaikis [*AES (A.S.M.E.),* **19,** 1990, pp. 13–19] developed a computer code for use with *h-s* and *T-s* diagrams. For heat pumps see Hihara and Sato, *ASME/JSME Thermal Eng. Proc.,* **3,** 1991, p. 297. For **supercritical heat pump** cycles see, e.g., Angelino and Invernizzi, *Int. J. Refrig.,* **17,** no. 8, 1991; pp. 543–554.

An analysis of industrial gas separation to yield minimum overall cost, i.e., taking into account both energy and capital cost, for the processes of distillation, absorption, adsorption, and membranes was given by Haselden, *Gas Separation & Purification,* **3,** Dec. 1989, pp. 209–216. Analysis of the thermodynamic regenerator cycle with compressed-gas throttling, called the **Linde cycle,** was made by Lavrenchenko, *Cryogenics,* **33,** no. 11, 1993, pp. 1040–1045.

Orifice pulse tube refrigerators are receiving more attention. Kittel (*Cryogenics,* **32,** no. 9, 1992, pp. 843–844) examines their thermodynamic efficiency and refers to Radebaugh (*Adv. Cryog. Eng.,* **35B,** 1990, pp. 1192–1205) for a review of these devices.

de Rossi et al. (*Proc Mtg. IIR–IIF Comm.* B1, Tel Aviv, 1990) gave an interactive computer code for refrigerant thermodynamic properties which was evaluated for 20 different refrigerants in vapor compression and a reversed Rankine cycle (*Appl. Energy,* **38,** 1991, pp. 163–180). The evaluation included an exergy analysis. A similar publication was *AES (A.S.M.E.),* **3,** no. 2, 1987, pp. 23–31. Other papers include Kumar et al. (*Heat Recovery Systems & CHP,* **9,** no. 2, 1989, pp. 151–157), Alefeld (*Int. J. Refrig.,* **10,** Nov. 1987, pp. 331–341), and Nikolaidis and Probert (*Appl. Energy,* **43,** 1992, pp. 201–220).

The problem of deciding which refrigerants will be used in the future is complex. Although recommendations exist as to the phasing out of existing substances, one cannot predict the extent to which the recommendations will be followed. The blends proposed by several manufacturers have yet to receive extensive testing. One must bear in mind that in addition to the thermodynamic suitability considerations of material compatibility, ozone depletion potential, etc. have to be taken into account. According to Dr. McLinden of the National Institute of Standards and Technology, Boulder, CO (private communication, March 1995), R 11, R 12, R 22, R 123, R 134a as well as ammonia (R 717) and propane/isobutane (R 290/R 600a) blends are likely to be important for many years. The presentation of the tables in Sec. 4.2 has been revised to include some of these plus a few other compounds used in ternary blends. The best single source for further information is the ''ASHRAE Handbook—Fundamentals,'' 1993 or latest edition.

STEAM CYCLES

Rankine Cycle The ideal Rankine cycle is generally employed by engineers as a standard of reference for comparing the performance of

actual steam engines and steam turbines. Figure 4.1.26 shows this cycle on the *T-S* and *p-V* planes. *AB* represents the heating of the water in the boiler, *BC* represents evaporation (and superheating if there is any), *CD* the assumed isentropic expansion in the engine cylinder, and *DA* condensation in the condenser.
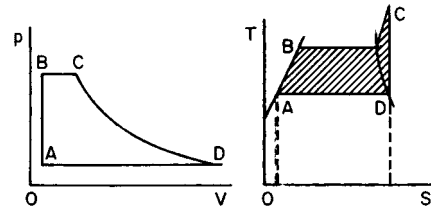
Fig. 4.1.26 Rankine cycle.

Let h_a, h_b, h_c, h_d represent the enthalpy per unit mass of steam in the four states *A*, *B*, *C*, and *D*, respectively. Then the energy transformed into work, represented by the area *ABCD*, is $h_c - h_d$ (enthalpies in Btu/lbm).

The energy expended on the fluid is $h_c - h_a$, hence the **Rankine cycle efficiency** is $e_t = (h_c - h_d)/(h_c - h_a)$.

The **steam consumption** of the ideal Rankine engine in pounds per horsepower-hour is $N_r = 2,544/(h_c - h_d)$. Expressed in pounds per kilowatthour, the steam consumption of the ideal Rankine cycle is $3,412.7/(h_c - h_d)$.

The performance of an engine is frequently stated in terms of the heat used per horsepower-hour. For the ideal Rankine engine, this is

$$Q_r = 2,544/e_t = 2,544(h_c - h_a)/(h_c - h_d)$$

Efficiency of the Actual Engine Let Q denote the heat transformed into work per pound of steam by the actual engine; then if Q_1 is the heat furnished by the boiler per pound of steam, the **thermal efficiency of the engine** is $e_t = Q/Q_1$.

The efficiency thus defined is misleading, as it takes no account of the conditions of boiler and condenser pressure, superheat, or quality of steam. It is customary therefore to define the efficiency as the ratio Q/Q_a, where Q_a is the **available heat,** or the heat that could be transformed under ideal conditions. For steam engines and turbines, the Rankine cycle is usually taken as the ideal, and the quantity $Q/Q_a = Q(h_c - h_d)$ is called the **engine efficiency.** For engines and turbines, this efficiency ranges from 0.50 to 0.85. The engine efficiency *e* may also be expressed in terms of steam consumed; thus, if N_a is the steam consumption of the actual engine and N_r is the steam consumption of the ideal Rankine engine under similar conditions, then $e = N_r/N_a$.

EXAMPLE.   Suppose the boiler pressure to be 180 psia, superheat 150°F, and the condenser pressure 3 in of mercury. From the steam tables or diagram, the following values are found: $h_c = 1,283.3$, $h_d = 942$, $h_a = 82.99$. The available heat is $Q_a = 1,283.3 - 942 = 341.3$ Btu, and the thermodynamic efficiency of the cycle is $341.3/(1,283.3 - 82.99) = 0.284$. The steam consumption per horsepower-hour is $2,544/341.3 = 7.46$ lb, and the heat used per horsepower-hour is $2,544/0.284 = 8,960$ Btu. If an actual engine working under the same conditions has a steam consumption of 11.4 lb/(hp · h), its efficiency is $7.46/11.4 = 0.655$, and its heat consumption per horsepower-hour is $8,960/0.655 = 13,680$ Btu.

Reheating Cycle Let the steam after expansion from p_1 to an intermediate pressure p_2 (*cd*, Fig. 4.1.27) be reheated at constant pressure p_2, as indicated by *de*. Then follows the isentropic expansion to pressure p_3, represented by *ef*.

The energy absorbed by 1 lb of steam is $h_c - h_a$ from the boiler, and $h_e - h_d$ from the reheating. The work done, neglecting the energy required to operate the boiler feed pump, etc., is $h_c - h_d + h_e - h_f$. Hence the efficiency of the cycle is

$$e_t = \frac{h_c - h_d + h_e - h_f}{h_c - h_a + h_e - h_d}$$

Bleeding Cycle In the **regenerative** or bleeding cycle, steam is drawn from the turbine at one or more stages and used to heat the feed water. Figure 4.1.28 shows a diagrammatic arrangement for bleeding at one stage. Entering the turbine is $1 + w$ lb of steam at p_1, t_1, and enthalpy

h_1. At the bleeding point w lb at p_2, t_2, h_2 enters the feedwater heater. The remaining 1 lb passes through the turbine and condenser and enters the feedwater heater as water at temperature t_3. Let t' denote the temperature of the water leaving the heater, and h' the corresponding en-
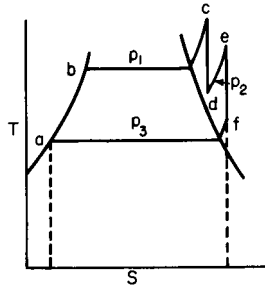
Fig. 4.1.27   Reheating cycle.

thalpy of the liquid. Then the equation for the interchange of heat in the heater is

$$w(h_2 - h') = h' - h_{f3}$$

The work done by the bled steam is $w(h_1 - h_2)$ and that by the 1 lb of steam going completely through the turbine is $h_1 - h_3$. Total work $= w(h_1 - h_2) + (h_1 - h_3)$ if work to the pumps is neglected. The heat supplied between feedwater heater and turbine is $(1 + w)(h_1 - h')$. Hence the ideal efficiency of the cycle is

$$e_t = \frac{w(h_1 - h_2) + h_1 - h_3}{(1 + w)(h - h')}$$

A **computer program** which is claimed to model the thermodynamic performance of any steam power system has been described by Thelen and Somerton [*AES, (A.S.M.E.),* **33,** 1994, pp. 167–175], extending an earlier analysis.
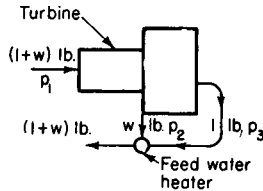
Fig. 4.1.28   Regenerative feedwater heating.

The use of selected fluid mixtures in Rankine cycles was proposed by Radermacher (*Int. J. Ht. Fluid Flow,* **10,** no. 2, June 1989, p. 90). Lee and Kim (*Energy Convsn. Mgmt.,* **33,** no. 1, 1992, pp. 59–67) describe the finite time optimization of a modified Rankine heat engine. For a steam Wankel engine see Badr et al. (*Appl. Energy,* **40,** 1991, pp. 157–190).

Heat from **nuclear reactors** can be used for heating services or, through thermodynamic cycles, for power purposes. The reactor coolant transfers the heat generated by fission so as to be used directly, or through an intermediate heat-exchange system, avoiding radioactive contamination. Steam is the preferred thermodynamic fluid in practice so that the Rankine-cycle performance standards with regenerative and reheat variations prevail. Adaptation of gas-turbine cycles, using various gases, can be expected as allowable reactor temperatures are raised.

Many engineers and scientists are actively engaged in research dealing with the location, production, utilization, transmission, storage, and distribution of new forms of energy. Examples are the study of the energy released in the fusion of hydrogen nuclei and research in solar energy. Considerable effort is being expended in studying the feasibility of combining the gas turbine with a steam-generating plant. The possi-

bility of efficiency improvement over the steam cycle is due to higher inlet temperatures associated with the gas turbine. Significant advances are predicted in the near future in expanding our energy sources and reserves.

THERMODYNAMICS OF FLOW OF COMPRESSIBLE FLUIDS

Important examples of the flow of compressible fluids are the following: (1) the flow of air and steam through orifices and short tubes or nozzles, as in the steam turbine, (2) the flow of compressed air, steam, and illuminating gas in long mains, (3) the flow of low-pressure gases, as furnace gases in ducts and chimneys or air in ventilating ducts, and (4) the flow of gases in moving channels, as in the centrifugal fan.

Notation

Let $A =$ area of section, ft^2
$C =$ empirically determined coefficient of discharge
$D =$ inside diameter of pipe, ft
$d = 12D =$ inside diameter of pipe, in
$F_{12} =$ energy expended in overcoming internal and external friction between sections A_1 and A_2
$F' =$ energy used in overcoming friction, $\text{ft} \cdot \text{lb/lb}$ of fluid flowing
$f =$ friction factor $= 4f'$
$g = 32.2 =$ local acceleration of gravity, ft/s^2
$g_c =$ a dimensional constant
$h =$ enthalpy, Btu/lb
$J = 778.3 \; \text{ft} \cdot \text{lb/Btu}$
$k = c_p/c_v$
$L =$ equivalent length of pipe, ft
$m =$ mass of fluid flowing past a given section per s, lb
$\mu =$ viscosity, cP
$P =$ pressure, lb/in^2 abs
$\Delta P =$ differential pressure across nozzle, lb/in^2
$p =$ pressure of fluid at given section, lb/ft^2 abs
$p_m =$ critical flow pressure
$Q_{12} =$ heat entering the flowing fluid between sections A_1 and A_2
$q =$ volume of fluid flowing past section, $\text{ft}^3\text{/min}$
$R =$ ideal gas constant
$\rho =$ density, lb/ft^3
$T =$ temperature, °R
$\bar{v} =$ mean velocity at the given section, ft/s
$v =$ specific volume
$w =$ weight of fluid power flowing past a given section per s, lb
$z =$ height from center of gravity of flow to fixed base level, ft

The cross sections of the tube or channel are denoted by A_1, A_2, etc. (Fig. 4.1.29), and the various magnitudes pertaining to these sections are denoted by corresponding subscripts. Thus, at section A_1, the velocity, specific volume, and pressure are, respectively, $\bar{v}_1$, v_1, p_1; at section A_2, they are $\bar{v}_2$, v_2, p_2.
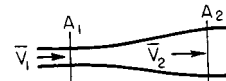
Fig. 4.1.29

Fundamental Equations   In the interpretation of fluid-flow phenomena, three fundamental equations are of importance.

1. The continuity equation, or material balance,

$$\frac{A_1 \bar{v}_1}{v_1} = \frac{A_2 \bar{v}_2}{v_2} \quad \text{or} \quad \frac{dv}{v} = \frac{dA}{A} + \frac{d\bar{v}}{\bar{v}}$$

2. The first law of energy balance for steady flow,

$$q = (h_2 - h_1) + \frac{\bar{v}_2^2 - \bar{v}_1^2}{2g_c} + \frac{g}{g_c}(z_2 - z_1)$$

3. The available energy balance for a steady-flow process, based on unit weight, is

$$v\,dp + \frac{\overline{v}\,d\overline{v}}{g} + dF + dz = 0$$

In the process here discussed, no net external or shaft work is performed.

For most actual processes, the third equation cannot be integrated because the actual path is not known. Usually, adiabatic flow is assumed, but occasionally the assumption of isothermal conditions may be more nearly correct.

For **adiabatic flow of imcompressible fluids,** the last equation above can be written in the more familiar form known as Bernoulli's equation:

$$(p_2 - p_1)/\rho + (\overline{v}_2^2 - \overline{v}_1^2)/2 + g/g_c(z_2 - z_1) = 0$$

Flow through Orifices and Nozzles   As a compressible fluid passes through a nozzle, drop in pressure and simultaneous increase in velocity result. By assuming the type of flow, e.g., adiabatic, it is possible to calculate from the properties of the fluid the required area for the cross section of the nozzle at any point in order that the flowing fluid may just fill the provided space. From this calculation, it is found that for all compressible fluids the nozzle form must first be converging but eventually, if the pressure drops sufficiently, a place is reached where to accommodate the increased volume due to the expansion the nozzle must become diverging in form. The smallest cross section of the nozzle is called the throat, and the pressure at the throat is the **critical flow pressure** (not to be confused with the critical pressure). If the nozzle is cut off at the throat with no diverging section and the pressure at the discharge end is progressively decreased, with fixed inlet pressure, the amount of fluid passing increases until the discharge pressure equals the critical, but further decrease in discharge pressure does not result in increased flow. This is not true for thin plate orifices. For any particular gas, the ratio of critical to inlet pressure is approximately constant. For gases, $p_m/p_1 = 0.53$ approx.; for saturated steam the ratio is about 0.575; and for moderately superheated steam it is about 0.55.

Formulas for Orifice Computations   The general fundamental relation is given by the energy balance $(\overline{v}_2^2 - \overline{v}_1^2)/(2g_c) = -h_{12}$. Referring to Fig. 4.1.30, let section 2 be taken at the orifice, section 3 is somewhat
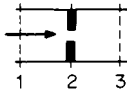
Fig. 4.1.30

beyond the orifice on the downstream side, and section 1 is before the orifice on the upstream side. Then

$$\overline{v}_2 = C\sqrt{2g_c(h_1 - h_2)} \bigg/ \sqrt{1 - \left(\frac{A_2}{A_1}\right)^2\left(\frac{v_1}{v_2}\right)^2}$$

The coefficient of discharge C is discussed in Secs. 3 and 16. The volume of gas passing is $\overline{v}_2 A_2$ ft³/s, and the quantity is $\overline{v}_2 A_2\rho$. For ideal gases, assuming reversible adiabatic expansion through the orifice,

$$\overline{v}_2 = C\,\frac{\sqrt{2g_c p_1 \overline{v}_1 \dfrac{k}{k-1}\left[1 - \left(\dfrac{p_2}{p_1}\right)^{(k-1)/k}\right]}}{\sqrt{1 - \left(\dfrac{A_2}{A_1}\right)^2\left(\dfrac{p_2}{p_1}\right)^{2/k}}}$$

$$m = CA_2 p_2\,\frac{\sqrt{\dfrac{2g_c}{RT_1}\dfrac{k}{k-1}\left(\dfrac{p_1}{p_2}\right)^{(k-1)/k}\left[\left(\dfrac{p_1}{p_2}\right)^{(k-1)/k} - 1\right]}}{\sqrt{1 - \left(\dfrac{A_2}{A_1}\right)^2\left(\dfrac{p_2}{p_1}\right)^{2/k}}}$$

Often $\overline{v}_1$ is small compared with $\overline{v}_2$, and under these conditions the denominators in the preceding equations become approximately equal to unity. For air, assuming $R = 53.3$, $k = 1.3937$, and $\overline{v}_1$ negligible,

$$m = 2.05CA_2 p_2 \sqrt{(1/T_1)(p_1/p_2)^{0.283}[(p_1/p_2)^{0.283} - 1]}$$

Although the preceding formulas are generally applicable under the assumed conditions, it must be remembered that irrespective of the value of p_3, p_2 cannot become less than p_m. When p_3 is less than p_m, the flow rate becomes independent of the downstream pressure; for ideal gases,

$$m = CA_2 p_1 \sqrt{\frac{g_c}{RT_1}\,k\left(\frac{2}{k+1}\right)^{(k+1)(k-1)}}$$

or for air

$$m = 0.53Cp_1\,\frac{A_2}{\sqrt{T_1}}$$

The following formula is useful for calculating the flow rate, in cubic feet per minute, of any gas (provided no condensation occurs) through a nozzle for pressure drops less than the critical range:

$$q_1 = \frac{31.5Cd_n^2 Y'}{\rho_1}\sqrt{\rho_1\,\Delta P}$$

In this equation,

$$Y' = \left(\frac{k}{k-1}\right)^{1/2}\left(\frac{P_2}{P_1}\right)^{1/k}$$

$$\times\sqrt{\left[1 - \left(\frac{P_2}{P_1}\right)^{(k-1)/k}\right]\bigg/\left(1 - \frac{P_2}{P_1}\right)\left[1 - \left(\frac{d_n}{d_1}\right)^4\left(\frac{P_2}{P_1}\right)^{2/k}\right]}$$

where P_1 = static pressure on upstream side of nozzle, psia; P_2 = static pressure on downstream side of nozzle, psia; d_1 = diameter of pipe upstream of nozzle, in; d_n = nozzle throat diameter, in; ρ_1 = specific weight of gas at upstream side of nozzle, lb/ft³. Values of Y' are given in Table 4.1.3.

Where the pressure drop through the orifice is small, the hydraulic formulas applicable to incompressible fluids may be employed for gases and other compressible fluids.

In general, the formulas of the preceding section are applicable to nozzles. When so used, however, the proper value of the discharge coefficient must be employed. For steam nozzles, this may be as high as 0.94 to 0.96, although for many orifice installations it is as low as 0.50 to 0.60. Steam nozzles constitute a most important type, and calculations for these are best carried out with the aid of a Mollier or similar chart.

Formulas for Discharge of Steam   When the back pressure p_3 is less than the critical pressure p_m, the discharge depends upon the area of orifice A_2 and reservoir pressure p_1. There are three formulas widely used to express, approximately, the discharge m of **saturated** steam in terms of A_2 and p_1 as follows:

1. Napier's equation, $m = A_2 p_1/70$.
2. Grashof's formula, $m = 0.0165 A_2 p_1^{0.97}$.
3. Rateau's formula, $m = A_2 p_1(16.367 - 0.96 \log p_1)/1,000$.

In these formulas, A_2 is to be taken in square inches, p_1 in pounds per square inch. Napier's formula is merely convenient as a rough check. Formulas 2 and 3 are applicable to well-rounded convergent orifices, in which case the coefficient of discharge may be taken as 1; i.e., no correction is required.

When the back pressure p_2 is greater than the critical flow pressure p_m, the velocity and discharge are found most conveniently from the general formulas of flow. From the steam tables or from the **Mollier chart,** find the initial enthalpy h_1 and the enthalpy h_2 after isentropic expansion; also the specific volume v_2 (see Fig. 4.1.31). Then

$$\overline{v}_2 = 223.7\sqrt{h_1 - h_2} \qquad\text{and}\qquad m = A_2\overline{v}_2/v_2$$

The same method is used in the case of steam initially superheated.

EXAMPLE.   Required the discharge through an orifice ½ in diam of steam at 140 psi superheated 110°F, back pressure, 90 psia.

Table 4.1.3 Values for Y′

| | k = 1.40 | | | | | k = 1.35 | | | | | k = 1.30 | | | | |
| | d_n/d_1 | | | | | d_n/d_1 | | | | | d_n/d_1 | | | | |
P_2/P_1	0	0.2	0.3	0.4	0.5	0	0.2	0.3	0.4	0.5	0	0.2	0.3	0.4	0.5
1.00	1.000	1.001	1.004	1.013	1.033	1.00	1.001	1.004	1.013	1.033	1.000	1.001	1.004	1.013	1.033
0.99	0.995	0.995	0.999	1.007	1.027	0.994	0.995	0.999	1.007	1.027	0.994	0.995	0.998	1.007	1.026
0.98	0.989	0.990	0.993	1.002	1.021	0.989	0.990	0.993	1.001	1.020	0.988	0.989	0.992	1.001	1.020
0.97	0.984	0.985	0.988	0.996	1.015	0.983	0.984	0.987	0.995	1.014	0.983	0.983	0.986	0.995	1.013
0.96	0.978	0.979	0.982	0.990	1.009	0.978	0.978	0.981	0.990	1.008	0.977	0.977	0.980	0.989	1.007
0.95	0.973	0.974	0.977	0.985	1.002	0.972	0.973	0.976	0.984	1.001	0.971	0.972	0.974	0.982	1.000
0.94	0.967	0.968	0.971	0.979	0.996	0.966	0.967	0.970	0.978	0.995	0.965	0.966	0.968	0.976	0.993
0.93	0.962	0.963	0.965	0.973	0.990	0.961	0.961	0.964	0.972	0.989	0.959	0.960	0.962	0.970	0.987
0.92	0.956	0.957	0.960	0.967	0.984	0.955	0.955	0.958	0.966	0.982	0.953	0.954	0.956	0.964	0.980
0.91	0.951	0.951	0.954	0.961	0.978	0.949	0.950	0.952	0.960	0.976	0.947	0.948	0.950	0.957	0.973
0.90	0.945	0.946	0.948	0.956	0.971	0.943	0.944	0.946	0.953	0.969	0.941	0.942	0.944	0.951	0.966
0.89	0.939	0.940	0.943	0.950	0.965	0.937	0.938	0.940	0.947	0.963	0.935	0.935	0.938	0.945	0.959
0.88	0.934	0.934	0.937	0.944	0.959	0.931	0.932	0.934	0.941	0.956	0.929	0.929	0.932	0.938	0.953
0.87	0.928	0.928	0.931	0.938	0.953	0.925	0.926	0.926	0.935	0.950	0.922	0.923	0.926	0.932	0.946
0.86	0.922	0.923	0.925	0.932	0.946	0.919	0.920	0.922	0.929	0.943	0.916	0.917	0.919	0.926	0.939
0.85	0.916	0.917	0.919	0.926	0.940	0.913	0.914	0.916	0.923	0.936	0.910	0.911	0.913	0.923	0.932
0.84	0.910	0.911	0.913	0.920	0.933	0.907	0.908	0.910	0.916	0.930	0.904	0.904	0.907	0.919	0.925
0.83	0.904	0.905	0.907	0.913	0.927	0.901	0.902	0.904	0.910	0.923	0.897	0.898	0.900	0.916	0.918
0.82	0.898	0.899	0.901	0.907	0.920	0.895	0.895	0.898	0.904	0.917	0.891	0.891	0.894	0.900	0.911
0.81	0.892	0.893	0.895	0.901	0.914	0.889	0.889	0.891	0.897	0.910	0.885	0.885	0.887	0.893	0.904
0.80	0.886	0.887	0.889	0.895	0.907	0.883	0.883	0.885	0.891	0.903	0.878	0.879	0.880	0.886	0.897
0.79	0.880	0.881	0.883	0.889	0.901	0.876	0.877	0.879	0.834	0.896	0.872	0.872	0.874	0.880	0.890
0.78	0.874	0.875	0.877	0.882	0.894	0.870	0.870	0.872	0.878	0.889	0.865	0.865	0.868	0.873	0.883
0.77	0.868	0.869	0.871	0.876	0.887	0.864	0.864	0.866	0.871	0.882	0.859	0.859	0.861	0.866	0.876
0.76	0.862	0.862	0.864	0.869	0.881	0.857	0.858	0.859	0.865	0.876	0.852	0.852	0.854	0.859	0.869
0.75	0.856	0.856	0.858	0.863	0.874	0.851	0.851	0.853	0.858	0.869	0.845	0.846	0.848	0.852	0.862
0.74	0.849	0.850	0.852	0.857	0.867	0.844	0.845	0.846	0.851	0.862	0.839	0.839	0.841	0.845	0.855
0.73	0.843	0.844	0.845	0.850	0.860	0.838	0.838	0.840	0.845	0.855	0.832	0.832	0.834	0.838	0.848
0.72	0.837	0.837	0.839	0.844	0.854	0.831	0.831	0.833	0.838	0.848	0.825	0.825	0.827	0.831	0.841
0.71	0.820	0.831	0.832	0.837	0.847	0.825	0.825	0.827	0.831	0.840	0.818	0.819	0.820	0.824	0.834
0.70	0.824	0.824	0.826	0.830	0.840	0.818	0.818	0.820	0.824	0.833	0.811	0.812	0.813	0.817	0.826

If the velocity of approach is zero (as with a nozzle taking in air from the outside), d_1 is infinite and d_n/d_1 is zero.

From the Mollier chart and the steam tables, $h_1 = 1,255.7$, $h_2 = 1,214$, $v_2 = 5.30$ ft³.

$$\bar{v}_2 = 233.7\sqrt{1,255.7 - 1,214} = 1,455$$
$$A_2 = 0.1964 \text{ in}^2 = (0.1964/144)\text{ft}^2$$
$$m = A_2\bar{v}_2/v_2 = (0.1964/144) \times (1,455/5.30) = 0.372 \text{ lb/s}$$

This calculation assumes ideal conditions, and the results must be multiplied by the correct coefficient of discharge to get actual results.

Flow through Converging-Diverging Nozzles At the throat, or smallest cross section of the nozzle (Fig. 4.1.32), the pressure of saturated steam takes the value $p_m = 0.57p_1$. The quantity discharged is fixed by the area A_2 of the throat and the initial pressure p_1. For saturated steam, Grashof's or Rateau's formula (see above) may be used. The diverging part of the nozzle permits further expansion to the break pressure p_3, the velocity of the jet meanwhile increasing from $\bar{v}_m(=\bar{v}_2)$, the critical velocity at the throat, to $\bar{v}_3$ given by the fundamental equation $\bar{v}_3 = 223.7\sqrt{h_1 - h_3}$.

The frictional resistances in the nozzle have the effect of decreasing the jet energy $\bar{v}_3^2/(2g_c)$ and correspondingly increasing the enthalpy of the flowing fluid. Thus, if h_3 is the enthalpy in the final state with
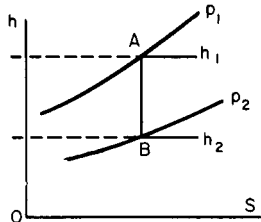
Fig. 4.1.31

frictionless expansion, h_3' ($>h_3$) is the enthalpy when friction is taken into account; hence $(\bar{v}_3')^2/(2g_c) = (h_1 - h_3')$ is less than $\bar{v}_3^2/g_c = h_1 - h_3$. The loss of kinetic energy, in Btu, is $h_3' - h_3$, and the ratio of this loss to the available kinetic energy, i.e., $(h_3' - h_3)/(h_1 - h_3)$, is denoted by y.
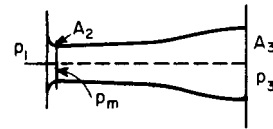
Fig. 4.1.32

The **design of a nozzle for a given discharge** m with pressures p_1 and p_3 is most conveniently effected with the aid of the Mollier chart. Determine p_m, the critical pressure, and h_1, h_m, h_3, assuming frictionless flow. Then

$$\bar{v}_m = 223.7\sqrt{h_1 - h_m}$$

and

$$\bar{v}_3' = 223.7\sqrt{(1 - y)(h_1 - h_3)}$$

Next find v_m and v_3'. Then, from the equation of continuity,

$$A_m = mv_m/\bar{v}_m$$

and

$$A_3' = mv_3'/\bar{v}_3'$$

The following example illustrates the method.

EXAMPLE. Required the throat and end sections of a nozzle to deliver 0.7 lb of steam per second. The initial pressure is 160 psia, the back pressure 15 psia, and the steam is initially superheated 100°F; y = 0.15.

The critical pressure is $160 \times 0.55 = 88$ lb. On the Mollier chart (Fig. 4.1.33), the point A representing the initial state is located, and line of constant entropy (frictionless adiabatic) is drawn from A. This cuts the curves $p = 88$ and $p = 15$ in the points B and C, respectively. The three values of h are found to be $h_1 = 1,253$, $h_m = 1,199$, $h_3 = 1,067$. Of the available drop in enthalpy, $h_1 - h_3 = 185.5$ Btu,
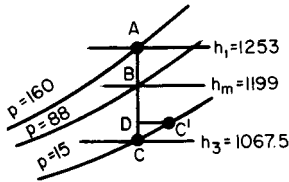
Fig. 4.1.33

15 percent or 27.9 Btu is lost through friction. Hence, $CD = 27.9$ is laid off and D is projected horizontally to point C' on the curve $p = 15$. Then C' represents the final state of the steam, and the quality is found to be $x = 0.943$. The specific volume in the state C' is $26.29 \times 0.943 = 24.8$ ft^3. Likewise, the specific volume for the state B is found to be 5.29 ft^3/lb.

For the velocities at throat and end sections,

$$\bar{v}_m = 223.7\sqrt{1,253 - 1,199} = 1,643 \text{ ft/s}$$
$$\bar{v}_3 = 223.7\sqrt{185.5 - 27.9} = 2,813 \text{ ft/s}$$
$$A_m = (0.7 \times 5.29)/1,643 = 0.00225 \text{ ft}^2 = 0.324 \text{ in}^2$$
$$A_3 = (0.7 \times 24.8)/2,813 = 0.00617 \text{ ft}^2 = 0.89 \text{ in}^2$$

The diameters are $d_m = 0.643$ in and $d_3 = 1.064$ in.

Divergence of Nozzles Figure 4.1.34 gives, for various ratios of expansion, the required ''divergence'' of nozzle, i.e., the ratio of the area of any section to the throat area. Thus in the case of saturated steam, if the final pressure is $\frac{1}{15}$ of the initial pressure the ratio of the areas is 3.25. The curves apply to frictionless flow; the effect of friction is to increase the divergence.
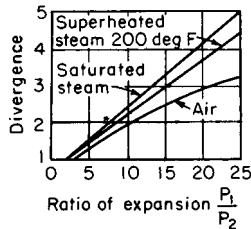
Fig. 4.1.34

Theory of Supersaturation Certain discrepancies between the discharge of saturated steam through an orifice as calculated from the preceding theory and the discharge actually observed are explained by a hypothesis first advanced by Martin, viz., that steam when expanded rapidly, as in turbine nozzles, becomes supersaturated; in other words, the condensation required by the ordinary theory of adiabatic expansion does not occur on account of the rapidity of the expansion.

The effect of supersaturation in turbines is a loss of energy, the amount of which may be 1.5 to 3 percent of the available energy of the steam.

Flow of Wet Steam When the steam entering a nozzle is wet, the speed of the water particles at exit is not the same as the speed of the steam. Denoting by $\bar{v}$ the speed of the steam, the speed of the water drop is $f\bar{v}$, and f may vary perhaps 0.20 to 0.05 or less, depending on the pressure. The actual velocity $\bar{v}$ of the steam is greater than the velocity $\bar{v}_0$ calculated on the usual assumption that steam and water have the same velocity. If x is the quality of the steam, the ratio of these velocities is

$$\bar{v}/\bar{v}_0 = 1/\sqrt{x + f^2(1 - x)}$$

Thus with $x = 0.92$, $f = 0.15$, $\bar{v}/\bar{v}_0 = 1.036$. Since the discharge is

practically proportional to the steam velocity, the actual discharge in this case is 3.6 percent greater than the discharge computed on the usual assumptions.

Velocity Coefficients, Loss of Energy y On account of friction losses, the actual velocity $\bar{v}$ attained by the jet is less than the velocity $\bar{v}_0$ calculated under ideal conditions. That is, $\bar{v} = x\bar{v}_0$, where $x \ (< 1)$ is a velocity coefficient. The coefficient x is connected with the coefficient y, giving the loss of energy, by the relation, $y = 1 - x^2$.

The elaborate and accurate experiments of the General Electric Co. on turbine nozzles give convergent nozzles values of x in excess of 0.98, with a corresponding loss of energy $y = 0.025$ to 0.04. For similar nozzles, the experiments of the Steam Nozzles Research Committee (of England) by a different method give values of x around 0.96, or $y = 0.08$. In the case of divergent nozzles, the velocity coefficient may be somewhat lower.

FLOW OF FLUIDS IN CIRCULAR PIPES

The fundamental equation as previously given on a unit weight bases, assuming the pipe horizontal, is

$$(\bar{v} \, d\bar{v}/g) + v \, dp + dF = 0$$

The friction term dF includes not only losses due to frictional flow along the pipe but also those due to fittings, valves, etc., as well as losses occasioned by any enlargement or contraction of the pipe as, for instance, the loss occurring when a fluid passes from a pipe into a tank. For long straight pipes of uniform diameter, dF is approximately equal to $2f' \, [\bar{v}^2 \, dL/(gD)]$. It is usual to express friction due to fittings, etc., in terms of additional length of pipe, adding this to the actual pipe length to get the equivalent pipe length.

Integration of the fundamental equation leads to two sets of formulas.

1. For pressure drops, small relative to the initial pressure, the specific volume v and the velocity $\bar{v}$ may be assumed constant. Then approximately

$$p_1 - p_2 = 2f'\bar{v}^2L/(vgD)$$

Expressing pressure in pounds per square inch, p', the diameter in inches, and $\bar{v}$ as a function of wv/d^2, this equation becomes

$$p_1' - p_2' = 174.2f'w^2vL/d^5$$

2. For considerable pressure drops, when dealing with approximately isothermal flow of gases and vapors to which the gas laws are applicable, the fundamental equation on a weight basis may be integrated to give

$$p_1^2 - p_2^2 = \frac{2w^2RT}{gA^2} \ln \frac{v_2}{v_1} + \frac{4f'RTw^2L}{gA^2D}$$

Coefficients of Friction The coefficient of friction f is not a constant but is a function of the dimensionless expression $\mu/(\rho\bar{v}a)$ or $\mu v/(\bar{v}d)$, which is the reciprocal of the Reynolds number. McAdams and Sherwood formulate the expression

$$f' = 0.0054 + 0.375[\mu v/(\bar{v}d)]$$

This formula is applicable to water and other fluids. For high-pressure steam, the second term in the expression is small and f' is approximately equal to 0.0054. Babcock has suggested the approximation $f' = 0.0027(1 + 3.6/d)$ for steam.

Values of $f = 4f'$ as a function of pipe surface are given in Sec. 3.3.

For predicting the capacity of a given pipe operating on a chosen fluid with fixed pressure drop, the use of Fig. 4.1.35 eliminates the trial-and-error methods usually involved.

Resistances due to fittings, expressed in terms of L/D, are as follows: 90° elbows, $1-2\frac{1}{2} \ (3-6) \ [7-10]$ in, 30 (40) [50]; 90° curves, radius of centerline of curve $2-8$ pipe diameters, 10; globe valves, $1-2\frac{1}{2} \ (3-6)$ $[7-10]$ in, 45 (60) [75]; tees, $1-4$ in, 60. The resistance in energy units, due to sudden enlargement in a pipe, is approximately $(\bar{v}_1 - \bar{v}_2)^2/(2g)$. For sudden contraction it is $1.5(1 - r)\bar{v}_2^2/[2g(3 - r)]$, where $r = A_2/A_1$.

(See ''Camerons Hydraulic Data,'' latest edition, Ingersoll Rand Co., Woodcliff Lake, NJ; Warring, ''Hydraulic Handbook,'' 8th ed., Gulf, Houston and Trade & Tech. Press, Morden, Surrey; Houghton and Brock, ''Tables for the Compressible Flow of Dry Air,'' 3d ed., E. Arnold, London, with a review of basic equations and tabular data for the isentropic flow of dry air with Prandtl-Meyer expansion angles, Rayleigh flow, Fanno flow, and plane normal and oblique shock wave tables; Shapiro, ''The Dynamics and Thermodynamics of Compressible Fluid Flow,'' Ronald Press, New York; Blevins, ''Applied Fluid Dynamics Handbook,'' Van Nostrand Reinhold.)
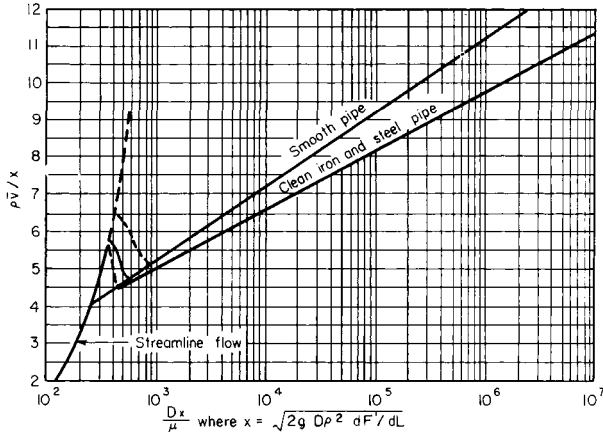
Fig. 4.1.35 Chart for estimating rate of flow from the pressure gradient.

THROTTLING

Throttling or Wire Drawing When a fluid flows from a region of higher pressure into a region of lower pressure through a valve or con- stricted passage, it is said to be throttled or wire-drawn. Examples are seen in the passage of steam through pressure-reducing valves, in the flow through ports and passages in the steam engine, and in the expan- sion valve of the refrigerating machine.

The **general equation applicable to throttling processes** is

$$(\bar{v}_2^2 - \bar{v}_1^2)/(2g_c) = h_1 - h_2$$

The velocities $\bar{v}_2$ and $\bar{v}_1$ are practically equal, and it follows that $h_1 = h_2$; i.e., in a throttling process there is no change in enthalpy.

For a mixture of liquid and vapor, $h = h_f + xh_{fg}$; hence the equation of throttling is $h_{f1} + x_1 h_{fg1} = h_{f2} + x_2 h_{fg2}$. In the case of a perfect gas, $h = c_p T + h_0$; hence the equation of throttling is $c_p T_1 + h_0 = c_p T_2 + h_0$, or $T_1 = T_2$.

Joule-Thomson Effect The investigations of Joule and Lord Kelvin showed that a gas drops in temperature when throttled. This is not universally true. For some gases, notably hydrogen, the temperature rises for throttling processes over ordinary ranges of temperature and pressure. Whether there is a rise or fall in temperature depends on the particular range of pressure and temperature over which the change
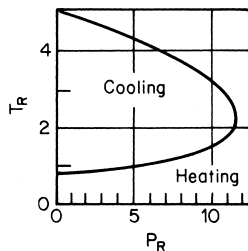
Fig. 4.1.36 Inversion curve.

occurs. For each gas, there are different values of pressure and tempera- ture at which no temperature change occurs during a Joule-Thomson expansion. That temperature is called the inversion temperature. Below this temperature, a gas cools on throttling; above it, its temperature rises. The ratio of the observed drop in temperature to the drop in pressure, i.e., dT/dP, is the Joule-Thomson coefficient. In actual design, the effect of heat leaks must be carefully evaluated before the theoreti- cal Joule-Thomson coefficients are applied.

Figure 4.1.36 shows the variation of inversion temperature with pres- sure and temperature; the exact values are shown in Table 4.1.4. The inversion locus for air is shown in Table 4.1.5.

The cooling **effect produced by throttling** has been applied to the lique- faction of gases.

Table 4.1.4 Approximate Inversion-Curve Locus in Reduced Coordinates ($T_R = T/T_c$; $P_R = P/P_c$)*

P_r	0	0.5	1	1.5	2	2.5	3	4
T_{RL}	0.782	0.800	0.818	0.838	0.859	0.880	0.903	0.953
T_{RU}	4.984	4.916	4.847	4.777	4.706	4.633	4.550	4.401

P_r	5	6	7	8	9	10	11	11.79
T_{RL}	1.01	1.08	1.16	1.25	1.35	1.50	1.73	2.24
T_{RU}	4.23	4.06	3.88	3.68	3.45	3.18	2.86	2.24

* Calculated from the best three-constant equation recommended by Miller, *Ind. Eng. Chem. Fundam.* **9**, 1970, p. 585. T_{RL} refers to the lower curve and T_{RU} to the upper curve.

Table 4.1.5 Approximate Inversion-Curve Locus for Air

P_r, bar	0	25	50	75	100	125	150	175	200	225
T_L, K	(112)*	114	117	120	124	128	132	137	143	149
T_U, K	653	641	629	617	606	594	582	568	555	541

P, bar	250	275	300	325	350	375	400	425	432
T_L, K	156	164	173	184	197	212	230	265	300
T_U, K	526	509	491	470	445	417	386	345	300

* Hypothetical low-pressure limit.

Loss due to Throttling A throttling process in a cycle of operations always introduces a loss of efficiency. If T_0 is the temperature corre- sponding to the back pressure, the loss of available energy is the product of T_0 and the increase of entropy during the throttling process. The following example illustrates the calculation in the case of ammonia passing through the expansion valve of a refrigerating machine.

EXAMPLE. The liquid ammonia at a temperature of 70°F passes through the valve into the brine coil in which the temperature is 20 deg and the pressure is 48.21 psia. The initial enthalpy of the liquid ammonia is $h_{f1} = 120.5$, and therefore the final enthalpy is $h_{f2} + x_2 h_{fg2} = 64.7 + 553.1x_2 = 120.5$, whence $x_2 = 0.101$. The initial entropy is $s_{f1} = 0.254$. The final entropy is $s_{f2} + (x_2 h_{fg2}/T_2) = 0.144 + 0.101 \times 1.153 = 0.260$. $T_0 = 20 + 460 = 480$; hence the loss of refrigerating effect is $480 \times (0.260 - 0.254) = 2.9$ Btu.

COMBUSTION

REFERENCES: Chigier, ''Energy, Combustion and Environment,'' McGraw-Hill. Campbell, ''Thermodynamic Analysis of Combustion Engines,'' Wiley. Glass- man, ''Combustion,'' Academic Press. Lefebvre, ''Gas Turbine Combustion,'' McGraw-Hill. Strehlow, ''Combustion Fundamentals,'' McGraw-Hill. Williams et al., ''Fundamental Aspects of Solid Propellant Rockets,'' *Agardograph,* **116,** Oct. 1969. Basic thermodynamic table type information needed in this area is found in Glushko et al., ''Thermodynamic and Thermophysical Properties of Combustion Products,'' Moscow, and IPST translation; Gordon, NASA Technical Paper 1906, 1982; ''JANAF Thermochemical Tables,'' NSRDS-NBS-37, 1971.

Fuels For special properties of various fuels, see Sec. 7. In general, fuels may be classed under three headings: (1) gaseous fuels, (2) liquid fuels, and (3) solid fuels.

The combustible elements that characterize fuels are carbon, hydrogen, and, in some cases, sulfur. The complete combustion of carbon gives, as a product, carbon dioxide, CO_2; the combustion of hydrogen gives water, H_2O.

Combustion of Gaseous and Liquid Fuels

Combustion Equations The approximate molecular weights of the important elements and compounds entering into combustion calculations are:

Material	C	H₂	O₂	N₂	CO	CO₂	H₂O	CH₄	C₂H₄	C₂H₆O	S	NO	NO₂	SO₂
Molecular weight	12	2	32	28	28	44	18	16	28	46	32	30	46	64

For the elements C and H, the equations of complete combustion are

$$C + O_2 = CO_2 \qquad H_2 + \tfrac{1}{2}O_2 = H_2O$$
$$12\ lb + 32\ lb = 44\ lb \qquad 2\ lb + 16\ lb = 18\ lb$$
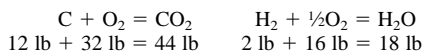
For a combustible compound, as CH_4, the equation may be written

$$CH_4 + x \cdot O_2 = y \cdot CO_2 + z \cdot H_2O$$
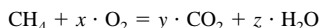
Taking, as a basis, 1 molecule of CH_4 and making a balance of the atoms on the two sides of the equation, it is seen that

$$y = 1 \qquad z = 2 \qquad 2x = 2y + z \qquad \text{or} \qquad x = 2$$

Hence,

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$
$$16\ lb + 64\ lb = 44\ lb + 36\ lb$$
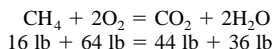
The coefficients in the combustion equation give the combining volumes of the gaseous components. Thus, in the last equation 1 ft³ of CH_4 requires for combustion 2 ft³ of oxygen and the resulting gaseous products of combustion are 1 ft³ of CO_2 and 2 ft³ of H_2O. The coefficients multiplied by the corresponding molecular weights give the combining weights. These are conveniently referred to 1 lb of the fuel. In the combustion of CH_4, for example, 1 lb of CH_4 requires $64/16 = 4$ lb of oxygen for complete combustion and the products are $44/16 = 2.75$ lb of CO_2 and $36/16 = 2.25$ lb of H_2O.

Air Required for Combustion The composition of air is approximately 0.232 O_2 and 0.768 N_2 on a pound basis, or 0.21 O_2 and 0.79 N_2 by volume. For exact analyses, it may be necessary sometimes to take account of the water vapor mixed with the air, but ordinarily this may be neglected.

The minimum amount of air required for the combustion of 1 lb of a fuel is the quantity of oxygen required, as found from the combustion equation, divided by 0.232. Likewise, the minimum volume of air required for the combustion of 1 ft³ of a fuel gas is the volume of oxygen divided by 0.21. For example, in the combustion of CH_4 the air required per pound of CH_4 is $4/0.232 = 17.24$ lb and the volume of air per cubic foot of CH_4 is $2/0.21 = 9.52$ ft³. Ordinarily, more air is provided than is required for complete combustion. Let a denote the minimum amount required and xa the quantity of air admitted; then $x - 1$ is the **excess coefficient**.

Products of Combustion The products arising from the complete combustion of a fuel are CO_2, H_2O, and if sulfur is present, SO_2. Accompanying these are the nitrogen brought in with the air and the oxygen in the excess of air. Hence the products of complete combustion are principally CO_2, H_2O, N_2, and O_2. The **presence of CO indicates incomplete combustion**. In simple calculations the reaction of nitrogen with oxygen to form noxious oxides, often termed NO_x, such as nitric oxide (NO), nitrogen peroxide (NO_2), etc., is neglected. In practice, an automobile engine is run at a lower compression ratio to reduce NO_x formation. The reduced pollution is bought at the expense of reduced operating efficiency. The composition of the products of combustion is readily calculated from the combustion equations, as shown by the following illustrative example. (See also Table 4.1.7.)

EXAMPLE. A producer gas having the volume composition given is burned with 20 percent excess of air; required the volume composition of the exhaust gases.

	V
H₂	0.08
CO	0.22
CH₄	0.024
CO₂	0.066
N₂	0.61
	1.0

Coefficients in reaction equations			Coefficients multiplied by V		
O₂	CO₂	H₂O	O₂	CO₂	H₂O
0.5	0	1	0.04	0	0.08
0.5	1	0	0.11	0.22	0
2	1	2	0.048	0.024	0.048
0	1	0	0	0.066	0
0	0	0	0	0	0
			0.198	0.31	0.128

For 1 ft³ of the producer gas, 0.198 ft³ of O_2 is required for complete combustion. The minimum volume of air required is $0.198/0.21 = 0.943$ ft³ and with 20 percent excess the air supplied is $0.943 \times 1.2 = 1.132$ ft³. Of this, 0.238 ft³ is oxygen and 0.894 ft³ is N_2. Consequently, for 1 ft³ of the fuel gas, the exhaust gas contains

CO_2		0.31 ft³
H_2O		0.128 ft³
N_2	$0.61 + 0.894 =$	1.504 ft³
O_2 (excess)	$0.238 - 0.198 =$	0.040 ft³
		1.982 ft³

or

CO_2	15.7 percent
H_2O	6.5 percent
N_2	75.8 percent
O_2	2.0 percent
	100.0 percent

Volume Contraction As a result of chemical action, there is often a change of volume; for example, in the reaction $2H_2 + O_2 = 2H_2O$, three volumes (two of H_2 and one of O_2) contract to two volumes of water vapor. In the example just given, the volume of producer gas and air supplied is 1 ft³ gas + 1.132 ft³ air = 2.132 ft³, and the corresponding volume of the exhaust gas is 1.982 ft³, showing a contraction of about 7 percent. For a hydrocarbon having the composition C_mH_n, the relative volume contraction is $1 - n/4$; thus for CH_4 and C_2H_4 there is no change of volume, for C_2H_2 the contraction is half the volume, and for C_2H_6 there is an increase of one-half in volume.

The change of volume accompanying a chemical reaction, such as a combustion, causes a corresponding change in the gas constant R. Let R' denote the constant for the mixture of gas and air (1 lb of gas and xa lb of air) before combustion, and R'' the constant of the mixture of resulting products of combustion. Then, if y is the resulting contraction of volume, $R''/R' = (1 + xa - y)/(1 + xa)$.

Heat of Combustion Usually, a chemical change is accompanied by the generation or absorption of heat. The union of a combustible with oxygen produces heat, and the heat thus generated when 1 lb of combustible is completely burned is called the **heat of combustion** or the **heat value** of the combustible. Heat values are determined experimentally by calorimeters in which the products of combustion are cooled to the

initial temperature and the heat absorbed by the cooling medium is measured. This is called the **high heat value**.

The heat transferred (heat of combustion) during a combustion reaction is computed on either a constant-pressure or a constant-volume basis. The first law is used in the analysis of either process.

1. The **heat value at constant volume** (Q_v). Consider a constant-volume combustion process where several reactants combine under proper conditions to form one or more products. The heat of combustion under constant-volume conditions (Q_v) according to the first law may be expressed as follows:

$$Q_v = \Sigma(Nu)_P - \Sigma(Nu)_R$$

The term N refers to the amount of material, and the symbol u signifies the internal energy per unit quantity of material. The subscripts P and R refer to the products and reactants, respectively. Hence, it may be concluded that Q_v is equal to the change in internal energy. The heat of combustion under constant-volume conditions may also be described as the quantity of heat transferred from a calorimeter to the external surroundings when the termperature and volume of the combustion products are brought to the temperature and volume, respectively, of the gaseous mixture before burning.

2. The **heat value at constant pressure** (Q_p). For a constant-pressure process the first law may be expressed as

$$Q_p = \Sigma(Nu)_P - \Sigma(Nu)_R + pV_P - pV_R$$

Here the symbols p and V refer to the pressure and total volume, respectively. Usually in combustion reactions that part of the change in internal energy resulting from a volume change is small in comparison to the total change; hence it may usually be neglected. Assuming therefore that the internal energy change for a constant-volume reaction is approximately equal to that for a constant-pressure change, the following equation results:

$$Q_p = Q_v + p(V_P - V_R)$$

Since Q_v is equal to the change in internal energy, this relation may be changed to enthalpy values, from which it may be concluded that Q_v is equal to the change in enthalpy. The heat of combustion under constant-pressure conditions may also be described as the heat transferred from a calorimeter when the pressure and temperature of the products are brought back to the pressure and temperature, respectively, of the gaseous mixture before burning.

If the reactants and products are assumed to be ideal gases, then the relation for (Q_p) may be expressed as follows, where ΔN represents the change in number of moles and R the universal gas constant:

$$Q_p = Q_v + \Delta N\, RT$$

From this relation the heat transferred (heat of combustion) at constant pressure may be found from the heat of reaction at constant volume, or vice versa, if the temperature and molar-volume change are known.

If there is no change of volume due to the combustion, the heat values Q_p and Q_v are the same. When there is a contraction of volume, Q_p exceeds Q_v by the heat equivalent of the work done on the gas during the contraction. For example, in the burning of CO according to the equation $CO + \frac{1}{2}O_2 = CO_2$, there is a contraction of $\frac{1}{2}$ volume. Taking 62°F as the temperature, the volume of 1 lb CO at atmospheric pressure is 13.6 ft³; hence the equivalent of the work done at atmospheric pressure is $\frac{1}{2} \times 13.6 \times 2{,}116/778 = 18.5$ Btu, which is about 0.4 percent of the heat value of CO. Since the difference between Q_p and Q_v is small in most fuels, it is usually neglected.

It is also to be noted that heat values vary with the initial temperature (which is also the final temperature), but the variation is usually negligible.

Heat Value per Unit Volume   Since the consumption of a fuel gas is more easily measured by volume than by mass, it is convenient to express heat values in terms of volumes. For this purpose, a standard temperature and pressure must be assumed. It is customary to take atmospheric pressure (14.70 psi) as standard, but there is diversity of practice in the matter of a **standard temperature**. The temperature of 68°F (20°C) is generally accepted in metric countries and has been recommended by the American delegates to the meeting of the International Committee of Weights and Measures and also by the ASME Power Test Codes Committee. The American Gas Assoc. uses 60°F as the standard temperature of reference. Conversion of density and heat values from 68 to 60°F of dry (saturated) gas is obtained by multiplying by the factor 1.0154 (1.0212). Conversion of specific volumes of dry (saturated) gas is obtained by multiplying by the factor 0.9848 (0.9792).

If the gas is at some other pressure and temperature, say p_1 psia and T_1 °R, the heat value per cubic foot is found by multiplying the heat value per cubic foot under standard conditions by $35.9 p_1/T_1$.

The heat values of a few of the more common fuels per pound and per cubic foot are given in Table 4.1.6.

Heat Value per Unit Volume of Mixture   Let a denote the volume of

Table 4.1.6   Heats of Combustion

Fuel	Chemical symbol	High heat value Btu/lb	High heat value *Btu/ft³	Low heat value Btu/lb	Low heat value *Btu/ft³
Carbon to CO_2	C	14,096			
Carbon to CO	C	3,960			
CO to CO_2	CO	4,346	316.0		
Sulfur to SO_2	S	3,984			
Hydrogen	H_2	61,031	319.4	51,593	270.0
Methane	CH_4	23,890	994.7	21,518	896.0
Ethane	C_2H_6	22,329	1,742.6	20,431	1,594.5
Propane	C_3H_8	21,670	2,480.1	19,944	2,282.6
Butane	C_4H_{10}	21,316	3,215.6	19,679	2,968.7
Pentane	C_5H_{12}	21,095	3,950.2	19,513	3,654.0
Hexane (liquid)	C_6H_{14}	20,675	....	19,130	
Octane (liquid)	C_8H_{18}	20,529	....	19,029	
n-Decane (liquid)	$C_{10}H_{22}$	20,371	....	19,175	
Ethylene	C_2H_4	21,646	1,576.1	20,276	1,477.4
Propene (propylene)	C_3H_6	21,053	2,299.4	19,683	2,151.3
Acetylene (ethyne)	C_2H_2	21,477	1,451.4	20,734	1,402.0
Benzene	C_6H_6	18,188	3,687.5	17,446	3,539.3
Toluene (methyl benzene)	C_7H_8	18,441	4,410.1	17,601	4,212.6
Methanol (methyl alcohol, liquid)	CH_4O	9,758	....	8,570	
Ethanol (ethyl alcohol, liquid)	C_2H_6O	12,770	....	11,531	
Naphthalene (solid)	$C_{10}H_8$	17,310	....	13,110	

* Measured as a gas at 68°F and 14.70 psia. Multiply by 1.0154 for 60°F and 14.70 psia.

air required for the combustion of 1 ft³ of fuel gas and xa the value of air actually admitted, $(x - 1)a$ being therefore the excess. Then the volume of the mixture of fuel gas and air is $1 + xa$, and the quotient $Q/(1 + xa)$ may be called the heat value per cubic foot of mixture. This magnitude is useful in comparing the relative volumes of mixture required with different fuel gases. Thus a lean gas, as blast-furnace gas or producer gas, has a low heat value Q, but the value of a is correspondingly low. On the other hand, a rich gas, like natural gas, has a high heat value but requires a large volume of air for combustion.

Low and High Heat Values Any fuel containing hydrogen yields water as one product of combustion. At atmospheric pressure, the partial pressure of the water vapor in the resulting combustion gas mixture will usually be sufficiently high to cause water to condense out if the temperature is allowed to fall below 120 to 140°F. This causes liberation of the heat of vaporization of any water condensed. The low heat value is evaluated assuming no water vapor condensed, whereas the high heat value is calculated assuming all water vapor condensed.

To facilitate calculations of the temperature attained by combustion, it is desirable to make use of the **low heat value**. The necessity of taking into account the heat of vaporization of the water vapor and the difference between the specific heats of liquid water and of water vapor is thus avoided. The high heat of combustion exceeds the low heat of combustion by the difference between the heat actually given up on cooling the products to the initial temperature and that which would have been given up if the products had remained in the gaseous state. A

bomb calorimeter (constant volume) gives practically correct values of the high heat value; a gas calorimeter (constant pressure) gives values which, for the usual fuels, may be incorrect by a fraction of 1 percent. The quantity to be subtracted from the high heat value to obtain the low heat value will vary with the composition of the fuel; an approximate value is $1,050m$, where m is the number of pounds of H_2O formed per pound of fuel burned.

In Germany, the low heat value of the fuel is used in calculating efficiencies of internal-combustion engines. In the United States, the high value is specified by the ASME Power Test Codes.

Heat of Formation The change in enthalpy resulting when a compound is formed from its elements isothermally and at constant pressure is numerically equal to, but of opposite sign to, the heat of formation, $\Delta H_f = -Q_f$. It is equal to the difference between the heats of combustion of the constituents forming the compound and the heat of combustion of the compound itself. The following values for heats of formation are in Btu per pound of the compound. The elements before the change and the compounds formed are assumed in their ordinary stable states at 65°F and 1 atm. A plus sign indicates heat evolved on forming the compound, a minus sign heat absorbed from the surroundings.

Fuels Methane, CH_4 (gas), 2,001.4; ethane, C_2H_6 (gas), 1,206.1; propane, C_3H_8 (vapor), 1,008.5; acetylene, C_2H_2 (gas), -3747; ethylene, C_2H_4 (gas), -805.3; benzene, C_6H_6 (vapor), -459; toluene, C_7H_8 (vapor), -234.9; methyl alcohol, CH_3OH (liquid), 3,227.3; ethyl alcohol, C_2H_5OH (liquid), 2623.3.

Table 4.1.7 Products of Combustion

Fuel	Chemical formula	Molecular weight $O_2 = 32$	Specific weight, lb/ft³ at 68°F and 14.70 lb/in²	Volume of air necessary for combustion of unit volume of fuel at same temperature and pressure	Products of combustion of 1 ft³ of fuel in theoretical amount of air, ft³			Weight of air necessary for combustion of unit weight of fuel	Products of combustion of 1 lb of fuel in theoretical amount of air, lb		
					CO_2	H_2O	N_2		CO_2	H_2O	N_2
Oxygen	O_2	32	0.0831								
Nitrogen	N_2	28.08	0.0727								
Air			0.0753								
Hydrogen	H_2	2.016	0.0052	2.39	0	1	1.89	34.2	0.0	8.94	26.28
Steam	H_2O	18.016									
Carbon monoxide	CO	28.00	0.0727	2.39							
Carbon dioxide	CO_2	44.00	0.1142								
Methane	CH_4	16.03	0.0416	9.55	1	2	7.55	17.21	2.75	2.248	13.22
Ethane	C_2H_6	30.05	0.0779	16.71	2	3	13.21	16.07	2.93	1.799	12.34
Propane	C_3H_8	44.06	0.1142	23.87	3	4	18.87	15.65	3.00	1.635	12.02
Butane	C_4H_{10}	58.1	0.1506	30.94	4	5	24.53	15.44	3.03	1.551	11.86
Pentane	C_5H_{12}	72.1	0.1869	38.08	5	6	30.2	15.31	3.05	1.499	11.76
Hexane	C_6H_{14}	86.1	0.2232	45.3	6	7	35.8	15.22	3.07	1.465	11.69
Heptane	C_7H_{16}	100.1	0.2596	52.5	7	8	41.5	15.15	3.08	1.439	11.64
Octane	C_8H_{18}	114.1	0.2959	59.7	8	9	47.2	15.11	3.08	1.421	11.60
Nonane	C_9H_{20}	128.2	0.3323	66.8	9	10	52.8	15.07	3.09	1.406	11.57
Benzene	C_6H_6	78.0	0.2025	35.8	6	3	28.3	13.26	3.38	0.693	10.18
Toluene	C_7H_8	92.1	0.2388	42.9	7	4	34.0	13.50	3.35	0.783	10.36
Xylene	C_8H_{10}	106.2	0.2752	50.1	8	5	39.6	13.57	3.31	0.845	10.42
Cyclohexane	C_6H_{12}	84.0	0.2180	43.0	6	6	34.0	14.76	3.14	1.285	11.34
Ethylene	C_2H_4	28.03	0.0728	14.32	2	2	11.32	14.76	3.14	1.285	11.34
Propylene	C_3H_6	42.0	0.1090	21.48	3	3	16.98	14.76	3.14	1.285	11.34
Butylene	C_4H_8	64.1	0.1454	28.64	4	4	22.64	14.76	3.14	1.285	11.34
Acetylene	C_2H_2	26.02	0.0675	11.93	2	1	9.43	13.26	3.38	0.693	10.18
Allylene	C_3H_4	40.0	0.1038	19.09	3	2	15.09	13.78	3.30	0.900	10.59
Naphthalene	$C_{10}H_8$	128.1	0.3322	57.3	10	4	45.28	12.93	3.44	0.563	9.93
Methyl alcohol	CH_4O	32.0	0.0830	7.16	1	2	5.66	6.46	1.37	1.125	4.96
Ethyl alcohol	C_2H_6O	46.0	0.1194	14.32	2	3	11.32	8.99	1.91	1.174	6.90

SOURCE: Marks, ''The Airplane Engine.''

Table 4.1.8   Internal Energy of Gases
Btu/(lb·mol) above 520°R

Temp. °R	O₂	N₂	Air	CO₂	H₂O	H₂	CO	Apv
520	0	0	0	0	0	0	0	1,033
540	100	97	97	139	122	96	97	1,072
560	200	196	196	280	244	193	196	1,112
580	301	295	295	424	357	291	295	1,152
600	402	395	395	570	490	390	396	1,192
700	920	896	897	1,320	1,110	887	896	1,390
800	1,449	1,399	1,403	2,120	1,734	1,386	1,402	1,589
900	1,989	1,905	1,915	2,965	2,366	1,886	1,913	1,787
1,000	2,539	2,416	2,431	3,852	3,009	2,387	2,430	1,986
1,100	3,101	2,934	2,957	4,778	3,666	2,889	2,954	2,185
1,200	3,675	3,461	3,492	5,736	4,399	3,393	3,485	2,383
1,300	4,262	3,996	4,036	6,721	5,030	3,899	4,026	2,582
1,400	4,861	4,539	4,587	7,731	5,740	4,406	4,580	2,780
1,500	5,472	5,091	5,149	8,764	6,468	4,916	5,145	2,979
1,600	6,092	5,652	5,720	9,819	7,212	5,429	5,720	3,178
1,700	6,718	6,224	6,301	10,896	7,970	5,945	6,305	3,376
1,800	7,349	6,805	6,889	11,993	8,741	6,464	6,899	3,575
1,900	7,985	7,393	7,485	13,105	9,526	6,988	7,501	3,773
2,000	8,629	7,989	8,087	14,230	10,327	7,517	8,109	3,972
2,100	9,279	8,592	8,698	15,368	11,146	8,053	8,722	4,171
2,200	9,934	9,203	9,314	16,518	11,983	8,597	9,339	4,369
2,300	10,592	9,817	9,934	17,680	12,835	9,147	9,961	4,568
2,400	11,252	10,435	10,558	18,852	13,700	9,703	10,588	4,766
2,500	11,916	11,056	11,185	20,033	14,578	10,263	11,220	4,965
2,600	12,584	11,682	11,817	21,222	15,469	10,827	11,857	5,164
2,700	13,257	12,313	12,453	22,419	16,372	11,396	12,499	5,362
2,800	13,937	12,949	13,095	23,624	17,288	11,970	13,144	5,561
2,900	14,622	13,590	13,742	24,836	18,217	12,549	13,792	5,759
3,000	15,309	14,236	14,394	26,055	19,160	13,133	14,443	5,958
3,100	16,001	14,888	15,051	27,281	20,117	13,723	15,097	6,157
3,200	16,693	15,543	15,710	28,513	21,086	14,319	15,754	6,355
3,300	17,386	16,199	16,369	29,750	22,066	14,921	16,414	6,554
3,400	18,080	16,855	17,030	30,991	23,057	15,529	17,078	6,752
3,500	18,776	17,512	17,692	32,237	24,057	16,143	17,744	6,951
3,600	19,475	18,171	18,356	33,487	25,067	16,762	18,412	7,150
3,700	20,179	18,833	19,022	34,741	26,085	17,385	19,082	7,348
3,800	20,887	19,496	19,691	35,998	27,110	18,011	19,755	7,547
3,900	21,598	20,162	20,363	37,258	28,141	18,641	20,430	7,745
4,000	22,314	20,830	21,037	38,522	29,178	19,274	21,107	7,944
4,100	23,034	21,500	21,714	39,791	30,221	19,911	21,784	8,143
4,200	23,757	22,172	22,393	41,064	31,270	20,552	22,462	8,341
4,300	24,482	22,845	23,073	42,341	32,326	21,197	23,140	8,540
4,400	25,209	23,519	23,755	43,622	33,389	21,845	23,819	8,738
4,500	25,938	24,194	24,437	44,906	34,459	22,497	24,499	8,937
4,600	26,668	24,869	25,120	46,193	35,535	23,154	25,179	9,136
4,700	27,401	25,546	25,805	47,483	36,616	23,816	25,860	9,334
4,800	28,136	26,224	26,491	48,775	37,701	24,480	26,542	9,533
4,900	28,874	26,905	27,180	50,069	38,791	25,418	27,226	9,731
5,000	29,616	27,589	27,872	51,365	39,885	25,819	27,912	9,930
5,100	30,361	28,275	28,566	52,663	40,983	26,492	28,600	10,129
5,200	31,108	28,961	29,262	53,963	42,084	27,166	29,289	10,327
5,300	31,857	29,648	29,958	55,265	43,187	27,842	29,980	10,526
5,400	32,607	30,337	30,655	56,569	44,293	28,519	30,674	10,724

SOURCE: L. C. Lichty, ''Internal Combustion Engines,'' p. 582, derived from data given by Hershey, Eberhardt, and Hottel, *Trans. SAE,* **31,** 1936, p. 409.

Inorganic Compounds Al_2O_3, 6,710; CaO, 4,869; $CaCO_3$, 5,206; FeO, 1,611; Fe_2O_3, 2,238; Fe_3O_4, 2,075; FeS_2, 532.7; HCl (gas), 1,089; HNO_3 (liquid), 1,190; H_2O (liquid), 6,827; H_2S (gas), 279.9; H_2SO_4 (liquid), 3,555.8; K_2O, 164.7; MgO, 6,522; MnO, 2,449; NO, $-1,296$; N_2O, -803.5; Na_2O, 2,888; NH_3, 1,163; NH_4CL, 1,480; NiO, 1,407; P_2O_5, 5,394; PbO (red), 423.0; PbO_2, 489.1; SO_2, 1,933; SO_3, 2,112; SnO, 904.7; ZnO, 1,847.

INTERNAL ENERGY AND ENTHALPY OF GASES

Table 4.1.8 gives the internal energy of various common gases in Btu/(lb·mol) measured above 520°R (60°F). The corresponding values of the enthalpy are obtained by adding the value of Apv from the last column.

TEMPERATURE ATTAINED BY COMBUSTION

Excluding the effect of dissociation, the temperature attained at the end of combustion may be calculated by a simple energy balance. The heat of combustion less the heat lost by conduction and radiation during the process is equal to the increase in internal energy of the products mixture if the combustion is at constant volume; or, if the combustion is at constant pressure, the difference is equal to the increase in enthalpy of the products mixture.

EXAMPLE.   To calculate the temperature of combustion of a fuel gas having the composition $H_2 = 0.50$, CO $= 0.46$, $CO_2 = 0.04$. The gas is burned with 15 percent excess air at constant volume, and the initial temperature is 62°F; i.e., $T = 522°R$.

The volume compositions of the initial mixture of fuel gas and air and of the mixture of products are, respectively,

Initial: H_2, 0.50; CO, 0.46; CO_2, 0.04; O_2, 0.552; N_2, 2.098
Products: H_2O, 0.50; CO_2, 0.50; O_2, 0.072; N_2, 2.098

Since a volume composition is also a mol composition, the products mixture may be regarded as made up of 0.5 mol each of H_2O and CO_2, 0.072 mol of O_2, and 2.098 mols of N_2. If values are taken from Tables 4.1.6 and 4.1.7, the heat generated by combustion of the fuel mixture is $0.50 \times 2 \times 51,593 + 0.46 \times 28 \times 4,346 = 107,569$ Btu. The internal energy u of the products mixture at $T = 522$ is now calculated (Table 4.1.8). For 0.5 mol H_2O + 0.5 mol CO_2 +

0.072 mol O_2 + 2.098 mol N_2 this is $6.1 + 6.95 + 0.72 + 20.34 = 34.11$ Btu.

The energy u of the mixture is next calculated for various assumed temperatures, the proper values being taken from Table 4.1.8.

If the heat of combustion, 107,569 Btu, is entirely used in the increase of energy, the temperature attained lies somewhere between 5,000 and 5,100; by interpolation, the value 5,073° is obtained.

Loss of heat during combustion may readily be taken into account; thus if 10 percent of the heat of combustion is lost, the amount available for increasing the energy of the products is $107,569 \times 0.90 = 96,812$ Btu, and this increase gives $T_2 = 4,671°$. If the fuel is burned at constant pressure, Q_p is used instead of Q_v and values of h are determined from Table 4.1.8 instead of values of u.

T_2 assumed	4,700	4,800	4,900	5,000	5,100
Energy 0.5 mol H_2O	18,308	18,851	19,396	19,943	20,429
Energy 0.5 mol CO_2	23,742	24,388	25,035	25,683	26,331
Energy 0.072 mol O_2	1,973	2,026	2,079	2,132	2,185
Energy 2.098 mol N_2	54,596	55,018	56,447	57,882	59,321
$u_2 =$	97,619	100,283	102,957	105,640	108,329
$u_1 =$	34	34	34	34	34
	97,585	100,249	102,923	105,606	108,295

EFFECT OF DISSOCIATION

The maximum temperature that can be obtained by the combustion of any fuel is limited by the dissociation of the products formed. The dissociation and equilibriums involved in high-temperature combustion are exceedingly complex, involving such chemical species as CO_2, CO, H_2O, H_2, H, OH, N_2, NO, N, O_2, and O. The equilibrium reached is a direct consequence of the second law of thermodynamics. However, the calculation of the equilibrium constant even for simple reactions is tedious. For all possible reactions $aA + bB \rightarrow cC + dD$ ($a, b, c, d \leq 2$), the excellent tables of the equilibrium constant k_p contained in the "American Institute of Physics Handbook," 3d edition, McGraw-Hill, pp. 4-31 and 4-32, are recommended to save time. Papers describing the calculation of k_p for multicomponent reacting gases are contained in the first *ASME Symposium on Thermophysical Properties Proceedings*.

Calculated flame temperatures, allowing for dissociation, for gaseous fuels with stated amounts of air present are given in Table 4.1.9. The combustion is assumed to be adiabatic and at 14.7 lb/in² absolute.

Table 4.1.9   Flame Temperatures, Deg R, at 14.7 psia, Allowing for Dissociation

	Percent of theoretical air				
Fuel	80	90	100	120	140
Hydrogen	4,210	4,330	4,390	4,000	3,670
Carbon monoxide	4,280	4,370	4,320	4,140	3,850
Methane	4,050	. . . . .	4,010	3,660	3,330
Carbureted water gas	3,940	. . . . .	4,150	3,820	3,510
Coal gas	3,920	. . . . .	4,050	3,780	3,440
Natural gas	4,010	. . . . .	4,180	3,840	3,520
Producer gas	3,040	. . . . .	3,330	3,130	2,970
Blast furnace gas	2,810	. . . . .	3,060	2,920	2,750

SOURCE: Satterfield, "Generalized Thermodynamics of High-Temperature Combustion," Sc.D. thesis, M.I.T., 1946.

The volumetric compositions of the fuels of Table 4.1.9 are given below:

Fuels	CO	H_2	CH_4	C_2H_4	Illuminants (assumed C_2H_4)	CO_2	O_2	N_2
H_2	. . . .	100.0						
CO	100.0							
CH_4	. . . .	. . . .	100.0					
Carbureted water gas	24.1	32.5	9.0	2.2	10.3	4.6	0.6	16.7
Coal gas	5.9	53.2	29.6	. . . .	2.7	1.4	0.7	6.5
Natural gas	. . . .	. . . .	78.8	14.0	. . . . . .	0.4	. . . . .	6.8
Producer gas	26.0	3.0	0.5	. . . .	. . . . . .	2.50	. . . . .	56.0
Blast furnace gas	26.5	3.5	0.2	. . . .	. . . . . .	12.8	0.1	56.9

In the case of **explosion** in the **internal-combustion engine,** the figures in Table 4.1.9 will be somewhat changed. The effect of compression is to increase both the initial temperature and the initial pressure. The resulting increase in the explosion temperature will tend to increase the dissociation; the increase of pressure will tend to reduce it. The net effect will be a small reduction.

COMBUSTION OF LIQUID FUELS

For properties of fuel oils, heat values, etc., see Sec. 7. Calculations for the burning of liquid fuels are fundamentally the same as for gaseous fuels. Liquid fuels are almost always gasified before or during actual combustion.

COMBUSTION OF SOLID FUELS

For **properties of solid fuels,** heat values, etc., see Sec. 7.

Air Required for Combustion Let c, h, and o, denote, respectively, the parts of carbon, hydrogen, and oxygen in 1 lb of the fuel. Then the **minimum amount of oxygen** required for complete combustion is $2.67c + 8h - o$ lb, and the **minimum quantity of air** required is $a = (2.67c + 8h - o)/0.23 = 11.6[c + 3(h - o/8)]$ lb.

With air at 62°F and at atmospheric pressure, the minimum volume of air required is $v_m = 147[c + 3(h - o/8]$ ft³. In practice, an excess of air over that required for combustion is admitted to the furnace. The actual quantity admitted per pound of fuel may be denoted by xa. Then x = amount admitted ÷ minimum amount.

Combustion Products If v_m is the minimum volume of air required for complete combustion and xv_m the actual volume supplied, then the products will contain per pound of fuel, $O_2 = 0.21v_m(x - 1)$ ft³, $N_2 = 0.79xv_m$ ft³.

From the reaction equation $C + O_2 = CO_2$, the volume of CO_2 formed is equal to the volume of oxygen required for the carbon constituent alone; hence volume of $CO_2 = 0.21v_mc/[c + 3(h - 0.125o)$.

Of the *dry* gaseous products (i.e., without water), the CO_2 content by volume is therefore given by the expression

$$CO_2 = 0.21c/[xc + (x - 0.21)3(h - 0.125o)]$$

The combined CO_2 and O_2 content is

$$CO_2 + O_2 = 0.21\left\{1 - 0.79 \Big/ \left[\frac{x + cx}{3(h - 0.125o) - 0.21}\right]\right\}$$

If the fuel is all carbon, the combined CO_2 and O_2 is by volume 21 percent of the gaseous products. The more hydrogen contained in the fuel, the smaller is the $CO_2 + O_2$ content. The CO_2 content depends in the first instance on the excess of air. Thus, for pure carbon, it is $CO_2 = 0.21/x$.

The excess of air may be calculated from the composition of the gases and that of the fuel. Thus

$$x = 0.21\left[\frac{c}{[CO_2]} + 3(h - 0.125o)\right] \Big/ [c + 3(h - 0.125o)]$$
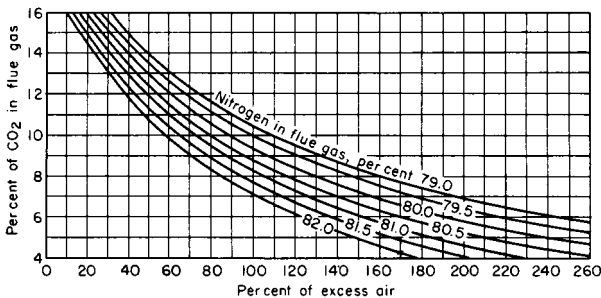
Fig. 4.1.37 Ratio of air supplied per pound of combustible to that theoretically required.

in which $[CO_2]$ denotes the percent by volume of the CO_2 in the dry gas.

The temperature of combustion is calculated by the same method as for gaseous fuels.

Loss due to Incomplete Combustion The loss due to incomplete combustion of the carbon in the fuel, in Btu/lb of fuel, is

$$L = 10,136C \times CO/(CO + CO_2)$$

where $10,136$ = difference in heat evolved in burning 1 lb of carbon to CO_2 and to CO; CO and CO_2 = percentages by volume of carbon monoxide and carbon dioxide as found by analysis; and C = fraction of quantity of carbon in the fuel which is actually burned and passes up the stack, either as CO or CO_2. The presence of 1 percent of CO in the flue gases will represent a decrease in the boiler efficiency of 4.5 percent. An additional loss is caused by passage through the grate to the ashpit of any unburned or partly burned fuel.

It is generally assumed that high CO_2 readings are indicative of good combustion and, hence, of high efficiencies. Such readings are not satisfactory when considered apart from the CO determination. The best percentage of CO_2 to maintain varies with different fuels and is lower for those with a high hydrogen content than for fuel mainly composed of carbon.

Hydrogen in a fuel increases the nitrogen content of the flue gases. This is due to the fact that the water vapor formed by the combustion of hydrogen will condense at the temperature at which the analysis is made, while the nitrogen which accompanied the oxygen maintains its gaseous form and passes in that form into the sampling apparatus. For this reason, where highly volatile coals containing considerable hydrogen are burned, the flue gas contains an apparently increased amount of nitrogen. The effect is even more pronounced when burning gaseous or liquid hydrocarbon fuels.

The amount of flue gases per pound of fuel, including moisture formed by the hydrogen component, is approximately $3.02[N/(CO_2 + CO)]C + (1 - A)$, where A = percent of ash found in test. The quantity of dry flue gases per pound of fuel may be approximated from the formula $W_2 = C[11CO_2 + 8O + 7(CO + N)]/3(CO_2 + CO)$. In these formulas, the amount of gas is per pound of dry or moist fuel as the percentage of C is referred to a dry or moist basis.
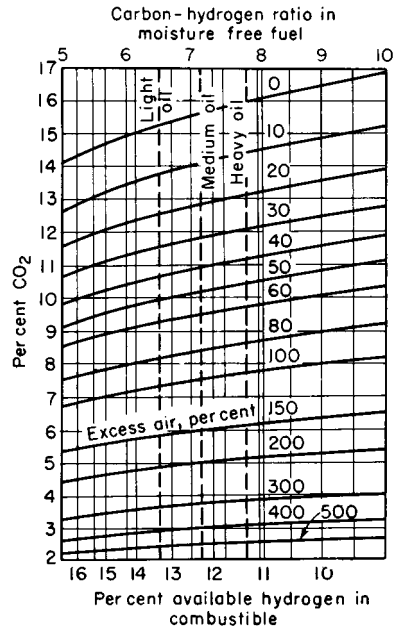
Fig. 4.1.38 Relation of CO_2 to excess air for fuels.

The ratio of air suppplied per pound of fuel to the air theoretically required is

$$\frac{W_1}{W} = \frac{3.02C[N/(CO_2 + CO)]}{34.56(C/3 + H - O/8)}$$

The ratio of air supplied per pound of combustible to that theoretically required is $N/[N - 3.782(O - \frac{1}{2}CO)]$, on the assumption that all the nitrogen in the flue gas comes from the air supplied. Figure 4.1.37 gives the value of this ratio for varying flue-gas analyses where there is no CO present.

For petroleum fuels with hydrogen content from 9 to 16 percent, the excess air can be determined from the CO_2 content of the flue gases (with no CO present) by the use of Fig. 4.1.38. The curves are based on the assumption of 0.4 percent sulfur in the oil.

4.2   THERMODYNAMIC PROPERTIES OF SUBSTANCES
by Peter E. Liley

NOTE: Thermodynamic properties of a variety of other specific materials are listed also in Secs. 4.1, 6.1, and 9.8.

Table 4.2.1   Enthalpy and Psi Functions for Ideal-Gas Air*

T, K	h, kJ/kg	Ψ	T, K	h, kJ/kg	Ψ	T, K	h, kJ/kg	Ψ
200	200.0	-0.473	800	821.9	1.679	1,400	1,515	2.653
220	220.0	-0.329	820	844.0	1.720	1,420	1,539	2.679
240	240.1	-0.197	840	866.1	1.760	1,440	1,563	2.705
260	260.1	-0.076	860	888.3	1.800	1,460	1,587	2.730
280	280.1	0.037	880	910.6	1.838	1,480	1,612	2.755
300	300.2	0.142	900	933.0	1.876	1,500	1,636	2.779
320	320.3	0.240	920	955.4	1.914	1,520	1,660	2.803
340	340.4	0.332	940	978.0	1.950	1,540	1,684	2.827
360	360.6	0.419	960	1,000.6	1.987	1,560	1,709	2.851
380	380.8	0.502	980	1,023.3	2.022	1,580	1,738	2.875
400	401.0	0.580	1,000	1,046.1	2.057	1,600	1,758	2.898
420	421.3	0.655	1,020	1,068.9	2.091	1,620	1,782	2.921
440	441.7	0.727	1,040	1,091.9	2.125	1,640	1,806	2.944
460	462.1	0.795	1,060	1,114.9	2.158	1,660	1,831	2.966
480	482.5	0.861	1,080	1,138.0	2.190	1,680	1,855	2.988
500	503.1	0.925	1,100	1,161.1	2.223	1,700	1,880	3.010
520	523.7	0.986	1,120	1,184.3	2.254	1,720	1,905	3.032
540	544.4	1.045	1,140	1,207.6	2.285	1,740	1,929	3.054
560	565.2	1.102	1,160	1,230.9	2.316	1,760	1,954	3.075
580	586.1	1.158	1,180	1,254.3	2.346	1,780	1,979	3.096
600	607.0	1.211	1,200	1,278	2.376	1,800	2,003	3.117
620	628.1	1.264	1,220	1,301	2.406	1,840	2,053	3.158
640	649.2	1.314	1,240	1,325	2.435	1,880	2,102	3.198
660	670.5	1.364	1,260	1,349	2.463	1,920	2,152	3.238
680	691.8	1.412	1,280	1,372	2.491	1,960	2,202	3.277
700	713.3	1.459	1,300	1,396	2.519	2,000	2,252	3.215
720	734.8	1.505	1,320	1,420	2.547	2,050	2,315	3.262
740	756.4	1.550	1,340	1,444	2.574	2,100	2,377	3.408
760	778.2	1.594	1,360	1,467	2.601	2,150	2,440	3.453
780	800.0	1.637	1,380	1,491	2.627	2,200	2,504	3.496

* Values rounded off from Chappell and Cockshutt, Nat. Res. Counc. Can. Rep. NRC LR 759 (NRC No. 14300), 1974. This source tabulates values of seven thermodynamic functions at 1-K increments from 200 to 2,200 K in SI units and at other increments for two other unit systems. An earlier report (NRC LR 381, 1963) gives a more detailed description of an earlier fitting from 200 to 1,400 K. In the above table h = specific enthalpy, kJ/kg, and $\Psi_2 - \Psi_1 = \log (P_2/P_1)$, for an isentrope. In terms of the Keenan and Kaye function ϕ, $\Psi = [\log (e/R)]\phi$.
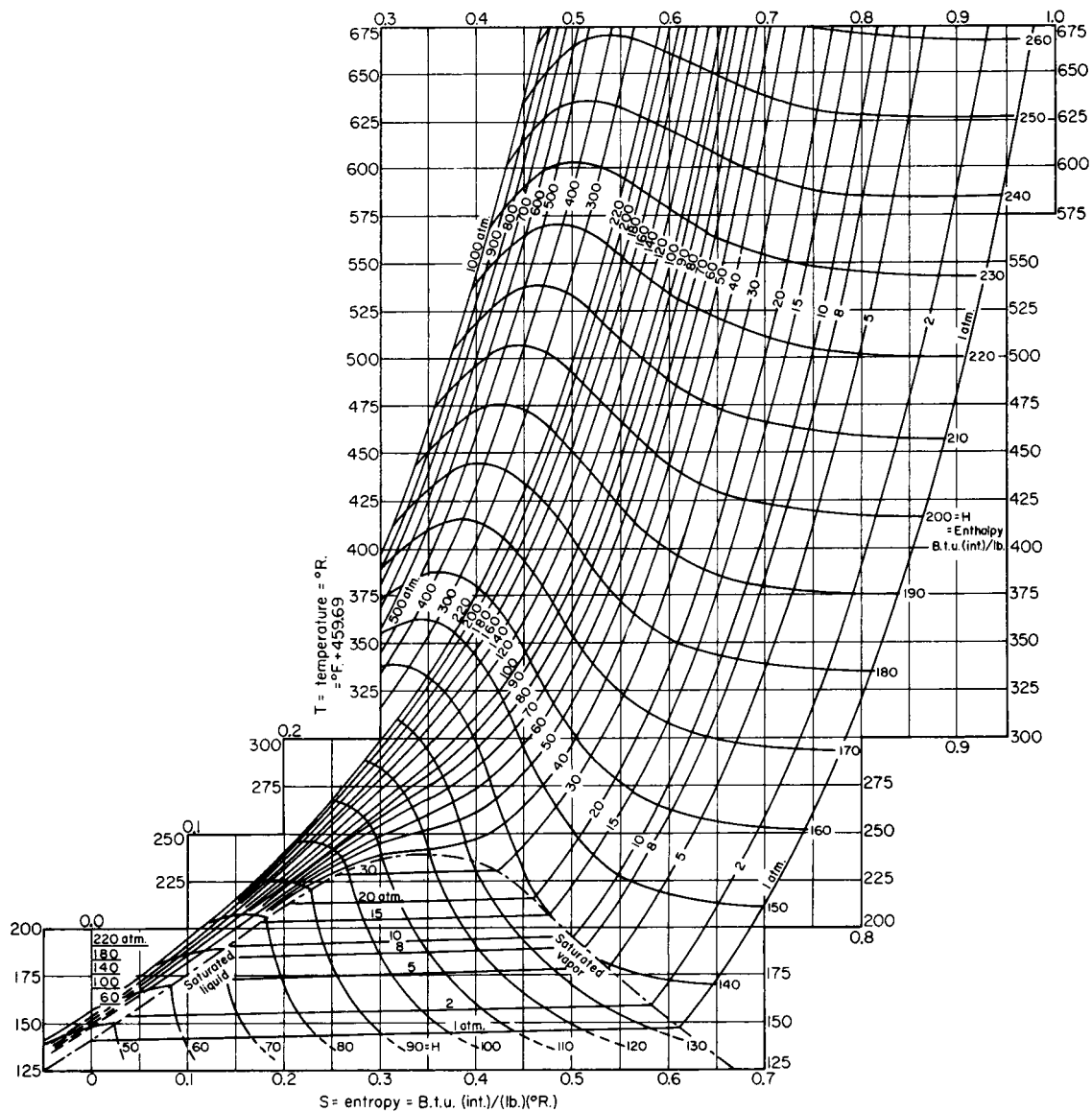
Fig. 4.2.1 Temperature-entropy diagram for air. (*Landsbaum et al., AIChE J.,* **1,** no. 3, 1955, p. 303.) *(Reproduced by permission of the authors and editor, AIChE.)*

Table 4.2.2   International ρ, Standard Atmosphere*

Z, m	T, K	P, bar	ρ, kg/m³	g, m/s²	M	a, m/s	λ, m	H, m
0	288.15	1.01325	1.2250	9.80665	28.964	340.29	6.63. − 8	0
1,000	281.65	0.89876	1.1117	9.8036	28.964	336.43	7.31. − 8	1,000
2,000	275.15	0.79501	1.0066	9.8005	28.964	332.53	8.07. − 8	1,999
3,000	268.66	0.70121	0.90925	9.7974	28.964	328.58	8.94. − 8	2,999
4,000	262.17	0.61660	0.81935	9.7943	28.964	324.59	9.92. − 8	3,997
5,000	255.68	0.54048	0.73643	9.7912	28.964	320.55	1.10. − 7	4,996
6,000	249.19	0.47217	0.66011	9.7882	28.964	316.45	1.23. − 7	5,994
7,000	242.70	0.41105	0.59002	9.7851	28.964	312.31	1.38. − 7	6,992
8,000	236.22	0.35651	0.52579	9.7820	28.964	308.11	1.55. − 7	7,990
9,000	229.73	0.30800	0.46706	9.7789	28.964	303.85	1.74. − 7	8,987
10,000	223.25	0.26499	0.41351	9.7759	28.964	299.53	1.97. − 7	9,984
15,000	216.65	0.12111	0.19476	9.7605	28.864	295.07	4.17. − 7	14,965
20,000	216.65	0.05529	0.08891	9.7452	28.964	295.07	9.14. − 7	19,937
25,000	221.55	0.02549	0.04008	9.7300	28.964	298.39	2.03. − 6	24,902
30,000	226.51	0.01197	0.01841	9.7147	28.964	301.71	4.42. − 6	29,859
40,000	250.35	2.87. − 3	4.00. − 3	9.6844	28.964	317.19	2.03. − 5	39,750
50,000	270.65	8.00. − 4	1.03. − 3	9.6542	28.964	329.80	7.91. − 5	49,610
60,000	247.02	2.20. − 4	3.10. − 4	9.6241	28.964	315.07	2.62. − 4	59,439
70,000	219.59	5.22. − 5	8.28. − 5	9.5942	28.964	297.06	9.81. − 4	69,238
80,000	198.64	1.05. − 5	1.85. − 5	9.5644	28.964	282.54	4.40. − 3	79,006
90,000	186.87	1.84. − 6	3.43. − 6	9.5348	28.95		2.37. − 2	88,744
100,000	195.08	3.20. − 7	5.60. − 7	9.5052	28.40		0.142	98,451
150,000	634.39	4.54. − 9	2.08. − 9	9.3597	24.10		33	146,542
200,000	854.56	8.47. − 10	2.54. − 10	9.2175	21.30		240	193,899
250,000	941.33	2.48. − 10	6.07. − 11	9.0785	19.19		890	240,540
300,000	976.01	8.77. − 11	1.92. − 11	8.9427	17.73		2,600	286,480
400,000	995.83	1.45. − 11	2.80. − 12	8.6799	15.98		1.6. + 4	376,320
500,000	999.24	3.02. − 12	5.22. − 13	8.4286	14.33		7.7. + 4	463,540
600,000	999.85	8.21. − 13	1.14. − 13	8.1880	11.51		2.8. + 5	548,252
800,000	999.99	1.70. − 13	1.14. − 14	7.7368	5.54		1.4. + 6	710,574
1,000,000	1,000.00	7.51. − 14	3.56. − 15	7.3218	3.94		3.1. + 6	864,071

* Extracted from *U.S. Standard Atmosphere, 1976, National Oceanic and Atmospheric Administration,* National Aeronautics and Space Administration and the U.S. Air Force, Washington, 1976. Z = geometric altitude, T = temperature, P = pressure, g = acceleration of gravity, M = molecular weight, a = velocity of sound, λ = mean free path, and H = geopotential altitude. The notation 1.79. − 5 signifies 1.79×10^{-5}.

Table 4.2.3   Saturated Ammonia (R 717)*

P, bar	T, °C	v_f	v_g	h_f	h_g	s_f	s_g	c_{pf}	c_{pg}	μ_f	μ_g	k_f	k_g	Pr_f	Pr_g
		m³/kg		kJ/kg		kJ/(kg · K)		kJ/(kg · K)		μPa · s		W/(m · K)			
0.5	− 46.5	0.001438	2.175	− 9.0	1,397.9	0.1643	6.3723	4.366	2.126		7.71	0.615	0.0161		
1	− 33.6	0.001466	1.138	47.9	1,418.3	0.4080	6.1286	4.429	2.233	262.9	8.09	0.588	0.0175	1.98	1.032
1.5	− 25.2	0.001488	0.779	86.1	1,430.5	0.5610	5.9867	4.447	2.266	236.1	8.33	0.572	0.0184	1.84	1.046
2	− 18.9	0.001507	0.595	113.8	1,439.2	0.6745	5.8863	4.507	2.393	218.4	8.52	0.554	0.0191	1.78	1.060
2.5	− 13.7	0.001523	0.482	137.4	1,445.9	0.7658	5.8085	4.535	2.460	205.4	8.69	0.548	0.0199	1.70	1.074
3	− 9.2	0.001536	0.406	157.5	1,451.3	0.8426	5.7449	4.561	2.521	195.0	8.81	0.539	0.0204	1.65	1.089
4	− 1.9	0.001560	0.309	191.3	1,459.8	0.9680	5.6443	4.605	2.630	179.5	9.03	0.524	0.0215	1.59	1.104
5	4.1	0.001580	0.250	219.2	1,466.1	1.0692	5.5660	4.463	2.728	168.0	9.21	0.512	0.0225	1.54	1.118
6	9.3	0.001598	0.210	243.2	1,471.0	1.1546	5.5017	4.678	2.818	158.8	9.38	0.501	0.0234	1.48	1.129
8	17.9	0.001630	0.160	283.7	1,478.2	1.2946	5.3994	4.741	2.983	147.4	9.59	0.487	0.0247	1.43	1.160
10	24.9	0.001658	0.1285	317.4	1,483.0	1.4080	5.3189	4.798	3.133	134.6	9.86	0.469	0.0263	1.38	1.174
15	38.7	0.001719	0.0862	384.7	1,489.5	1.6258	5.1683	4.929	3.479	115.6	10.34	0.438	0.0292	1.34	1.233
20	49.4	0.001773	0.0644	437.9	1,491.1	1.7909	5.0564	5.057	3.809	104.9	10.68	0.417	0.0315	1.30	1.292
25	58.2	0.001823	0.0512	483.0	1,489.9	1.9259	4.9651	5.192	4.142	96.2	11.01	0.398	0.0335	1.26	1.360
30	65.8	0.001871	0.0421	522.6	1,486.7	2.0415	4.8864	5.340	4.488	89.3	11.31	0.381	0.0356	1.25	1.426
35	72.4	0.001918	0.03564	558.4	1,482.0	2.1434	4.8161	5.505	4.856	83.7	11.61	0.366	0.0375	1.26	1.50
40	78.4	0.001965	0.03069	591.5	1,476.1	2.2354	4.7516	5.692	5.255	78.8	11.90	0.352	0.0397	1.28	1.57
45	83.9	0.002012	0.02680	622.4	1,469.0	2.3198	4.6912	5.904	5.692	74.6	12.20	0.338	0.0419	1.30	1.66
50	88.9	0.002060	0.02364	651.7	1,461.0	2.3985	4.6338	6.148	6.181	70.8	12.49	0.326	0.0441	1.33	1.75
60	97.9	0.002161	0.01883	706.8	1,442.0	2.5431	4.5244	6.764	7.375	64.3	13.14	0.302	0.0489	1.36	1.98
80	112.9	0.002406	0.01253	810.6	1,390.7	2.8052	4.3076	9.005	11.548	53.4	14.78				
100	125.2	0.002793	0.00826	920.3	1,309.8	3.0715	4.4131	17.08	26.04	42.9	17.76				
113.4†	132.3	0.004260	0.00426	1,105.5	1,105.5	3.5006	3.5006								

* The T, P, v, h, and s values interpolated, rounded, and converted from "ASHRAE Handbook — Fundamentals," 1993. The c_p, μ, and k values from Liley and Desai, CINDAS Rep. 106, 1992. Similar values can be found in "ASHRAE Handbook — Fundamentals," 1993.
† Critical point.
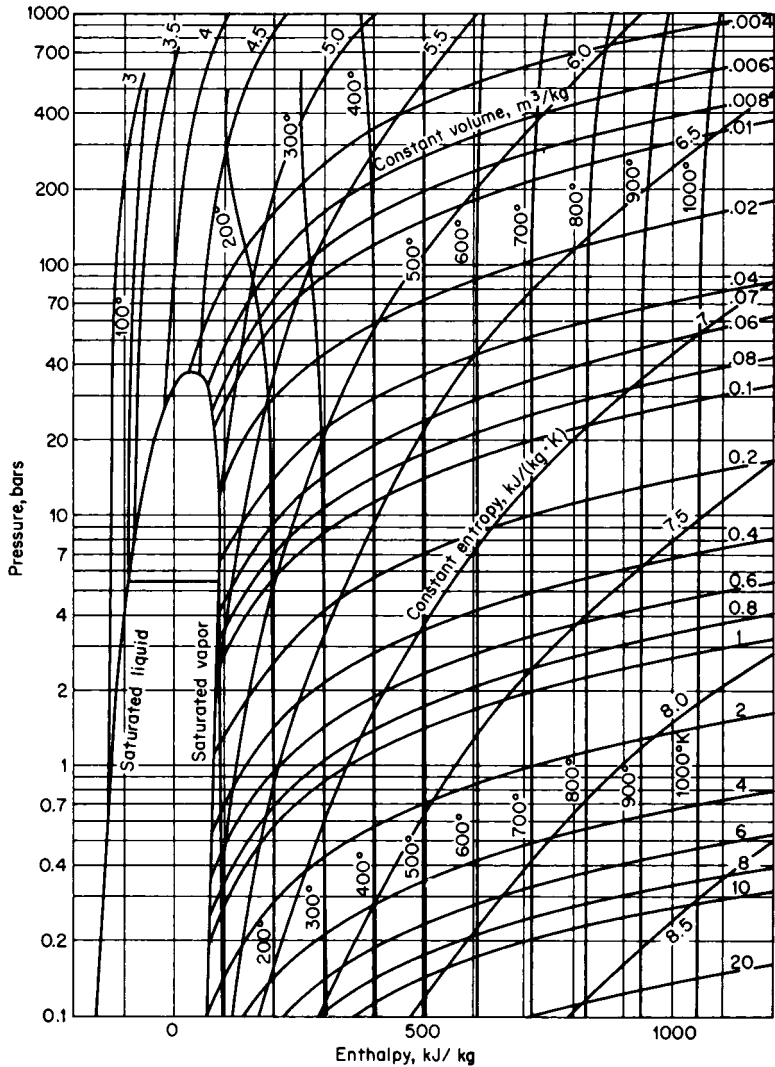
Fig. 4.2.2 Enthalpy–log pressure diagram for air.

Fig. 4.2.3 Enthalpy–log pressure diagram for ammonia (R717).

Table 4.2.4   Saturated Carbon Dioxide*

T, K	P, bar	v_f, m³/kg	v_g, m³/kg	h_f, kJ/kg	h_g, kJ/kg	s_f, kJ/(kg · K)	s_g, kJ/(kg · K)	c_{pf}, kJ/(kg · K)
216.6	5.180	8.484. − 4	0.0712	386.3	731.5	2.656	4.250	1.707
220	5.996	8.574. − 4	0.0624	392.6	733.1	2.684	4.232	1.761
225	7.357	8.710. − 4	0.0515	401.8	735.1	2.723	4.204	
230	8.935	8.856. − 4	0.0428	411.1	736.7	2.763	4.178	1.879
235	10.75	9.011. − 4	0.0357	402.5	737.9	2.802	4.152	
240	12.83	9.178. − 4	0.0300	430.2	738.9	2.842	4.128	1.933
245	15.19	9.358. − 4	0.0253	440.1	739.4	2.882	4.103	
250	17.86	9.554. − 4	0.0214	450.3	739.6	2.923	4.079	1.992
255	20.85	9.768. − 4	0.0182	460.8	739.4	2.964	4.056	
260	24.19	1.000. − 3	0.0155	471.6	738.7	3.005	4.032	2.125
270	32.03	1.056. − 3	0.0113	494.4	735.6	3.089	3.981	2.410
275	36.59	1.091. − 3	0.0097	506.5	732.8	3.132	3.954	
280	41.60	1.130. − 3	0.0082	519.2	729.1	3.176	3.925	2.887
290	53.15	1.241. − 3	0.0058	547.6	716.9	3.271	3.854	3.724
300	67.10	1.470. − 3	0.0037	585.4	690.2	3.393	3.742	
304.2†	73.83	2.145. − 3	0.0021	636.6	636.6	3.558	3.558	∞

* The notation 8.484. − 4 signifies 8.484×10^{-4}.
† Critical point.

Table 4.2.5   Superheated Carbon Dioxide*

P, bar		Temperature , K								
	300	350	400	450	500	600	700	800	900	1,000
v	0.5639	0.6595	0.7543	0.8494	0.9439	1.1333	1.3324	1.5115	1.7005	1.8894
1 h	809.3	853.1	899.1	947.1	997.0	1,102	1,212	1,327	1,445	1,567
s	4.860	4.996	5.118	5.231	5.337	5.527	5.697	5.850	5.990	6.120
v	0.1106	0.1304	0.1498	0.1691	0.1882	0.2264	0.2645	0.3024	0.3403	0.3782
5 h	805.5	850.3	897.0	945.5	995.8	1,101	1,211	1,326	1,445	1,567
s	4.548	4.686	4.810	4.925	5.031	5.222	5.392	5.546	5.685	5.814
v	0.0539	0.0642	0.0742	0.0841	0.0938	0.1131	0.1322	0.1513	0.1703	0.1893
10 h	800.7	846.9	894.4	943.5	994.1	1,100	1,211	1,326	1,445	1,567
s	4.405	4.548	4.674	4.790	4.897	5.089	5.260	5.414	5.555	5.683
v	0.0255	0.0311	0.0364	0.0416	0.0466	0.0564	0.0661	0.0757	0.0853	0.0948
20 h	790.2	839.8	889.3	939.4	990.8	1,098	1,209	1,325	1,444	1,567
s	4.249	4.402	4.534	4.653	4.762	4.955	5.127	5.282	5.423	5.551
v	0.0159	0.0201	0.0238	0.0274	0.0309	0.0375	0.0441	0.0505	0.0570	0.0633
30 h	778.5	832.4	883.8	935.2	987.3	1,096	1,208	1,324	1,444	1,566
s	4.144	4.341	4.447	4.569	4.679	4.876	5.049	5.204	5.346	5.474
v	0.0110	0.0146	0.0175	0.0203	0.0230	0.0281	0.0331	0.0379	0.0428	0.0476
40 h	764.9	824.6	878.3	931.1	984.3	1,094	1,205	1,323	1,443	1,566
s	4.055	4.239	4.380	4.507	4.619	4.818	4.993	5.148	5.291	5.419
v	0.0080	0.0112	0.0138	0.0161	0.0183	0.0224	0.0265	0.0304	0.0343	0.0382
50 h	748.2	816.3	872.6	926.9	981.1	1,091	1,205	1,322	1,443	1,566
s	3.968	4.179	4.330	4.457	4.572	4.773	4.948	5.104	5.247	5.377
v	0.0058	0.0090	0.0113	0.0133	0.0151	0.0187	0.0221	0.0254	0.0286	0.0318
60 h	726.9	807.7	866.9	922.7	977.8	1,089	1,204	1,321	1,442	1,565
s	3.878	4.126	4.314	4.416	4.532	4.736	4.912	5.069	5.212	5.341
v		0.0062	0.0081	0.0097	0.0112	0.0140	0.0166	0.0191	0.0216	0.0240
80 h		788.4	855.1	914.2	971.3	1,085	1,201	1,320	1,441	1,565
s		4.029	4.208	4.347	4.468	4.675	4.854	5.011	5.155	5.286

Table 4.2.5   Superheated Carbon Dioxide*   (Continued)

P, bar		300	350	400	450	500	600	700	800	900	1,000
						Temperature, K					
100	v		0.0045	0.0062	0.0076	0.0089	0.0111	0.0133	0.0153	0.0173	0.0193
	h		766.2	843.0	905.7	964.9	1,081	1,198	1,318	1,440	1,564
	s		3.936	4.144	4.290	4.417	4.627	4.808	4.967	5.111	5.241
150	v		0.0023	0.0038	0.0049	0.0058	0.0074	0.0089	0.0103	0.0117	0.0130
	h		704.5	811.9	884.8	949.4	1,072	1,192	1,314	1,437	1,562
	s		3.716	4.005	4.177	4.313	4.536	4.722	4.884	5.030	5.162
200	v		0.0017	0.0027	0.0035	0.0043	0.0056	0.0067	0.0078	0.0088	0.0099
	h		670.0	783.2	865.2	934.9	1,063	1,186	1,310	1,435	1,561
	s		3.591	3.894	4.088	4.234	4.468	4.668	4.824	4.970	5.104
300	v			0.0018	0.0023	0.0029	0.0038	0.0046	0.0053	0.0060	0.0067
	h			745.3	834.0	910.6	1,047	1,176	1,303	1,431	1,559
	s			3.747	3.956	4.118	4.367	4.573	4.743	4.886	5.021
400	v			0.0015	0.0018	0.0022	0.0029	0.0035	0.0041	0.0047	0.0052
	h			728.1	814.6	893.3	1,035	1,168	1,298	1,428	1,558
	s			3.663	3.867	4.033	4.292	4.497	4.671	4.824	4.960
500	v				0.0016	0.0018	0.0024	0.0029	0.0034	0.0038	0.0043
	h				803.5	881.9	1,027	1,162	1,294	1,426	1,557
	s				3.805	3.970	4.234	4.443	4.620	4.774	4.913

* Interpolated and rounded from Vukalovich and Altunin, ''Thermophysical Properties of Carbon Dioxide,'' Atomizdat, Moscow, 1965; and Collett, England, 1968. Note: v, h, and s units are the same as in Table 4.2.4.

Table 4.2.6   Saturated Iso-Butane (R 600a)*

P, bar	T, °C	v_f	v_g	h_f	h_g	s_f	s_g	c_{pf}	c_{pg}	μ_f	μ_g	k_f	k_g	Pr_f	Pr_g
		m³/kg		kJ/kg		kJ/(kg · K)		kJ/(kg · K)		μPa · s		W/(m · K)			
1	−12.13	0.001683	0.3601	288.2	655.5	3.4552	4.8626	2.24	1.56	229	6.63	0.112	0.0125	4.58	0.827
1.5	−1.42	0.001720	0.2468	312.8	668.2	3.5470	4.8615	2.30	1.63	203	6.93	0.108	0.0136	4.31	0.831
2	6.82	0.001746	0.1886	332.3	681.2	3.6166	4.8631	2.35	1.68	184	7.18	0.104	0.0145	4.16	0.832
2.5	13.60	0.001771	0.1528	348.5	690.5	3.6734	4.8658	2.38	1.73	171	7.38	0.101	0.0153	4.03	0.834
3	19.38	0.001793	0.1290	362.6	698.3	3.7214	4.8689	2.42	1.78	160	7.57	0.098	0.0159	3.95	0.847
4	29.17	0.001834	0.0978	382.3	711.5	3.8020	4.8757	2.49	1.86	144	7.89	0.094	0.0170	3.81	0.863
5	37.32	0.001870	0.0785	407.6	722.3	3.8688	4.8824	2.54	1.93	132	8.18	0.090	0.0181	3.73	0.872
6	44.28	0.001904	0.0657	425.7	731.5	3.9254	4.8889	2.60	1.99	122	8.44	0.087	0.0190	3.65	0.884
8	56.08	0.001966	0.0490	456.6	746.7	4.0213	4.9008	2.70	2.11	108	8.91	0.083	0.0206	3.51	0.913
10	65.88	0.002026	0.0389	484.2	758.8	4.1010	4.9112	2.76	2.23	97	9.34	0.079	0.0221	3.39	0.942
15	85.29	0.002220	0.0222	556.3	786.1	4.3020	4.9345	3.04	2.56	78	10.4	0.072	0.0252	3.29	1.057
20	100.38	0.002332	0.0175	588.7	795.1	4.3878	4.9405	3.38	3.01	64	11.4	0.067	0.0284	2.99	1.208
25	112.83	0.002522	0.0135	631.9	802.6	4.4980	4.9403	3.92	3.79	54	12.7	0.063	0.0326	3.36	1.476
30	123.33	0.002786	0.0095	673.7	802.2	4.6008	4.9251	6.3	7.4	44	14.3	0.061	0.0414	4.54	2.556
35	132.33	0.003312	0.0064	720.8	782.0	4.7155	4.8663			33	17.6	0.075	0.0723		
35.5†	134.85	0.004464	0.0045	752.5	752.4	4.791	4.791								

* P, T, v, h, and s are interpolated and rounded from ''ASHRAE Handbook—Fundamentals,'' 1993. c_p, μ, and k from Liley and Desai, CINDAS Rep. 106, 1992. Substantially similar values appear in the ''ASHRAE Thermophysical Properties of Refrigerants,'' 1993.
† Critical point.

Table 4.2.7   Saturated Normal Hydrogen*

T	P	v_f	v_g	h_f	h_g	s_f	s_g	c_{pf}	c_{pg}
13.95	0.072	0.0130	7.974	218.3	565.4	14.08	46.64	6.36	10.52
14	0.074	0.0130	7.205	219.6	669.3	14.17	46.30	6.47	10.54
15	0.127	0.0132	4.488	226.4	678.2	14.64	44.76	6.91	10.67
16	0.204	0.0133	2.954	233.8	686.7	15.10	43.42	7.36	10.85
17	0.314	0.0135	2.032	241.6	694.7	15.57	42.23	7.88	11.07
18	0.461	0.0137	1.449	249.9	702.1	16.03	41.16	8.42	11.34
19	0.654	0.0139	1.064	258.8	708.8	16.50	40.19	8.93	11.66
20	0.901	0.0141	0.802	268.3	714.8	16.97	39.30	9.45	12.04
21	1.208	0.0143	0.618	278.4	720.2	17.44	38.49	10.13	12.49
22	1.585	0.0146	0.483	289.2	724.4	17.92	37.71	10.82	13.03
23	2.039	0.0148	0.383	300.8	727.6	18.41	36.97	11.69	13.69
24	2.579	0.0151	0.307	313.3	729.8	18.90	36.27	12.52	14.49
25	3.213	0.0155	0.243	326.7	730.7	19.41	35.58	13.44	15.52
26	3.950	0.0159	0.203	341.2	730.2	19.93	34.90	14.80	16.85
27	4.800	0.0164	0.167	357.0	728.0	20.47	34.22	16.17	18.66
28	5.770	0.0170	0.137	374.3	723.7	21.04	33.52	18.48	21.24
29	6.872	0.0177	0.113	393.6	716.6	21.65	32.80	22.05	25.19
30	8.116	0.0185	0.092	415.4	705.9	22.31	32.00	26.59	31.99
31	9.510	0.0198	0.074	441.3	689.7	23.08	31.09	36.55	46.56
32	11.068	0.0217	0.057	474.7	663.2	24.03	29.93	65.37	87.02
33.18^c	13.130	0.0318	0.032	565.4	565.4	26.68	26.68		

* T = temperature, K; P = pressure, bar; c = critical point; v = specific volume, m³/kg; h = specific enthalpy, kJ/kg; s = specific entropy, kJ/(kg · K); c_p = specific heat at constant pressure, kJ/(kg · K); subscript f represents saturated liquid and subscript g represents saturated vapor.

Table 4.2.8   Saturated Propane (R 290)*

P, bar	T, °C	v_f	v_g	h_f	h_g	s_f	s_g	c_{pf}	c_{pg}	μ_f	μ_g	k_f	k_g	Pr_f	Pr_g
		m³/kg		kJ/kg		kJ/(kg · K)		kJ/(kg · K)		μPa · s		W/(m · K)			
0.5	− 56.95	0.001674	0.8045	388.5	831.5	3.7263	5.7747	2.181	1.374	233	6.05	0.139	0.0101	3.66	0.823
1	− 42.38	0.001721	0.4186	420.9	849.0	3.8705	5.7258	2.246	1.457	198	6.46	0.130	0.0113	3.42	0.833
1.5	− 32.83	0.001755	0.2871	442.8	860.5	3.9636	5.7015	2.294	1.517	178	6.74	0.124	0.0122	3.29	0.838
2	− 25.48	0.001783	0.2194	460.1	869.2	4.0341	5.6861	2.336	1.568	164	6.97	0.119	0.0130	3.22	0.841
2.5	− 19.43	0.001807	0.1778	474.5	876.3	4.0916	5.6753	2.371	1.610	154	7.16	0.116	0.0136	3.15	0.848
3	− 14.23	0.001828	0.1498	487.1	882.4	4.1404	5.6672	2.406	1.652	146	7.33	0.113	0.0141	3.11	0.859
4	− 5.53	0.001867	0.1138	508.5	892.3	4.2213	5.6556	2.467	1.723	134	7.61	0.108	0.0151	3.06	0.868
5	1.66	0.001901	0.0918	526.6	900.4	4.2875	5.6477	2.522	1.787	124	7.86	0.104	0.0160	3.01	0.878
6	7.82	0.001932	0.0771	542.4	907.1	4.3437	5.6418	2.574	1.847	116	8.08	0.101	0.0168	2.96	0.888
8	18.20	0.001990	0.0580	569.7	917.9	4.4379	5.6333	2.674	1.961	104	8.48	0.096	0.0182	2.90	0.914
10	26.86	0.002044	0.04609	593.1	926.4	4.5161	5.6270	2.769	2.072	95	9.04	0.092	0.0195	2.86	0.961
15	43.84	0.002173	0.03009	641.6	941.1	4.6697	5.6148	3.013	2.363	79	9.63	0.084	0.0225	2.83	1.011
20	57.14	0.002304	0.02165	682.3	949.9	4.7923	5.6026	3.290	2.717	67	10.4	0.078	0.0256	2.83	1.104
25	68.15	0.002450	0.01642	719.0	954.1	4.8979	5.5872	3.665	3.216	58	11.6	0.073	0.0295	2.91	1.265
30	77.67	0.002627	0.01269	753.8	953.8	4.9950	5.5654	4.270	4.041	50	12.4	0.071	0.0355	3.01	1.412
35	85.99	0.002866	0.00978	788.7	947.5	5.0895	5.5318	5.594	5.848	44	13.6	0.073	0.0412	3.37	1.93
40	93.38	0.00336	0.00685	830.0	928.9	5.200	5.470	12.12	14.25	33	17.8	0.084	0.0728	4.76	3.48
42.4†	96.65	0.00457	0.00457	879.2	879.2	5.330	5.330								

* The T, P, v, h, and s values are interpolated, rounded, and converted from ''ASHRAE Handbook—Fundamentals,'' 1993. The c_p, μ, and k values are from Liley and Desai, CINDAS Rep. 106, 1992. Similar values can be found in ''ASHRAE Handbook—Fundamentals,'' 1993.
   † Critical point.

Table 4.2.9   Saturated Refrigerant 11*

P, bar	T, °C	v_f	v_g	h_f	h_g	s_f	s_g	c_{pf}	c_{pg}	μ_f	μ_g	k_f	k_g	Pr_f	Pr_g
		m³/kg		kJ/kg		kJ/(kg · K)		kJ/(kg · K)		μPa · s		W/(m · K)			
0.5	5.18	0.000657	0.3298	204.5	392.4	1.0162	1.6916	0.873	0.560	537	10.3	0.094	0.0083	4.35	0.695
1	23.55	0.000676	0.1731	220.3	401.8	1.0711	1.6833	0.887	0.580	440	11.0	0.090	0.0088	4.01	0.725
1.5	35.26	0.000689	0.1186	230.9	407.9	1.1060	1.6800	0.896	0.594	385	11.4	0.089	0.0091	3.80	0.736
2	44.42	0.000700	0.0908	239.1	412.5	1.1322	1.6783	0.905	0.604	341	11.8	0.085	0.0096	3.63	0.740
2.5	51.90	0.000709	0.0737	245.9	416.3	1.1532	1.6774	0.913	0.614	315	12.0	0.083	0.0099	3.47	0.745
3	58.37	0.000718	0.0620	251.8	419.4	1.1711	1.6768	0.920	0.623	288	12.3	0.081	0.0102	3.27	0.751
4	69.18	0.000733	0.0470	261.9	424.7	1.2008	1.6764	0.934	0.637	252	12.8	0.079	0.0107	2.98	0.762
5	78.07	0.000746	0.0380	270.2	428.9	1.2247	1.6763	0.947	0.652	228	13.1	0.077	0.0111	2.80	0.770
6	85.76	0.000759	0.0317	277.6	432.4	1.2482	1.6764	0.959	0.669	211	13.5	0.076	0.0115	2.66	0.779
8	98.59	0.000781	0.0239	290.1	438.0	1.2790	1.6768	0.983	0.689	187	14.1	0.073	0.0122	2.52	0.792
10	109.3	0.000802	0.0190	300.8	442.3	1.3069	1.6771	1.008	0.713	170	14.6	0.070	0.0129	2.45	0.807
15	130.3	0.000853	0.0124	322.6	449.9	1.3614	1.6770	1.076	0.783	138	15.7	0.065	0.0143	2.28	0.860
20	146.6	0.000903	0.0090	340.5	454.5	1.4038	1.6754	1.153	0.876	118	16.9	0.062	0.0158	2.19	0.937
25	160.2	0.000959	0.0068	356.4	457.0	1.4399	1.6721	1.256	1.021	101	18.1	0.059	0.0174	2.15	1.062
30	171.9	0.001024	0.0053	371.1	457.6	1.4722	1.6670	1.384	1.317	86	19.3	0.058	0.0193	2.13	1.317
35	182.2	0.001105	0.0042	385.5	456.1	1.5032	1.6583	1.82	1.84						
40	191.3	0.001246	0.0031	401.1	451.3	1.5352	1.6432	2.95	2.31						
44.1†	198.0	0.00181	0.0018	428.6	428.6	1.5933	1.5933								

* The *T, P, v, h,* and *s* values are interpolated, converted, and rounded from ''ASHRAE Handbook—Fundamentals,'' 1993. The c_p, μ, and k are from Liley and Desai, CINDAS Rep. 106, 1992. Similar values appear in ''ASHRAE Handbook—Fundamentals,'' 1993.
  † Critical point.
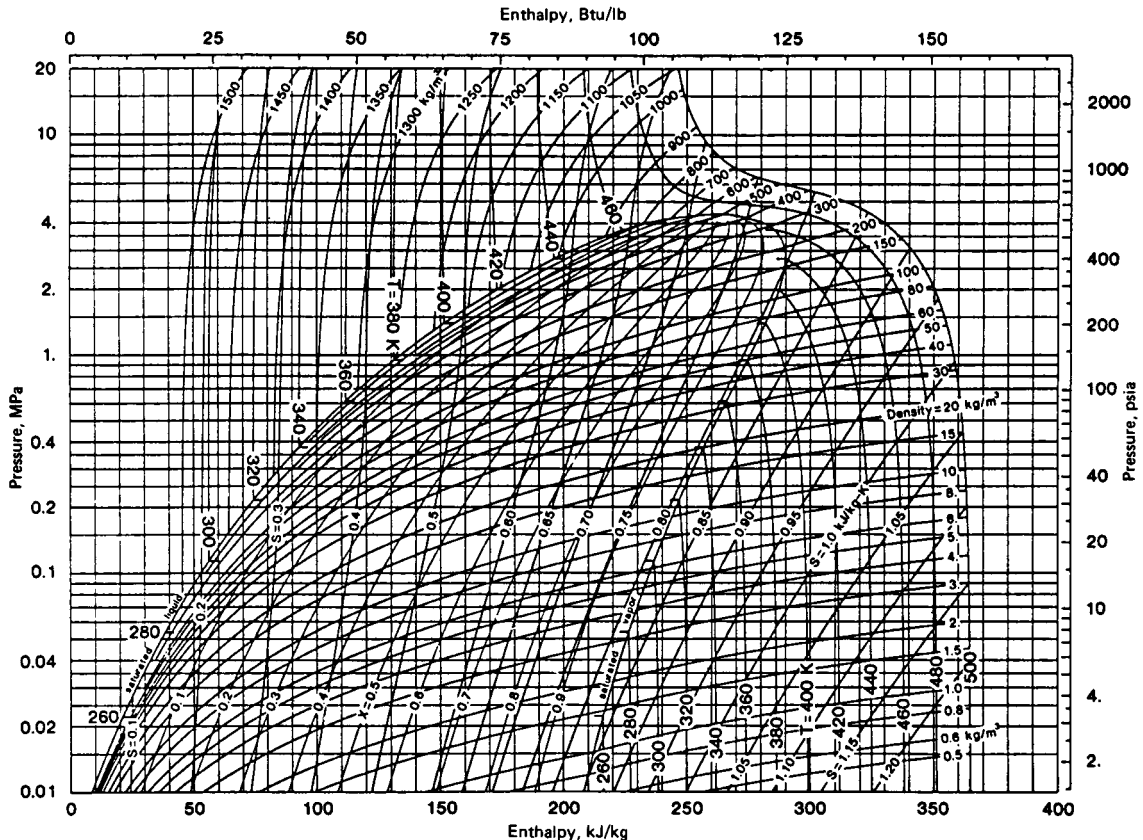
Fig. 4.2.4   Enthalpy–log pressure diagram for refrigerant 11. 1 MPa = 10 bar. (*Copyright 1981 by ASHRAE and reproduced by permission.*)

Table 4.2.10   Saturated Refrigerant 12*

P, bar	T, °C	v_f	v_g	h_f	h_g	s_f	s_g	c_{pf}	c_{pg}	μ_f	μ_g	k_f	k_g	Pr_f	Pr_g
		m³/kg		kJ/kg		kJ/(kg · K)		kJ/(kg · K)		µPa · s		W/(m · K)			
0.5	−45.24	0.000653	0.3072	159.5	331.5	0.8386	1.5936	0.883	0.545	420	9.8	0.0940	0.0062	4.08	0.861
1	−30.11	0.000672	0.1611	172.7	338.8	0.8947	1.5780	0.895	0.575	358	10.4	0.0883	0.0070	3.63	0.854
1.5	−20.15	0.000686	0.1103	181.6	345.3	0.9304	1.5702	0.906	0.595	322	11.0	0.0846	0.0075	3.45	0.873
2	−12.52	0.000697	0.0843	188.5	347.0	0.9571	1.5654	0.913	0.612	297	11.4	0.0817	0.0079	3.32	0.883
2.5	−6.22	0.000707	0.0682	194.2	349.9	0.9788	1.5619	0.921	0.627	277	11.7	0.0793	0.0083	3.22	0.834
3	−0.84	0.000715	0.0574	199.2	352.3	0.9972	1.5594	0.929	0.640	262	12.0	0.0774	0.0086	3.13	0.893
4	8.19	0.000731	0.0436	207.7	356.3	1.0275	1.5556	0.945	0.663	238	12.4	0.0739	0.0091	3.04	0.903
5	15.64	0.000744	0.0351	214.8	359.4	1.0522	1.5530	0.959	0.683	221	12.8	0.0714	0.0095	2.97	0.920
6	22.01	0.000757	0.0294	220.9	362.0	1.0731	1.5510	0.969	0.702	207	13.2	0.0692	0.0098	2.90	0.946
8	32.79	0.000780	0.0221	231.7	366.2	1.1082	1.5479	0.995	0.738	186	13.9	0.0653	0.0105	2.83	0.977
10	41.70	0.000802	0.0176	240.8	369.4	1.1370	1.5455	1.021	0.773	170	14.5	0.0621	0.0111	2.80	1.01
15	59.30	0.000854	0.0141	259.6	374.7	1.1938	1.5400	1.107	0.868	143	15.9	0.0558	0.0125	2.84	1.10
20	72.99	0.000907	0.0082	275.2	377.5	1.2386	1.5341	1.225	0.993	124	17.3	0.0512	0.0137	2.97	1.25
25	84.33	0.000967	0.0062	289.2	378.4	1.2770	1.5265	1.36	1.029	108	18.9	0.0469	0.0151	3.13	1.40
30	94.05	0.001040	0.0048	302.4	377.3	1.3120	1.5162	1.51	1.55	92	20.7	0.0429	0.0167	3.24	1.92
35	102.6	0.001141	0.0036	315.7	373.5	1.3437	1.4975		2.50	75	23.2	0.0389	0.0191	3.04	3.04
40	110.1	0.001360	0.0025	332.3	362.5	1.3871	1.4659		10.9	55	28.2	0.0346	0.0222		
41.2†	111.8	0.001771	0.0018	347.4	347.4	1.4272	1.4272								

*The T, P, v, h, and s values are interpolated, converted, and rounded from ''ASHRAE Handbook—Fundamentals,'' 1993. The c_p, μ, and k values are from Liley and Desai, CINDAS Rep. 106, 1992. Similar values appear in ''ASHRAE Handbook—Fundamentals,'' 1993.
† Critical point.
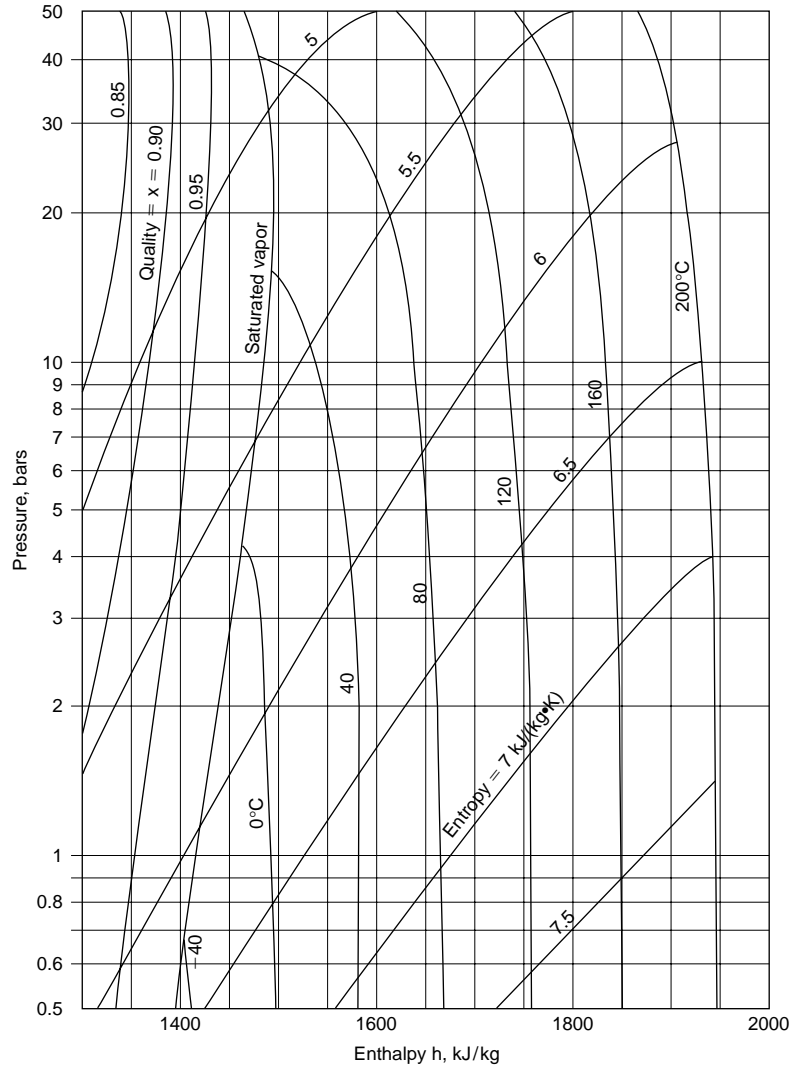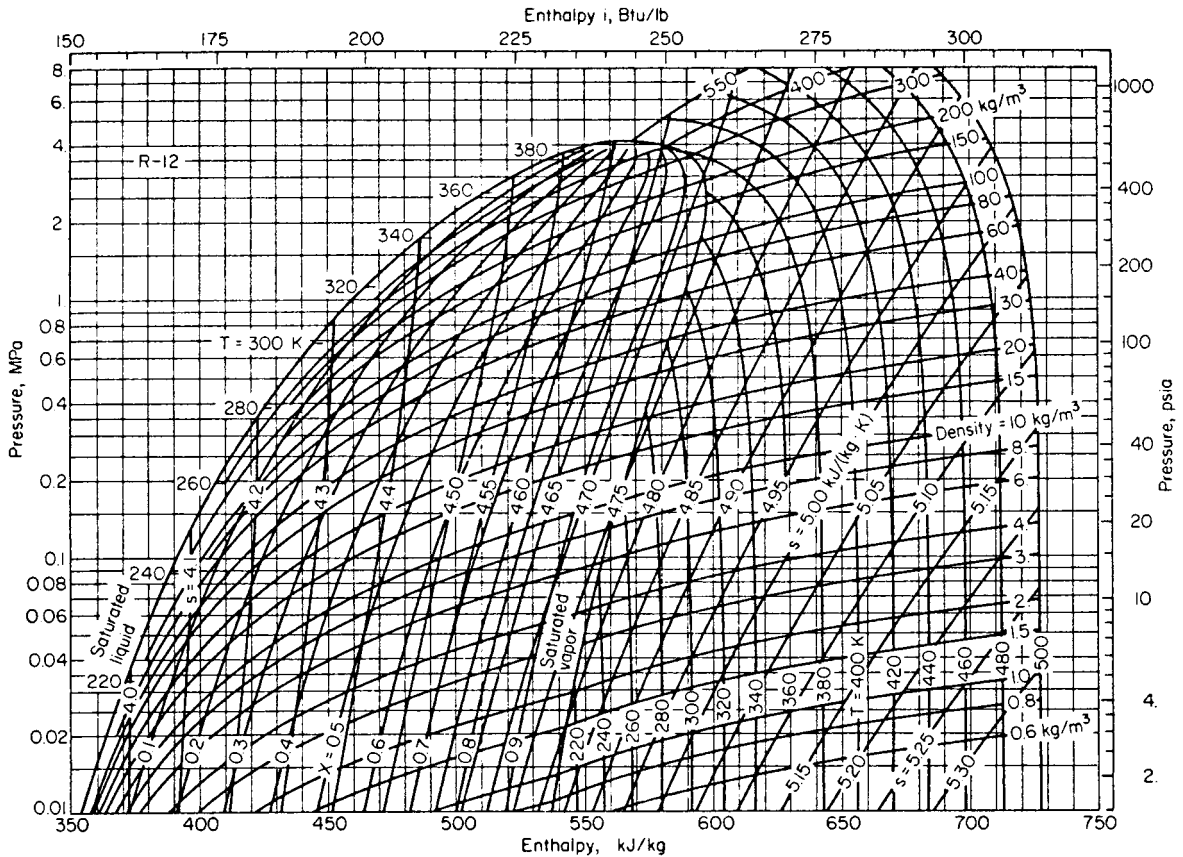

Fig. 4.2.5   Enthalpy–log pressure diagram for refrigerant 12. Prepared at the Center for Applied Thermodynamic Studies, University of Idaho, Moscow. *(Copyright by ASHRAE and reproduced by permission.)*

Table 4.2.11   Saturated Refrigerant 22*

P, bar	T, °C	v_f	v_g	h_f	h_g	s_f	s_g	c_{pf}	c_{pg}	μ_f	μ_g	k_f	k_g	Pr_f	Pr_g
		m³/kg		kJ/kg		kJ/(kg · K)		kJ/(kg · K)		μPa · s		W/(m · K)			
0.5	−54.80	0.000690	0.4264	138.7	381.1	0.7510	1.8619	1.080	0.574			0.121	0.0060		
1	−41.39	0.000709	0.2153	153.6	387.6	0.8173	1.8256	1.092	0.605			0.114	0.0069		
1.5	−32.07	0.000723	0.1472	163.6	393.5	0.8591	1.8056	1.104	0.630			0.110	0.0075		
2	−25.19	0.000734	0.1125	171.2	394.7	0.8902	1.7919	1.115	0.650			0.107	0.0079		
2.5	−19.52	0.000743	0.0910	177.5	397.2	0.9155	1.7814	1.126	0.669	258.6	11.02	0.105	0.0083	2.78	0.888
3	−14.66	0.000752	0.0766	183.1	399.2	0.9368	1.7730	1.136	0.686	245.9	11.21	0.103	0.0086	2.71	0.894
4	−6.57	0.000767	0.0582	192.3	402.4	0.9718	1.7599	1.155	0.716	225.6	11.54	0.099	0.0091	2.63	0.907
5	0.11	0.000780	0.0469	200.1	404.9	1.0005	1.7498	1.171	0.745	209.9	11.80	0.096	0.0095	2.56	0.924
6	5.85	0.000789	0.0392	206.9	405.7	1.0327	1.7417	1.189	0.771	197.2	11.97	0.094	0.0099	2.50	0.936
8	15.44	0.000815	0.0295	218.5	410.0	1.0650	1.7287	1.221	0.819	177.7	12.42	0.090	0.0104	2.42	0.974
10	23.39	0.000835	0.0236	228.3	412.3	1.0981	1.7185	1.252	0.871	163.0	12.82	0.086	0.0109	2.36	1.026
15	39.07	0.000883	0.0155	248.5	415.7	1.1628	1.6985	1.332	1.000	137.7	13.9	0.080	0.0118	2.29	1.12
20	51.23	0.000929	0.0113	265.0	417.1	1.2132	1.6822	1.426	1.149						
25	61.33	0.000978	0.0087	279.6	417.0	1.2560	1.6670	1.550	1.341						
30	70.05	0.001030	0.0068	301.3	415.7	1.2942	1.6517	1.613	2.070						
35	77.70	0.001087	0.0056	305.0	413.7	1.3275	1.6371	2.03	2.05						
40	84.53	0.001174	0.0044	318.9	408.3	1.3648	1.6150	2.67	2.96						
45	90.67	0.001326	0.0033	335.8	397.9	1.4100	1.5810	4.47	5.19						
49.9†	96.14	0.001909	0.0019	366.6	366.6	1.4918	1.4918								

* Values are interpolated and rounded from ''ASHRAE Handbook—Fundamentals,'' 1993.
† Critical point.
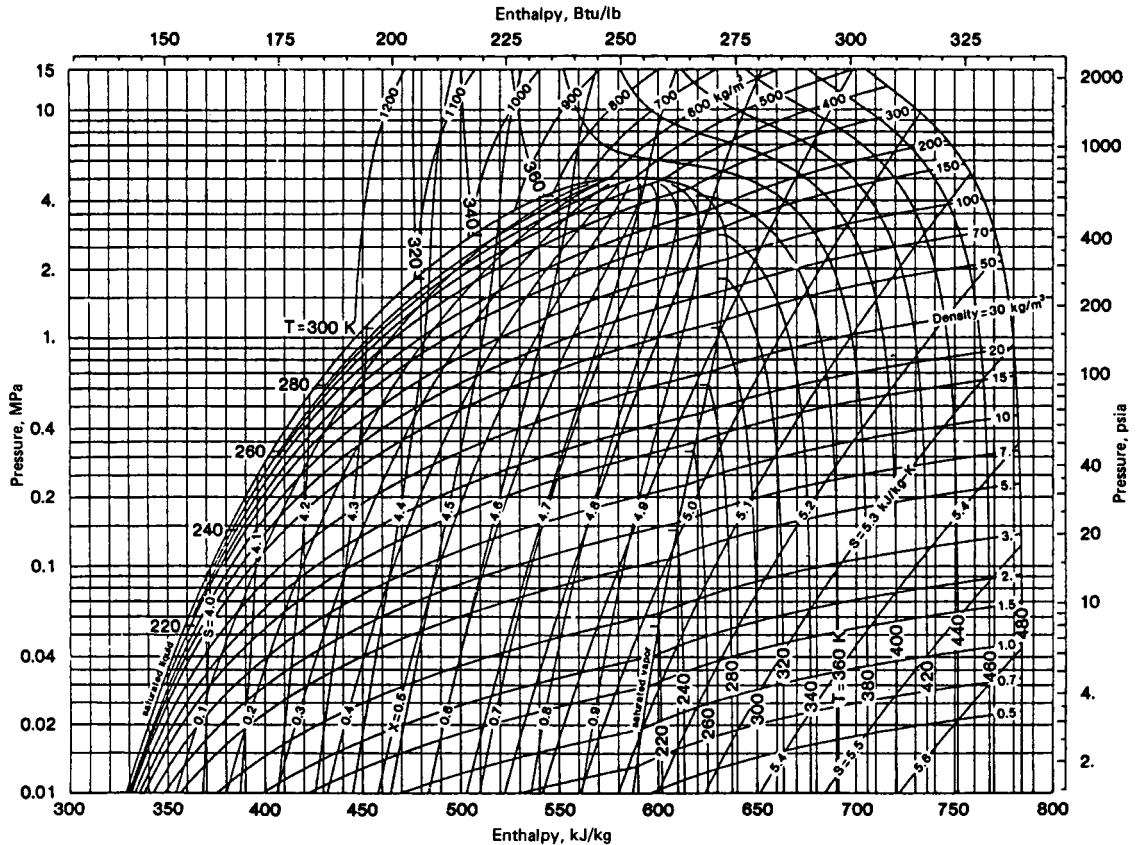
Fig. 4.2.6   Enthalpy–log pressure diagram for refrigerant 22. 1 MPa = 10 bar. *(Copyright 1981 by ASHRAE and reproduced by permission.)*

Table 4.2.12   Saturated Refrigerant 32*

P, bar	T, °C	v_f	v_g	h_f	h_g	s_f	s_g	c_{pf}	c_{pg}	μ_f	μ_g	k_f	k_g	Pr_f	Pr_g
		m³/kg		kJ/kg		kJ/(kg · K)		kJ/(kg · K)		μPa · s		W/(m · K)			
1	−51.68	0.000832	0.3361	114.6	497.5	0.6565	2.3855	1.559	0.873	278.5	10.50	0.189	0.0082	2.30	1.12
1.5	−43.66	0.000847	0.2394	127.2	501.5	0.7123	2.3435	1.576	0.911	251.6	10.61	0.181	0.0085	2.19	1.14
2	−37.35	0.000860	0.1773	137.3	504.5	0.7555	2.3127	1.601	0.955	226.6	10.70	0.175	0.0088	2.10	1.16
2.5	−32.16	0.000870	0.1433	145.7	506.8	0.7906	2.2888	1.615	1.003	218.8	10.77	0.171	0.0091	2.06	1.18
3	−27.74	0.000880	0.1205	152.7	508.6	0.8202	2.2693	1.627	1.020	207.7	10.83	0.167	0.0094	2.02	1.18
4	−20.39	0.000897	0.0914	165.2	511.3	0.8689	2.2383	1.653	1.074	192.7	10.93	0.161	0.0100	1.98	1.18
5	−14.34	0.000912	0.0736	175.3	513.3	0.9084	2.2140	1.678	1.123	180.8	11.02	0.156	0.0104	1.94	1.19
6	−9.16	0.000925	0.0616	184.2	514.7	0.9418	2.1940	1.701	1.169	170.1	11.10	0.152	0.0109	1.90	1.19
8	−0.51	0.000950	0.0463	199.1	516.7	0.9968	2.1616	1.743	1.255	154.8	11.32	0.145	0.0117	1.86	1.21
10	6.63	0.000972	0.0369	211.7	517.8	1.0415	2.1356	1.784	1.337	142.4	11.53	0.139	0.0124	1.83	1.24
15	20.64	0.001023	0.0242	237.0	518.3	1.1282	2.0855	1.895	1.541	120.7	12.08	0.128	0.0141	1.79	1.32
20	31.45	0.001072	0.0176	257.5	516.7	1.1949	2.0460	2.009	1.761	105.7	12.67	0.119	0.0156	1.78	1.43
25	40.36	0.001122	0.0136	275.3	513.7	1.2506	2.0112	2.151	2.026	94.0	13.29	0.112	0.0171	1.81	1.57
30	48.00	0.001175	0.0102	291.4	509.4	1.2997	1.9786	2.314	2.352	84.9	13.98	0.107	0.0186	1.84	1.77
35	54.69	0.001232	0.0088	306.6	503.9	1.3447	1.9463	2.524	2.791	77.7	14.74	0.101	0.0200	1.94	2.06
40	60.66	0.001299	0.0072	322.1	496.7	1.3876	1.9128	2.744	3.367	71.4	15.60	0.095	0.0215	2.06	2.44
45	66.05	0.001380	0.0060	336.5	487.8	1.4304	1.8763		4.49	66.0	16.61	0.089	0.0191		3.90
50	70.95	0.001490	0.0048	352.8	475.6	1.4759	1.8328			61.8	17.85	0.082	0.0167		
58.6†	78.41	0.002383	0.0024	413.8	413.8	1.6465	1.6465								

* The P, T, v, h, and s values are interpolated and rounded from ''ASHRAE Handbook—Fundamentals,'' 1993; c_p values are interpolated and converted from Defbaugh et al., *J. Chem. Eng. Data,* **39,** 1994, pp. 333–340; μ_f and μ_g are interpolated from Oliveira and Wakeham, *Int. J. Thermophys.,* **14,** no. 6, 1993, pp. 1131–1143.
† Critical point.

Table 4.2.13   Saturated Refrigerant 123*

P, bar	T, °C	v_f	v_g	h_f	h_g	s_f	s_g	c_{pf}	c_{pg}	μ_f	μ_g	k_f	k_g	Pr_f	Pr_g
		m³/kg		kJ/kg		kJ/(kg · K)		kJ/(kg · K)		μPa · s		W/(m · K)			
0.5	9.72	0.000666	0.2995	209.9	387.3	1.0348	1.6626	1.002	0.668	503		0.0811		6.21	
1	27.46	0.000686	0.1564	227.7	398.0	1.0963	1.6629	1.023	0.700	410		0.0759		5.53	
1.5	39.10	0.000701	0.1068	239.7	405.0	1.1353	1.6649	1.037	0.722	362	11.36	0.0726	0.0111	5.16	0.738
2	48.05	0.000713	0.0813	249.0	410.3	1.1647	1.6670	1.049	0.741	330	11.65	0.0699	0.0119	4.78	0.728
2.5	55.38	0.000723	0.0657	256.8	414.7	1.1884	1.6692	1.059	0.756	306	11.90	0.0678	0.0122	4.78	0.736
3	61.68	0.000732	0.0552	263.5	418.4	1.2086	1.6713	1.069	0.770	287	12.11	0.0660	0.0127	4.65	0.739
4	73.20	0.000749	0.0417	274.8	424.5	1.2418	1.6751	1.086	0.796	259	12.47	0.0629	0.0134	4.47	0.742
5	80.87	0.000764	0.0335	284.3	429.4	1.2687	1.6784	1.101	0.818	238	12.75	0.0604	0.0140	4.33	0.746
6	88.34	0.000778	0.0280	292.6	433.5	1.2916	1.6815	1.116	0.840	221	13.00	0.0582	0.0145	4.23	0.754
8	100.81	0.000804	0.0217	306.7	439.3	1.3246	1.6865	1.145	0.881	195	13.41	0.0547		4.08	
10	111.15	0.000828	0.0165	318.7	445.5	1.3607	1.6906	1.175	0.922	176	13.74	0.0504		4.10	
15	131.50	0.000887	0.0106	343.2	454.7	1.4218	1.6974	1.262	1.037						
20	147.25	0.000951	0.0075	363.4	460.3	1.4697	1.7001	1.383	1.198						
25	160.24	0.001027	0.0055	381.6	463.0	1.5109	1.6990	1.590	1.481						
30	171.30	0.001131	0.0041	398.8	462.6	1.5491	1.6926	2.08	2.18						
35	180.88	0.001361	0.0027	418.4	455.4	1.5915	1.6730	5.71	7.22						
36.6†	183.68	0.001818	0.0018	437.4	437.4	1.6290	1.6290								

* The P, T, v, h, s, and c_p values are interpolated and rounded from YoungIove and McLinden, *J. Phys. Chem. Ref. Data,* **23,** no. 5, 1994, pp. 731–779; μ and k interpolated from ''ASHRAE Handbook—Fundamentals,'' 1993.
† Critical point.
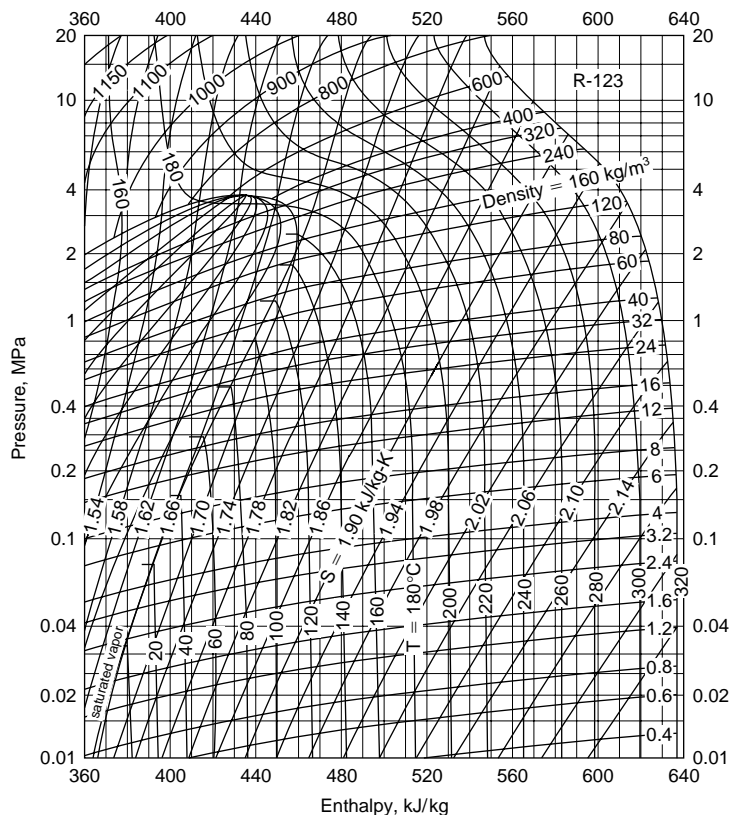
Fig. 4.2.7 Enthalpy–log pressure diagram for refrigerant 123. 1 MPa = 10 bar. *(Reprinted by permission of the ASHRAE from the 1993 ''ASHRAE Handbook—Fundamentals.'')*

Table 4.2.14 Saturated Refrigerant 134a*

P, bar	T, K	Spec. vol., m³/kg		Enthalpy, kJ/kg		Entropy, kJ/(kg · K)		Spec. ht. const., P, kJ/(kg · K)	
		Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor
0.5	232.7	0.000706	0.3572	148.4	374.1	0.7966	1.7640	1.254	0.748
1	246.8	0.000726	0.1926	165.4	382.6	0.8675	1.7474	1.279	0.793
1.5	256.0	0.000741	0.1313	177.4	388.3	0.9148	1.7388	1.299	0.826
2	263.1	0.000753	0.0999	186.6	392.6	0.9502	1.7334	1.315	0.854
2.5	268.9	0.000764	0.0807	194.3	396.1	0.9789	1.7295	1.330	0.878
3	273.8	0.000774	0.0677	200.9	399.0	1.0032	1.7267	1.343	0.900
4	282.1	0.000791	0.0512	212.1	403.7	1.0433	1.7225	1.367	0.940
5	288.9	0.000806	0.0411	221.5	407.5	1.0759	1.7196	1.389	0.976
6	294.7	0.000820	0.0343	229.7	410.6	1.1037	1.7184	1.411	1.010
8	304.5	0.000846	0.0256	243.6	415.5	1.1497	1.7140	1.453	1.075
10	312.5	0.000870	0.0203	255.5	419.2	1.1876	1.7112	1.495	1.139
15	328.4	0.000928	0.0131	279.8	425.2	1.2621	1.7048	1.611	1.313
20	340.6	0.000989	0.00929	300.0	428.3	1.3208	1.6975	1.761	1.539
25	350.7	0.001057	0.00694	317.8	429.0	1.3711	1.6880	1.983	1.647
30	359.4	0.001141	0.00528	334.7	427.3	1.4170	1.6748	2.388	2.527
35	366.9	0.001263	0.00237	351.9	422.2	1.4626	1.6549	3.484	4.292
40	373.5	0.001580	0.00256	375.6	405.4	1.5247	1.6045	26.33	37.63
40.6†	374.3	0.001953	0.00195	389.6	389.6	1.5620	1.5620		

* Values are rounded, converted, and interpolated from Tillner-Roth and Baehr, *J. Phys. Chem. Ref. Data,* **23,** no. 5, 1994, pp. 657–730. Liquid enthalpy and entropy at 0°C = 273.15 K are 200 kJ/kg and 1.0000 kJ/kg · K, respectively.
  † Critical point.
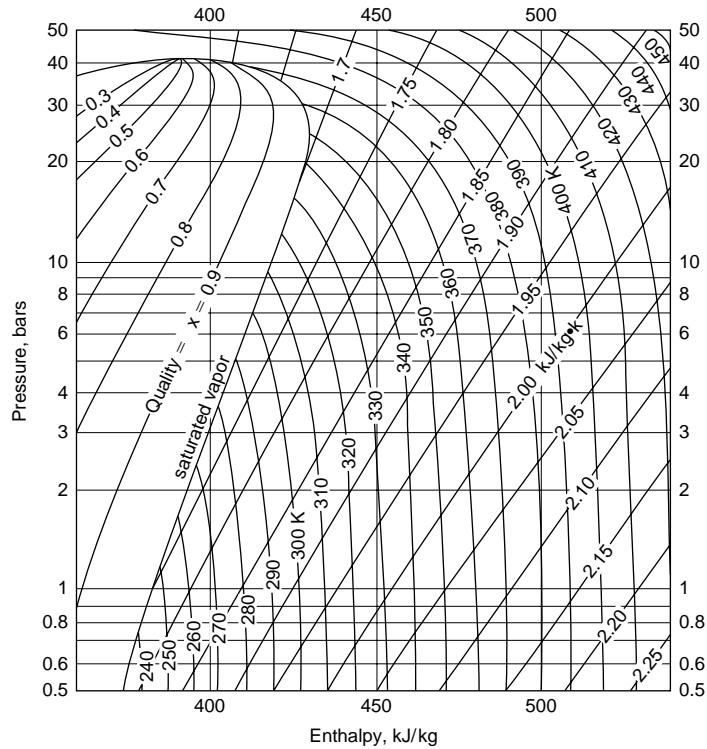
Fig. 4.2.8 Enthalpy–log pressure diagram for refrigerant 134a.

Table 4.2.15   Saturated Refrigerant 143a*

P, bar	T, °C	v_f	v_g	h_f	h_g	s_f	s_g	c_{pf},	μ_f,	k_f,	Pr_f
		m³/kg		kJ/kg		kJ/(kg · K)		kJ/(kg · K)	μPa · s	W/(m · K)	
0.5	− 61.06	0.000840	0.4160	115.8	352.1	0.6541	1.769	1.291	314.6	0.1214	3.34
1	− 47.49	0.000861	0.1977	136.4	361.9	0.7474	1.738	1.327	262.4	0.1121	3.11
1.5	− 38.59	0.000875	0.1486	145.5	366.1	0.7865	1.728	1.346	243.4	0.1080	3.03
2	− 31.77	0.000889	0.1113	154.7	370.2	0.8253	1.718	1.366	225.6	0.1039	2.97
2.5	− 26.16	0.000903	0.0908	162.4		0.8567	1.710	1.384	212.5	0.1005	2.93
3	− 21.35	0.000915	0.0755	169.2	376.3		1.706	1.401	201.8	0.0976	2.90
4	− 13.34	0.000936	0.0566	180.5	380.8	0.9277	1.698	1.430	185.6	0.0928	2.86
5	− 6.72	0.000955	0.0461	190.1	384.3	0.9636	1.693	1.459	173.7	0.0889	2.85
6	− 1.04	0.000973	0.0382	198.5	387.2	0.9944	1.688	1.486	163.6	0.0856	2.84
8	8.47	0.001005	0.0284	212.8	391.8	1.0457	1.681	1.538	147.0	0.0800	2.83
10	16.34	0.001036	0.0224	225.1	395.2	1.088	1.675	1.590	134.2	0.0755	2.83
15	31.80	0.001112	0.0144	250.6	400.3	1.171	1.664	1.741	113.0	0.0667	2.95
20	43.75	0.001191	0.0102	271.8	402.4	1.238	1.651	1.943	99.1	0.0598	3.22
25	53.83	0.001288	0.0074	291.4	401.5	1.297	1.634	2.369	87.0	0.0538	3.83
30	61.96	0.001405	0.0056	308.9	398.0	1.350	1.616	2.93			
35	69.26	0.001616	0.0040	329.8	338.9	1.403	1.576				
38.3†	73.60	0.002311	0.0023	360.6	360.6	1.471	1.471				

* The P, T, v, h, and s values are interpolated from a tabulation as a function of temperature supplied by Dr. Friend, NIST, Boulder, CO, based on REFROP 5.
† Critical point.

Table 4.2.16 Saturated Refrigerant 152a*

P, bar	T, °C	v_f	v_g	h_f	h_g	s_f	s_g	c_{pf}	c_{pg}	μ_f	μ_g	k_f,	Pr_f
		m³/kg		kJ/kg		kJ/(kg · K)		kJ/(kg · K)		μPa · s		W/(m · K)	
0.5	− 38.88	0.000960	0.5737	135.9	478.5	0.7477	2.2103	1.593	0.951	346.9			
1	− 24.29	0.000989	0.2997	159.4	489.3	0.8448	2.1710	1.632	1.030	286.1	8.65	0.1280	3.65
1.5	− 13.05	0.001012	0.1923	178.0	497.5	0.9177	2.1464	1.665	1.098	249.2	8.98	0.1231	3.37
2	− 7.68	0.001025	0.1569	187.1	501.4	0.9523	2.1360	1.682	1.134	233.8	9.14	0.1199	3.28
2.5	− 1.60	0.001039	0.1267	197.3	505.6	0.9900	2.1254	1.702	1.175	218.3	9.32	0.1164	3.18
3	3.59	0.001052	0.1057	206.2	509.1	1.0222	2.1169	1.720	1.211	205.9	9.47	0.1134	3.10
4	12.12	0.001074	0.0800	221.8	514.7	1.0747	2.1042	1.751	1.275	187.5	9.67	0.1084	3.03
5	19.14	0.001094	0.0644	233.4	519.1	1.1173	2.0947	1.781	1.331	174.2	9.91	0.1046	2.97
6	25.17	0.001113	0.0546	244.3	522.7	1.1527	2.0871	1.809	1.383	163.6	10.12	0.1010	2.93
8	35.25	0.001146	0.0402	262.8	528.4	1.2140	2.0752	1.862	1.314	147.4	10.48	0.0953	2.88
10	43.57	0.001177	0.0320	278.5	532.6	1.2635	2.0658	1.915	1.567	135.5	10.81	0.0907	2.86
15	59.95	0.001251	0.0207	310.7	539.2	1.3608	2.0470	2.055	1.800	114.6	11.56	0.0820	2.87
20	72.61	0.001325	0.0148	337.3	542.2	1.4371	2.0299	2.224	2.083		12.32	0.0758	
25	83.07	0.001405	0.0112	360.7	542.5	1.5021	2.0125	2.456	2.476		13.18		
30	92.03	0.001498	0.0087	382.6	540.3	1.5605	1.9927	2.814	3.101				
35	99.87	0.001615	0.0068	403.8	535.0	1.6161	1.9699	3.42	4.32				
40	106.76	0.001840											
45.2†	113.26	0.002717	0.0027	476.7	476.7	1.8019	1.8019						

† The P, T, v, h, s, c_p, μ, and k values are interpolated from ''ASHRAE Handbook—Fundamentals,'' 1993.
‡ Critical point.

Table 4.2.17 Saturated Water Substance

T, K	P, bar	v_c, m³/kg	v_g, m³/kg	h_c, kJ/kg	h_g, kJ/(kg · K)	s_c, kJ/(kg · K)	s_g, kJ/(kg · K)
250	0.00076	1.087. − 3	1520	− 381.5	2,459	− 1.400	9.954
260	0.00196	1.088. − 3	612.2	− 360.5	2,477	− 1.323	9.590
270	0.00469	1.090. − 3	265.4	− 339.6	2,496	− 1.296	9.255
273.15	0.00611	1.091. − 3	206.3	− 333.5	2,502	− 1.221	9.158
273.15	0.00611	1.000. − 3	206.3	0.0	2,502	0.000	9.158
280	0.00990	1.000. − 3	130.4	28.8	2,514	0.104	8.980
290	0.01917	1.001. − 3	69.7	70.7	2,532	0.251	8.740
300	0.03531	1.003. − 3	39.13	112.5	2,550	0.393	8.520
310	0.06221	1.007. − 3	22.93	154.3	2,568	0.530	8.318
320	0.1053	1.011. − 3	13.98	196.1	2,586	0.649	8.151
330	0.1719	1.016. − 3	8.82	237.9	2,604	0.791	7.962
340	0.2713	1.021. − 3	5.74	279.8	2,622	0.916	7.804
350	0.4163	1.027. − 3	3.846	321.7	2,639	1.038	7.657
360	0.6209	1.034. − 3	2.645	363.7	2,655	1.156	7.521
370	0.9040	1.041. − 3	1.861	405.8	2,671	1.271	7.394
373.15	1.0133	1.044. − 3	1.679	419.1	2,676	1.307	7.356
380	1.2869	1.049. − 3	1.337	448.0	2,687	1.384	7.275
390	1.794	1.058. − 3	0.980	490.4	2,702	1.494	7.163
400	2.455	1.067. − 3	0.731	532.9	2,716	1.605	7.058
420	4.370	1.088. − 3	0.425	618.6	2,742	1.810	6.865
440	7.333	1.110. − 3	0.261	705.3	2,764	2.011	6.689
460	11.71	1.137. − 3	0.167	793.5	2,782	2.205	6.528
480	17.90	1.167. − 3	0.111	883.4	2,795	2.395	6.377
500	26.40	1.203. − 3	0.0766	975.6	2,801	2.581	6.233
520	37.70	1.244. − 3	0.0525	1,071	2,801	2.765	6.093
540	52.38	1.294. − 3	0.0375	1,170	2,792	2.948	5.953
560	71.08	1.355. − 3	0.0269	1,273	2,772	3.132	5.808
580	94.51	1.433. − 3	0.0193	1,384	2,737	3.321	5.654
600	123.5	1.541. − 3	0.0137	1,506	2,682	3.520	5.480
620	159.1	1.705. − 3	0.0094	1,647	2,588	3.741	5.259
647.3*	221.2	3.170. − 3	0.0032	2,107	2,107	4.443	4.443

Above the solid line the condensed phase is solid; below it is liquid. The notation $1.087. − 3$ signifies 1.087×10^{-3}. * Critical temperature.
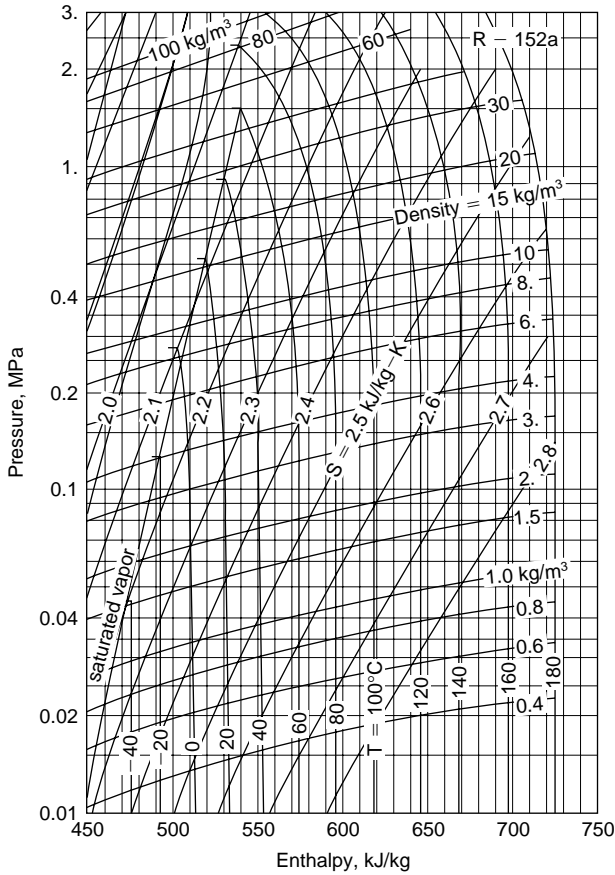
Fig. 4.2.9 Enthalpy–log pressure diagram for refrigerant 152a. *(Reprinted by permission of the ASHRAE from the 1993 ''ASHRAE Handbook— Fundamentals.'')*
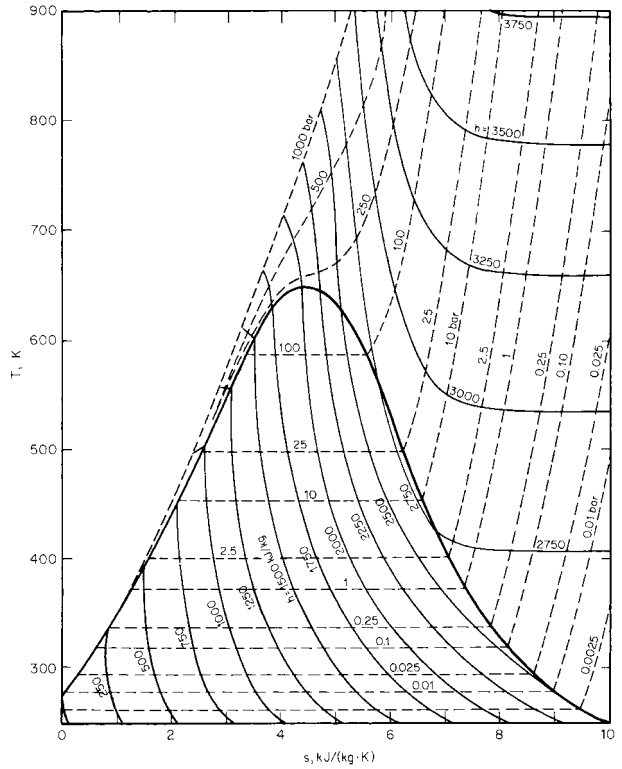
Fig. 4.2.10 Temperature-entropy diagram for water substance, SI units.

Table 4.2.18 Compressed Steam*

Temperature, K		1	10	20	40	60	80	100	200	400	600	800	1,000	Temperature, K
							Pressure, bar							
350	v	1.027.−3	1.027.−3	1.026.−3	1.025.−3	1.024.−3	1.023.−3	1.023.−3	1.018.−3	1.009.−3	1.002.−3	9.937.−4	9.865.−4	350
	h	231.8	322.5	323.3	324.9	326.4	328.1	329.7	337.7	353.8	369.7	385.7	401.7	
	s	1.037	1.037	1.036	1.035	1.034	1.032	1.031	1.025	1.013	1.001	0.991	0.979	
400	v	1.827	1.067.−3	1.066.−3	1.065.−3	1.064.−3	1.063.−3	1.061.−3	1.056.−3	1.045.−3	1.035.−3	1.027.−3	1.018.−3	400
	h	2,730	533.4	534.1	535.4	536.8	538.2	539.6	546.5	560.6	574.9	589.3	603.8	
	s	7.502	1.600	1.599	1.597	1.595	1.593	1.592	1.583	1.565	1.549	1.533	1.518	
450	v	2.063	1.124.−3	1.123.−3	1.121.−3	1.119.−3	1.118.−3	1.116.−3	1.108.−3	1.094.−3	1.082.−3	1.070.−3	1.059.−3	450
	h	2,830	749.0	749.8	750.8	751.9	753.0	754.1	759.5	771.0	783.0	795.3	807.9	
	s	7.736	2.110	2.107	2.105	2.102	2.099	2.097	2.085	2.061	2.039	2.019	2.002	
500	v	2.298	0.221	0.104	1.201.−3	1.198.−3	1.196.−3	1.193.−3	1.181.−3	1.160.−3	1.142.−3	1.126.−3	1.112.−3	500
	h	2,929	2,891.2	2,839.4	975.9	976.3	976.8	977.3	980.3	987.4	995.9	1005.3	1015.4	
	s	7.944	6.823	6.422	2.578	2.575	2.571	2.567	2.549	2.517	2.488	2.461	2.437	
600	v	2.76	0.271	0.133	0.0630	0.0396	0.0276	0.0201	1.483.−3	1.392.−3	1.337.−3	1.296.−3	1.265.−3	600
	h	3,129	3,109	3,087	3,036	2,976	2,906	2,820	1,489	1,462	1,452	1,447	1,447	
	s	8.309	7.223	6.875	6.590	6.224	5.997	5.775	3.469	3.379	3.316	3.266	3.223	
700	v	3.23	0.319	0.158	0.0769	0.0500	0.0346	0.0283	1.157.−2	2.630.−3	1.831.−3	1.639.−3	1.536.−3	700
	h	2,334	3,322	3,307	3,278	3,247	3,214	3,179	2,965	2,233	2,021	1,962	1,931	
	s	8.625	7.550	7.215	6.864	6.644	6.431	6.334	5.770	4.554	4.192	4.058	3.972	
800	v	3.69	0.367	0.182	0.0689	0.0589	0.0436	0.0343	1.575.−2	6.391.−3	3.496.−3	2.484.−3	2.072.−3	800
	h	3,546	3,537	3,526	3,506	3,485	3,464	3,442	3,325	3,047	2,734	2,567	2,465	
	s	8.908	7.837	7.507	7.151	6.965	6.809	6.685	6.252	5.654	5.175	4.864	4.701	
900	v	4.15	0.414	0.206	0.102	0.0674	0.0501	0.0398	1.899.−2	8.619.−3	5.257.−3	3.704.−3	2.907.−3	900
	h	3,764	3,757	3,750	3,737	3,719	3,704	3,688	3,609	3,440	3,269	3,113	2,995	
	s	9.165	8.097	7.770	7.462	7.237	7.092	6.975	6.587	6.119	5.780	5.510	5.305	
1,000	v	4.15	0.414	0.206	0.102	0.0674	0.0501	0.0398	2.186.−2	1.038.−2	6.605.−3	4.792.−3	3.763.−3	1,000
	h	3,990	3,984	3,978	3,967	3,955	3,944	3,935	3,874	3,756	3,640	3,532	3,435	
	s	9.402	8.336	8.011	7.682	7.486	7.345	7.233	6.867	6.453	6.172	5.951	5.727	
1,500	v	6.92	0.692	0.341	0.1730	0.1153	0.0865	0.0692	0.0346	0.0173	0.0116	0.00871	0.00700	1,500
	h	5,227	5,224	5,221	5,217	5,212	5,207	5,203	5,198	5,171	5,144	5,120	5,095	
	s	10.40	9.34	9.015	8.693	8.503	8.368	8.262	7.936	7.597	7.391	7.239	7.118	
2,000	v	9.26	0.925	0.462	0.231	0.1543	0.1157	0.0926	0.0465	0.0234	0.0157	0.0119	0.0096	2,000
	h	6,706	6,649	6,639	6,629	6,623	6,619	6,616	6,610	6,599	6,590	6,581	6,574	
	s	11.25	10.15	9.828	9.503	9.313	9.178	9.073	8.748	8.418	8.222	8.082	7.971	
2,500	v	11.90	1.171	0.583	0.291	0.1942	0.1457	0.1166	0.0584	0.0294	0.0197	0.0149	0.0120	2,500
	h	9,046	8,504	8,413	8,342	8,307	8,285	8,269	8,269	8,267	8,261	8,250	8,240	
	s	12.28	10.80	10.62	10.26	10.06	9.920	9.810	9.468	9.129	8.930	8.788	8.677	

* v = specific volume, m³/kg; h = specific enthalpy, kJ/kg; s = specific entropy, kJ/(kg · K). The notation 1.027. − 3 signifies 1.027×10^{-3}.

Table 4.2.19 Saturated Water Substance, fps Units

Abs press, lb/in²	Temp., °F	Specific volume, ft³/lb		Enthalpy, Btu/lb			Entropy, Btu/(lb · R)			Internal energy, evap., Btu/lb
		Liquid	Vapor	Liquid	Evap.	Vapor	Liquid	Evap.	Vapor	
0.08866	32.02	0.016022	3,302	0.01	1,075.4	1,075.4	0.00000	2.1869	2.1869	1,021.2
1.0	101.70	0.016136	333.6	69.74	1,036.0	1,105.8	0.13266	1.8453	1.9779	974.3
1.5	115.65	0.016187	227.7	83.65	1,028.0	1,111.7	0.15714	1.7867	1.9438	964.8
2	126.04	0.016230	173.75	94.02	1,022.1	1,116.1	0.17499	1.7448	1.9198	957.8
3	141.43	0.016300	118.72	109.39	1,013.1	1,122.5	0.20089	1.6852	1.8861	947.2
4	152.93	0.016358	90.64	120.89	1,006.4	1,127.3	0.21983	1.6426	1.8624	939.3
5	162.21	0.016407	73.53	130.17	1,000.9	1,131.0	0.23486	1.6093	1.8441	932.9
10	193.19	0.016590	38.42	161.23	982.1	1,143.3	0.28358	1.5041	1.7877	911.0
14.696	211.99	0.016715	26.80	180.15	970.4	1,150.5	0.31212	1.4446	1.7567	897.5
15	213.03	0.016723	26.29	181.19	969.7	1,150.9	0.31367	1.4414	1.7551	896.8
20	227.96	0.016830	20.09	196.26	960.1	1,156.4	0.33580	1.3962	1.7320	885.8
25	240.08	0.016922	16.306	208.52	952.2	1,160.7	0.35345	1.3607	1.7142	876.9
30	250.34	0.017004	13.748	218.93	945.4	1,164.3	0.36821	1.3314	1.6996	869.2
35	259.30	0.017078	11.900	228.04	939.3	1,167.4	0.38093	1.3064	1.6873	862.4
40	267.26	0.017146	10.501	236.16	933.8	1,170.0	0.39214	1.2845	1.6767	856.2
45	274.46	0.017209	9.403	243.51	928.8	1,172.3	0.40218	1.2651	1.6673	850.7
50	281.03	0.017269	8.518	250.24	924.2	1,174.4	0.41129	1.2476	1.6589	845.5
55	287.10	0.017325	7.789	256.46	919.9	1,176.3	0.41963	1.2317	1.6513	840.8
60	292.73	0.017378	7.177	262.25	915.8	1,178.0	0.42733	1.2170	1.6444	836.3
65	298.00	0.017429	6.657	267.67	911.9	1,179.6	0.43450	1.2035	1.6380	832.1
70	302.96	0.017478	6.209	272.79	908.3	1,181.0	0.44120	1.1909	1.6321	828.1
75	307.63	0.017524	5.818	277.61	904.8	1,182.4	0.44749	1.1790	1.6265	824.3
80	312.07	0.017570	5.474	282.21	901.4	1,183.6	0.45344	1.1679	1.6214	820.6
85	316.29	0.017613	5.170	286.58	898.2	1,184.8	0.45907	1.1574	1.6165	817.1
90	320.31	0.017655	4.898	290.76	895.1	1,185.9	0.46442	1.1475	1.6119	813.8
95	324.16	0.017696	4.654	294.76	892.1	1,186.9	0.46952	1.1380	1.6076	810.6
100	327.86	0.017736	4.434	298.61	889.2	1,187.8	0.47439	1.1290	1.6034	807.5
150	358.48	0.018089	3.016	330.75	864.2	1,194.9	0.51422	1.0562	1.5704	781.0
200	381.86	0.018387	2.289	355.6	843.7	1,199.3	0.5440	1.0025	1.5464	759.6
250	401.04	0.018653	1.8448	376.2	825.8	1,202.1	0.5680	0.9594	1.5274	741.4
300	417.13	0.018896	1.5442	394.1	809.8	1,203.9	0.5883	0.9232	1.5115	725.1
350	431.82	0.019124	1.3267	409.9	795.0	1,204.9	0.6060	0.8917	1.4978	710.3
400	444.70	0.019340	1.1620	424.2	781.2	1,205.5	0.6218	0.8638	1.4856	696.7
450	456.39	0.019547	1.0326	437.4	768.2	1,205.6	0.6360	0.8385	1.4746	683.9
500	467.13	0.019748	0.9283	449.5	755.8	1,205.3	0.6490	0.8154	1.4645	671.7
550	477.07	0.019943	0.8423	460.9	743.9	1,204.8	0.6611	0.7941	1.4551	660.2
600	486.33	0.02013	0.7702	471.7	732.4	1,204.1	0.6723	0.7742	1.4464	649.1
700	503.23	0.02051	0.6558	491.5	710.5	1,202.0	0.6927	0.7378	1.4305	628.2
800	518.36	0.02087	0.5691	509.7	689.6	1,199.3	0.7110	0.7050	1.4160	608.4
900	532.12	0.02123	0.5009	526.6	669.5	1,196.0	0.7277	0.6750	1.4027	589.6
1,000	544.75	0.02159	0.4459	542.4	650.0	1,192.4	0.7432	0.6471	1.3903	571.5
1,500	596.39	0.02346	0.2769	611.5	557.2	1,168.7	0.8082	0.5276	1.3359	486.9
2,000	636.00	0.02565	0.18813	671.9	464.4	1,136.3	0.8623	0.4238	1.2861	404.2
2,500	668.31	0.02860	0.13059	730.9	360.5	1,091.4	0.9131	0.3196	1.2327	313.4
3,000	695.52	0.03431	0.08404	802.5	213.0	1,015.5	0.9732	0.1843	1.1575	185.4
3,203.6	705.44	0.05053	0.05053	902.5	0	902.5	1.0580	0	1.0580	0

SOURCE: Abstracted from Keenan, Keyes, Hill, and Moore, ''Steam Tables,'' 1969.

Table 4.2.20   Compressed Water Substance, fps Units

Pressure, psia (saturation temp., °F)		Temperature of steam, °F							
		200	300	400	500	600	800	1,000	1,200
10	v	38.85	44.99	51.03	57.04	63.03	74.98	86.91	98.84
(193.19)	h	1,146.6	1,193.7	1,240.5	1,287.7	1,335.5	1,433.3	1,534.6	1,639.4
	s	1.7927	1.8592	1.9171	1.9690	2.0164	2.1009	2.1755	2.2428
50	v	0.01663		8.772	10.061	11.305	14.949	17.352	19.747
(281.03)	h	168.1	1,332.8	1,184.4	1,235.0	1,284.0	1,431.7	1,533.5	1,638.7
	s	0.2940	1.8371	1.6722	1.7348	1.7887	1.9225	1.9975	2.0650
100	v	0.01663	0.01745	4.934	5.587	6.216	7.445	8.657	9.861
(327.86)	h	168.2	269.7	1,227.5	1,279.1	1,329.3	1,429.6	1,532.1	1,637.7
	s	0.2939	0.4372	1.6517	1.7085	1.7582	1.8449	1.9204	1.9882
150	v	0.01663	0.01744	3.221	3.679	4.111	4.944	5.759	6.566
(358.48)	h	168.4	269.8	1,219.5	1,274.1	1,325.7	1,427.5	1,530.7	1,454.5
	s	0.2938	0.4371	1.5997	1.6598	1.7110	1.7989	1.8750	1636.7
200	v	0.01662	0.01744	2.361	2.724	3.058	3.693	4.310	4.918
(381.86)	h	168.5	269.9	1,210.8	1,268.8	1,322.1	1,425.3	1,529.3	1,635.7
	s	0.2938	0.4370	1.5600	1.6239	1.6767	1.7660	1.8425	1.9109
300	v	0.01662	0.01743	0.01863	1.7662	2.004	2.442	2.860	3.270
(417.43)	h	168.8	270.1	375.2	1,257.5	1,314.5	1,421.0	1,526.5	1,633.8
	s	0.2936	0.4368	0.5665	1.5701	1.6266	1.7187	1.7964	1.8653
400	v	0.01661	0.01742	0.01862	1.2843	1.4760	1.8163	2.136	2.446
(444.70)	h	169.0	270.3	375.3	1,245.2	1,306.6	1,416.6	1,523.6	1,631.8
	s	0.2935	0.4366	0.5662	1.5282	1.5892	1.6844	1.7632	1.8327
500	v	0.01661	0.01741	0.01861	.9924	1.1583	1.4407	1.7008	1.9518
(467.13)	h	169.2	270.5	375.4	1,231.5	1,298.3	1,412.1	1,520.7	1,629.8
	s	0.2934	0.4364	0.5660	1.4923	1.5585	1.6571	1.7371	1.8072
600	v	0.01660	0.01740	0.01860	.7947	.9456	1.1900	1.4108	1.6222
(486.33)	h	169.4	270.7	375.5	1,216.2	1,289.5	1,407.6	1,517.8	1,627.8
	s	0.2933	0.4362	0.5657	1.4592	1.5320	1.6343	1.7155	1.7861
700	v	0.01660	0.01740	0.01859	0.02042	.7929	1.0109	1.2036	1.3868
(503.23)	h	169.6	270.9	375.6	487.6	1,280.2	1,402.9	1,514.9	1,625.8
	s	0.2932	0.4360	0.5655	0.6887	1.5081	1.6145	1.6970	1.7682
800	v	0.01659	0.01739	0.01857	0.02040	.6776	.8764	1.0482	1.2102
(518.36)	h	169.9	271.1	375.8	487.6	1,270.4	1,398.2	1,511.9	1,623.8
	s	0.2930	0.4359	0.5652	0.6883	1.4861	1.5969	1.6807	1.7526
900	v	0.01658	0.01739	0.01856	0.02038	.5871	.7717	.9273	1.0729
(532.14)	h	170.1	271.3	375.9	487.5	1,260.0	1,393.4	1,508.9	1,621.7
	s	0.2929	0.4355	0.5650	0.6878	1.4652	1.5810	1.6662	1.7386
1,000	v	0.01658	0.01738	0.01855	0.02036	0.5140	0.6878	0.8305	0.9630
(544.75)	h	170.3	271.5	376.0	487.5	1,248.8	1,388.5	1,505.9	1,619.7
	s	0.2928	0.4355	0.5647	0.6874	1.4450	1.5664	1.6530	1.7261
1,500	v	0.01655	0.01734	0.01849	0.02024	0.2816	0.4350	0.5400	0.6334
(596.39)	h	171.5	272.4	376.6	487.4	1,174.8	1,362.5	1,490.3	1,609.3
	s	0.2922	0.4346	0.5634	0.6853	1.3416	1.5058	1.6001	1.6765
2,000	v	0.01653	0.01731	0.01844	0.02014	0.02330	0.3071	0.3945	0.4685
(636.00)	h	172.6	273.3	377.2	487.3	614.0	1,333.8	1,474.1	1,598.6
	s	0.2916	0.4338	0.5622	0.6832	0.8046	1.4562	1.5598	1.6398
2,500	v	0.01650	0.01727	0.01839	0.02004	0.02300	0.2291	0.3069	0.3696
(668.31)	h	173.8	274.3	377.8	487.3	611.6	1,301.7	1,457.2	1,587.7
	s	0.2910	0.4329	0.5609	0.6813	0.8043	1.4112	1.5262	1.6101
3,000	v	0.01648	0.01724	0.01833	0.01994	0.02274	0.17572	0.2485	0.3036
(695.52)	h	174.9	275.2	378.5	487.3	609.6	1,265.2	1,439.6	1,576.6
	s	0.2905	0.4321	0.5597	0.6794	0.8004	1.3675	1.4967	1.5848
4,000	v	0.01643	0.01717	0.01824	0.01977	0.02229	0.1052	0.1752	0.2213
	h	177.2	277.2	379.9	487.5	606.5	1,172.9	1,402.6	1,553.9
	s	0.2931	0.4304	0.5573	0.6758	0.7936	1.2740	1.4449	1.5423
5,000	v	0.01638	0.01711	0.01814	0.01960	0.02191	0.05932	0.1312	0.1720
	h	179.5	279.1	381.3	487.9	604.2	1,042.1	1,363.4	1,530.8
	s	0.2882	0.4288	0.5551	0.6724	0.7876	1.1583	1.3988	1.5066

v = specific volume, ft³/lb; h = enthalpy, Btu/lb; s = entropy, Btu/(lb · R).
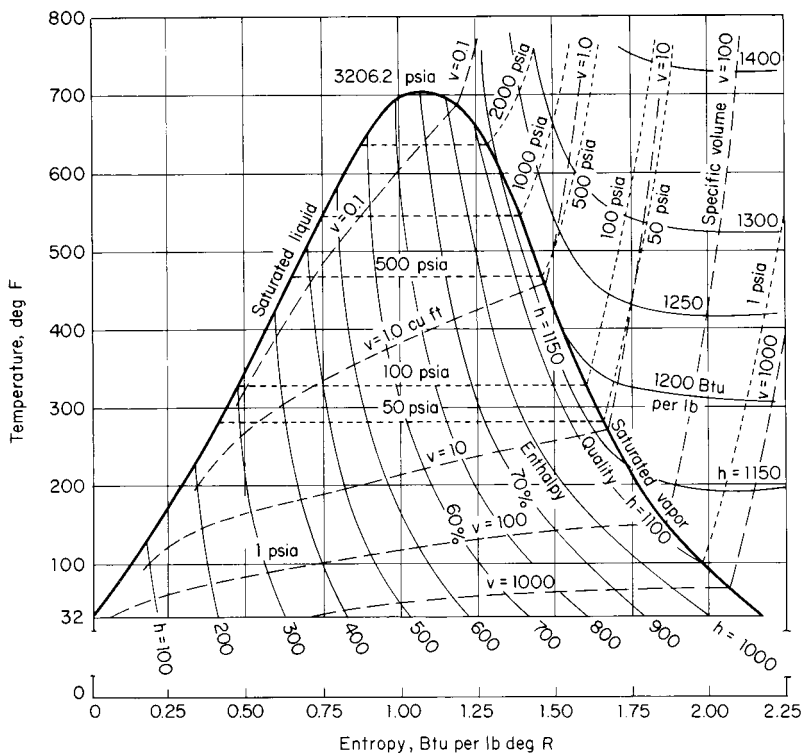
Fig. 4.2.11   Temperature-entropy diagram for water substance, fps units. *(Data from Keenan and Keyes, "Thermodynamic Properties of Steam," Wiley.)*

Table 4.2.21 Phase Transition and Other Data for 100 Fluids*

Name	Formula	M	T_m, K	Δh_{fus}, kJ/kg	T_b, K	Δh_{vap}, kJ/kg	P_c, bar	v_c, m³/kg	T_c, K	Z_c
Acetaldehyde	C_2H_4O	44.053	149.7	73.2	293.7	584.0	55.4	0.00382	461	0.243
Acetic acid	$C_2H_4O_2$	60.053		195.2	391.2	404.7	57.9	0.00285	594.5	0.200
Acetone	C_3H_6O	58.080	178.5	98.5	329.3	500.9	47.2	0.00360	508.2	0.232
Acetylene	C_2H_2	26.038	179.0	96.5	189.2	687.0	62.4	0.00435	308.3	0.276
Air	Mixed	28.966	60.0		79, 82	206.5	37.7	0.00320	132.6	0.263
Ammonia	NH_3	17.031	195.4	331.9	239.7	1,368	112.9	0.00427	405.7	0.244
Aniline	C_6H_7N	93.129	266.8	113.2	457.5	484.9	53.0	0.00340	698.8	0.289
Argon	A	39.948	83.8	29.4	87.5	163.2	48.7	0.00187	150.8	0.290
Benzene	C_6H_6	78.114	278.7	125.9	353.3	394.0	49.2	0.00332	562.1	0.273
Bromine	Br_2	159.81	264.9	66.2	331.6	187.7	103.4	0.00079	584.2	0.270
Butane, n	C_4H_{10}	58.124	113.7	78.2	261.5	366.4	36.5	0.00452	408.1	0.283
Butane, iso	C_4H_{10}	58.124	137.0	80.2	272.7	385.5	38.0	0.00439	425.2	0.274
Butanol	$C_4H_{10}O$	74.123	183.9	121.2	390.8	593.2	44.1	0.00370	562.9	0.259
Butylene	C_4H_8	56.108	87.8	68.6	266.9	391.0	40.2	0.00428	419.6	0.277
Carbon dioxide	CO_2	44.010	216.6	18.4	194.7	573.2	73.8	0.00214	304.1	0.274
Carbon disulfide	CS_2	76.131	161.1	57.7	319.4	351.6	79.0	0.00223	552.0	0.293
Carbon monoxide	CO	28.010	68.1	29.8	81.6	215.1	35.0	0.00332	132.9	0.295
Carbon tetrachloride	CCl_4	153.82	250.3	16.3	349.8	195.0	45.6	0.00170	556.4	0.258
Carbon tetrafluoride	CF_4	88.005	89.5	8.0	145.2	138	37.4	0.00156	228.0	0.272
Cesium	Cs	132.91	301.6	16.4	942.4	494.3	153.7	0.00230	2,043	0.240
Chlorine	Cl_2	70.906	172.2	90.4	238.6	287.5	77.0	0.00175	417.2	0.278
Chloroform	$CHCl_3$	119.38	209.7	77.1	334.5	248.5	54.5	0.00202	536.0	0.294
o-Cresol	C_7H_8O	108.14	303.8		464.1		50.0	0.00291	697.6	0.271
Cyclohexane	C_6H_{12}	84.162	279.8	31.7	353.9	357.4	40.7	0.00366	553.4	0.273
Cyclopropane	C_3H_6	42.081	145.5	129.4	240.3	477	55.0	0.00387	397.8	0.271
Decane	$C_{10}H_{22}$	142.29	243.4	201.8	447.3	276.2	21.0	0.00424	617.5	0.247
Deuterium	D_2	4.028	18.71	48.9	23.7	304.4	16.7	0.00143	38.34	0.301
Diphenyl	$C_{12}H_{10}$	154.21	342.4	120.6	527.6	317.3	38.5	0.00326	789.0	0.295
Ethane	C_2H_6	30.070	89.9	45.0	184.6	488.4	48.8	0.00486	305.4	0.281
Ethanol	C_2H_6O	46.069	159.0	109.0	351.5	840.9	63.8	0.00362	516.2	0.248
Ethyl acetate	$C_4H_8O_2$	88.107	189.4	119.0	350.3	366.2	38.3	0.00325	523.2	0.252
Ethyl bromide	C_2H_5Br	108.97	153.5	54.0	311.5	218	62.3	0.00197	503.9	0.320
Ethyl chloride	C_2H_5Cl	64.515	134.9	68.9	285.4	382.5	52.0	0.00309	460.4	0.270
Ethyl ether	$C_4H_{10}O$	74.123	150.0	93.1	307.8	358.9	36.8	0.00377	466.8	0.262
Ethyl formate	$C_3H_6O_2$	74.080	193.8	124.3	327.4	405.8	47.4	0.00310	508.5	0.257
Ethylene	C_2H_4	28.054	104.0	119.5	169.5	480.0	50.5	0.00455	283.1	0.274
Ethylene oxide	C_2H_4O	44.054	160.6	117.5	283.6	580.0	71.9	0.00318	468.9	0.258
Fluorine	F_2	37.997	53.5	13.4	85.1	172.1	52.2	0.00174	144.3	0.288
Helium 4	He	4.003			4.3	20.6	2.3	0.0144	5.189	0.303
Heptane	C_7H_{16}	100.20	182.5	139.9	371.6	316.3	27.4	0.0043	540.2	0.263
Hexane	C_6H_{14}	86.178	177.8	151.2	341.9	334.8	30.3	0.0043	507.6	0.265
Hydrazine	N_2H_4	32.045	274.7	395.0	386.7	1,207	147.0		653.2	0.284
Hydrogen	H_2	2.016	14.0	58.0	20.4	454.0	13.0	0.0323	33.3	0.305
Hydrogen bromide	HBr	80.912	186.3	37.4	206.4	217.5	85.5	0.00124	363.2	0.284
Hydrogen chloride	HCl	36.461	160.0	54.7	188.1	443.0	83.1	0.00022	324.7	0.249
Hydrogen fluoride	HF	20.006	181.8	196.3	272.7	374.3	64.9	0.00345	461.2	0.120
Hydrogen iodide	HI	127.91	222.4	22.4	237.8	154.0	83.1	0.00106	423.9	0.318
Hydrogen sulfide	H_2S	34.076	187.5	69.8	213.0	248.0	89.4	0.00289	373.1	0.283

Table 4.2.21   Phase Transition and Other Data for 100 Fluids*   (*Continued*)

Name	Formula	M	T_m, K	Δh_{fus}, kJ/kg	T_b, K	Δh_{vap}, kJ/kg	P_c, bar	v_c, m³/kg	T_c, K	Z_c
Iodine	I_2	253.81	387.0	62.1	457.5	164.3	117.5	0.00054	785.0	0.248
Krypton	Kr	83.80	116.0	19.5	121.4	107.9	55.0	0.00109	209.4	0.288
Lithium	Li	6.940	453.8		1,615	1,945			3,750	
Mercury	Hg	200.59	234.3	11.4	630.1	295.6	1,510	0.00018	1,763	
Methane	CH_4	16.043	90.7	58.4	111.5	511.8	46.0	0.00617	190.5	0.287
Methanol	CH_4O	32.042	175.5	98.9	337.7	1,104	79.5	0.00368	512.6	0.220
Methyl acetate	$C_3H_6O_2$	74.080	175		330.3	410.0	46.9	0.00308	506.9	0.254
Methyl bromide	CH_3Br	94.939	179.5	62.8	276.7	252.0		0.00173	467.2	
Methyl chloride	CH_3Cl	50.49	175.4	127.4	249.4	428.5	66.8	0.00270	416.3	0.277
Methyl formate	$C_2H_4O_2$	60.053	173.4	125.5	304.7	481.2	60.0	0.00287	487.2	0.255
Methylene chloride	CH_2Cl_2	84.922	176.5	54.4	312.9	328	61.3	0.00197	510.	0.255
Naphthalene	$C_{10}H_8$	128.17	353.4	148.1	491.1	341	40.5	0.00321	748.4	0.270
Neon	Ne	20.179	24.5	16.6	27.3	91.3	27.6	0.00207	44.4	0.311
Nitric oxide	NO	30.006	111	76.6	121.4	460	64.9	0.00192	180	0.249
Nitrogen	N_2	28.013	63.1	25.7	77.3	197.6	34.0	0.00318	126.2	0.287
Nitrogen peroxide	NO_2	46.006	263	159.5	294.5	414.4	101.3	0.00180	431.4	0.233
Nitrous oxide	N_2O	44.013	176	148.6	184.7	376.0	72.4	0.00221	309.6	0.274
Octane	C_8H_{18}	114.23	216.4	161.6	398.9	302.7	25.0	0.00426	508.9	0.258
Oxygen	O_2	31.999	54.4	13.9	90.0	212.5	50.4	0.00229	154.6	0.288
Pentane, iso	C_5H_{12}	72.151	113.7	71.1	301.0	341.0	33.5	0.00427	460.4	0.270
Pentane, n	C_5H_{12}	72.151	143.7	116.6	309.2	357.2	33.7	0.00431	469.6	0.268
Potassium	K	39.098	336.4	59.8	1,030		167		2,265	
Propane	C_3H_8	44.097	86	80.0	231.1	425.7	42.6	0.00453	369.8	0.277
Propanol	C_3H_8O	60.096	147.0	86.5	370.4	695.8	51.7	0.00364	536.7	0.253
Propylene	C_3H_6	42.081	87.9	71.4	225.5	437.5	46.0	0.00429	365.1	0.275
Radon	Rn	224	201	12.3	211	82.8	65.5	0.00063	377.0	0.293
Refrigerant 11	$CFCl_3$	137.37	162.2	50.2	296.9	180.2	44.1	0.00181	471.2	0.280
Refrigerant 12	CF_2Cl_2	120.91	115.4	34.3	243.4	165.1	41.2	0.00179	385.2	0.278
Refrigerant 13	CF_3Cl	104.46	92.1		191.7	148.4	38.7	0.00173	302.0	0.279
Refrigerant 13B1	CF_3Br	148.91	105.4		215.4	118.7	39.6	0.00134	340.2	0.280
Refrigerant 21	$CHFCl_2$	102.91	138.2		282.1	242.1	51.7	0.00192	451.4	0.271
Refrigerant 22	CHF_2Cl	86.469	113.2	47.6	232.4	233.6	49.8	0.00191	369.2	0.267
Refrigerant 23	CHF_3	70.014	118.0	58.0	191.2	239	48.4	0.00190	299.1	0.259
Refrigerant 113	$C_2F_3Cl_3$	187.38	238.2		320.8	146.8	34.1	0.00174	487.3	0.274
Refrigerant 114	$C_2F_4Cl_2$	170.92	179.2		276.7	136.0	32.6	0.00172	418.9	0.275
Refrigerant 115	C_2F_5Cl	154.47	171	12.2	234.0	124.1	31.6	0.00163	353.1	0.271
Refrigerant 142b	$C_2F_2H_3Cl$	100.50	142.4	26.7	263.9	223	41.5	0.00232	410.0	0.279
Refrigerant 152a	$C_2F_2H_4$	66.051	156		248	326	45.0	0.00274	386.7	0.253
Refrigerant 216	$C_3F_6Cl_2$	220.93			308	117.3	27.5	0.00174	453.2	0.281
Refrigerant C318	C_4F_8	200.03	233.0		267	116	27.8	0.00161	388.5	0.272
Refrigerant 500	Mix	99.303	114.3		239.7	201.1	44.3	0.00201	378.7	0.281
Refrigerant 502	Mix	111.63			237	172.2	40.7	0.00178	355.3	0.275
Refrigerant 503	Mix	87.267			184	172.9			293	
Refrigerant 504	Mix	79.240			216	242.9			339	
Refrigerant 505	Mix	103.43			243.6		47.3		391	
Refrigerant 506	Mix	93.69			260.7		51.6		416	
Rubidium	Rb	85.468	312.6		959.4	811.3		0.00288	2,083	
Sodium	Na	22.990	371.0		1,155	3,880			2,730	
Sulfur dioxide	SO_2	64.059	197.8		268.4	368.3	78.8	0.00190	430.7	0.269
Sulfur hexafluoride	SF_6	146.051					37.8	0.00137	318.7	0.285
Toluene	C_7H_8	92.141	178.2		383.8	339.0	40.5	0.00345	594.0	0.260
Water	H_2O	18.015	273.2		373.2	2,256	221.2	0.00315	647.3	0.234
Xenon	Xe	131.36	161.5		165	99.2	58.7	0.00091	290	0.290

* M = molecular weight, T_m = normal melting temperature, Δh_{fus} = enthalpy (or latent heat) of fusion, T_b = normal boiling point temperature, Δh_{vap} = enthalpy (or latent heat) of vaporization, T_c = critical temperature, P_c = critical pressure, v_c = critical volume, Z_c = critical compressibility factor.
SOURCE: Prepared by the author and abstracted from Rohsenow et al., ''Handbook of Heat Transfer Fundamentals,'' McGraw-Hill.

Table 4.2.22   Specific Heat at Constant Pressure [kJ/(kg · K)] of Liquids and Gases

Substance	Temperature, K												
	200	225	250	275	300	325	350	375	400	425	450	475	500
Acetylene	1.457	1.517	1.575	1.635	1.695	1.747							
Air	1.048	1.036	1.029	1.025	1.021	1.021	1.020	1.021	1.022	1.024	1.027	1.030	1.035
Ammonia	4.605	4.360	2.210	2.176	2.169	2.183	2.210	2.247	2.289	2.331	2.381	2.429	2.477
Argon	0.524	0.523	0.522	0.522	0.522	0.521	0.521	0.521	0.521	0.521	0.521	0.521	0.521
Butane, i	1.997	2.099	2.207	1.590	1.694	1.810	1.921	2.035	2.149	2.258	2.367	2.436	2.571
Butane, n	2.066	2.134	2.214	1.642	1.731	1.835	1.941	2.047	2.154	2.253	2.361	2.461	2.558
Carbon dioxide		0.763	0.791	0.818	0.845	0.870	0.894	0.917	0.938	0.958	0.978	0.995	1.014
Ethane	1.419	1.492	1.574	1.658	1.762	1.871	1.968	2.081	2.184	2.287	2.393	2.492	2.590
Ethylene	1.296	1.340	1.397	1.475	1.560	1.656	1.748	1.839	1.928	2.014	2.097	2.179	2.258
Fluorine	0.785	0.793	0.803	0.815	0.827								
Helium	5.193	5.193	5.193	5.193	5.193	5.193	5.193	5.193	5.193	5.193	5.193	5.193	5.193
Hydrogen, n	13.53	13.83	14.05	14.20	14.31	14.38	14.43	14.46	14.48	14.49	14.50	14.50	14.51
Krypton	0.252	0.251	0.250	0.249	0.249	0.249	0.249	0.249	0.249	0.249	0.249	0.249	0.248
Methane	2.105	2.122	2.145	2.184	2.235	2.297	2.375	2.454	2.534	2.617	2.709	2.797	2.892
Neon	1.030	1.030	1.030	1.030	1.030	1.030	1.030	1.030	1.030	1.030	1.030	1.030	1.030
Nitrogen	1.043	1.042	1.042	1.041	1.041	1.041	1.042	1.043	1.045	1.047	1.050	1.053	1.056
Oxygen	0.915	0.914	0.915	0.917	0.920	0.924	0.929	0.935	0.942	0.949	0.956	0.964	0.972
Propane	2.124	2.220	1.500	1.596	1.695	1.805	1.910	2.030	2.140	2.249	2.355	2.458	2.558
Propylene	2.094	2.132	1.436	1.481	1.536	1.625	1.709	1.793	1.890	1.981	2.070	2.153	2.245
Refrigerant 12			0.549	0.578	0.602	0.625	0.647	0.666	0.685	0.701	0.716	0.728	0.741
Refrigerant 21	0.973	0.982	0.991	1.015	0.594	0.617	0.641	0.661	0.683	0.701	0.720	0.735	0.752
Refrigerant 22	1.065	1.085	0.588	0.617	0.647	0.676	0.704	0.729	0.757	0.782	0.806	0.826	0.848
Water substance	1.545	1.738	1.935	4.211	4.179	4.182	4.195	2.035	1.996	1.985	1.981	1.980	1.983
Xenon	0.165	0.163	0.162	0.161	0.160	0.160	0.160	0.159	0.159	0.159	0.159	0.159	0.159

Values for the saturated liquid are tabulated up to the normal boiling point. Higher temperature values are for the dilute gas. Values for water substance below 275 K are for ice.

Table 4.2.23   Specific Heat Ratio c_p/c_v for Liquids and Gases at Atmospheric Pressure

Substance	Temperature, K												
	200	225	250	275	300	325	350	375	400	425	450	475	500
Acetylene	1.313	1.289	1.269	1.250	1.234	1.219	1.205						
Air	1.399	1.399	1.399	1.399	1.399	1.399	1.398	1.397	1.395	1.393	1.391	1.388	1.386
Ammonia					1.327	1.302	1.295	1.285	1.278	1.269	1.262	1.256	1.249
Argon	1.663	1.665	1.666	1.666	1.666	1.666	1.666	1.666	1.666	1.666	1.666	1.666	1.666
Butane, i	1.357	1.356	1.359	1.116	1.103	1.094	1.086	1.080	1.075	1.070	1.066	1.063	1.060
Butane, n	1.418	1.412	1.407	1.114	1.103	1.094	1.086	1.080	1.075	1.071	1.067	1.063	1.061
Carbon dioxide		1.344	1.323	1.302	1.290	1.279	1.269	1.260	1.252	1.245	1.239	1.233	1.229
Carbon monoxide	1.405	1.404	1.403	1.402	1.401	1.401	1.400	1.398	1.396	1.394	1.392	1.390	1.387
Ethane		1.246	1.226	1.210	1.193	1.180	1.167	1.157	1.148	1.139	1.132	1.126	1.120
Ethylene			1.275	1.254	1.236	1.220	1.206	1.194	1.183	1.173	1.165	1.158	1.151
Fluorine	1.393	1.386	1.377	1.370	1.362								
Helium	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667
Hydrogen, n	1.439	1.426	1.415	1.410	1.406	1.403	1.401	1.400	1.399	1.398	1.398	1.397	1.397
Krypton	1.649	1.655	1.658	1.660	1.662	1.662	1.662	1.662	1.662	1.663	1.664	1.665	1.667
Methane	1.337	1.332	1.325	1.316	1.306	1.295	1.282	1.271	1.258	1.247	1.237	1.228	1.219
Neon	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667	1.667
Nitrogen	1.399	1.399	1.399	1.399	1.399	1.399	1.399	1.398	1.397	1.396	1.394	1.393	1.391
Oxygen	1.398	1.397	1.396	1.395	1.394	1.391	1.388	1.385	1.381	1.377	1.373	1.369	1.365
Propane	1.513	1.504	1.164	1.148	1.135	1.124	1.114	1.107	1.100	1.094	1.089	1.085	1.081
Propylene			1.171	1.160	1.150	1.140	1.131	1.123	1.116	1.110	1.105	1.100	1.096
Refrigerant 12			1.165	1.114	1.101	1.088	1.077	1.065	1.055	1.044	1.034	1.025	1.071
Refrigerant 21					1.179	1.164	1.152	1.144	1.137	1.132	1.127	1.124	1.120
Refrigerant 22				1.207	1.190	1.172	1.164	1.155	1.148	1.143	1.138	1.133	1.129
Steam								1.322	1.319	1.317	1.314	1.312	1.309
Xenon	1.623	1.634	1.642	1.650	1.655	1.659	1.662	1.662	1.662	1.662	1.662	1.662	1.662

Table 4.2.24   Saturation Temperature, in Kelvins, of Selected Substances

Pressure, bar	Acetone C_3H_6O	Acetylene, C_2H_2	Air, sat. liquid	Air, sat. vapor	Ammonia, NH_3	Aniline C_6H_7N	Argon, Ar	Benzene, C_6H_6	Butanol, $C_4H_{10}O$	n-Butane, C_4H_{10}	Carbon dioxide, CO_2	Carbon tetrachloride, CCl_4	Carbon tetrafluoride, CF_4
0.010	237.8					337.2			299.1			255.1	
0.015	243.8					344.2			305.4	196.5		259.7	
0.020	247.1					350.0			310.0	200.3		263.2	106.4
0.025	251.6					353.6			313.8	203.1		266.0	107.9
0.030	254.3					357.1			316.9	205.7			109.3
0.04	259.0					363.1		276.5	321.8	209.8		270.9	111.5
0.05	262.7					368.1		280.0	325.6	212.9		275.0	113.2
0.06	266.8					372.3		283.2	328.8	215.8		278.5	114.7
0.08	270.9				198.9	379.0		288.6	333.9	220.3		284.6	117.2
0.10	275.1		62.3	66.3	201.9	385.2		293.0	337.8	224.1		289.1	119.1
0.15	283.2		64.6	68.5	207.6	397.1		301.7	345.8	231.0		298.1	122.9
0.20	289.6		66.4	70.2	211.8	404.5		308.3	351.8	236.3		304.8	125.8
0.25	294.1		67.9	71.5	215.2	410.6		313.7	356.8	240.7		310.2	128.1
0.30	298.0		69.1	72.7	218.1	415.8		318.2	360.8	244.4		314.9	130.1
0.40	304.7		71.2	74.6	222.8	424.8		325.8	367.4	250.5		322.2	133.3
0.5	310.1		72.8	76.2	226.6	432.1		331.8	372.8	255.4		327.8	136.0
0.6	315.0		74.3	77.5	229.9	438.2		337.1	377.2	259.6		333.1	138.2
0.8	322.8		76.6	79.7	235.2	448.8	85.1	345.7	384.3	266.6		342.0	142.0
1.0	329.0		78.6	81.6	239.6	456.5	87.2	352.7	390.0	272.2		349.2	145.0
1.5	341.0	195.1	82.3	85.3	247.9	472.1	91.2	366.5	402.6	283.4		363.8	151.0
2.0	350.1	200.1	85.2	88.1	254.3	484.2	94.3	377.0	412.0	291.9		374.7	155.6
2.5	358.9	204.8	87.6	90.4	259.5	494.0	96.8	385.7	419.8	299.0		383.0	159.3
3.0	365.9	208.8	89.7	92.4	263.9	502.0	99.0	393.1	426.1	305.0		390.2	162.1
4.0	377.1	215.3	93.1	95.7	271.3	516.0	102.6	405.6	436.8	315.1		402.0	168.0
5.0	386.1	220.9	96.0	98.4	277.3	527.0	105.8	415.8	445.1	323.4		412.8	172.5
6	393.9	225.8	98.4	100.8	282.4	536.2	108.4	424.7	452.9	330.6	220.0	422.0	175.5
8	406.4	233.9	102.7	104.8	291.0	551.5	110.8	439.9	465.4	342.6	227.1	433.0	182.9
10	417.3	240.3	106.1	108.1	298.1	564.7	116.6	451.6	475.8	352.6	233.0	449.5	187.7
15	435.9	252.5	113.1	114.7	311.9	593.0	124.0	475.8	496.0	372.2	244.6	474.3	199.0
20	452.0	262.3	118.5	119.9	322.5	613.6	129.8	494.6	510.1	387.6	253.6	495.0	207.4
25	465.8	270.3	123.0	124.1	331.3	631.2	134.6	510.1		400.2	260.6	511.2	214.3
30	476.9	277.6	127.0	127.8	338.9	645.8	138.7	523.5		410.9	269.6	524.0	220.2
40	496.0	289.5			351.6	672.0	145.7	545.8			278.5	547.6	
50		299.0			362.1	693.0					287.4		
60		306.9			371.1						295.1		
80					386.1								
100					398.4								

Table 4.2.24   Saturation Temperature, in Kelvins, of Selected Substances   (*Continued*)

Pressure, bar	Chlorine, Cl_2	Cyclohexane, C_6H_{12}	Cyclopropane, C_3H_6	Diphenyl, $C_{12}H_{10}$	Ethane, C_2H_6	Ethanol, C_2H_6O	Ethyl chloride C_2H_5Cl	Ethylene, C_2H_4	Fluorine, F_2	Helium, He	Heptane, C_7H_{16}	Hexane, C_6H_{14}	Hydrazine, N_2H_4
0.010			172.9	384.3	127.6	266.7		117.4	58.2		266.9	244.2	285.9
0.015	173.4		176.9	393.5	131.1	272.7	207.9	120.4	59.8		273.2	250.0	293.2
0.020	176.6		179.9	400.1	133.6	277.1	212.0	122.8	61.0		277.9	254.2	298.3
0.025	179.1		182.3	405.9	135.7	280.6	215.1	124.7	62.0		281.8	257.7	302.4
0.030	181.2		184.4	410.2	137.3	283.1	217.6	126.1	62.7		285.0	260.7	306.0
0.04	184.7		187.7	418.0	140.4	287.7	221.9	128.8	64.1		290.1	265.6	311.7
0.05	186.4		190.1	423.8	142.5	291.2	225.0	130.8	65.1		294.4	269.7	315.9
0.06	189.8	282.2	192.5	428.9	144.6	294.3	227.8	132.6	66.1	2.25	298.1	273.0	319.7
0.08	193.8	288.0	196.2	436.8	147.6	299.2	232.4	136.9	67.6	2.38	304.2	278.4	325.5
0.10	197.0	292.6	199.2	443.6	150.4	303.1	236.1	138.0	68.8	2.49	309.0	282.6	330.1
0.15	203.0	301.4	205.0	456.3	155.3	310.4	243.4	143.0	71.1	2.71	318.3	291.5	339.1
0.20	207.7	308.0	209.5	466.1	158.9	315.7	248.8	146.6	72.9	2.82	325.1	298.3	345.9
0.25	211.4	313.6	213.2	473.9	161.9	320.1	253.1	149.3	74.3	3.03	330.5	304.0	350.8
0.30	214.8	318.1	216.1	480.4	164.6	323.9	256.9	151.7	75.5	3.15	335.0	308.6	355.2
0.40	219.9	325.7	221.2	491.5	168.8	330.1	263.1	155.3	77.6	3.37	343.0	316.6	362.3
0.5	224.0	331.8	225.1	499.6	172.4	335.2	267.9	158.3	79.2	3.55	349.2	321.4	368.1
0.6	227.7	337.3	228.7	506.6	175.3	339.2	272.1	161.0	80.6	3.71	354.8	326.4	372.8
0.8	233.8	346.9	234.6	518.2	180.2	345.9	279.5	165.6	82.9	3.98	363.9	334.6	380.2
1.0	238.8	353.7	239.3	528.7	184.3	351.4	285.1	169.2	84.8	4.21	371.0	341.3	386.9
1.5	248.3	368.3	249.0	548.0	192.2	362.3	297.6	176.5	88.6	4.67	385.3	355.2	399.1
2.0	255.9	378.9	260	562.2	198.2	370.6	306.9	181.9	91.4	5.03	396.7	361.0	408.1
2.5	262.1	387.7	269	573.8	203.1	377.5	314.6	186.3	93.7		406.0	373.7	415.6
3.0	267.2	395.0	275	583.8	207.4	382.9	319.6	190.6	95.8		413.5	381.7	422.0
4.0	275.9	407.9	282	600.3	214.5	392.0	329.4	197.7	99.2		426.0	393.3	432.4
5.0	283.0	418.6	287	614.3	220.4	399.1	337.0	202.9	102.0		431.9	404.0	441.2
6	289.2	427.8	292	626.6	225.5	405.0	343.5	207.2	104.4		441.5	412.2	449.0
8	290.6	443.0	301	646.6	234.0	415.6	354.7	215.0	108.4		462.1	427.0	462.5
10	307.8	455.2	309	664.2	241.1	424.1	364.1	221.2	111.8		474.9	438.9	473.7
15	325.0	481.1	327	697.8	255.1	442.4	385.9	234.1	118.5		498.9	462.0	494.3
20	338.0	499.9	342	722.5	266.0	456.0	400.4	243.9	123.7		518.9	479.1	510.2
25	349.4	516.3	355	744.2	275.1	467.0	412.8	252.3	128.1		535.0	495.0	522.2
30	359.2	528.8	365	763.4	282.9	476.0	422.2	259.9	131.8			506.3	531.7
40	376.0	551.1	379	794.0	296.0	490.4	442.4	272.7	138.1				547.8
50	389.0			818.2		502.8	456.5	282.7	143.3				561.8
60	400.7					513.4							574.0
80													598.0
100													616.2

Table 4.2.24   Saturation Temperature, in Kelvins, of Selected Substances   (*Continued*)

Pressure, bar	n-Hydrogen, H_2	Hydrochloric acid, HCl	Hydrogen sulfide, H_2S	Mercury, Hg	Methane, CH_4	Methanol	Methyl chloride, CH_3Cl	Naphthalene	Nitrogen, N_2	Octane, C_8H_{18}	Oxygen, O_2	Pentane, C_5H_{12}	Potassium, K
0.010				448.6		252.6	173.2	353.0		286.4	62.2	219.1	699
0.015				460.5		258.2	178.4	361.2		293.8	63.0	225.0	719
0.020				468.9		262.3	182.6	367.6		299.4	64.3	228.8	732
0.025				475.3		265.6	185.9	372.8		303.7	65.2	232.0	743
0.030				481.6		268.4	188.6	376.9		306.8	66.2	234.7	752
0.04				491.2		272.9	192.7	384.3		312.4	67.6	239.2	764
0.05				498.2		276.5	196.0	389.9		316.9	68.8	242.8	776
0.06				504.7		278.8	198.6	394.8		320.8	69.8	245.9	788
0.08	14.0			515.2		284.4	202.8	402.7		327.1	71.4	250.8	811
0.10	14.4			523.6		288.4	206.0	408.9		332.0	72.7	254.9	829
0.15	15.2	161.0		538.9	92.6	295.9	211.9	420.9	64.1	341.6	75.2	263.0	861
0.20	15.8	164.5		551.0	95.0	301.4	216.5	429.5	65.8	348.7	77.1	269.1	883
0.25	16.3	167.2	189.8	561.0	97.0	305.9	220.5	437.1	67.2	354.6	78.7	274.0	899
0.30	16.7	169.3	192.5	569.0	98.6	309.7	223.8	443.3	68.3	359.7	80.0	277.9	916
0.40	17.5	172.7	197.0	582.2	101.4	315.9	229.1	454.0	70.2	368.3	82.2	284.9	940
0.5	18.1	175.2	200.4	592.7	103.7	320.8	233.4	462.1	71.8	374.9	83.9	290.0	960
0.6	18.6	177.5	203.1	601.8	105.6	325.0	237.0	469.4	73.2	380.6	85.5	294.7	977
0.8	19.5	181.0	208.0	616.8	108.8	331.9	243.1	481.1	75.4	390.2	88.0	302.1	1,006
1.0	20.2	187.8	212.5	628.9	111.5	337.5	248.0	490.2	77.2	398.0	90.1	308.6	1,029
1.5	21.7	195.6	222.0	652.1	116.6	348.1	257.9	509.0	80.8	413.3	94.1	321.6	1,074
2.0	22.8	201.5	227.9	670.0	120.6	356.1	265.4	523.3	83.6	424.6	97.2	331.1	1,108
2.5	23.8	206.1	234.3	684.5	123.9	362.6	271.5	535.0	85.9	434.4	99.8	339.2	1,137
3.0	24.6	210.0	237.9	696.7	126.7	368.1	276.6	544.8	87.9	442.1	102.0	345.7	1,176
4.0	26.0	216.7	245.1	717.1	131.4	377.2	285.5	560.3	91.2	456.3	105.7	356.7	1,203
5.0	27.1	222.0	250.9	733.5	135.3	384.6	292.6	573.2	94.0	467.4	108.8	365.4	1,238
6	28.1	226.2	256.1	747.8	138.7	390.9	298.9	584.7	96.4	477.0	111.4	373.6	1,268
8	29.8	233.6	264.9	770.8	144.4	401.4	309.4	605.0	100.4	494.0	115.9	387.6	1,318
10	31.2	241.6	272.1	790.2	149.1	410.0	318.1	620.7	103.8	507.0	119.6	398.2	1,359
15		254.2	283.3	827.5	158.5	426.5	332.7	652.6	110.4	532.4	127.0	420.7	1,440
20		263.7	299.8	857.2	165.8	439.1	348.6	677.9	115.6	553.6	132.8	436.8	1,505
25		272.3	309.4	879.2	172.0	449.4	359.4	699.0	119.9		137.6	450.4	1,558
30		279.9	316.7	901.0	177.2	458.2	368.6	718.4	123.6		141.7	462.1	1,606
40		291.9	330.0	934.4	186.1	473.0	384.3				148.6		1,689
50		301.1	340.4	962.8		484.9	397.2				154.4		1,759
60		309.5	350.3	987.6		495.3	408.5						1,819
80		322.9	366.9	1,028		511.9							1,920
100				1,065									2,000

Table 4.2.24   Saturation Temperature, in Kelvins, of Selected Substances   (*Continued*)

Pressure, bar	Propane, C_3H_8	Propanol, C_3H_8O	Propylene, C_3H_6	Refrigerant 11, $CFCl_3$	Refrigerant 12, CF_2Cl_2	Refrigerant 13, CF_3Cl	Refrigerant 21, $CHFCl_2$	Refrigerant 22, CHF_2Cl	Sodium, Na	Sulfur dioxide, SO_2	Toluene, C_7H_8	Water, H_2O
0.010	162.0	284.0	157.8	209.9	171.5	134.1	201.8	165.7	804	190.6	275.1	280.1
0.015	166.2	289.8	161.9	215.0	175.8	137.6	206.6	170.0	825	195.9	282.0	286.1
0.020	169.4	294.0	165.1	219.1	179.1	140.3	210.5	173.1	841	199.6	286.3	290.6
0.025	171.9	297.3	167.4	222.2	181.8	142.4	212.9	175.6	854	202.6	290.0	294.2
0.030	174.1	299.9	169.6	224.7	184.1	144.2	215.5	177.8	865	204.8	293.4	297.2
0.04	177.4	304.2	172.8	229.0	187.8	147.1	219.6	180.9	883	208.7	298.9	302.1
0.05	180.1	307.8	175.7	232.6	190.3	149.4	222.9	183.5	898	211.8	303.3	306.0
0.06	182.4	310.7	177.9	235.5	193.0	151.3	225.7	185.8	910	214.3	307.1	309.3
0.08	186.2	315.7	181.7	240.7	197.0	154.6	230.2	189.6	930	218.6	313.7	314.7
0.10	189.4	319.7	184.9	244.7	200.1	157.1	233.9	192.6	946	222.0	318.6	319.0
0.15	195.6	327.4	190.7	252.1	206.3	162.1	241.0	198.5	977	228.2	328.5	327.3
0.20	200.1	333.2	195.2	257.8	211.1	165.9	246.3	202.9	1,000	232.9	335.1	333.2
0.25	203.9	337.8	198.7	262.4	214.9	169.0	250.6	206.6	1,019	236.2	341.6	338.1
0.30	207.0	341.7	201.7	266.4	218.2	171.7	254.2	209.6	1,034	239.8	346.3	342.3
0.40	212.1	348.1	206.8	273.1	223.5	176.0	260.2	214.7	1,061	244.8	354.1	349.0
0.5	216.3	352.9	211.0	278.2	227.9	179.5	265.1	218.6	1,082	248.7	360.3	354.5
0.6	219.9	357.3	214.5	282.8	231.7	182.5	269.2	220.2	1,099	252.2	366.1	359.1
0.8	225.9	364.6	221.4	290.3	237.9	187.1	276.1	227.7	1,129	258.0	375.6	366.7
1.0	230.7	370.1	225.2	296.6	243.0	191.4	281.7	232.2	1,153	262.8	383.2	372.8
1.5	240.3	381.4	234.5	308.6	253.0	199.3	292.6	241.2	1,199	272.6	398.2	384.5
2.0	247.7	389.9	241.6	317.9	260.6	205.4	299.4	248.1	1,235	279.6	409.3	393.4
2.5	253.2	396.9	247.3	325.5	266.9	210.4	307.8	253.8	1,264	285.4	419.0	400.6
3.0	258.9	402.3	252.6	331.8	272.3	214.6	313.6	258.6	1,289	290.0	427.0	406.7
4.0	267.6	411.9	262.6	342.7	281.3	221.8	323.5	266.5	1,330	298.6	441.7	416.8
5.0	274.8	419.8	267.2	351.1	288.8	227.1	331.6	273.0	1,364	305.3	451.4	425.0
6	281.0	426.8	273.9	358.8	295.2	232.8	338.5	279.0	1,393	311.1	460.9	432.0
8	291.4	438.5	284.0	372.2	306.0	241.4	350.2	289.1	1,430	320.7	476.8	445.6
10	300.0	447.8	292.3	382.7	314.9	248.5	361.0	297.1	1,480	328.6	490.0	453.0
15	317.0	466.6	308.9	403.7	332.6	262.7	379.1	312.3	1,556	345.2	515.8	472.0
20	330.3	481.4	321.8	419.2	346.3	273.7	394.0	324.9	1,623	357.8	535.5	485.5
25		493.6	332.5	432.1	357.5	282.8	406.4	335.1	1,676	368.2	552.3	497.1
30		503.8	341.7	444.8	367.2	290.7	417.1	343.4	1,720	377.0	566.4	507.0
40		511.3	357.0	463.9	383.3		434.7	358.3	1,795	391.6	589.6	523.5
50		536.1					449.2		1,859	403.8		537.1
60									1,913	414.5		548.7
80									2,010			568.1
100									2,085			584.1

Table 4.2.25   Color Scale of Temperature for Iron or Steel

	Temperature	
Color	°F	K
Dark blood red, black red	1,000	810
Dark red, blood red, low red	1,050	840
Dark cherry red	1,175	910
Medium cherry red	1,250	950
Cherry, full red	1,375	1,020
Light cherry, light red	1,550	1,120
Orange, free scaling heat	1,650	1,170
Light orange	1,725	1,210
Yellow	1,825	1,270
Light yellow	1,975	1,350
White	2,200	1,475

Table 4.2.26   Melting Points of Refractory Materials

	Temperature	
Material	°F	K
Aluminum nitride, AlN	4,060	2,500
Aluminum oxide, Al_2O_3	3,720	2,320
Aluminum oxide–beryllium oxide, Al_2O_3-BeO	3,400	2,140
Beryllium carbide, Be_2C	3,810	2,370
Beryllium nitride, Be_3N_4	4,000	2,480
Beryllium oxide, BeO	4,570	2,790
Beryllium silicide, $2BeO \cdot SiO_2$	3,630	2,270
Borazon, BN	5,430	3,270
Calcia (lime), CaO	4,660	2,840
Graphite, C	6,700	3,980
Hafnia, HfO_2	5,090	3,090
Magnesia, MgO	5,070	3,070
Niobium carbide, NbC	6,330	3,770
Silica, SiO_2	3,110	1,980
Silicon carbide, SiC	3,990	2,470
Thoria, ThO_2	5,830	3,490
Titanium carbide, TiC	5,680	3,410
Zirconium aluminide, $ZrAl_2$	3,000	1,920
Zirconium beryllide, $ZrBe_{13}$	3,180	2,020
Zirconium carbide, ZrC	6,400	3,810
Zirconium disilicide, $ZrSi_2$	3,090	1,970
Zirconium nitride, ZrN	5,400	3,260
Zirconium oxide, ZrO_2	4,900	2,980
Zirconium silicides, Zr_3Si_2, Zr_4Si_3, Zr_6Si_5	≈4,050	≈2,500

Table 4.2.27   Mean Specific Heats of Various Solids (32–212°F, 273–373 K)

Solid	c, Btu/(lb · °F)	c, kJ/(kg · K)
Alumina	0.183	0.77
Asbestos	0.20	0.84
Ashes	0.20	0.84
Bakelite	≈0.35	1.50
Basalt (lava)	0.20	0.84
Bell metal	0.086	0.36
Bismuth-tin	0.043	0.18
Borax	0.229	0.96
Brass, yellow	0.088	0.37
Brass, red	0.090	0.38
Brick	0.22	0.92
Bronze	0.104	0.44
Carbon-coke	0.203	0.85
Chalk	0.215	0.90
Charcoal	0.20	0.84
Cinders	0.18	0.75
Coal	≈0.30	≈1.25
Concrete	0.156	0.65
Constantan	0.098	0.41
Cork	0.485	2.03
Corundum	0.198	0.83
D'Arcet's metal	0.050	0.21
Dolomite	0.222	0.93
Ebonite	0.33	1.38
German silver	0.095	0.40
Glass, crown	0.16	0.70
Glass, flint	0.12	0.50
Glass, normal	0.20	0.84
Gneiss	0.18	0.75
Granite	0.20	0.84
Graphite	0.20	0.84
Gypsum	0.26	1.10
Hornblende	0.20	0.84
Humus (soil)	0.44	1.80
India rubber (para)	≈0.37	1.50
Kaolin	0.224	0.94
Lead oxide (PbO)	0.055	0.23
Limestone	0.217	0.91
Lipowitz's metal	0.040	0.17
Magnesia	0.222	0.93
Magnesite (Fe_3O_4)	0.168	0.70
Marble	0.210	0.88
Nickel steel	0.109	0.46
Paraffin wax	0.69	2.90
Porcelain	0.22	0.92
Quartz	≈0.23	0.96
Quicklime	0.217	0.91
Rose's metal	0.050	0.21
Salt, rock	0.21	0.88
Sand	0.195	0.82
Sandstone	0.22	0.92
Serpentine	0.25	1.05
Silica	0.191	0.80
Soda	0.231	0.97
Solders (Pb + Sn)	0.043	0.18
Sulfur	0.180	0.75
Talc	0.209	0.87
Tufa	0.33	1.40
Type metal	0.039	0.16
Vulcanite	0.331	1.38
Wood, fir	0.65	2.70
Wood, oak	0.57	2.40
Wood, pine	0.67	2.80
Wood's metal	0.040	0.17

Table 4.2.28   Phase Transition and Other Data for the Elements

Name	Symbol	Formula weight	T_m, K	Δh_{fus}, kJ/kg	T_b, K	Δh_{vap}, kJ/kg	T_c, K	P_c, bar	T_{tr}, K
Actinium	Ac	227.028	1,323	63	3,475	1,750			
Aluminum	Al	26.9815	933.5	398	2,750	10,875	7,850	4,800	
Antimony	Sb	121.75	903.9	163	1,905		5,700	3,200	368, 686
Argon	Ar	39.948	83	30	87.2	163	151	50	
Arsenic	As	74.9216				1,703	2,100		
Barium	Ba	137.33	1,002	55.8		1,099	4,450	720	643
Beryllium	Be	9.01218	1,560	1,355	2,750	32,450	6,200	4,600	1,530
Bismuth	Bi	208.980	544.6	54.0	1,838	725	4,450	1,400	
Boron	B	10.81	2,320	1,933	4,000		3,300		1,473
Bromine	Br	159.808	266	66.0	332	188	584		
Cadmium	Cd	112.41	594	55.1	1,040	886	2,690	1,680	
Calcium	Ca	40.08	1,112	213.1	1,763	3.833	4,300	1,000	720
Carbon	C	12.011	3,810		4,275		7,200	11,500	
Cerium	Ce	140.12	1,072	390		2,955	9,750	3,350	103, 263, 1,003
Cesium	Cs	132.905	301.8	16.4	951	496	2,015	125	
Chlorine	Cl$_2$	70.906	172	180.7	239	576	417		
Chromium	Cr	51.996	2,133	325.6	2,950	6.622	5,500		2,113
Cobalt	Co	58.9332	1,766	274.7	3,185	6,390	6,300		700, 1,400
Copper	Cu	63.546	1,357	206.8	2,845	4,726	8,280	7,400	
Dysprosium	Dy	162.50	1,670	68.1	2,855	1,416	6,925	2,500	1,659
Erbium	Er	167.26	1,795	119.1	3,135	1,563	7,250		1,643
Europium	Eu	151.96	1,092	60.6	1,850	944	4,350	690	
Fluorine	F$_2$	37.997	53.5	13.4	85.0	172	144		46
Gadolinium	Gd	157.25	1,585	63.8	3,540	2,285	8,670		1,537
Gallium	Ga	69.72	303	80.1	2,500	3,688	7,125	4,150	276
Germanium	Ge	72.59	1,211	508.9	3,110	4,558	8,900	5,300	
Gold	Au	196.967	1,337	62.8	3,130	1,701	7,250	5,450	
Hafnium	Hf	178.49	2,485	134.8	4,885	3,211	10,400		2,000
Helium	He	4.00260	3.5	2.1	4.22	21	5.2	2.3	2.2
Holmium	Ho	164.930	1,744	73.8	2,968	1,461	7,575		1,703
Hydrogen	H$_2$	2.0159	14.0		20.4				
Indium	In	114.82	430	28.5	2,346	2,019	6,150	2,550	
Iodine	I$_2$	253.809	387	125.0	457	785			
Iridium	Ir	192.22	2,718	13.7	4,740	3,185	7,800		
Iron	Fe	55.847	1,811	247.3	3,136	6,259	8,500	10,000	1,183, 1,671
Krypton	Kr	83.80	115.8	19.6	119.8	108	209.4	55	
Lanthanum	La	138.906	1,194	44.6	3,715	2,978	10,500		550, 1,134
Lead	Pb	207.2	601	23.2	2,025	858	5,500	1,650	
Lithium	Li	6.941	454		1,607	21,340	3,700	1,000	80
Lutetium	Lu	174.967	1,937	106.6	3,668	2,034			
Magnesium	Mg	24.305	922	368.4	1,364	5,242	3,850	1,750	
Manganese	Mn	54.9380	1,518	219.3	2,334	4,112	4,325	560	1,374, 1,447
Mercury	Hg	200.59	234.6	11.4	630	293	1,720	1,500	194
Molybdenum	Mo	95.94	2,892	290.0	4,900		1,450	12,000	
Neodymium	Nd	144.24	1,290	49.6	3,341	1,891	7,900		1,132, 1,297
Neon	Ne	20.179	24.5	16.4	27.1	89	44.5	26.6	
Neptunium	Np	237.048	910		4,160		12,000		551, 847
Nickel	Ni	58.70	1,728	297.6	3,190	6,308	8,000	11,100	631
Niobium	Nb	92.9064	2,740	283.7	5,020	7,341	12,500		
Nitrogen	N$_2$	28.013	63.2	25.7	77.3	198	126.2	34.0	35.6
Osmium	Os	190.2	3,310	150.0	5,300	3,310	12,700		
Oxygen	O$_2$	31.9988	54.4	13.8	90.2	213	154.8		23.8, 43.8
Palladium	Pd	106.4	1,826	165.0	3,240	3,358	7,700	7,100	
Phosphorus	P	30.9738	317		553		995	81	196, 298
Platinum	Pt	195.09	2,045	101	4,100	2,612	10,700	11,000	
Plutonium	Pu	244	913	11.7	3,505	1,409	10,500	3,250	395, 480, 588, 730
Potassium	K	39.0983	336.4	60.1	1,032	2,052	2,210	170	
Praseodymium	Pr	140.908	1,205	49	3,785	2,105	8,900		1,066
Promethium	Pm	145	1,353		2,730				
Protactinium	Pa	231	1,500	64.8	4,300	2,036			
Radium	Ra	226.025	973		1,900				
Radon	Rn	222	202	12.3	211	83	377	66	
Rhenium	Re	186.207	3,453	177.8	5,920	3,842	18,900	14,900	
Rhodium	Rh	102.906	2,236	209.4	3,980	4,798	7,000		
Rubidium	Rb	85.4678	312.6	26.4	964	810	2,070	168	

Table 4.2.28   Phase Transition and Other Data for the Elements   (*Continued*)

Name	Symbol	Formula weight	T_m, K	Δh_{fus}, kJ/kg	T_b, K	Δh_{vap}, kJ/kg	T_c, K	P_c, bar	T_{tr}, K
Ruthenium	Ru	101.07	2,525	256.3	4,430	5,837	9,600		1,300, 1,475, 1,775
Samarium	Sm	150.4	1,345	57.3	2,064	1,107	5,050	1,780	1,190
Scandium	Sc	44.9559	1,813	313.6	3,550	6,989	6,410	3,750	1,608
Selenium	Se	78.96	494	66.2	958	1,210	1,810	320	398, 425
Silicon	Si	28.0855	1,684	1,802	3,540	14,050	5,160	540	
Silver	Ag	107.868	1,234	104.8	2,435	2,323	6,400	4,450	
Sodium	Na	22.9898	371	113.1	1,155	4,263	2,500	370	
Strontium	Sr	87.62	1,043	1,042	1,650	1,585	4,275	375	505, 893
Sulfur	S	32.06	388	53.4	718		1,210	130	369, 374
Tantalum	Ta	180.948	3,252	173.5	5,640	4,211	16,500	12,000	
Technetium	Tc	98	2,447	232	4,550	5,830	11,500		
Tellurium	Te	127.60	723	137.1	1,261	895	2,330		
Terbium	Tb	158.925	1,631	67.9	3,500	2,083	8,470		228, 1,575
Thallium	Tl	204.37	577	20.1	1,745	806	4,550	1,700	507
Thorium	Th	232.038	2,028	69.4	5,067	2,218	14,400	6,165	1,670
Thulium	Tm	168.934	1,819	99.6	2,220	1,129	6,450		
Tin	Sn	118.69	505	58.9	2,890	2,496	7,700	2,250	286, 476
Titanium	Ti	47.90	1,943	323.6	3,565	8,787	5,850		1,162, 1,353
Tungsten	W	183.85	3,660	192.5	5,890	4,483	15,500	15,000	
Uranium	U	238.029	1,406	35.8	4,422	1,949	12,500	5,000	938, 1,046
Vanadium	V	50.9415	2,191	410.7	3,680	8,870	11,300	10,300	
Xenon	Xe	131.30	161.3	17.5	164.9	96	290	58	
Ytterbium	Yb	173.04	1,098	44.2	1,467	745	4,080	1,150	1,050
Yttrium	Y	88.9059	1,775	128.2	3,610	4,485	8,950		1,758
Zinc	Zn	65.38	692.7	113.0	1,182	1,768			
Zirconium	Zr	91.22	2,125	185.3	4,681	6,376	10,500		1,135

Formula weight = molecular weight, T_m = normal melting temperature, Δh_{fus} = enthalpy (or latent heat) of fusion, T_b = normal boiling-point temperature, Δh_{vap} = enthalpy (or latent heat) of vaporization, T_c = critical temperature, P_c = critical pressure, T_{tr} = transition temperature.
SOURCE: Prepared by the author and abstracted from Rohsenow et al., ''Handbook of Heat Transfer Fundamentals,'' McGraw-Hill.

Table 4.2.29 Thermophysical Properties of Selected Solid Elements

Element	Property	Temperature, K							
		100	200	300	400	500	600	800	1,000
Al	P, bar			2.1. − 43	4.9. − 31	1.1. − 23	1.0. − 18	1.4. − 12	6.6. − 9
	ρ, kg/m³	2,732	2,719	2,701	2,681	2,661	2,639	2,591	2,365
	h, kJ/kg			4,623	4,716	4,812	4,913	5,131	5,768
	s, kJ/(kg · K)			1.056	1.323	1.539	1.723	2.035	2.728
	c_p, kJ/(kg · K)	0.481	0.797	0.902	0.949	0.997	1.042	1.134	0.921
	λ, W/(m · K)	300	237	237	240	236	231	218	
	α, m²/s	2.3. − 4	1.1. − 4	9.7. − 5	9.4. − 5	8.9. − 5	8.4. − 5	7.4. − 5	6.6. − 5
Cr	P, bar			4.6. − 62	8.9. − 45	2.1. − 34	1.6. − 27	6.3. − 19	9.1. − 14
	ρ, kg/m³	7,155	7,145	7,135	7,120	7,110	7,080	7,040	7,000
	h, kJ/kg			4,113	4,160	4,210	4,263	4,375	4,495
	s, kJ/(kg · K)			0.457	0.591	0.703	0.800	0.962	1.094
	c_p, kJ/(kg · K)	0.190	0.382	0.450	0.501	0.537	0.565	0.611	0.653
	λ, W/(m · K)	160	110	94	91	86	81	71	65
	α, m²/s	1.2. − 4	4.1. − 5	2.9. − 5	2.6. − 5	2.3. − 5	2.0. − 5	1.7. − 5	1.4. − 5
Cu	P, bar			1.1. − 52	9.0. − 38	5.5. − 29	3.8. − 23	7.6. − 16	1.7. − 11
	ρ, kg/m³	9,009	8,973	8,930	8,884	8,837	8,787	8,686	8,568
	h, kJ/kg			5,067	5,106	5,146	5,188	5,273	5,361
	s, kJ/(kg · K)			0.524	0.637	0.726	0.802	0.924	1.022
	c_p, kJ/(kg · K)	0.254	0.357	0.386	0.396	0.406	0.431	0.448	0.466
	λ, W/(m · K)	480	413	401	393	386	379	366	352
	α, m²/s	2.2. − 4	1.3. − 4	1.2. − 4	1.1. − 4	1.1. − 4	1.0. − 4	9.0. − 5	8.0. − 5
Au	P, bar			6.7. − 58	6.3. − 42	2.8. − 32	3.6. − 25	6.5. − 18	3.7. − 13
	ρ, kg/m³	19,460	19,380	19,300	19,210	19,130	19,040	18,860	18,660
	h, kJ/kg			6,046	6,059	6,072	6,086	6,113	6,142
	s, kJ/(kg · K)			0.241	0.279	0.309	0.333	0.373	0.404
	c_p, kJ/(kg · K)	0.109	0.124	0.129	0.131	0.133	0.136	0.141	0.147
	λ, W/(m · K)	327	323	317	311	304	298	284	270
	α, m²/s	1.5. − 4	1.34. − 4	1.27. − 4	1.23. − 4	1.19. − 4	1.15. − 4	1.07. − 4	9.8. − 5
Fe	P, bar			3.1. − 65	6.3. − 54	3.9. − 47	1.5. − 36	6.6. − 20	1.5. − 14
	ρ, kg/m³	7,900	7,880	7,860	7,830	7,800	7,760	7,690	7,650
	h, kJ/kg			4,523	4,570	4,621	4,676	4,801	4,958
	s, kJ/(kg · K)			0.491	0.626	0.740	0.840	1,018	1.193
	c_p, kJ/(kg · K)	0.216	0.384	0.450	0.491	0.524	0.555	0.692	1.034
	λ, W/(m · K)	134	94	80	70	61	55	43	32
	α, m²/s	8.2. − 5	3.1. − 5	2.2. − 5	1.8. − 5	1.5. − 5	1.3. − 5	1.1. − 5	1.0. − 5
Pb	P, bar			6.3. − 29	1.8. − 20	2.2 − 15	5.4. − 12	6.2. − 8	1.6. − 5
	ρ, kg/m³	11,520	11,430	11,330	11,230	11,130	11,010	10,430	10,190
	h, kJ/kg			6,929	6,942	6,955	6,969	7,022	7,050
	s, kJ/(kg · K)			0.314	0.351	0.381	0.406	0.487	0.519
	c_p, kJ/(kg · K)	0.118	0.125	0.129	0.132	0.137	0.142	0.145	0.142
	λ, W/(m · K)	39.7	36.7	35.3	34.0	32.8	31.4		
	α, m²/s	2.9. − 5	2.6. − 5	2.4. − 5	2.3. − 5	2.2. − 5	2.0. − 5	1.3. − 5	1.5. − 5
Li	P, bar								
	ρ, kg/m³	546	541	533	526	492	482	462	442
	h, kJ/kg				4,615	4,919	5,844	6,274	7,113	7,945
	s, kJ/(kg · K)			4.214	5.289	7.182	7.967	9.173	10.102
	c_p, kJ/(kg · K)	1.923	3.105	3.54	3.76	4.34	4.26	4.17	4.15
	λ, W/(m · K)	105	90	85	80				
	α, m²/s	1.0. − 4	5.4. − 5	4.5. − 5	3.2. − 5	2.1. − 5	2.3. − 5	2.8. − 5	3.3. − 5
Ni	P, bar			1.1. − 67	5.8. − 49	9.8. − 38	2.7. − 30	5.5. − 21	2.1. − 15
	ρ, kg/m³	8,960	8,930	8,900	8,860	8,820	8,780	8,690	8,610
	h, kJ/kg			4,837	4,883	4,934	4,990	5,099	5,207
	s, kJ/(kg · K)			0.512	0.645	0.758	0.859	1.017	1.137
	c_p, kJ/(kg · K)	0.232	0.383	0.444	0.490	0.540	0.590	0.530	0.556
	λ, W/(m · K)	165	105	91	80	72	66	68	72
	α, m²/s	8.0. − 5	3.1. − 5	2.3. − 5	1.9. − 5	1.5. − 5	1.3. − 5	1.4. − 5	1.5. − 5
Pt	P, bar			3.2. − 91	1.3. − 66	7.3. − 52	5.0. − 42	9.7. − 30	2.3. − 22
	ρ, kg/m³	21,550	21,500	21,450	21,380	21,330	21,270	21,140	21,010
	h, kJ/kg			5,837	5,850	5,864	5,878	5,907	5,937
	s, kJ/(kg · K)			0.214	0.253	0.283	0.309	0.350	0.383
	c_p, kJ/(kg · K)	0.101	0.127	0.134	0.136	0.138	0.140	0.146	0.152
	λ, W/(m · K)	78	73	72	72	72	73	76	79
	α, m²/s	3.6. − 5	2.7. − 5	2.5. − 5	2.5. − 5	2.5. − 5	2.5. − 5	2.5. − 5	2.5. − 5

Table 4.2.29 Thermophysical Properties of Selected Solid Elements (*Continued*)

Element	Property	Temperature, K							
		100	200	300	400	500	600	800	1,000
Rh	P, bar			5.5. − 89	6.5. − 65	1.8. − 50	7.1. − 41	7.0. − 29	1.1. − 21
	ρ, kg/m³	12,480	12,460	12,430	12,400	12,360	12,330	12,250	12,170
	h, kJ/kg			4,921	4,946	4,972	4,999	5,055	5,115
	s, kJ/(kg · K)			0.308	0.380	0.437	0.487	0.568	0.635
	c_p, kJ/(kg · K)	0.147	0.220	0.246	0.257	0.265	0.274	0.290	0.307
	λ, W/(m · K)	190	154	150	146	141	136	127	121
	α, m²/s	1.0. − 4	5.6. − 5	4.9. − 5	4.6. − 5	4.3. − 5	4.0. − 5	3.6. − 5	3.2. − 5
Ag	P, bar			2.1. − 43	4.9. − 31	1.1. − 23	1.0. − 18	1.4. − 12	6.6. − 9
	ρ, kg/m³	10,600	10,550	10,490	10,430	10.360	10,300	10,160	10,010
	h, kJ/kg			5,791	5,815	5,839	5,864	5,915	5,968
	s, kJ/(kg · K)			0.3959	0.4641	0.5180	0.5630	0.6365	0.6964
	c_p, kJ/(kg · K)	0.187	0.225	0.236	0.240	0.245	0.251	0.264	0.276
	λ, W/(m · K)	450	430	429	425	419	412	396	379
	α, m²/s	2.3. − 4	1.8. − 4	1.7. − 4	1.7. − 4	1.7. − 4	1.6. − 4	1.5 − 4	1.3. − 4
Ti	P, bar			1.0. − 74	4.6. − 54	5.2. − 42	7.2. − 35	1.2. − 23	1.4. − 17
	ρ, kg/m³	4,530	4,520	4,510	4,490	4,480	4,470	4,440	4,410
	h, kJ/kg			4,857	4,911	4,967	5,025	5,147	5,278
	s, kJ/(kg · K)			0.643	0.797	0.922	1.028	1.205	1.350
	c_p, kJ/(kg · K)	0.295	0.464	0.525	0.555	0.578	0.597	0.627	0.670
	λ, W/(m · K)	31	25	21	20	20	19	19	21
	α, m²/s								
W	P, bar			3.2. − 141	2.9. − 104	4.3. − 82	2.7. − 67	8.7. − 49	1.1. − 37
	ρ, kg/m³	19,310	19,290	19,270	19,240	19,220	19,190	19,130	19,080
	h, kJ/kg			6,255	6,268	6,282	6,296	6,325	6,354
	s, kJ/(kg · K)			0.178	0.217	0.248	0.273	0.315	0.347
	c_p, kJ/(kg · K)	0.089	0.125	0.135	0.137	0.139	0.140	0.144	0.148
	λ, W/(m · K)	208	185	174	159	146	137	125	118
	α, m²/s								
V	P, bar			3.0. − 82	7.1. − 60	1.9. − 46	1.6. − 37	2.4. − 26	1.2. − 19
	ρ, kg/m³	6,074	6,062	6,050	6,030	6,010	6,000	5,960	5,920
	h, kJ/kg			4,740	4,790	4,843	4,896	5,006	5,121
	s, kJ/(kg · K)			0.571	0.716	0.832	0.930	1.088	1.216
	c_p, kJ/(kg · K)	0.257	0.434	0.483	0.512	0.528	0.540	0.563	0.598
	λ, W/(m · K)	36	31	31	31	32	33	36	38
	α, m²/s	2.3. − 5	1.2. − 5	1.1. − 5	1.0. − 5	1.0. − 5	1.0. − 5	1.1. − 5	1.1. − 5
Zn	P, bar			3.7. − 17	1.6. − 11	3.7. − 8	6.7. − 6	3.4. − 3	1.2. − 1
	ρ, kg/m³	7,260	7,200	7,135	7,070	7,000	6,935	6,430	6,260
	h, kJ/kg			5,690	5,730	5,771	5,813	5,970	6,114
	s, kJ/(kg · K)	0.295		0.639	0.753	0.844	0.922	1.216	1.323
	c_p, kJ/(kg · K)	117	0.366	0.389	0.404	0.419	0.435	0.479	0.479
	λ, W/(m · K)	5.5. − 5	118	116	111	107	103		
	α, m²/s		4.7. − 5	4.1. − 5	3.9. − 5	3.7. − 5	3.4. − 5	1.8. − 5	2.2. − 5
Zr	P, bar			2.8. − 99	8.6. − 73	6.6. − 57	2.7. − 46	4.6. − 33	4.1. − 25
	ρ, kg/m³	6,535	6,525	6,515	6,510	6,490	6,480	6,450	6,420
	h, kJ/kg			5,540	5,569	5,600	5,632	5,698	5,768
	s, kJ/(kg · K)			0.429	0.513	0.590	0.640	0.735	0.813
	c_p, kJ/(kg · K)	0.120	0.126	0.130	0.136	0.143	0.153	0.153	0.153
	λ, W/(m · K)	33	25	23	22	21	21	21	23
	α, m²/s								

P = saturation vapor pressure; ρ = density; h = enthalpy; s = entropy; c_p = specific heat at constant pressure; λ = thermal conductivity; α = thermal diffusivity.

4.3 RADIANT HEAT TRANSFER

by Hoyt C. Hottel and Adel F. Sarofim

REFERENCES: Hottel and Sarofim, ''Radiative Transfer,'' McGraw-Hill. Siegel and Howell, ''Thermal Radiation Heat Transfer,'' McGraw-Hill, 3d ed. Modest, ''Radiative Heat Transfer,'' McGraw-Hill.

A heated body loses energy continuously by radiation, at a rate dependent on the shape, the size, and, particularly, the temperature of the body. In contrast to conductive energy transport, such emitted radiation is capable of passage to a distant body, where it may be absorbed, reflected, scattered, or transmitted.

Consider a pencil of radiation, defined as all the rays passing through each of two small, widely separated areas dA_1 and dA_2. The rays at dA_1 will have a solid angle of divergence $d\Omega_1$, equal to the apparent area of dA_2 viewed from dA_1, divided by the square of the separating distance. Let the normal to dA_1 make the angle θ_1 with the pencil. The flux density q [energy/(time)(area normal to beam)] is called the **intensity I,** and the flux dQ_1 (energy/time) through area dA_1 (of apparent area $dA_1 \cos \theta_1$ normal to the beam) is therefore given by

$$d\dot{Q}_1 = dA_1 \cos \theta_1 q_1 = I \, dA_1 \cos \theta_1 \, d\Omega_1 \qquad (4.3.1)$$

The intensity I along a pencil, in the absence of absorption or scatter is constant (unless the beam passes into a medium of different refractive index n; $I_1/n_1^2 = I_2/n_2^2$). The **emissive power*** of a surface is the flux density [energy/(time)(surface area)] due to emission from it throughout a hemisphere. If the intensity I of emission from a surface is independent of the angle of emission, Eq. (4.3.1) may be used to show that the surface emissive power is πI, though the emission is throughout 2π steradians.

BLACKBODY RADIATION

Engineering calculations of thermal radiation from surfaces are best keyed to the radiation characteristics of the **blackbody,** or **ideal radiator**. The characteristic properties of a blackbody are that it absorbs all the radiation incident on its surface and that the quality and intensity of the radiation it emits are completely determined by its temperature. The total radiative flux throughout a hemisphere from a black surface of area A and absolute temperature T is given by the **Stefan-Boltzmann law:** $\dot{Q} = A\sigma T^4$ or $q = \sigma T^4$. The Stefan-Boltzmann constant σ has the value 5.67×10^{-8} W/m²(K)⁴, 0.1713×10^{-8} Btu/(ft)²(h)(°R)⁴ or 1.356×10^{-12} cal/(cm)²(s)(K)⁴. From the above definition of emissive power, σT^4 is the total emissive power of a blackbody, called E; and the intensity I_B of emission from a blackbody is E/π, or $\sigma T^4/\pi$.

The spectral distribution of energy flux from a blackbody is expressed by Planck's law

$$E_\lambda \, d\lambda = \frac{2\pi hc^2 n^2 \lambda^{-5}}{e^{hc/(k\lambda T)} - 1} \, d\lambda \equiv \frac{n^2 c_1 \lambda^{-5}}{e^{c_2/(\lambda T)} - 1} \qquad (4.3.2)$$

wherein $E_\lambda \, d\lambda$ is the hemispherical flux density in W/m² lying in the wavelength range λ to $\lambda + d\lambda$; h is Planck's constant, 6.6262×10^{-34} J·s; c is the velocity of light in vacuo, 2.9979×10^8 m/s; k is the Boltzmann constant, 1.3807×10^{-23} J/K; λ is the wavelength measured in vacuo, m; n is the refractive index of the emitter; c_1 and c_2, the first and second Planck's law constants, are 3.7418×10^{-16} W·m² and 1.4388×10^{-2} m·K. To show how E_λ varies with wavelength or temperature, Planck's law may be cast in the form

$$\frac{E_\lambda}{n^2 T^5} = \frac{c_1 (\lambda T)^{-5}}{e^{c_2/(\lambda T)} - 1} \qquad (4.3.3)$$

* Variously called, in the literature, **emittance, total hemispherical intensity, radiant flux density** or **exitance**.

i.e., when $n \cong 1$ (e.g., in a gas), E_λ/T^5 is a unique function of λT. And E_λ is a maximum at $\lambda T = 2,898$ μm·K (Wien's displacement law). A more useful displacement law: Half of blackbody radiation lies on either side of $\lambda T = 4,107$ μm·K. Another: The maximum intensity per unit fractional change in wavelength *or* frequency is at $\lambda T = 3,670$ μm·K. Integration of E_λ over λ shows that the fraction f of blackbody radiation lying at wavelengths below λ depends only on λT. Values of f versus λT appear in Table 4.3.1. A twofold range of λT geometrically centered on $\lambda T = 3,670$ μm·K spans about half the energy.

A limiting form of the Planck equation as $\lambda T \to 0$ is $E_\lambda = n^2 c_1 \lambda^{-5} e^{-c_2/(\lambda T)}$, the Wien equation, less than 1 percent in error when λT is less than $3,000$ μm·K. This is useful for optical pyrometry (red screen $\lambda = 0.65$ μm) when $T < 4,800$ K.

Table 4.3.1 Fraction f of Blackbody Radiation below λ
$\lambda T = \mu$m · K

λT	1,200	1,600	1,800	2,000	2,200	2,400	2,600	2,800
f	0.002	0.020	0.039	0.067	0.101	0.140	0.183	0.228
λT	3,000	3,200	3,400	3,600	3,800	4,000	4,200	4,500
f	0.273	0.318	0.362	0.404	0.443	0.480	0.516	0.564
λT	4,800	5,100	5,500	6,000	6,500	7,000	7,600	8,400
f	0.608	0.646	0.691	0.738	0.776	0.808	0.839	0.871
λT	10,000	12,000	14,000	20,000	50,000			
f	0.914	0.945	0.963	0.986	0.999			

RADIATIVE EXCHANGE BETWEEN SURFACES OF SOLIDS

The ratio of the total radiating power of a real surface to that of a black surface at the same temperature is called the **emittance** of the surface (for a perfectly plane surface, the **emissivity**), designated by ε. Subscripts λ, θ, and n may be assigned to differentiate monochromatic, directional, and surface-normal values, respectively, from the total hemispherical value. If radiation is incident on a surface, the fraction absorbed is called the **absorptance (absorptivity),** a term in which two subscripts may be appended, the first to identify the temperature of the surface and the second to identify the quality of the incident radiation. According to **Kirchhoff's law,** the emissivity and absorptivity of a surface *in surroundings at its own temperature* are the same, for both monochromatic and total radiation. When the temperatures of the surface and its surroundings differ, the total emissivity and absorptivity of the surface are found often to be different, but because absorptivity is substantially independent of irradiation density, the monochromatic emissivity and absorptivity of surfaces are for all practical purposes the same. The difference between total emissivity and absorptivity depends on the variation, with wavelength, of ε_λ and on the difference between the emitter temperature and the effective source temperature.

Consider radiative exchange between a body of area A_1 and temperature T_1 and its black surroundings at T_2. The net interchange is given by

$$\dot{Q}_{1=2} = A_1 \int_0^\alpha [\varepsilon_\lambda E_\lambda(T_1) - \alpha_\lambda E_\lambda(T_2)] \, d\lambda$$

$$= A_1(\varepsilon_1 \sigma T_1^4 - \alpha_{12} \sigma T_2^4) \qquad (4.3.4)$$

where

$$\varepsilon_1 = \int_0^1 \varepsilon_\lambda \, df_{\lambda T_1} \quad \text{and} \quad \alpha_{12} = \int_0^1 \varepsilon_\lambda \, df_{\lambda T_2} \qquad (4.3.5)$$

i.e., ε_1 (or α_{12}) is the area under a curve of ε_λ versus f, read as a function of λT at T_1 (or T_2) from Table 4.3.1. If ε_λ does not change with wave-

length, the surface is called **gray**, and $\varepsilon_1 = \alpha_{12} = \varepsilon_\lambda$. A selective surface is one whose ε_λ changes dramatically with wavelength. If this change is monotonic, ε_1 and α_{12} are, according to Eqs. (4.3.4) and (4.3.5), markedly different when the absolute temperature ratio is far from 1; e.g., when $T_1 = 293$ K (ambient temperature) and $T_2 = 5,800$ K (effective solar temperature), $\varepsilon_1 = 0.9$ and $\alpha_{12} = 0.1-0.2$ for a white paint, but ε_1 can be as low as 0.12 and α_{12} above 0.9 for a thin layer of copper oxide on bright aluminum, or of chromic oxide on bright nickel.

Although values of emittances and absorptances depend in very complex ways on the real and imaginary components of the refractive index and on the geometric structure of the surface layer, some generalizations are possible.

Polished Metals   (1) ε_λ is quite low in the infrared and, for $\lambda > 8$ μm, can be adequately approximated by $0.00365\sqrt{r/\lambda}$, where r is the resistivity in ohm·cm and λ is in micrometres; at shorter wavelengths, ε_λ increases and, for many metals, has values of 0.4 to 0.8 in the visible (0.4–0.7 μm). ε_λ is approximately proportional to the square root of the absolute temperature ($\varepsilon_\lambda \propto \sqrt{r}$ and $r \propto T$) in the far infrared ($\lambda > 8$ μm), is temperature insensitive in the near infrared (0.7–1.5 μm) and, in the visible, decreases slightly as temperature increases. (2) Total emittance is substantially proportional to absolute tempera-ture; at moderate temperature, $\varepsilon_n = 0.58T\sqrt{r_0/T_0}$, where T is in kelvins. (3) Total absorptance of a metal at T_1 for radiation from a black or gray source at T_2 is equal to the emissivity evaluated at the geometric mean of T_1 and T_2. (4) The ratio of hemispherical to normal emittance (absorptance) varies from 1.33 at very lower ε's (α's) to about 1.03 at an ε (α) of 0.4.

Unless extraordinary pains are taken to prevent oxidation, however, a metallic surface may exhibit several times the emittance or absorptance of a polished specimen. The emittance of iron and steel, for example, varies widely with degree of oxidation and roughness—clean metallic surfaces have an emittance of from 0.05–0.45 at ambient temperatures to 0.4–0.7 at high temperatures; oxidized and/or rough surfaces range from 0.6–0.95 at low temperatures to 0.9–0.95 at high temperatures.

Refractory Materials   Grain size and concentration of trace impurities are important. (1) Most refractory materials have an ε_λ of 0.8 to 1.0 at wavelengths beyond 2 to 4 μm; ε_λ decreases rapidly toward shorter wavelengths for materials that are white in the visible but retains its high value for black materials such as FeO and Cr_2O_3. Small concentrations of FeO and Cr_2O_3 or other colored oxides can cause marked increases in the emittance of materials that are normally white. ε_λ for refractory materials varies little with temperature. (2) Refractory materials generally have a total emittance which is high (0.7 to 1.0) at ambient temperatures and decreases with increase in temperature; a change from 1,000 to 1,600°C may cause a decrease in ε of one-fourth to one-third. (3) The emittance and absorptance increase with increase in grain size over a grain-size range of 1–200 μm. (4) The ratio $\varepsilon/\varepsilon_n$ of hemispherical to normal emissivity of polished surfaces varies with refractive index from 1 at $n = 1$ to 0.95 at $n = 1.5$ (common glass) and back to 0.98 at $n = 3.5$. (5) The ratio $\varepsilon/\varepsilon_n$ for a surface composed of particulate matter which scatters isotropically varies with ε from 1 when $\varepsilon = 1$ to 0.8 when $\varepsilon = 0.07$. (6) The total absorptance shows a decrease with increase in temperature of the radiation source similar to the decrease in emittance with increase in the specimen temperature. Figure 4.3.1 shows the effect of the temperature of the radiation source on the absorptance of surfaces of various materials at room temperature. It will be noted that polished aluminum (line 15) and anodized aluminum (line 13), representative of metals and nonmetals, respectively, respond oppositely to a change in the temperature of the radiation source. The absorptance of surfaces for sunlight may be read from the right of Fig. 4.3.1, assuming sunlight to consist of blackbody radiation from a source at 10,440°R (5,800 K).

When T_2 is not too different from T_1, α_{12} may be expressed as $\varepsilon_1(T_2/T_1)^n$, with n determined from Fig. 4.3.1. For this case, Eq. (4.3.4) becomes

$$\dot{Q}_{1,\text{net}} = \sigma A_1 \varepsilon_{AV}(1 + n/4)(T_1^4 - T_2^4) \tag{4.3.6}$$

where ε_{AV} is evaluated at the arithmetic mean of T_1 and T_2.

Table 4.3.2 gives the emittance of various surfaces and emphasizes the variation possible in a single material. The values in the table apply, with a few exceptions, to normal radiation from the surface.

For opaque materials, the **reflectance** ρ is the complement of the absorptance. The directional distribution of the reflected radiation depends on the material, its degree of roughness or grain size, and if a metal, its state of oxidation. Polished surfaces of homogeneous materials reflect specularly. In contrast, the intensity of the radiation reflected from a **perfectly diffuse,** or **Lambert,** surface is independent of direction. The directional distribution of reflectance of many oxidized metals, refractory materials, and natural products approximates that of a perfectly diffuse reflector. A better model, adequate for many calculational purposes, is achieved by assuming that the total reflectance ρ is the sum of diffuse and specular components ρ_D and ρ_S (Hottel and Sarofim, p. 180).

Black Surface Enclosures   When several surfaces are present, the need arises for evaluating a geometric factor F, called the **direct-view factor.** Restriction is temporarily to black surfaces, the intensity from which is independent of angle of emission. Define F_{12} as the fraction of the radiation leaving surface A_1 in all directions which is intercepted by
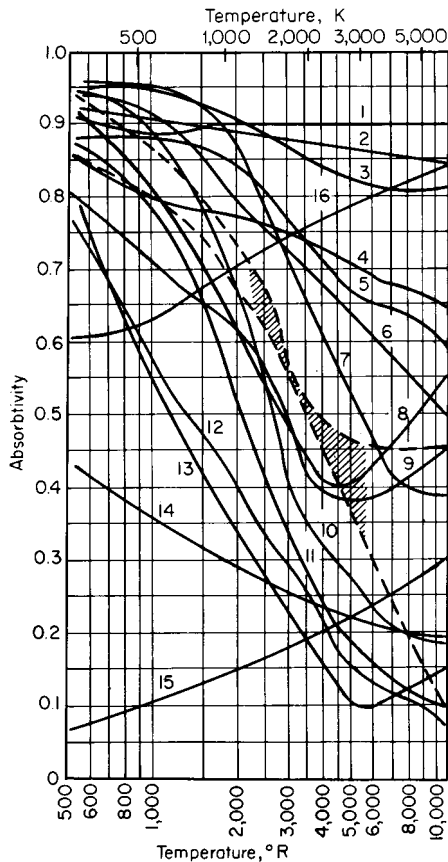
Fig. 4.3.1   Variation of absorptivity with temperature of radiation source. (1) Slate composition roofing; (2) linoleum, red-brown; (3) asbestos slate (asbestos use is obsolete, but may be encountered in existing construction); (4) soft rubber, gray; (5) concrete; (6) porcelain; (7) vitreous enamel, white; (8) red brick; (9) cork; (10) white Dutch tile; (11) white chamotte; (12) MgO, evaporated; (13) anodized aluminum; (14) aluminum paint; (15) polished aluminum; (16) graphite. The two dashed lines bound the limits of data for gray paving brick, asbestos paper (asbestos use is obsolete, but may be encountered in existing construction), wood, various cloths, plaster of paris, lithopone, and paper.

Table 4.3.2 Emissivity of Surfaces

Surface	Temp.,* °C	Emissivity*
Metals and their oxides		
Aluminum:		
Highly polished	230–580	0.039–0.057
Polished	23	0.040
Rough plate	26	0.055–0.07
Oxidized at 600°C	200–600	0.11–0.19
Oxide	280–830	0.63–0.26
Alloy 75ST	24	0.10
75ST, repeated heating	230–480	0.22–0.16
Brass:		
Highly polished	260–380	0.03–0.04
Rolled plate, natural	22	0.06
Rolled, coarse-emeried	22	0.20
Oxidized at 600°C	200–600	0.61–0.59
Chromium	40–540	0.08–0.26
Copper:		
Electrolytic, polished	80	0.02
Comm'l plate, polished	20	0.030
Heated at 600°C	200–600	0.57–0.57
Thick oxide coating	25	0.78
Cuprous oxide	800–1,100	0.66–0.54
Molten copper	1,080–1,280	0.16–0.13
Dow metal, cleaned, heated	230–400	0.24–0.20
Gold, highly polished	230–630	0.02–0.04
Iron and steel:		
Pure Fe, polished	180–980	0.05–0.37
Wrought iron, polished	40–250	0.28
Smooth sheet iron	700–1,040	0.55–0.60
Rusted plate	20	0.69
Smooth oxidized iron	130–530	0.78–0.82
Strongly oxidized	40–250	0.95
Molten iron and steel	1,500–1,770	0.40–0.45
Lead:		
99.96%, unoxidized	130–230	0.06–0.08
Gray, oxidized	24	0.28
Oxidized at 190°C	190	0.63
Mercury, pure clean	0–100	0.09–0.12
Molybdenum filament	730–2590	0.10–0.29
Monel metal, K5700		
Washed, abrasive soap	24	0.17
Repeated heating	230–875	0.46–0.65
Nickel and alloys:		
Electrolytic, polished	23	0.05
Electroplated, not polished	20	0.11
Wire	190–1,010	0.10–0.19
Plate, oxid. at 600°C	200–600	0.37–0.48
Nickel oxide	650–1,250	0.59–0.86
Copper-nickel, polished	100	0.06
Nickel-silver, polished	100	0.14
Nickelin, gray oxide	21	0.26
Nichrome wire, bright	50–1,000	0.65–0.79
Nichrome wire, oxide	50–500	0.95–0.98
ACI-HW (60Ni, 12Cr); firm black ox, coat	270–560	0.89–0.82
Platinum, polished plate	230–1,630	0.05–0.17
Silver, pure polished	230–630	0.02–0.03
Stainless steels:		
Type 316, cleaned	24	0.28
316, repeated heating	230–870	0.57–0.66
304, 42 h at 520°C	220–530	0.62–0.73
310, furnace service	220–530	0.90–0.97
Allegheny #4, polished	100	0.13
Tantalum filament	1,330–3,000	0.194–0.33
Thorium oxide	280–830	0.58–0.21
Tin, bright	24	0.04–0.06
Tungsten, aged filament	25–3,320	0.03–0.35
Zinc, 99.1%, comm'l, polished	230–330	0.05
Galv., iron, bright	28	0.23
Galv. gray oxide	24	0.28

Table 4.3.2 Emissivity of Surfaces (*Continued*)

Surface	Temp.,* °C	Emissivity*
Refractories, building materials, paints, misc.		
Alumina	260–680	0.6–0.33
Alumina, 50-μm grain size	1,010–1,570	0.39–0.28
Alumina-silica, cont'g	1,010–1,570	
0.4% Fe_2O_3		0.61–0.43
1.7% Fe_2O_3		0.73–0.62
2.9% Fe_2O_3		0.78–0.68
Al paints (vary with amount of lacquer body, age)	100	0.27–0.67
Asbestos	40–370	0.93–0.95
Calcium oxide	750–1,100	0.29–0.28
Candle soot; lampblack-waterglass	20–370	0.95 ± 0.01
Carbon plate, heated	130–630	0.81–0.79
Ferric oxide (Fe_2O_3)	500–900	0.8–0.43
Magnesium oxide, 1 μm	260–760	0.67–0.41
Oil layers		
Lube oil, 0.01 in on pol. Ni	20	0.82
Linseed, 1–2 coats on Al	20	0.56–0.57
Rubber, soft gray reclaimed	24	0.86
Silica, 3 μm	260–740	0.7–0.5
Misc. I: shiny black lacquer, planed oak, white enamel, serpentine, gypsum, white enamel paint, roofing paper, lime plaster, black matte shellac	21	0.87–0.91
Misc. II: glazed porcelain, white paper, fused quartz, polished marble, rough red brick, smooth glass, hard glossy rubber, flat black lacquer, water, electrographite	21	0.92–0.96

*When two temperatures and two emissivities are given they correspond, first to first and second to second, and linear interpolation is suggested.

surface A_2. Since the net interchange between A_1 and A_2 must be zero when their temperatures are alike, it follows that $A_1F_{12} = A_2F_{21}$. From the definition of F and Eq. (4.3.1),

$$A_1F_{12} = \int_{A1} \int_{\Omega} \frac{dA_1 \cos \theta_1 \, d\Omega_1}{\pi}$$

$$= \int_{A1} \int_{A2} \frac{dA_1 \cos \theta_1 \, dA_2 \cos \theta_2}{\pi r^2} \qquad (4.3.7)$$

where $dA \cos \theta$ is the projection of dA normal to r, the line connecting dA_1 and dA_2. The product A_1F_{12}, having the dimensions of area, will be called the **direct-interchange area** and be designated by $\overline{s_1s_2}$, sometimes for brevity by $\overline{12}$ ($\equiv \overline{21}$). Clearly, $\overline{11} + \overline{12} + \overline{13} + \cdots = A_1$; and when A_1 cannot ''see'' itself, $\overline{11} = 0$. Values of F or $\overline{ss}$ have been calculated for various surface arrangements.

Direct-View Factors and Direct Interchange Areas

CASE 1. Directly opposed parallel rectangles of equal dimensions, and with lengths of sides X and Y divided by separating distance z:

$$\overline{s_1s_2} \, (\equiv A_1F_{12} \equiv A_2F_{21}) = \frac{z^2}{2} \left[\frac{1}{2} \ln \frac{(1 + X^2)(1 + Y^2)}{1 + X^2 + Y^2} \right.$$
$$+ X\sqrt{1 + Y^2} \tan^{-1} \frac{X}{\sqrt{1 + Y^2}} + Y\sqrt{1 + X^2} \tan^{-1} \frac{Y}{\sqrt{1 + X^2}}$$
$$\left. - X \tan^{-1} X - Y \tan^{-1} Y \right]$$

See also Fig. 4.3.2.

CASE 2. Parallel circular disks with centers on a common normal and with radii R_1 and R_2 divided by separating distance z:

$$\overline{s_1s_2} \, (\equiv A_1F_{12} \equiv A_2F_{21}) = \frac{\pi z^2}{2} \left[1 + R_1^2 + R_2^2 \right.$$
$$\left. - \sqrt{(1 + R_1^2 + R_2^2)^2 - 4R_1^2R_2^2} \right]$$
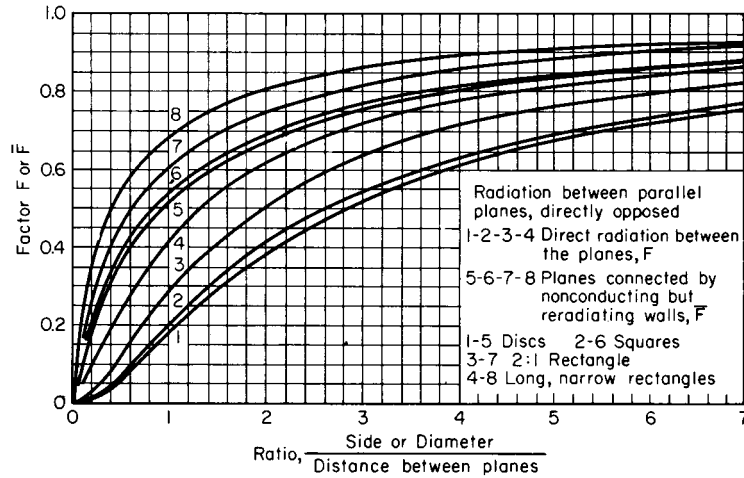
Fig. 4.3.2 Variation of the factor F or $\bar{F}$ for parallel planes directly opposed.

CASE 3. Rectangles in perpendicular planes of area A_1 and A_2, with a common edge l and with other dimension divided by $l = W_1$ and W_2:

$$\overline{s_1 s_2} \; (\equiv A_1 F_{12} \equiv A_2 F_{21})$$

$$= \frac{l^2}{\pi} \left(\frac{1}{4} \ln \frac{(1 + W_1^2)(1 + W_2^2)}{1 + W_1^2 + W_2^2} \left[\frac{W_1^2(1 + W_1^2 + W_2^2)}{(1 + W_1^2)(W_1^2 + W_2^2)} \right]^{W_1^2} \right.$$

$$\times \left. \left[\frac{W_2^2(1 + W_1^2 + W_2^2)}{(1 + W_2^2)(W_1^2 + W_2^2)} \right]^{W_2^2} \right]$$

$$\left. + W_1 \tan^{-1} \frac{1}{W_1} + W_2 \tan^{-1} \frac{1}{W_2} - \sqrt{W_1^2 + W_2^2} \tan^{-1} \frac{1}{\sqrt{W_1^2 + W_2^2}} \right)$$

CASE 4. Circular cylinder of radius r_1 surrounded by cylinder of radius r_2, both of equal length l and on a common axis:

$$A_1 = 2\pi r_1 l \qquad A_2 = 2\pi r_2 l$$

Let $r_1/l = R_1$; $r_2/l = R_2$; $[1/R_1^2 - (R_2/R_1)^2 + 1] = B$; $[1/R_1^2 + (R_2/R_1)^2 + 1] = D$; and $r_2/r_1 = R$.

$$\overline{s_1 s_2} \; (\equiv A_1 F_{12} \equiv A_2 F_{21})$$

$$= l^2 \left\{ R_1^2 \left[\sqrt{(D + 2)^2 - 4R^2} \cos^{-1} \frac{B}{DR} + B \sin^{-1} \frac{1}{R} - \frac{\pi}{2} D \right] \right.$$

$$\left. + 2R_1 \left(\pi - \cos^{-1} \frac{B}{D} \right) \right\}$$

$$\overline{s_2 s_2} \; (\equiv A_2 F_{22}) = l^2 R_1 \left\{ 2\pi(R - 1) + 4 \tan^{-1}(2R_1 \sqrt{R^2 - 1}) \right.$$

$$- \sqrt{4R^2 + \frac{1}{R_1^2}} \left(\frac{\pi}{2} + \sin^{-1} \frac{4(R^2 - 1) + 1/[R_1^2(1 - 2/R^2)]}{4(R^2 - 1) + 1/R_1^2} \right)$$

$$\left. + \frac{1}{R_1} \left[\sin^{-1} \left(1 - \frac{2}{R^2} \right) + \frac{\pi}{2} \right] \right\}$$

CASE 5. Two closed surfaces, one enclosing the other and neither having any negative curvature; A_1 is inside. Since $F_{12} = 1$,

$$\overline{s_1 s_2} \; (\equiv A_1 F_{12} \equiv A_2 F_{21}) = A_1$$

$$F_{21} = \frac{A_1}{A_2} \qquad F_{22} = 1 - \frac{A_1}{A_2}$$

CASE 6. Sphere of total inside area A_T; radiative exchange between sphere segments of areas A_1 and A_2. Application of Eq. (4.3.7) shows that, independent of relative position,

$$\overline{s_1 s_2} \; (\equiv A_1 F_{12} \equiv A_2 F_{21}) = \frac{A_1 A_2}{A_T} \qquad F_{12} = \frac{A_2}{A_T}$$

CASE 7. Two dimensional surfaces A_1 and A_2 per unit length normal to cross section, with each area defined by the length of stretched string, on inside face, between ends (i.e., elimination of negative curvature). Graphical exact solution: $\overline{s_1 s_2}$ (per unit normal length) = sum of lengths of crossed stretched strings between ends of A_1 and A_2 minus sum of uncrossed strings, all divided by 2. If an obstruction lies between A_1 and A_2, there may be two sets of strings to represent views on both sides of the obstruction, with results added. The relations for cases 8, 9, and 10 are the results of three among many applications of this principle.

CASE 8. Exchange among inside surfaces of hollow triangular shape of infinite length and areas A_1, A_2, and A_3:

$$\overline{s_1 s_2} \; (\equiv A_1 F_{12} \equiv A_2 F_{21}) = \frac{A_1 + A_2 - A_3}{2} \qquad F_{12} = \frac{A_1 + A_2 - A_3}{2A_1}$$

CASE 9. Exchange between two long parallel circular tubes of diameter D and center-to-center distance C, having areas A_{1a} and A_{1b} per unit length:

$$\overline{s_{1a} s_{1b}} \; (\text{per unit length}) = D \left[\sin^{-1} \frac{D}{C} + \sqrt{\left(\frac{C}{D}\right)^2 - 1} - \frac{C}{D} \right]$$

$$F_{1a \to 1b} = \frac{1}{\pi} \left[\sin^{-1} \frac{D}{C} + \sqrt{\left(\frac{C}{D}\right)^2 - 1} - \frac{C}{D} \right]$$

CASE 10. Exchange between a row of tubes and a plane parallel to it. Consider a unit length along tube axes, with single tube area $A_{1a} = \pi D$ and associated plane area $A_p = C$. A tube sees two tubes and two plane areas:

$$A_{1a} = 2\overline{s_{1a} s_{1b}} + 2\overline{s_{1a} s_p}$$

$$\overline{s_{1a} s_p} \; (\equiv \overline{s_p s_{1a}} \equiv A_p F_{p1}) = \frac{A_{1a}}{2} - \overline{s_{1a} s_{1b}}$$

Substituting from previous example (case 9) yields

$$F_{p1} = 1 - \frac{D}{C} \left[\sin^{-1} \frac{D}{C} + \sqrt{\left(\frac{C}{D}\right)^2 - 1} - \frac{\pi}{2} \right]$$

The value from case 10 appears as line 1 of Fig. 4.3.3. The same figure gives the fraction going to the second row. Additional curves in Fig. 4.3.3 can be obtained by considering the refractory backing as radiatively adiabatic, i.e., by assuming that the radiation that is not absorbed directly is reflected or reradiated, undergoing the same fractional absorption as the incoming beam. In a furnace chamber one zone of which is one or two rows of tubes backed by a refractory, one may visualize the zone as a continuous plane of area A_p at a temperature T_T,
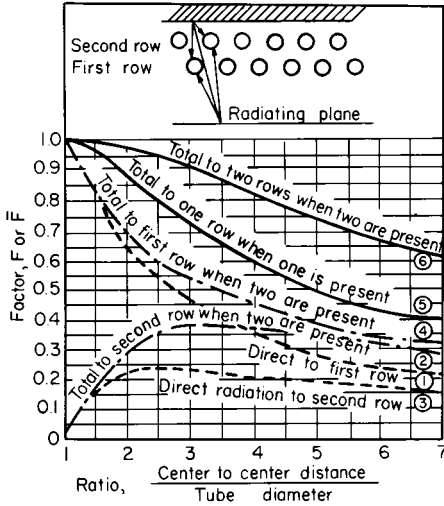
Fig. 4.3.3 Values of F or $\overline{F}$ for a plane parallel to rows of tubes.

the tube surface-temperature, and having an effective absorptivity or emissivity $\varepsilon(=\mathscr{F}_{pT})$ that is equal to the value read from Fig. 4.3.3, line 5 or 6; in total exchange area nomenclature, it is $(\overline{S_pS_T})_R/A_p$. Its complement is headed back toward the emitter, which is whatever faces the replaced tube zone—radiating gas or surfaces or a mixture of them.

When the tubes are gray,

$$\frac{A_p}{(\overline{S_pS_T})_R} = \frac{A_p}{(\overline{S_pS_T})_R}\Bigg)_{\substack{\text{black} \\ \text{tubes}}} + \frac{\rho_T}{\varepsilon_T} \qquad (4.3.8)$$

When $C/D = 2$, the treatment of a single tube row system with the tubes divided into two zones, front and rear half, reduces $(\overline{S_pS_T})_R$ or $\mathscr{F}_{pT}$ below the value given by Eq. (4.3.8) by only 1.7 percent (3 percent) when ε_T is 0.8 (0.6).

For other cases, see References.

The view factor F may often be evaluated from that for simpler configurations by the application of three principles: that of reciprocity, $A_iF_{ij} = A_jF_{ji}$; that of conservation, $\Sigma F_{ij} = 1$; and that due to Yamauti, showing that the exchange areas AF between two pairs of surfaces are equal when there is a one-to-one correspondence for all sets of symmetrically placed pairs of elements in the two surface combinations (Hottel and Sarofim, p. 60).

EXAMPLE. The exchange area between the two squares 1 and 4 of Fig. 4.3.4 is to be evaluated. The following exchange areas may be obtained from the values of F for common-side rectangles (case 3, direct-view factors): $\overline{13} = 0.24$, $\overline{24} = 2 \times 0.29 = 0.58$, $\overline{(1+2)(3+4)} = 3 \times 0.32 = 0.96$. Expression of $\overline{(1+2)(3+4)}$ in terms of its components yields $\overline{(1+2)(3+4)} = \overline{13} + \overline{14} + \overline{23} + \overline{24}$. And by the Yamauti principle $\overline{14} = \overline{23}$, since for every pair of elements in 1 and 4, there is a corresponding pair in 2 and 3. Therefore,

$$\overline{14} = [\overline{(1+2)(3+4)} - \overline{13} - \overline{24}]/2 = 0.07$$

Case 1 may be modified in the same way. Another example is the evaluation of AF for exchange between the outside of the smaller of two coaxial cylinders and the
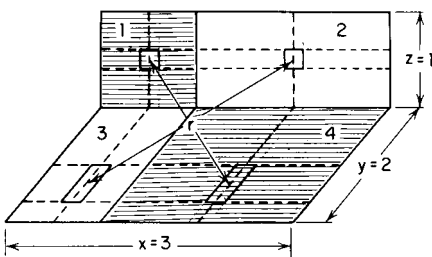
Fig. 4.3.4 Illustration of the Yamauti principle.

inside of the larger when they are *not* coextensive, given the view factor for coextensive cylinders (case 4).

Enclosures Containing Gray Source and Sink Surfaces, Refractory Surfaces, and No Absorbing Gas The calculation of interchange between a source and a sink under conditions involving successive multiple reflections from other source-sink surfaces in the enclosure, as well as reradiation from refractory surfaces, can become complicated. Let a **zone** of a furnace enclosure be an area small enough to make all elements of itself have substantially equivalent ''views'' of the rest of the enclosure. (In a furnace containing a symmetry plane, parts of a single zone would lie on either side of the plane.) Zones are of two classes, source-sink surfaces, designated by numerical subscripts and having areas $A_1, A_2, \ldots$ and emissivities $\varepsilon_1, \varepsilon_2, \ldots$; and surfaces at which the net radiant-heat flux is zero (fulfilled by the average refractory wall where difference between internal convection and external loss is minute compared with incident radiation), designated by letter subscripts starting with r, and having areas $A_r, A_s, \ldots$. It may be shown that the net radiation interchange between source-sink zones i and j is given by

$$\dot{Q}_{i=j} = \overline{S_iS_j}\sigma T_i^4 - \overline{S_jS_i}\sigma T_j^4 \qquad (4.3.9)$$

The term $\overline{S_iS_j}$ is called the **total interchange area** shared by areas A_i and A_j and depends on the shape of the enclosure and the emissivity and absorptivity of the source and sink zones. It is sometimes called $A_i\mathscr{F}_{ij}$. Restriction here is to gray source-sink zones, for which $\overline{S_iS_j} = \overline{S_jS_i}$; the more general case is treated elsewhere (Hottel and Sarofim, Chaps. 3 and 5).

Evaluation of the $\overline{SS}$'s that characterize an enclosure involves solution of a system of radiation balances on the surfaces. If at a surface the total **leaving flux density,** emitted plus reflected, is denoted by W, radiation balances take the form for source-sink surface j:

$$A_j\varepsilon_jE_j + \rho_j\sum_i \overline{(ij)}W_i = A_jW_j \qquad (4.3.10)$$

and for adiabatic surface r:

$$\sum_i \overline{(ir)}W_i = A_rW_r \qquad (4.3.11)$$

where ρ is reflectance and the summation is over all surfaces in the enclosure. These equations apply to surfaces which emit and reflect diffusely (i.e., their leaving intensity W_i/π is independent of its direction. Most nonmetallic, tarnished, or rough metal surfaces correspond reasonably well to this restriction (but see p. 4-72). In matrix notation, Eqs. (4.3.10) and (4.3.11) become

$$\begin{bmatrix} \overline{11}-\dfrac{A_1}{\rho_1} & \overline{12} & \cdots & \overline{1r} & \overline{1s} & \cdots \\ \overline{12} & \overline{22}-\dfrac{A_2}{\rho_2} & \cdots & \overline{2r} & \overline{2s} & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \overline{1r} & \overline{2r} & \cdots & \overline{rr}-A_r & \overline{rs} & \cdots \\ \overline{1s} & \overline{2s} & \cdots & \overline{rs} & \overline{ss}-A_s & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \end{bmatrix}\begin{bmatrix} W_1 \\ W_2 \\ \cdots \\ W_r \\ W_s \\ \cdots \end{bmatrix} = \begin{bmatrix} -\dfrac{A_1\varepsilon_1}{\rho_1}E_1 \\ -\dfrac{A_2\varepsilon_2}{\rho_2}E_2 \\ \cdots \\ 0 \\ 0 \\ \cdots \end{bmatrix}$$

$$(4.3.12)$$

This represents a system of simultaneous equations equal in number to the number of rows of the square matrix. Each equation consists, on the left, of the sum of the products of the members of a row of the square matrix and the corresponding members of the W-column matrix, and, on the right, of the member of that row in the third matrix. With the above set of equations solved for W_i, the net flux at any surface A_i is given by

$$\dot{Q}_{i,\text{net}} = \frac{A_1\varepsilon_i}{\rho_i}(E_i - W_i) \qquad (4.3.13)$$

Refractory temperature is obtained from $W_r = E_r = \sigma T_r^4$.

The more general use of Eq. (4.3.12) is to obtain the set of total-interchange areas $\overline{SS}$ which constitute a complete description of the

effect of shape, size, and emissivity on radiative flux, independent of the presence or absence of other transfer mechanisms. It may be shown that

$$\overline{S_iS}_j \equiv \overline{S_jS}_i \equiv A_i\mathscr{F}_{ij} = \frac{A_i\varepsilon_i}{\rho_i}\frac{A_j\varepsilon_i}{\rho_j}\left(-\frac{D_{ij}'}{D}\right) \quad (4.3.14)$$

where D is the determinant of the square coefficient matrix in Eq. (4.3.12) and D_{ij}' is the cofactor of its ith row and jth column, or -1^{i+j} times the minor of D formed by crossing out the ith row and jth column.

As an example, consider radiation between two surfaces A_1 and A_2 which together form a complete enclosure. Equation (4.3.12) takes the form

$$A_1\mathscr{F}_{12} = \frac{A_1\varepsilon_1}{\rho_1}\frac{A_2\varepsilon_2}{\rho_2}\frac{\overline{12}}{\begin{vmatrix} \overline{11} - \dfrac{A_1}{\rho_1} & \overline{12} \\ \overline{12} & \overline{22} - \dfrac{A_2}{\rho_2} \end{vmatrix}} \quad (4.3.15)$$

Only one direct-view factor F_{12} or direct exchange area $\overline{12}$ is needed because F_{11} equals $1 - F_{12}$ and F_{22} equals $1 - F_{21}$ or $1 - F_{12}A_1/A_2$. Then $\overline{11}$ equals $A_1 - \overline{12}$, and $\overline{22}$ equals $A_2 - \overline{21}$. With the above substitutions, Eq. (4.3.15) becomes

$$A_1\mathscr{F}_{12} = \frac{A_1}{1/F_{12} + 1/\varepsilon_1 - 1 + (A_1/A_2)(1/\varepsilon_2 - 1)} \quad (4.3.16)$$

Special cases include:
1. Parallel plates, large compared to clearance. Substitution of $F_{12} = 1$ and $A_1 = A_2$ gives

$$A_1\mathscr{F}_{12} = \frac{A_1}{1/\varepsilon_1 + 1/\varepsilon_2 - 1} \quad (4.3.17)$$

2. Sphere of area A_1 concentric with surrounding sphere of area A_2. $F_{12} = 1$. Then

$$A_1\mathscr{F}_{12} = \frac{A_1}{1/\varepsilon_1 + (A_1/A_2)(1/\varepsilon_2 - 1)} \quad (4.3.18)$$

3. Body of surface A_1 having no negative curvature, surrounded by very much larger surface A_2. $F_{12} = 1$ and $A_1/A_2 \to 0$. Then

$$\mathscr{F}_{12} = \varepsilon_1 \quad (4.3.19)$$

Many furnace problems are adequately handled by dividing the enclosure into but two source-sink zones A_1 and A_s, and any number of no-flux zones, $A_r, A_s, \ldots$. For this case Eq. (4.3.14) yields

$$\frac{1}{\overline{S_1S_2}}\left(\equiv\frac{1}{\overline{S_2S_1}}\right) = \frac{1}{A_1}\left(\frac{1}{\varepsilon_1} - 1\right)$$
$$+ \frac{1}{A_2}\left(\frac{1}{\varepsilon_2} - 1\right) = \frac{1}{(\overline{S_1S_2})_B} \quad (4.3.20)$$

Here the expression $(\overline{S_1S_2})_B [\equiv (\overline{S_2S_1})_B]$ represents the total interchange area for the limiting case of a black source and black sink (the refractory emissivity is of no moment). The factor $(\overline{S_1S_2})_B/A_1$, called $\overline{F}_{12}$, is known exactly for a few geometrically simple cases and may be approximated for others. If A_1 and A_2 are equal parallel disks, squares, or rectangles, connected by nonconducting but reradiating refractory walls, then $\overline{F}$ is given by Fig. 4.3.2, lines 5 to 8. If A_1 represents an infinite plane and A_2 is one or two rows of infinite parallel tubes in a parallel plane, and if the only other surface is a refractory surface behind the tubes, $\overline{F}_{12}$ is given by line 5 or 6 of Fig. 4.3.3. If an enclosure may be divided into several radiant-heat sources or sinks A_1, A_2, etc., and the rest of the enclosure (reradiating refractory surface) may be lumped together as A_r at a uniform temperature T_r, then the total interchange area for zone pairs in the black system is given by

$$(\overline{S_1S_2})_B(\equiv A_1\overline{F}_{12}) = \overline{12} + \frac{(\overline{1r})\,(\overline{r2})}{A_r - \overline{rr}} \quad (4.3.21)$$

For the two-source-sink-zone system to which Eq. (4.3.20) applies, Eq. (4.3.21) simplifies to $(\overline{S_1S_2})_B = \overline{12} + 1/[1/\overline{1r} + 1/(\overline{2r})]$; and if A_1 and A_2 each can see none of itself, there is further simplification to

$$(\overline{S_1S_2})_B = \overline{12} + \frac{1}{1/(A_1 - \overline{12}) + 1/(A_2 - \overline{12})}$$
$$= \frac{A_1A_2 - (\overline{12})^2}{A_1 + A_2 - 2(\overline{12})} \quad (4.3.22)$$

which necessitates the evaluation of but one direct-view factor F.

Equation (4.3.20) covers many problems of radiant heat interchange between source and sink in furnace enclosures involving no radiating gas. The error due to single zoning of source and sink is small even if the "views" of the enclosure from different parts of each zone are quite different, provided the emissivity is fairly high; the error in $\overline{F}$ is zero if it is obtainable from Fig. 4.3.2 or 4.3.3, small if Eq. (4.3.21) is used and the variation in temperature over the refractory is small. Approach to any desired accuracy can be made by use of Eq. (4.3.14) with division of the surfaces into more zones.

From the definitions of F, $\overline{F}$, and $\mathscr{F}$ or of $\overline{ss}$, $(\overline{SS})_B$, and $\overline{SS}$ it is to be noted that

$$\left.\begin{array}{l} F_{11} + F_{12} + \cdots + F_{1r} + F_{1s} + \cdots = 1 \\ \overline{F}_{11} + \overline{F}_{12} + \cdots \qquad\qquad\quad = 1 \\ \mathscr{F}_{11} + \mathscr{F}_{12} + \cdots \qquad\qquad\quad = \varepsilon_1 \end{array}\right\}$$

$$\overline{s_1s_2} + \overline{s_1s_2} + \cdots + \overline{s_1s_r} + \overline{s_1s_s} + \cdots = A_1$$
or
$$(\overline{S_1S_1})_B + (\overline{S_1S_2})_B + \cdots = A_1$$
$$\overline{S_1S_1} + \overline{S_1S_2} + \cdots = A_1\varepsilon_1$$

EXAMPLE. A furnace chamber of rectangular parallelpipedal form is heated by the combustion of gas inside vertical radiant tubes lining the side walls. The tubes are on centers 2.4 diameters apart. The stock forms a continuous plane on the hearth. Roof and end walls are refractory. Dimensions are shown in Fig. 4.3.5. The radiant tubes and stock are gray bodies having emissivities 0.8 and 0.9, respectively. What is the net rate of heat transmission to the stock by radiation when the mean temperature of the tube surface is 1,500°F (1,089 K) and that of the stock is 1,200°F (922 K)?
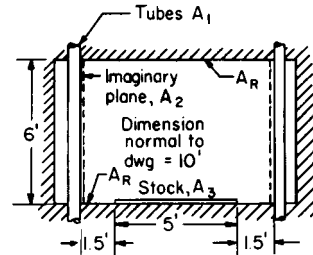
Fig. 4.3.5   Dimensions of a furnace chamber.

This problem must be broken up into two parts, first considering the walls with their refractory-backed tubes. To imaginary planes A_2 of area 6×10 ft located parallel to and inside the rows of radiant tubes, the tubes emit radiation $\sigma T_1^4A_1\mathscr{F}_{12}$, which equals $\sigma T_1^4A_2\mathscr{F}_{21}$. To find $\mathscr{F}_{21}$ use Fig. 4.3.3, line 5, from which $\overline{F}_{21} = 0.81$. Then from Eq. (4.3.20).

$$\mathscr{F}_{21} = 1/[(1/0.81) + (1/1 - 1) + (2.4/\pi)(1/0.8 - 1)] = 0.702$$

This amounts to saying that the system of refractory-backed tubes is equal in radiating power to a continuous plane A_2 replacing the tubes and refractory back of them, having a temperature equal to that of the tubes and an equivalent or effective emissivity of 0.702.

The new simplified furnace now consists of an enclosure formed by two 6×10 ft radiating side walls (area A_2, of emissivity 0.702), a 5×10 ft receiving plane on the floor (A_3), and refractory surfaces (A_R) to complete the enclosure (ends, roof, and floor side strips); the desired heat transfer is

$$q_{2=3} = \sigma(T_1^4 - T_3^4)A_2\mathscr{F}_{23}$$

To evaluate $\mathscr{F}_{23}$, start with the direct interchange factor F_{23}. $F_{23} = F$ from A_2 to $(A_3 + $ a strip of A_R alongside A_3 which has a common edge with A_2) minus F from

A_2 to the strip only. These two F's may be evaluated from case 3 for direct-view factors. For the first F, $Y/X = 6/10$, $Z/X = 6.5/10$, $F = 0.239$; for the second F, $Y/X = 6/10$, $Z/X = 1.5/10$, $F = 0.100$. Then $F_{23} = 0.239 - 0.10 = 0.139$. Now $\overline{F}$ may be evaluated. From Eq. (4.3.21) et seq.,

$$A_2\overline{F}_{23} = \overline{23} + \frac{1}{1/2r + 1/3r}$$

$$\overline{F}_{23} = F_{23} + \frac{1}{1/F_{2r} + (A_2/A_3)(1/F_{3r})}$$

Since A_2 ''sees'' A_r, A_3, and some of itself (the plane opposite), $F_{2r} = 1 - F_{22} - F_{23}$. F_{22}, the direct interchange factor between parallel 6×10 ft rectangles separated by 8 ft, may be taken as the geometric mean of the factors for 6-ft squares separated by 8 ft, and 10-ft squares separated by 8 ft. These come from Fig. 4.3.2, line 2, according to which $F_{22} = \sqrt{0.13 \times 0.255} = 0.182$. Alternatively, the first of the 10 cases listed above under ''Direct-View Factors'' may be used. Then $F_{2r} = 1 - 0.182 - 0.139 = 0.679$. The other required direct factor is $F_{3r} = 1 - F_{32} = 1 - F_{23}A_2/A_3 = 1 - 0.139 \times {}^{120}/{}_{50} = 0.666$. Then $\overline{F}_{23} = 0.139\ \{1/[(1/0.679) + (120/50)(1/0.666)]\} = 0.336$. Having $\overline{F}_{23}$, we may now evaluate the factor $\mathscr{F}_{23}$ using Eq. (4.3.20) with $A_1 \rightarrow A_2$, $A_2 \rightarrow A_3$, and $[\overline{S_1S_2}]_{13} \rightarrow A_2\ \overline{F}_{23}$.

$$\mathscr{F}_{23} = \frac{1}{1/0.336 + 1/0.702 - 1 + (120/50)(1/0.9 - 1)}$$

$$= 0.273$$

$$\dot{Q}_{net} = \sigma(T_1^4 - T_3^4)A_2\mathscr{F}_{23} = 0.171(19.6^4 - 16.6^4)(120)(0.273)$$

$$= 402,000 \text{ Btu/h}$$

In SI units

$$\dot{Q}_{net} = 5.67(10.89^4 - 9.22^4)(120 \times .3048^2)(0.273) = 118,000 \text{ W}$$

A result of interest is obtained by dividing the term $A_2\mathscr{F}_{23}(120 \times 0.273$, or 32.7 ft^2) by the actual area A_1 of the radiating tubes [$(\pi/2.4) \times 60 \times 2 = 157$ ft^2]. This is $32.7/157 = 0.208$; i.e., the net radiation from a tube to the stock is 20.8 percent as much as if the tube were black and completely surrounded by black stock.

Enclosures of Surfaces That Are Not Diffuse Reflectors The total interchange-area concept has been generalized to include surfaces the reflectance ρ of which can be divided into a diffuse, or Lambert-reflecting, component ρ_D and a specular component ρ_S independent of angle of incidence, with $\varepsilon + \rho_S + \rho_D = 1$. In application to concentric spheres or infinite cylinders, with A_1 the inner surface, the method yields (Hottel and Sarofim, p. 181)

$$A_1\mathscr{F}_{12} \equiv \overline{S_1S_2}$$

$$= \frac{1}{\dfrac{1}{A_1\varepsilon_1} + \dfrac{1}{A_2}\left(\dfrac{1}{\varepsilon_2} - 1\right) + \dfrac{\rho_{S2}}{1 - \rho_{S2}}\left(\dfrac{1}{A_1} - \dfrac{1}{A_2}\right)} \quad (4.3.23)$$

When there is no specular reflectance, the third term in the denominator drops out, in agreement with Eq. (4.3.18). When the reflectance is exclusively specular, the denominator becomes $1/(A_1\varepsilon_1) + \rho_{S2}/[A_1(1 - \rho_{S2})]$, easily derivable from first principles.

RADIATION FROM FLAMES, COMBUSTION PRODUCTS, AND PARTICLE CLOUDS

The radiation from a flame consists of (1) radiation throughout the spectrum from burning soot particles of microscopic and submicroscopic dimensions, from suspended larger particles of coal, coke, or ash, all contributing to what is spoken of as flame luminosity, (2) infrared radiation, mostly from the water vapor and carbon dioxide in the hot gaseous combustion products, and (3) nonequilibrium radiation associated with the combustion process itself, called chemiluminescence and not a significant contributor to the total radiation. A major problem is the effect of the shape of the emitting volume on the radiative flux; this will be considered first.

Mean Beam Lengths Evaluation of radiation from a nonisothermal volume is beyond the scope of this section (see Hottel and Sarofim, Chap. 11). If a volume emitter is isothermal and at a temperature T, the ratio of the emission from an element of its volume subtending the solid angle $d\Omega$ at a receiver element dA, and making the angle θ with the

normal thereto, to blackbody radiation arriving from within the same solid angle is called the **gas emissivity.** Clearly, ε depends on the path length L through the volume to dA. A hemispherical volume radiating to a spot on the center of its base represents the case in which L is independent of direction. Flux at that spot relative to hemispherical blackbody flux is thus an alternative way to visualize emissivity. The flux density to an area of interest on the envelope of an emitter volume of any shape can be matched by that at the base of a hemispherical volume of some radius L, which will be called the **mean beam length.** It is found that, although the ratio of L to a characteristic dimension D of the shape varies with opacity, the variation is small enough for most engineering purposes to permit use of a constant ratio, L_M/D, where L_M is the **average mean beam length.** L_M can be defined to apply either to a spot on the envelope or to any finite portion of its area. An important limiting case is that of opacity approaching zero ($pD \rightarrow 0$, where p = partial pressure of the emitter constituent). For this case, L (called L_0) equals $4 \times$ ratio of gas volume to bounding area when interest is in radiation to the entire envelope. For the range of pD encountered in practice, L (now L_M) is always less. For various shapes, 0.8 to 0.95 times L_0 has been found optimum (see Table 4.3.3); for shapes not reported in Table 4.3.3, a factor of 0.88 (or $L_M = 0.88L_0 = 3.5V/A$) is recommended.

Soot luminosity is important where combustion occurs under such conditions that the hydrocarbons in the flame are subject to heat in the absence of sufficient air well mixed on a molecular scale. Because soot particles are small relative to the wavelength of radiation of interest (diameters 20 to 140 nm), the monochromatic emissivity ε_λ depends on the total particle volume per unit volume of space f_v, regardless of particle size. It is given by

$$\varepsilon_\lambda = 1 - e^{-Kf_vL/\lambda}$$

where L is the path length.

Use of the perfect gas law and a material balance enables the restatement of the above as

$$\varepsilon_\lambda = 1 - e^{-KPSL/(\lambda T)} \quad (4.3.24)$$

where P is the total pressure, atm, and S is the mole fraction of soot in the gas. Here S depends on the fractional conversion of f_c of the fuel carbon to soot, and it is the mole fraction, wet basis, of carbon in gaseous form (CO_2, CO, CH_4, etc.) times $f_c/(1 - f_c)$ or, with negligible error, times f_c, which is a very small number (more later on this). Evaluation of K is complex, and its numerical value depends somewhat on the age of the soot, the temperature at which it is formed, and its hydrogen content. It is recommended that $K = 0.526$ [K/atm] be used in the absence of specific information on the soot in question.

The total emissivity of soot ε_s is obtained by integration over the wavelength spectrum (Felske and Tien, *Comb. Sci. & Tech.,* **7,** no. 2, 1973), giving

$$\varepsilon_s = 1 - \frac{15}{4}\ [\psi^{(3)}(1 + KPSL/c_2)] \quad (4.3.25)$$

where $\psi^{(3)}(x)$ is the pentagamma function of x. It may be shown that an excellent approximation to Eq. (4.3.25) is

$$\varepsilon_s = 1 - (1 + 34.9SPL)^{-4} \quad (4.3.26)$$

where PL is in atm $\cdot$ m. The error is less the lower ε_s and is only 0.5 percent at $\varepsilon_s = 0.5$; 0.8 percent at 0.67. Expression of ε_s in e-power form is feasible but of lower accuracy than Eq. (4.3.25) or (4.3.26). In that form, with L in metres,

$$\varepsilon_s = 1 - e^{-143SPL} \pm 8\% \quad (4.3.27)$$

There is at present no method of predicting soot concentration of a luminous flame analytically; reliance must be placed on experimental measurement on flames similar to that of interest. Visual observation is misleading; a flame so bright as to hide the wall behind it may be far from a ''black'' radiator. The International Flame Foundation at Ijmuiden has recorded data on many luminous flames from gas, oil, and coal (see *Jour. Inst. Fuel,* 1956–present).

Table 4.3.3   Mean Beam Lengths for Volume Radiation

Shape	Characteristic dimension D	L_0/D	L_M/D
Sphere	Diameter	0.67	0.63
Infinite cylinder	Diameter	1	0.94
Semi-infinite cylinder, radiating to:			
Center of base	Diameter	1	0.90
Entire base	Diameter	0.81	0.65
Right-circle cylinder, ht = diam, radiating to:			
Center of base	Diameter	0.76	0.71
Whole surface	Diameter	0.67	0.60
Right-circle cylinder, ht = 0.5 diam, radiating to:			
End	Diameter	0.47	0.43
Side	Diameter	0.52	0.46
Total surface	Diameter	0.50	0.45
Right-circle cylinder, ht = 2 × diam, radiating to:			
End	Diameter	0.73	0.60
Side	Diameter	0.82	0.76
Total surface	Diameter	0.80	0.73
Infinite cylinder, half-circle cross section, radiating to spot on middle of flat side	Radius		1.26
Rectangular parallelepipeds			
1:1:1 (cube)	Edge	0.67	0.60
1:1:4, radiating to:			
1 × 4 face	Shortest edge	0.90	0.82
1 × 1 face	Shortest edge	0.86	0.71
Whole surface	Shortest edge	0.89	0.81
1:2:6, radiating to:			
2 × 6 face	Shortest edge	1.18	
1 × 6 face	Shortest edge	1.24	
1 × 2 face	Shortest edge	1.18	
Whole surface	Shortest edge	1.2	
Infinite parallel planes	Clearance	2.00	1.76
Space outside infinite bank of tubes, centers on equilateral triangles; tube diam = clearance	Clearance	3.4	2.8
Same, except tube diam = 0.5 clearance	Clearance	4.45	3.8
Same, except tube centers on squares, diam = clearance	Clearance	4.1	3.5

The chemical kinetics and fluid mechanics of soot burnout have not progressed far enough to evaluate the soot fraction f_c for relatively complex systems. Additionally, the soot in a combustion chamber is highly localized, and a mean value is needed for calculation of the radiative heat transfer performance of the chamber. On the basis of limited experience with fitting data to a model, the following procedure is recommended when total combustion chamber performance is being estimated: (1) When pitch or a highly aromatic fuel is burned, 1 percent of the fuel carbon appears as soot. This produces values of ε_s of 0.4 to 0.5 and ε_{G+s} of 0.6 to 0.7. These values are lower than some measurements on pitch flames, but the measurements are usually taken through the flame at points of high luminosity. (2) When no. 2 fuel oil is burned, ⅓ percent of the fuel carbon appears as soots, but that number varies greatly with burner design. (3) When natural gas is burned, any soot contribution to emissivity may be ignored. Admittedly the numbers given should be functions of burner design and excess air, and they should be considered tentative, subject to change when good data show they are off target.

Clouds of Large Black Particles   The emissivity of a cloud of particles depends on their area projected along the line of sight. The projected area per unit volume of space is the projected area A of a particle times the particle number concentration c, or the volume fraction f_v of space occupied by particles times b/d, the projected-surface/volume ratio, where d is the characteristic dimension. [For any randomly oriented particles without dimples, $A/$(total area) is ¼; for spheres, $b = ³⁄₂$.] The emissivity of a particle cloud is then given by the alternative formulations

$$\varepsilon = 1 - e^{-bf_vL/d} = 1 - e^{-cAL} \qquad (4.3.28)$$

As an example, consider heavy fuel oil ($CH_{1.5}$, s.g. 0.95) atomized to a surface mean particle diameter of d μm, burned with 20 percent excess

air to produce coke residue particles having the original drop diameter, and suspended in combustion products at 1,500 K. From stoichiometry, $f_v = 1.27 \times 10^{-5}$. For spherical particles $b = ³⁄₂$, and the flame emissivity due to the particles along a path L will be $1 - e^{-1.9 \times 10^{-2}L/d}$. With 200-$\mu$m particles and an L of 3 m, the particle contribution to emissivity will be 0.25. Soot luminosity will increase this; particle burnout will decrease it. The combined emissivity due to several kinds of emitters will be treated later. The correction for nonblackness of the particles is complicated by multiple scatter of the radiation reflected by each particle. The emissivity ε_M of a cloud of gray particles of individual surface emissivity ε_1 can be estimated by the use of Eq. (4.3.28) with its exponent multiplied by ε_1 if the optical thickness cAL does not exceed about 2.

Gaseous Combustion Products   Radiation from water vapor and carbon dioxide occurs in spectral bands in the infrared. Its magnitude is 3 to 10 times that of convection at furnace temperatures. It depends on gas temperature T_G, on the partial pressure-beam length products p_wL and p_cL (subscripts w and c refer to water vapor and carbon dioxide), and to a much lesser extent on total and partial pressure. The gas emissivity ε_G is the sum of the separate contributions due to H_2O and CO_2, corrected for pressure broadening of the spectral bands and for band overlap (Hottel and Sarofim, Chap. 6). The elaborate calculations can be combined for a restricted set of conditions, here taken to be the practically important cases of 1-atm total pressure and partial pressures representative of fossil fuel combustion in air. In the range of furnace operating conditions the product $\overline{\varepsilon_G T_G}$ varies much less than ε_G with T_G, and $\overline{\varepsilon_G T_G}$ depends primarily on $(p_w + p_c)L$, much less on $p_w/(p_w + p_c)$, and so little on T_G as to permit linear interpolation between widely separated T_G's. An equation of the form

$$\log \overline{\varepsilon_G T_G} = a_0 + a_1 \log pL + a_2 \log^2 pL + a_3 \log^3 pL \qquad (4.3.29)$$

where p is the sum of partial pressures $p_w + p_c$ atm and L is the mean beam length, has been found capable of fitting emissivity data over a 1000-fold range of pL, from 0.01 to 10 m · atm (0.03 to 30 ft · atm).

Table 4.3.4, section 2, gives values of the constants representing the results of an averaging of all the available total and integrated spectral data on CO_2 and H_2O, together with corrections for spectral band broadening and overlap. Equation (4.3.29) represents the original data with a precision greater than their accuracy. The constants are given for computation in either metres and kelvins or feet and degrees Rankine for mixtures, in nonradiating gases, of water vapor alone, CO_2 alone, and four p_w/p_c mixtures. Four suffice, since a change halfway from one mixture ratio to the adjacent one changes the emissivity by a maximum of only 5 percent; linear interpolation may be used if necessary. The constants are given for only three temperatures, which is adequate for linear interpolation since $\overline{\varepsilon_G T}$ changes a maximum of only one-sixth due to a change from one temperature base halfway to the adjacent one. Based on metre atmospheres and kelvins, the interpolation relation, with T_H and T_L representing the higher and lower base temperatures bracketing T, and with the brackets in the term $[A(x)]$ indicating that the parentheses refer not to a multiplier but to an argument, is

$$\overline{\varepsilon_G T_G} = \frac{[\overline{\varepsilon_G T_H}(pL)](T_G - T_L) + [\overline{\varepsilon_G T_L}(pL)](T_H - T_G)}{500} \quad (4.3.30)$$

Extrapolation to a temperature which is above the highest or below the lowest of the three base temperatures in Table 4.3.4 uses the same

Table 4.3.4   Emissivity of ε_G of H_2O-CO_2 Mixtures
Section 1: Limited range for furnaces, valid over 25-fold range of $p_{w+c}L$, 0.046–1.15 m · atm (0.15–3.75 ft · atm)

p_w/p_c	0		0.5		1		2		3		∞	
$\dfrac{p_w}{p_w + p_c}$	0		⅓(0.2–0.42)		½(0.42–0.6)		⅔(0.6–0.7)		¾(0.7–0.8)		1	
	CO_2 only		Corresponding to $(CH)_x$, covering coal, heavy oils, pitch		Corresponding to $(CH_2)_x$, covering distillate oils, paraffins, olefines		Corresponding to CH_4, covering natural gas and refinery gas		Corresponding to $(CH_6)_x$, covering future high-H_2 fuels		H_2O only	

Constants b and n of equation $\overline{\varepsilon_G T} = b(pL - 0.015)^n$, pL in m · atm, T in K

T, K	b	n	b	n	b	n	b	n	b	n	b	n
1,000	188	0.209	384	0.33	416	0.34	444	0.34	455	0.35	416	0.400
1,500	252	0.256	448	0.38	495	0.40	540	0.42	548	0.42	548	0.523
2,000	267	0.316	451	0.45	509	0.48	572	0.51	594	0.52	632	0.640

Constants b and n of equation $\overline{\varepsilon_G T} = b(pL - 0.05)^n$, pL in ft · atm, T in °R

T, °R	b	n	b	n	b	n	b	n	b	n	b	n
1,800	264	0.209	467	0.33	501	0.34	534	0.34	541	0.35	466	0.400
2,700	335	0.256	514	0.38	555	0.40	591	0.42	600	0.42	530	0.523
3,600	330	0.316	476	0.45	519	0.48	563	0.51	577	0.52	532	0.640

Section 2: Full range, valid over 2000-fold range of $p_{w+c}L$, 0.005–10.0 m · atm (0.016–32.0 ft · atm)
Constants of equation, $\log \overline{\varepsilon_G T} = a_0 + a_1 \log pL + a_2 \log^2 pL + a_3 \log^3 pL$

$\dfrac{p_w}{p_c}$	$\dfrac{p_w}{p_w + p_c}$	T, K	a_0	a_1	a_2	a_3	T, °R	a_0	a_1	a_2	a_3
					pL in m · atm, *T* in K				*pL* in ft · atm, *T* in °R		
0	0	1,000	2.2661	0.1742	−0.0390	0.0040	1,800	2.4206	0.2176	−0.0452	0.0040
		1,500	2.3954	0.2203	−0.0433	0.00562	2,700	2.5248	0.2695	−0.0521	0.00562
		2,000	2.4104	0.2602	−0.0651	−0.00155	3,600	2.5143	0.3621	−0.0627	−0.00155
½	⅓	1,000	2.5754	0.2792	−0.0648	0.0017	1,800	2.6691	0.3474	−0.0674	0.0017
		1,500	2.6461	0.3418	−0.0685	−0.0043	2,700	2.7074	0.4091	−0.0618	−0.0043
		2,000	2.6504	0.4279	−0.0674	−0.0120	3,600	2.6686	0.4879	−0.0489	−0.0120
1	½	1,000	2.6090	0.2799	−0.0745	−0.0006	1,800	2.7001	0.3563	−0.0736	−0.0006
		1,500	2.6862	0.3450	−0.0816	−0.0039	2,700	2.7423	0.4261	−0.0756	−0.0039
		2,000	2.7029	0.4440	−0.0859	−0.0135	3,600	2.7081	0.5210	−0.0650	−0.0135
2	⅔	1,000	2.6367	0.2723	−0.0804	0.0030	1,800	2.7296	0.3577	−0.0850	0.0030
		1,500	2.7178	0.3386	−0.0990	−0.0030	2,700	2.7724	0.4384	−0.0944	−0.0030
		2,000	2.7482	0.4464	−0.1086	−0.0139	3,600	2.7461	0.5474	−0.0871	−0.0139
3	¾	1,000	2.6432	0.2715	−0.0816	0.0052	1,800	2.7359	0.3599	−0.0896	0.0052
		1,500	2.7257	0.3355	−0.0981	0.0045	2,700	2.7811	0.4403	−0.1051	0.0045
		2,000	2.7592	0.4372	−0.1122	−0.0065	3,600	2.7599	0.5478	−0.1021	−0.0065
∞	1	1,000	2.5995	0.3015	−0.0961	0.0119	1,800	2.6720	0.4102	−0.1145	0.0119
		1,500	2.7083	0.3969	−0.1309	0.00123	2,700	2.7238	0.5330	−0.1328	0.00123
		2,000	2.7709	0.5099	−0.1646	−0.0165	3,600	2.7215	0.6666	−0.1391	−0.0165

NOTE: Values of $p_w/(p_w + p_c)$ of ⅓, ½, ⅔, ¾ may be used to cover the ranges 0.2–0.42, 0.42–0.6, 0.6–0.7, and 0.7–0.8, respectively, with a maximum error in ε_G of 5 percent at $pL = 6.5$ m · atm, less at lower pL's. Linear interpolation reduces the error generally to less than 1 percent. Linear interpolation or extrapolation on T introduces an error generally below 2 percent, less than the accuracy of the original data.

formulation, but one of the terms becomes negative. Linearization on the constants a_0 to a_3 rather than on $\overline{\varepsilon_G T}$ may be preferable if fuel quality is unchanging.

When pL lies in the 25-fold range of 0.046 to 1.15 m · atm (0.15 to 3.75 ft · atm), adequate for furnaces, a much simpler two-constant relation is adequate.

$$\overline{\varepsilon_G T} = \begin{cases} b(pL - 0.015)^n & \text{with } T = \text{K}, \ pL = \text{m} \cdot \text{atm} \\ b(pL - 0.05)^n & \text{with } T = {}^\circ\text{R}, \ pL = \text{ft} \cdot \text{atm} \end{cases}$$

The constants are given in Table 4.3.4, section 1.

Combined Radiation from Gases and Suspended Solids

The total emissivity of gases and suspended solids is less than the sum of the separate contributions because of interference between overlapping spectral emissions. The spectral overlap of H_2O and CO_2 radiation has been taken into account by the constants of Table 4.3.4 used for obtaining ε_G. Additional overlap occurs when soot emissivity ε_s is added. If the emission bands of water vapor and CO_2 were randomly placed in the spectrum and soot radiation were gray, the combined emissivity would be $\varepsilon_G + \varepsilon_s$ minus an overlap correction $\varepsilon_G\varepsilon_s$. Monochromatic soot emissivity is higher as the wavelength gets shorter, and in a highly sooted flame at 1,500 K half the soot emission lies below 2.5 μm where H_2O and CO_2 emission is negligible. Then the correction $\varepsilon_G\varepsilon_s$ must be reduced, and the following is recommended:

$$\varepsilon_{G+s} = \varepsilon_G + \varepsilon_s - M\varepsilon_G\varepsilon_s \qquad (4.3.31)$$

where M depends mostly on T_G and to a much less extent on the optical density SPL. Values that have been calculated from this simple model can be represented with acceptable error by

$$M = 1.07 + 18SPL - 0.27(T/1,000)$$

If, in addition to gas and soot, massive particles such as fly ash, coal char, or carbonaceous cenospheres from heavy fuel oil of emissivity ε_M are present, it is recommended that the total emissivity be approximated by

$$\varepsilon_{\text{total}} = \varepsilon_{G+s} + \varepsilon_M - \varepsilon_{G+s}\varepsilon_M \qquad (4.3.32)$$

Radiant interchange between a gas and a *completely bounding black surface* at T_1 produces a surface flux density q given by

$$q = \sigma(\varepsilon_G T_G^4 - \alpha_{G1} T_1^4) \qquad (4.3.33)$$

where α_{G1} is the **absorptivity** of the gas at T_G for radiation from a surface at T_1. The absorptivity of water vapor–CO_2 mixtures may also be obtained from the constants for emissivities. The product $\overline{\alpha_{G1}T_1}$—the absorptivity of gas at T_G for black radiation at T_1 times the surface temperature—is the product $\overline{\varepsilon_G T_1}$ with ε_G evaluated at surface temperature T_1 instead of T_G and at pLT_1/T_G instead of pL, then multiplied by $(T_G/T_1)^{0.5}$, or

$$\overline{\alpha_{G1}T_1} = [\overline{\varepsilon_G T_1}(pLT_1/T_G)](T_G/T_1)^{0.5} \qquad (4.3.34)$$

The exponent 0.5 is an adequate average of the exponents for the pure components. The interpolation relation for absorptivity is

$$\overline{\alpha_{G1}T_1} = \left[\overline{\varepsilon_G T_H\left(\frac{pLT_H}{T_G}\right)}\right]\left(\frac{T_G}{T_H}\right)^{0.5}\frac{T_1 - T_L}{500}$$
$$+ \left[\overline{\varepsilon_G T_L\left(\frac{pLT_L}{T_G}\right)}\right]\left(\frac{T_G}{T_L}\right)^{0.5}\frac{T_H - T_1}{500} \qquad (4.3.35)$$

The base temperature pair T_H and T_L can be different for the evaluation of ε_G and α_{G1} if T_G and T_1 are far enough apart. Extrapolation from the lowest T_G in Eq. (4.3.35) to a much lower T_1 to obtain α_{G1} may yield too high a value for it. That occurs, however, only when $T_1 \ll T_G$, and the fourth-power temperature relation makes the error in q negligible.

If the surface is not black, the right-hand side of Eq. (4.3.33) must be modified. If the surface is gray, multiplication by $\alpha_1(\equiv \varepsilon_1)$ allows for reduction in the primary beam from gas to surface and surface to gas, but some of the gas radiation initially reflected from the surface has further opportunity for absorption at the surface because the surface is but

incompletely opaque to the reflected beam. Consequently, the factor to allow for surface lies between absorptance α_1 and unity, nearer the latter the more transparent the gas (low pL) and the more convoluted the surface. In the absorptance range of most industrial surfaces, 0.7 to 1.0, an adequate approximation consists in use of an effective absorptance α_1' halfway between the actual value and unity. If the surface is not gray, q depends much more on surface absorptance, which modifies $\varepsilon_G T_G^4$, than on emittance, which modifies $\alpha_{G1}T_1^4$. Absorption is treated more rigorously later in the section.

EXAMPLE.   Flue gas containing 9.5 percent CO_2 and 7.1 percent H_2O, wet basis, flows through a bank of tubes of 1.5-in OD on equilateral triangular centers 4.5 in apart. In a section in which the gas and tube surface temperatures are 1,700 and 1,000°F, what is the heat transfer rate per square foot of tube area, due to gas radiation only? Tube surface absorptance = 0.8.
$T_G = 2,160°\text{R}$ (1,200 K); $T_S = 1,460°\text{R}$ (811 K)
$p_w/(p_w + p_c) = 7.1/16.6 = 0.428$; use 0.5
$pL = 0.166 \ [3.8(4.5 - 1.5)/12] = 0.158$ ft · atm (0.0480 m · atm)
$pL(Ts/T_G) = 0.1580(1,460/2,160) = 0.1066$ ft · atm (0.0325 m · atm)
From Table 4.3.4, for $T_G = 1,500$ K and $pL = 0.0480$ and 0.0325, $\varepsilon T = 125$ and 101 K, and for $T_G = 1,000$ K and $pL = 0.0480$ and 0.0325, $\varepsilon T = 129$ and 107 K. Then

$$\varepsilon_G = \frac{1}{1,200}\frac{125(1,200 - 1,000) + 129(1,500 - 1,200)}{1,500 - 1,000} = 0.106$$

$$\alpha_{G1} = \frac{1}{811}\frac{101(811 - 1,000) + 107(1,500 - 811)}{1,500 - 1,000} = 0.135$$

The effective surface absorptance factor $\alpha_1 = (0.8 + 1)/2 = 0.9$. From Eq. (4.3.33), modified,

$$q = 0.9 \times 0.1713(0.106 \times 21.6^4 - 0.135 \times 14.6^4)$$
$$= 2,612 \text{ Btu/(ft}^2 \cdot \text{h)}$$

or

$$q = 0.9 \times 5.67(0.106 \times 12^4 - 0.135 \times 8.111^4) = 8,235 \text{ W/m}^2$$

This is equivalent to a convection coefficient of $2,612/700$ or 3.73 Btu/(ft² · F · h) or 21.2 W/(m² · K). The emissivity of an equivalent gray flame is $(0.106 \times 21.6^4 - 0.135 \times 14.6^4)/(21.6^4 - 14.6^4) = 0.098$.

RADIATIVE EXCHANGE IN ENCLOSURES OF RADIATING GAS

The so-called *radiant section* of a furnace presents a heat-transfer problem in which there enters the combined action of direct radiation from the flame to the stock or heat sink and radiation from the flame to refractory surfaces and thence back through the flame (with partial absorption) to the sink, convection, and external losses. Solutions of the problem based on varying degrees of simplification are available, including allowance for temperature variation in both gas and refractory walls (Hottel and Sarofim, Chap. 14). A less rigorous treatment suffices, however, for handling many problems. There are two limiting cases: the long chamber with gas temperature varying only in the direction of gas flow and the compact chamber containing a gas or flame at a uniform temperature. The latter, with variations, will be considered first.

Total Exchange Areas $\overline{SS}$ and $\overline{GS}$ The arguments leading to the development of the interchange factor $A_i\mathscr{F}_{ij}(= \overline{S_iS_j})$ between surface zones [Eq. (4.3.14) et seq.] apply to the case of absorption within the gas volume if, in the evaluation of the direct exchange area, allowance is made for attenuation of the radiant beam through the gas. This necessitates nothing more than the redefinition, in Eqs. (4.3.7) to (4.3.22), of every term $\overline{ij} \ (\equiv \overline{s_i s_j} = A_iF_{ij})$ to represent, per unit of black emissive power, flux from A_i through an absorbing gas to A_j; that is, the prior F_{ij} must be multiplied by a mean transmittance τ_{ij} of the gas ($= 1 - \overline{\alpha}_{ij} = 1 - \varepsilon_G$ for a gray gas). In a system containing an isothermal gas and source-sink boundaries of areas $A_1, A_2, \ldots, A_n$, the total emission from A_1 per unit of its black emissive power is $A_1\varepsilon_1$, of which $\overline{S_1S_1} + \overline{S_1S_2} + \cdots + \overline{S_1S_n}$ is absorbed in the surfaces by all mechanisms, direct and indirect. The difference has been absorbed in the gas; it is called the **gas surface total exchange area $\overline{GS_1}$**:

$$\overline{GS_1} = A_1\varepsilon_1 - \sum_i \overline{S_1S_i} \qquad (4.3.36)$$

The letters identifying total exchange areas are, of course, commutative; $\overline{GS_1} \cong \overline{S_1G}$. Note that although $\overline{S_1S_1}$ is never used in calculating radiative interchange, its value is needed for use of Eq. (4.3.36) in calculating $\overline{GS_1}$. $\overline{GS_1}$ embraces the full effect of radiation complexities on radiative exchange between gas and A_1, including multiple reflection at all surfaces, and it is capable of including the effects of gas nongrayness and of assistance given by refractory surfaces to gas-A_1 interchange. It is but mildly temperature-sensitive and is independent of any changes in conduction, convection, mass flow, and energy balances except for their effect on the temperature used in evaluating it.

If the gas volume is not isothermal, the principles used here can be extended to setting up balances on a zoned gas volume (see, e.g., Hottel and Sarofim, ''Radiative Transfer,'' McGraw-Hill, Chap. 11).

Systems with a Single Gas Zone and Two Surface Zones

An enclosure consisting of but one isothermal gas zone and two gray surface zones, when properly specified, can model so many industrially important radiation problems as to merit presentation. One can evaluate the total radiation flux between any two of the three zones, including multiple reflection at all surfaces.

$$\dot{Q}_{G\leftrightarrow1} = \overline{GS_1}\sigma(T_G^4 - T_1^4)$$
$$\dot{Q}_{1\leftrightarrow2} = \overline{S_1S_2}\sigma(T_1^4 - T_2^4) \tag{4.3.37}$$

The total exchange area takes a relatively simple closed form, even when important allowance is made for gas radiation not being gray and when a reduction of the number of system parameters is introduced by assuming that one of the surface zones, if refractory, is radiatively adiabatic (see later). Before allowance is made for these factors, the case of a **gray gas** enclosed by two source-sink surface zones will be presented. Modification of Eqs. (4.3.7) to (4.3.22), discussed previously, combined with the assumption that a single mean beam length applies to all transfers, i.e., that there is but one gas transmittance $\tau (= 1 - \varepsilon_G)$, gives

$$\overline{S_1S_2} = \frac{A_1\varepsilon_1\varepsilon_2F_{12}}{1/\tau + \tau\rho_1\rho_2(1 - F_{12}/C_2) - \rho_1(1 - F_{12}) - \rho_2(1 - F_{21})} \tag{4.3.38}$$

$$\overline{S_1S_1} = \frac{A_1\varepsilon_1^2[F_{11} + \rho_2\tau(F_{12}/C_2 - 1)]}{\text{same denominator}} \tag{4.3.39}$$

$$\overline{GS_1} = \frac{A_1\varepsilon_1\varepsilon_G[1/\tau + \rho_2(F_{12}/C_2 - 1)]}{\text{same denominator}} \tag{4.3.40}$$

(Here C is the area expressed as a ratio to the total enclosure area A_T; $C_1 = A_1/A_T$, $C_2 = A_2/A_T$; $C_1 + C_2 = 1$.) The three equations above suffice to formulate total exchange areas for gas-enclosing arrangements which include, e.g., the four geometric cases illustrated in Table 4.3.5, to be discussed later.

An additional surface arrangement of importance is a single zone surface fully enclosing gas. With the gas assumed gray, the simplest derivation of $\overline{GS_1}$ is to note that the emission from surface A_1 per unit of its blackbody emissive power is $A_1\varepsilon_1$, of which the fractions ε_G and $(1 - \varepsilon_G)\varepsilon_1$ are absorbed by the gas and the surface, respectively, and the surface reflected residue always repeats this distribution. Therefore,

$$\overline{GS}_{\substack{\text{single surface} \\ \text{zone surrounding} \\ \text{gray gas}}} \equiv \overline{GS_1} = A_1\varepsilon_1\frac{\varepsilon_G}{\varepsilon_G + (1 - \varepsilon_G)\varepsilon_1} = \frac{A_1}{1/\varepsilon_G + 1/\varepsilon_1 - 1} \tag{4.3.41}$$

Alternatively, $\overline{GS_1}$ could be obtained from case 1 of Table 4.3.5 by letting plane area A_1 approach 0, leaving A_2 as the sole surface zone.

Although departure of gas from grayness has a marked effect on radiative transfer, the subject is complex and will be presented in stages, as the cases shown in Table 4.3.5 are discussed.

Partial Allowance for the Effect of Gas Nongrayness on Total Exchange Areas

A radiating gas departs from grayness in two ways: (1) Gas emissivity ε_G and absorptivity α_{G1} are not the same unless T_1 equals T_G. (2) The

fractional transmittance τ of radiation through successive path lengths L_m due to surface reflection, instead of being constant, keeps increasing because at the wavelengths of high absorption the incremental absorption decreases with increasing path length. The first of these effects is sufficiently straightforward to be introduced at this point, coupled with allowance for refractory surfaces being substantially radiatively adiabatic. The second, much more complicated effect will be introduced later; it sometimes changes the computed flux significantly.

In the simplest case of gas-surface radiative exchange—a gas at T_G completely enclosed by a black surface at T_1—the net flux $\dot{Q}_{G\leftrightarrow1}$ is given by

$$\dot{Q}_{G\leftrightarrow1} = \sigma(\varepsilon_G T_G^4 - \alpha_{G1}T_1^4) \equiv \sigma\varepsilon_{G,e}(T_G^4 - T_1^4)$$

The evaluation of the absorptivity α_G was covered in Eqs. (4.3.34) and (4.3.35). The second form of the above equation defines $\varepsilon_{G,e}$, the equivalent gray-gas emissivity

$$\varepsilon_{G,e} = \frac{\varepsilon_G - \alpha_{G1}(T_1^4/T_G^4)}{1 - (T_1/T_G)^4} \tag{4.3.42}$$

Although this introduction of $\varepsilon_{G,e}$ has added no information, the evaluation of $\dot{Q}_{G\leftrightarrow1}$ in terms of $\varepsilon_{G,e}$ rather than ε_G and α_{G1} gives a better structure for trial-and-error solutions of problems in which either T_G or T_1 is not known and a second energy relation is available.

With partial allowance for gas nongrayness having been made, the evaluation of radiative flux $\dot{Q}_{G\leftrightarrow1}$ or $\dot{Q}_{1\leftrightarrow2}$ [Eq. (4.3.37)] for cases falling in one of the categories of Table 4.3.5 is straightforward if both A_1 and A_2 are source-sink surfaces. Wherever ε_G or τ appears in the table, or in Eqs. (4.3.38) to (4.3.41), use $\varepsilon_{G,e}$ or $1 - \varepsilon_{G,e}$ instead.

EXAMPLE (FIRST APPROXIMATION TO NONGRAYNESS). Methane is burned to completion with 20 percent excess air (air half saturated with water vapor at 298 K (60°F), 0.0088 mol H_2O/mol dry air) in a furnace chamber with floor dimensions of 3×10 m and 5 m high. The whole surface is a gray energy sink of emissivity 0.8 at 1,000 K, surrounding gas at 1,500 K, well stirred. Find the effective gas emissivity $\varepsilon_{G,e}$ and the surface radiative flux density, assuming that the only correction necessary for gas nongrayness is use of $\varepsilon_{G,e}$ rather than ε_G.

SOLUTION. Combustion is 1 CH_4 + 2 × 1.2 O_2 + 1.2 × (79/21)N_2 + 2 × 1.2 × 100/21 × 0.0088 H_2O going to 1 CO_2 + [2 + 2 × 1.2 × (100/21) × 0.0088] H_2O + 0.4 O_2 + 9.03 N_2 = 12.53 mol/mol of CH_4. And $P_C + P_W$ = (1 + 2.1)/12.53 = 0.2474 atm. The mean beam length $L_m = 0.88 \times 4V/A_T = 0.88 \times 4(10 \times 3 \times 5)/\{2[2 \times (10 \times 3 + 10 \times 5 + 3 \times 5)]\}$ = 2.779 m. And pL_m = 0.2474 × 2.779 = 0.6875 m·atm. From emissivity Table 4.3.4, $b(1,500)$ = 540; $n(1,500)$ = 0.42; $b(1,000)$ = 444; $n(1,000)$ = 0.34. Also $\varepsilon_G(pL)$ = 540(0.6875 − 0.015)$^{0.42}$/1,500 = 0.3047, and $\alpha_{G1}(pL)$ = 444(0.6875 × 1,000/1,500 − 0.015)$^{0.34}$(1,500/1,000)$^{0.5}$/1,000 = 0.4124. Then $\varepsilon_{G,e}(pL)$ = [0.3047 − 0.4124(1,000/1,500)^4]/[1 − (1,000/1,500)^4] = 0.2782. From Eq. (4.3.41), with ε_G replaced by $\varepsilon_{G,e}$, $(\overline{GS_1}/A_1)$ = 1/(1/0.2782 + 1/0.8 − 1) = 0.2601. Then $\dot{Q}_{G\leftrightarrow1}/A_1$ = 56.7 × 0.2601[(1,500/1,000)^4 − (1,000/1,000)^4] = 59.91 kW/ m^2 [18,990 Btu/(ft^2·h)].

Refractory Surfaces If one of the surfaces A_r of an enclosure of gas is refractory, an extra temperature T_{refr} and an extra heat transfer equation are needed to determine the fluxes *unless* A_r can be assumed to be radiatively adiabatic. Consider the facts that irradiation of A_r plus convection from gas to it must equal back radiation plus conduction through it if steady state exists, and irradiation is enormous compared to convection. It then follows that the difference between convection and conduction is so minute compared to irradiation or back radiation as to make A_r substantially radiatively adiabatic; assume that A_1 is a source-sink zone and A_2 a radiatively adiabatic zone, and call it A_r. The condition for adiabaticity of A_r is
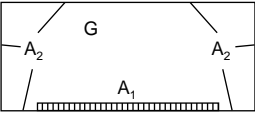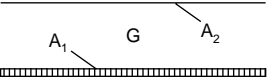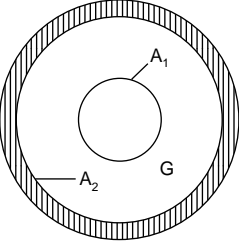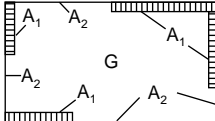
$$\overline{GS_r}(T_G^4 - T_r^4) = \overline{S_rS_1}(T_r^4 - T_1^4)$$

or, to eliminate T_r,

$$\frac{T_G^4 - T_r^4}{1/\overline{GS_r}} = \frac{T_r^4 - T_1^4}{1/\overline{S_rS_1}} = \frac{T_G^4 - T_1^4}{1/\overline{GS_r} + 1/\overline{S_rS_1}} \tag{4.3.43}$$

The net flux from gas G is $\overline{GS_1}\sigma(T_G^4 - T_1^4) + \overline{GS_r}\sigma(T_G^4 - T_r^4)$ which, with replacement of the last term, using Eq. (4.3.43), gives the single

Table 4.3.5   Total Exchange Areas for Four Arrangements of Two-Zone-Surface Enclosures of a Gray Gas*

Case 1	Case 2	Case 3	Case 4

Case 1

A plane surface A_1 and a surface A_2 complete the enclosure

$F_{12} = 1$

$$\frac{\overline{S_1 S_2}}{A_1} = \frac{\varepsilon_1 \varepsilon_2}{D_1}$$

$$\frac{\overline{GS_1}}{A_1} = \frac{\varepsilon_1 \varepsilon_G (1/\tau + \rho_2 C_1 / C_2)}{D_1}$$

$$\frac{\overline{GS_2}}{A_2} = \frac{\varepsilon_2 \varepsilon_G (1/\tau + \rho_1 C_1 / C_2)}{D_1}$$

$$\frac{\overline{S_1 S_1}}{A_1} = \frac{\varepsilon_1^2 \tau \rho_2 C_1 / C_2}{D_1}$$

$$D_1 \equiv \frac{1}{\tau} - \rho_2 \left[1 - \frac{C_1}{C_2} (1 - \tau \rho_1) \right]$$

$\tau = 1 - \varepsilon_G$

Case 2

Infinite parallel planes

$F_{12} = F_{21} = 1$

$$\frac{\overline{S_1 S_2}}{A_1} = \frac{\varepsilon_1 \varepsilon_2}{D_2}$$

$$\frac{\overline{GS_1}}{A_1} = \frac{\varepsilon_1 \varepsilon_G (1/\tau + \rho_2)}{D_2}$$

$$\frac{\overline{S_1 S_1}}{A_1} = \frac{\varepsilon_1^2 \rho_2 \tau}{D_2}$$

$$D_2 \equiv \frac{1}{\tau} - \tau \rho_1 \rho_2$$

Case 3

Concentric spherical or infinite cylindrical surface zones, A_1 inside

$F_{12} = 1 \qquad F_{21} = \frac{A_1}{A_2} = \frac{C_1}{C_2}$

$$\frac{\overline{S_1 S_2}}{A_1} = \frac{\varepsilon_1 \varepsilon_2}{D_3}$$

$$\frac{\overline{GS_1}}{A_1} = \frac{\varepsilon_1 \varepsilon_G (1/\tau + \rho_2 C_1 / C_2)}{D_3}$$

$$\frac{\overline{GS_2}}{A_2} = \frac{\varepsilon_2 \varepsilon_G (1/\tau + \rho_1 C_1 / C_2)}{D_3}$$

$$\frac{\overline{S_1 S_1}}{A_1} = \frac{\varepsilon_1^2 \rho_2 \tau C_1 / C_2}{D_3}$$

$$D_3 \equiv \frac{1}{\tau} - \rho_2 \left[1 - \frac{C_1}{C_2} (1 - \tau \rho_1) \right]$$

Case 4

Two-surface-zone enclosure, each zone in one or more parts, any shape

Case A

Rigorous evaluation of F's, with i and j representing parts of A_1 and A_2.

$$A_1 F_{12} = \sum_i \left(A_i \sum_j F_{ij} \right)$$

$$\left. \begin{array}{c} \overline{S_1 S_2} \\ \overline{GS_1} \\ \overline{S_1 S_1} \end{array} \right\} = \left\{ \begin{array}{l} \text{same as in base} \\ \text{case, Eqs. (4.3.38)} \\ \text{to (4.3.40)} \end{array} \right.$$

Case B

Assume that enclosing surface is a speckled enclosure, or spherical

$F_{12} = F_{22} = C_2$

$F_{21} = F_{11} = C_1$

$$\frac{\overline{S_1 S_2}}{A_1} = \frac{\varepsilon_1 \varepsilon_2 C_2}{D_4}$$

$$\frac{\overline{GS_1}}{A_1} = \frac{\varepsilon_1 \varepsilon_G / \tau}{D_4}$$

$$\frac{\overline{S_1 S_1}}{A_1} = \frac{\varepsilon_1^2 C_1}{D_4}$$

$$D_4 \equiv \frac{1}{\tau} - \rho_1 C_1 - \rho_2 C_2$$

* All equations above come from Eqs. (4.3.38) to (4.3.40), with substitutions for view factor F given before equations.

term multiplying a fourth-power temperature difference:

$$\dot{Q}_{G\leftrightarrow 1} = \sigma(T_G^4 - T_1^4) \left[\overline{GS_1} + \frac{1}{1/\overline{GS_r} + 1/\overline{S_rS_1}} \right]$$

$$\equiv (\overline{GS_1})_R \sigma(T_G^4 - T_1^4) \quad (4.3.44)$$

The bracketed term is called $(\overline{GS_1})_R$, the total exchange area from G to A_1 with assistance from a refractory surface. Table 4.3.5 supplies the forms for the three total exchange area terms needed to formulate $(\overline{GS_1})_R$, with A_r substituted for A_2 and with ε_G or τ replaced by $\varepsilon_{G,e}$ or $1 - \varepsilon_{G,e}$.

A general expression for a gray gas enclosure of two surfaces, one of which is radiatively adiabatic, comes from Eq. (4.3.44), in which $(\overline{GS_1})_R$ becomes $\overline{GS_1}$ because $\overline{S_rS_1}$ and $\overline{GS_r}$ are zero, and then from Eq. (4.3.36), which becomes $\overline{GS_1} [= (\overline{GS_1})_R] = A_1\varepsilon_1 - \overline{S_1S_1}$. With $\overline{S_1S_1}$ coming from Eq. (4.3.39), one finally obtains

$$\frac{(\overline{GS_1})_R}{A_1} = \frac{1}{\rho_1/\varepsilon_1 + 1/\{\varepsilon_G[1 + 1/(C_1/C_2 + \varepsilon_G/\tau\,F_{1r})]\}} \quad (4.3.45)$$

Note that since the first denominator term is zero when A_1 is black, the denominator of the second term is $(\overline{GS_1})_R/A_1$ for a black surface.

The above equation is perfectly general when the **gas is gray** and the two enclosing surfaces are a sink and a radiatively adiabatic surface. When A_1 is a plane (simulation of slab or billet heating furnaces and glass tanks), $(\overline{GS_1})_R/A_1$ is Eq. (4.3.45) with $F_{1r} = 1$. A different but completely equivalent form is

$$\left[\frac{(\overline{GS_1})_R}{A_1} \right]_{\substack{A_i \text{ is} \\ \text{plane}}} = \frac{1}{1/\varepsilon_1 + (1/\varepsilon_G - 1)^2/[1/(C_1\varepsilon_G) - 1]} \quad (4.3.46)$$

For most refinery **processing furnaces,** with sink and refractory assumed to form a **speckled** enclosure, $(\overline{GS_1})_R/A_1$ is Eq. (4.3.45) with $F_{1r} = C_r$. A better but completely equivalent form is

$$\left[\frac{(\overline{GS_1})_R}{A_1} \right]_{\substack{\text{surface is} \\ \text{speckled}}} = \frac{1}{1/\varepsilon_1 + C_1(1/\varepsilon_G - 1)} \quad (4.3.47)$$

As previously stated, partial allowance for the gas not being gray is made by evaluating $\overline{GS}$ or $(\overline{GS})_R$ with use of $\varepsilon_{G,e}$ rather than ε_G, and $1 - \varepsilon_{G,e}$ rather than τ, in Eqs. (4.3.45) to (4.3.47). A slightly better but more tedious allowance for partial **nongrayness** in evaluating $\dot{Q}_{\text{rad}}$ is to replace $\overline{GS_1}\sigma(T_G^4 - T_1^4)$, with $\overline{GS_1}$ evaluated by using $\varepsilon_{G,e}$, by $\overline{GS_1}T_G^4 - \overline{GS_1}T_1^4$, where $\overline{GS}$, and $\overline{GS}$, are evaluated by using ε_G and $\alpha_{G,1}$, respectively.

This completes the presentation of procedures for evaluating the total exchange area between gas and sink surface when the gas is gray or by making approximate allowance for the nongrayness by using ε_G and $\alpha_{G,1}$. These exchange areas can be used in the formulations below on furnace chamber performance. Methods will be presented first for a more rigorous treatment of gas nongrayness.

Full Allowance for Gas Nongrayness The above paragraphs failed to allow for the previously discussed change in gas transmittance on successive passages of reflected radiation through the gas. In many radiative transfer problems, interchange between many different pairs of radiators creates a system of simultaneous equations to be solved for the energy fluxes, and a shift from use of the Stefan-Boltzmann to the Planck equation would enormously increase the difficulty of solution. Use will be made of the fact that the total emissivity of a real gas, the spectral emissivity and absorptivity ε_λ of which vary in any way with λ, can be expressed *rigorously* as the a-weighted mean of a suitable number, n, of gray gas emissivity or absorptivity terms $\varepsilon_{G,i}$ or $\alpha_{G,i}$ representing the gray gas emissivity or absorptivity in the energy fractions a_i of the blackbody spectrum. Then

$$\varepsilon_G = \sum_0^n a_i\varepsilon_{G,i} = \sum_0^n a_i(1 - e^{-k_ipL}) \quad (4.3.48)$$

The linearity between flux $\dot{Q}$ and blackbody emissive power E_B allows the above relations to be used for converting $\overline{GS}$ or $\overline{SS}$ for a gray gas

to a form allowing for nongrayness. For a real gas $\overline{GS}$ or $\overline{SS}$ is the a_i-weighted sum of its values based on each of the $\varepsilon_{G,i}$ values of Eq. (4.3.48). Into an expression for $\overline{GS}_{\text{gray}}$ replace ε_G by $\varepsilon_{G,i}$, or τ by $1 - \varepsilon_{G,i}$, multiply the result by a_i and sum the resultant $\overline{GS}$ values to obtain $\overline{GS}_{\text{real gas}}$. Obviously, the number of terms n should be as small as possible while consistent with small error. Consider an n of 2, with the gas modeled as the sum of one gray gas plus a clear gas, with the gray gas of absorption coefficient k occupying the energy fraction a of the blackbody spectrum and the clear gas ($k = 0$) the fraction $1 - a$. Then, at path lengths L and $2L$,

$$[\varepsilon_G(pL)] = a(1 - e^{-kpL}) + (1 - a)(0)$$
$$[\varepsilon_G(2pL)] = a(1 - e^{-2kpL}) + (1 - a)(0) \quad (4.3.49)$$

Solution of these gives

$$a = \frac{\varepsilon_G(pL)}{2 - \varepsilon_G(2pL)/\varepsilon_G(pL)}$$

$$kpL = -\ln\left[1 - \frac{\varepsilon_G(pL)}{a} \right] \quad (4.3.50)$$

The equivalent gray gas emissivity in the spectral range a is $1 - e^{-kpL}$, from Eq. (4.3.48), and from Eq. (4.3.49) that is $\varepsilon_G(pL)/a$; in the spectral range $1 - a$, the equivalent gray gas emissivity is zero. This simple model will be correct for the contribution of the direct gas emission from path length L and for that of the once-reflected emission (path length $2L$); and the added contributions due to increasing numbers of reflections will be attenuated sufficiently by surface reflections to make errors in them unimportant. Note that a and k are not general constants; they are specific to the **subject mean beam length L_m** and come from basic data, such as Table 4.3.4. Note also that when full allowance for nongrayness is to be made by replacing ε_G by $\varepsilon_{G,e}$, then a is also changed to a_e, which comes from Eq. (4.3.50), with $\varepsilon_{G,e}$ replacing ε_G.

Conversion of gray gas total exchange areas $\overline{GS}$ and $\overline{SS}$ to their nongray forms is carried out as follows when the nongray model is gray-plus-clear gas: From Eq. (4.3.49) the equivalent gray gas emissivity in the spectral energy fraction a_e is $\varepsilon_{G,e}(pL)/a_e$, which replaces ε_G wherever it or its complement τ occurs in $\overline{GS}$; the result is then multiplied by a_e. There is no contribution from the clear gas energy fraction. Conversion of $\overline{SS}$ from gray to gray plus clear involves making the same substitution, but for $\overline{SS}$ another term must be added. For the clear gas contribution, 0 and 1 are substituted for ε_G and τ, and the result is multiplied by the weighting factor $1 - a_e$; this $\overline{SS}$ is added to the preceding one to give $\overline{SS}_{g+c}$.

The simplest application of this gray-plus-clear model of gas radiation is the case of a single gas zone surrounded by a single surface zone, the case covered for a gray gas by Eq. (4.3.51) and illustrated in the last numerical example, where radiation from methane combustion products is surrounded by a single-zone sink surface. That example will be repeated using the gray-plus-clear gas model, for which the total exchange area is

$$\frac{\overline{GS_1}}{A_1} = \frac{a_e}{a_e/\varepsilon_{G,e} + 1/\varepsilon_1 - 1} \quad (4.3.51)$$

EXAMPLE (GRAY-PLUS-CLEAR GAS RADIATION FROM METHANE COMBUSTION PRODUCTS). The computations of the previous example, radiative flux from methane combustion products, will be repeated with the more rigorous treatment of nongrayness, and the results will be compared with the more approximate calculations for the case of a wall emissivity ε_1 of 0.4 and 0.8.

SOLUTION. Repeat the calculations given, in the earlier example, of $\varepsilon_G(pL)$, $\alpha_{G1}(pL)$, and $\varepsilon_{G,e}(pL)$ for $pL = 2 \times 0.6875$, to give $\varepsilon_G(2pL) = 0.4096$, $\alpha_{G1}(2pL) = 0.5250$, and $\varepsilon_{G,e}(2pL) = 0.3812$. Then $a_e = 0.2782/(2 - 0.3812/0.2782) = 0.4418$, and the emissivity substitute for the gray gas portion of the gray-plus-clear gas model is $0.2782/0.4418 = 0.6297$. For a single enveloping surface zone, the total exchange area comes from Eq. (4.3.51): $\overline{GS_1}/A_1 = a_e/(a_e/\varepsilon_{G,e} + 1/\varepsilon_1 - 1) = 0.4418/(0.4418/0.2782 + 1/0.8 - 1) = 0.2404$. The flux density is $Q/A = q = (\overline{GS_1}/A)\sigma(T_G^4 - T_1^4) = 0.2404 \times 56.7 \times [(1,500/1,000)^4 - (1,000/1,000)^4] = 55.37$ kW/m² [17,550 Btu/(ft² · h)]. This is 7.6 percent lower than it is when only

the difference between ε_G and $\alpha_{G,1}$ is allowed for in finding the effect of gas nongrayness. In some problems the difference is as high as 20 percent. (Note that allowing for average humidity in air adds 5 percent to H_2O and about 2 percent to the gas emissivity.) Changing ε_1 from 0.8 to 0.4 changes the approximate solution for $\overline{GS_1}/A_1$ from 0.2501 to 0.1963 and the gray-plus-clear treatment from 0.2404 to 0.1431.

The procedures for introducing the nongray gas model can be used to convert the total exchange areas for the basic one-gas two-surface model, Eqs. (4.3.38) to (4.3.40), as used to evaluate the cases in Table 4.3.5, to the following gray-plus-clear-gas model forms:

$$\frac{\overline{S_1S_2}}{A_1} = F_{12}\varepsilon_1\varepsilon_2\left(\frac{a_e}{D_a} + \frac{1-a_e}{D_b}\right) \tag{4.3.52}$$

$$\frac{\overline{S_1S_2}}{A_1} = F_{12}\varepsilon_1^2\left\{\frac{a_e[1 - F_{12} + \rho_2(1 - \varepsilon_{G,e}/a_e)(F_{12}/C_2 - 1)]}{D_a}\right.$$
$$\left. + \frac{(1 - a_e)[1 - F_{12} + \rho_2(F_{12}/C_2 - 1)]}{D_b}\right\} \tag{4.3.53}$$

$$\frac{\overline{GS_1}}{A_1} = \frac{\varepsilon_1\varepsilon_{G,e}[1/(1 - \varepsilon_{G,e}/a_e)] + \rho_2(F_{12}/C_2 - 1)}{D_a} \tag{4.3.54}$$

$$D_a = \frac{1}{1 - \varepsilon_{G,e}/a_e} + \left(1 - \frac{\varepsilon_{G,e}}{a_e}\right)\rho_1\rho_2(1 - F_{12}C_2)$$
$$- \rho_1(1 - F_{12}) - \rho_2(1 - F_{21})$$

$$D_b = 1 + \rho_1\rho_2\left(1 - \frac{F_{12}}{C_2}\right) - \rho_1(1 - F_{12}) - \rho_2(1 - F_{21})$$

$$\text{or} \quad = \varepsilon_1\varepsilon_2 + F_{12}\left[\varepsilon_2 + \frac{\varepsilon_1(C_1 - \varepsilon_2)}{C_2}\right]$$

The above relations, with the view factor F_{12} specified, may be used to convert the geometric cases of Table 4.3.5 to their more nearly correct forms with gray gas replaced by the gray-plus-clear gas model. That has been done in Table 4.3.6, which covers a moderate idealization of many practical industrial systems.

Effect of Gas Nongrayness on Refractory Zones   Full allowance for the effect of gas nongrayness on enclosures in which part of the enclosing surface is radiatively adiabatic is straightforward but sometimes tedious. The term of Eq. (4.3.44) must be evaluated. It is tempting to use Eq. (4.3.45), but that is invalid because, although total radiative interchange at zone A_r is 0, the gas nongrayness makes A_r a net absorber in the spectral energy fraction a (or a_e) and a net emitter in the clear gas fraction $1 - a$. It is necessary, then, to use the basic equation

$$(\overline{GS_1})_R = \left(\overline{GS_1} + \frac{1}{1/\overline{GS_r} + 1/\overline{S_rS_1}}\right) \tag{4.3.55}$$

evaluating each of the right-hand members of a geometric system of interest, such as found in Table 4.3.5 (where A_r is A_2). As previously discussed, $\varepsilon_{G,e}/a_e$ is substituted for ε_G (or its complement for τ), and the result is weighted by the factor a_e; and for $\overline{S_rS_1}$ an additional term based on ε_G being replaced by 0 or τ by 1, with weighting $1 - a_e$, is added.

Of the cases covered in Table 4.3.5, only two will be evaluated to make A_2 represent the radiatively adiabatic zone A_r. The first is for the case of heat sink A_1 in a plane—the simulation of a slab-heating furnace. Insertion into Eq. (4.3.44) of the gray-plus-clear terms $\overline{GS_1}$, $\overline{GS_r}$, and $\overline{S_rS_1}$ from Table 4.3.6 (with subscript r replacing subscript 2) and rearrangement gives:

$$\left[\frac{(\overline{GS_1})_R}{A_1}\right]_{\substack{A_1 \text{ in a} \\ \text{plane}}} = \frac{\varepsilon_G}{D_1}\left[\varepsilon_1\left(\rho_r\frac{C_1}{C_r} + \frac{1}{1 - \varepsilon_G/a}\right)\right.$$
$$\left. + \frac{\varepsilon_r}{\rho_1 + \frac{C_r}{C_1}\left(1 - \frac{\varepsilon_G}{a}\right) + \frac{\varepsilon_G/\varepsilon_1}{a + \frac{(1-a)D_1}{\varepsilon_r + \rho_r\varepsilon_1C_1/C_r}}}\right] \tag{4.3.56}$$

where $D_1 = 1/(1 - \varepsilon_G/a) - \rho_r[1 - (C_1/C_r)(\varepsilon_1 + \rho_1\varepsilon_G/a)]$. Although ε_G and a are used here, $\varepsilon_{G,e}$ and a_e should be used if allowance is to be made for the difference between gas emissivity and absorptivity. Com-

parison of Eq. (4.3.56) with it gray gas equivalent, Eq. (4.3.46), shows the complexity introduced by allowance for gas nongrayness. [$(\overline{GS_1})_R$ for the gray-plus-clear gas model is about 15 percent higher than for gray gas when $\varepsilon_1 = 0.8$, $\varepsilon_G = 0.3$, $C_1 = \frac{1}{3}$, $a = 0.4$, and $\varepsilon_r = 0.6$, but only 1 percent higher when $\varepsilon_r = 1$.]

The second conversion of $\overline{GS}$ to $(\overline{GS_1})_R$ will be case 4B of Table 4.3.5, the two-surface-zone enclosure with the computation simplified by assuming that the direct-view factor from any spot to a surface equals the fraction of the whole enclosure which the surface occupies (the speckled furnace model). This case can be considered an idealization of many processing furnaces such as distilling and cracking coil furnaces, with parts of the enclosure tube-covered and part left refractory. (The refractory under the tubes is not to be classified as part of the refractory zone.) Again, one starts with substitution, into Eq. (4.3.44), of the terms $\overline{GS_1}$, $\overline{GS_r}$, and $\overline{S_rS_1}$ from Table 4.3.5, case 4B, with all terms first converted to their gray-plus-clear form. To indicate the procedure, one of the components, $\overline{S_rS_1}$, will be formulated.

$$\frac{\overline{S_rS_1}}{A_1} = a\frac{C_r\varepsilon_1\varepsilon_r}{D_4'} + (1 - a)\frac{C_r\varepsilon_1\varepsilon_r}{1 - \rho_1C_1 - \rho_rC_r}$$
$$= \frac{C_r\varepsilon_1\varepsilon_r}{D_4'}\left[1 + \frac{\varepsilon_G(1 - a)(a - \varepsilon_G)}{1 - \rho_1C_1 - \rho_rC_r}\right]$$

With $D_4' = 1/(1 - \varepsilon_G/a) - \rho_1C_1 - \rho_rC_r$, the result of the full substitution simplifies to

$$\frac{(\overline{GS_1})_R}{A_1} = \frac{1}{C_1\left(\frac{1}{\varepsilon_G} - \frac{1}{a}\right) + \frac{1}{\varepsilon_1} + \frac{1/a - 1}{\varepsilon_1 + \varepsilon_r(C_r/C_1)}} \tag{4.3.57}$$

For a gray gas ($a = 1$) the above becomes

$$\frac{(\overline{GS_1})_R}{A_1} = \frac{1}{C_1(1/\varepsilon_G - 1) + 1/\varepsilon_1} \tag{4.3.58}$$

Equation (4.3.57) has wide applicability.

The beginning of this subsection mentions compact chambers (just treated) and long chambers as limiting cases. The latter will now be treated.

The Long Combustion Chamber   If a chamber is long enough in the x direction compared to its mean hydraulic radius, the local flux from gas to wall sink comes substantially from gas at its local temperature, with $\overline{GS_1}$ [or $(GS_1)_R$] calculated by methods just described but based on a two-dimensional structure; i.e., the opposed upstream and downstream fluxes through the flow cross section will substantially cancel. That limiting case will be considered, with $(\overline{GS_1})_R/A_1$ evaluated by using local mean values of T_G and T_1. The local $(\overline{GS_1})_R$ applicable to a surface element of length dx and perimeter P is then $[(\overline{GS_1})_R/A_1]P\,dx$. Let $T_{G,\text{in}}$, $T_{G,\text{out}}$, $T_{1,\text{in}}$, and $T_{1,\text{out}}$ be specified; furnace length L is to be determined. Assume a constant sink temperature T_1 equal to the arithmetic mean gas temperature minus the logarithmic mean of the temperature difference, gas to sink, at the ends. The equation of heat transfer in the furnace length element $P\,dx$ is then

$$-\dot{m}C_p\,dT_G = P\,dx\left[\frac{(\overline{GS_1})_R}{A_1}\right]\sigma(T_G^4 - T_1^4) + h(T_G - T_1)] \tag{4.3.59}$$

The second of the heat-transfer terms is an order of magnitude smaller than the first, and to permit ready integration, $h(T_G - T_1)$ will be set equal to $b\sigma(T_G^4 - T_1^4)$, from which

$$b\sigma = \frac{h}{T_G^3 + T_G^2T_1 + T_GT_1^2 + T_1^3} = \frac{h}{4T_{G1}^3}$$

T_{G1} is the mean value of T_G and T_1, and a 10 percent error in T_1 will make but a 1 percent error in the calculated heat transfer. Then Equation (4.3.59) becomes

$$-\dot{m}C_p\,dT_G = P\,dx\left[\frac{(\overline{GS_1})_R}{A_1} + \frac{h}{4\sigma T_{G1}^3}\right]\sigma(T_G^4 - T_1^4) \tag{4.3.60}$$

Table 4.3.6   Conversion of Total Exchange Areas for Cases of Table 4.3.5 to Their Gray-plus-Clear Values

Case 1: Plane slab A_1 and surface A_2 completing an enclosure of gas; $F_{12} = 1$

$$\frac{\overline{S_1 S_2}}{A_1} = \frac{a\varepsilon_1\varepsilon_2}{D_1} + \frac{(1-a)\varepsilon_1\varepsilon_2}{1 - \rho_2(1 - \varepsilon_1 C_1/C_2)}$$

where

$$D_1 = \frac{1}{(1 - \varepsilon_G/a)} - \rho_2\left[1 - \frac{C_1}{C_2}\left(\varepsilon_1 + \frac{\rho_1\varepsilon_G}{a}\right)\right]$$

$$\frac{\overline{GS_1}}{A_1} = \varepsilon_1\varepsilon_G\left[\frac{1/(1 - \varepsilon_G/a) - \rho_2 C_1/C_2}{D_1}\right]$$

$$\frac{\overline{GS_2}}{A_2} = \varepsilon_2\varepsilon_G\left[\frac{1/(1 - \varepsilon_G/a) + \rho_1 C_1/C_2}{D_1}\right]$$

Case 2: Infinite parallel planes, gas between; $F_{12} = F_{21} = 1$

$$\frac{\overline{S_1 S_2}}{A_1} = \frac{a\varepsilon_1\varepsilon_2}{D_2} + \frac{(1-a)\varepsilon_1\varepsilon_2}{1 - \rho_1\rho_2}$$

where

$$D_2 = \frac{1}{1 - \varepsilon_G/a} - \left(1 - \frac{\varepsilon_G}{a}\right)\rho_1\rho_2$$

$$\frac{\overline{GS_1}}{A_1} = \varepsilon_1\varepsilon_G\left[\frac{1/(1 - \varepsilon_G/a) + \rho_2}{D_2}\right]$$

Case 3: Concentric spherical or infinite cylindrical surface zones, A_1 inside; $F_{12} = 1$; $F_{21} = A_1/A_2 \equiv C_1/C_2$

$$\frac{\overline{S_1 S_2}}{A_1} = \frac{a\varepsilon_1\varepsilon_2}{D_3} + \frac{(1-a)\varepsilon_1\varepsilon_2}{1 - \rho_2(1 - \varepsilon_1 C_1/C_2)}$$

where

$$D_3 = \frac{1}{1 - \varepsilon_G/a} - \rho_2\left[1 - \left(\frac{C_1}{C_2}\right)\left(\varepsilon_1 + \frac{\rho_1\varepsilon_G}{a}\right)\right]$$

$$\frac{\overline{GS_1}}{A_1} = \varepsilon_1\varepsilon_G\left[\frac{1/(1 - \varepsilon_G/a) + \rho_2 C_1/C_2}{D_3}\right]$$

$$\frac{\overline{GS_2}}{A_2} = \varepsilon_2\varepsilon_G\left[\frac{1/(1 - \varepsilon_G/a) + \rho_1 C_1/C_2}{D_3}\right]$$

Case 4A: Two-surface-zone enclosure, with F values exact

$$\frac{\overline{S_1 S_1}}{A_T} = \frac{aC_1\varepsilon_1^2[1 - F_{12} + \rho_2(1 - \varepsilon_G/a)(F_{12}/C_2 - 1)]}{D_a} + \frac{(1-a)C_1\varepsilon_1^2[1 + F_{12} + \rho_2(F_{12}/C_2 - 1)]}{(F_{12}/C_2)(C_1\varepsilon_1\rho_2 + C_2\varepsilon_2\rho_1) + \varepsilon_1\varepsilon_2}$$

$$\frac{\overline{S_1 S_2}}{A_T} = \frac{aC_1\varepsilon_1\varepsilon_2 F_{12}}{D_a} + \frac{(1-a)C_1\varepsilon_1\varepsilon_2 F_{12}}{(F_{12}/C_2)(C_1\varepsilon_1\rho_2 + C_2\varepsilon_2\rho_1) + \varepsilon_1\varepsilon_2}$$

$$\frac{\overline{GS_1}}{A_T} = \frac{C_1\varepsilon_1\varepsilon_G[1/(1 - \varepsilon_G/a) + \rho_2(F_{12}/C_2 - 1)]}{D_a}$$

where $\quad D_a \equiv \dfrac{\varepsilon_G}{a}\left[\dfrac{1}{1 - \varepsilon_G/a} + \rho_1\rho_2\left(\dfrac{F_{12}}{C_2} - 1\right)\right] + \dfrac{F_{12}}{C_2}(C_1\varepsilon_1\rho_2 + C_2\varepsilon_2\rho_1) + \varepsilon_1\varepsilon_2$

Case 4B: Spherical enclosure of two surface zones *or* speckled $A_1 : A_2$ enclosure; $F_{12} = F_{22} = C_2$; $F_{21} = F_{11} = C_1$

$$\frac{\overline{S_1 S_2}}{A_1} = \frac{a\varepsilon_1\varepsilon_2 C_2}{D_4} + \frac{(1-a)\varepsilon_1\varepsilon_2 C_2}{1 - \rho_1 C_1 - \rho_2 C_2}$$

where

$$D_4 = \frac{1}{1 - \varepsilon_G/a} - \rho_1 C_1 - \rho_2 C_2$$

$$C_1 = \frac{A_1}{A_1 + A_2}$$

$$\frac{\overline{GS_1}}{A_1} = \frac{\varepsilon_1\varepsilon_G/(1 - \varepsilon_G/a)}{D_4}$$

Integration of T_G from $T_{G,\text{in}}$ to $T_{G,\text{out}}$ and of x from 0 to L, and solution for L give

$$L = \frac{\dot{m}\overline{C}_p\left(\tan^{-1}\dfrac{T_{G,\text{out}}}{T_1} - \tan^{-1}\dfrac{T_{G,\text{in}}}{T_1} - \dfrac{1}{2}\ln\dfrac{T_{G,\text{out}} - T_1 T_{G,\text{in}} + T_1}{T_{G,\text{out}} + T_1 T_{G,\text{in}} - T_1}\right)}{2PT_1^3\sigma\left[\dfrac{(\overline{GS_1})_R}{A_1} + \dfrac{h}{4\sigma T_{G1}^3}\right]}$$

(4.3.61)

Trial and error are necessary if L is specified and $T_{G,\text{out}}$ is to be found. If L is not long, axial radiative flux becomes important and a much more complex treatment is necessary. Use of a multigas zone system is one possibility.

Partially Stirred Model of Furnace Chamber Performance   An equation representing an energy balance on a combustion chamber of two surface zones—a heat sink A_1 at temperature T_1 and a refractory surface A_r assumed radiatively adiabatic at T_r—is most simply solved if the total enthalpy input H is expressed as $\dot{m}\overline{C}_p(T_F - T_0)$; $\dot{m}$ is the mass rate of fuel plus air, and T_F is a pseudo-adiabatic flame temperature

based on a mean specific heat from base temperature T_0 *up to the gas exit temperature* T_E rather than up to T_F. Assume that enough stirring occurs in the chamber to produce two temperatures—the heat-transfer temperature T_G and the leaving gas enthalpy temperature T_E—the two differing by an empirical amount, zero if the stirring were perfect.

Of the many ways tried to introduce this empiricism, the best is to assume that $T_G - T_E$, expressed as a ratio to T_F, is a constant Δ. Although Δ will vary with burner type, the effects of excess air and firing rate are small, except that for very small chambers or abnormally low firing rates the predicted radiative transfer is excessive. For such an abnormal situation, wall cooling reduces the effective size of the chamber. These conditions excepted and in the absence of performance data on the subject furnace type, assume $\Delta = 0.08$, or

$$\frac{T_G - T_E}{T_F} = \Delta = 0.08$$

This assumption bypasses complex allowance for temperature variations in the chamber gas and for the effects of fluid mechanics and combustion kinetics, but at the cost of not permitting evaluation of **flux distribution** over the surface. The heat-transfer rate Q out of the gas is then $H - \dot{m}\overline{C}_p(T_E - T_0)$ or $\dot{m}\overline{C}_p(T_F - T_E)$. A combination of energy balance and heat transfer, with the ambient temperature taken as the enthalpy base temperature T_0, gives

$$(\dot{Q} =)\ \dot{H} - \dot{m}\overline{C}_p(T_E - T_0) = (\overline{GS_1})_R\ \sigma(T_G^4 - T_1^4)$$
$$+ h_1A_1(T_G - T_1) + A_0F_0\ \sigma(T_G^4 - T_0^4) + UA_r(T_G - T_0) \quad (4.3.62)$$

where U is the overall convection coefficient, gas through refractory to ambient.

To make the relations dimensionless, divide through by $(\overline{GS_1})_R\sigma T_F^4$, and let all temperatures, expressed as ratios to T_F, be called T^*. For clarity the terms are tabulated:

$$\dot{m}\overline{C}_p/(\overline{GS_1})_R\sigma T_F^3\ [\equiv \dot{H}/(\overline{GS_1})_R\ \sigma T_F^4(1 - T_E^*)]$$
$$= \text{dimensionless firing density } D$$

After the division, the left-hand side term of Eq. (4.3.62) = $D(1 - T_E^*)$ and the first right-hand side term = $T_G^{*4} - T_1^{*4}$.

$$\frac{h_1A_1}{(\overline{GS_1})_R\sigma T_F^3} = N_c, \text{ convection number (dimensionless)}$$

$$\frac{A_oF_o}{(\overline{GS_1})_R} = L_o, \text{ wall openings loss number (dimensionless)}$$

$$\frac{UA_r}{(\overline{GS_1})_R\sigma T_F^3} = L_r, \text{ refractory wall loss number (dimensionless)}$$

The equation then becomes

$$D(1 - T_E^*) = T_G^{*4} - T_1^{*4} + N_c(T_G^* - T_1^*)$$
$$+ L_o(T_G^{*4} - T_o^{*4}) + L_r(T_G^* - T_o^*) \quad (4.3.63)$$

The two unknowns T_G^* and T_E^* are reduced to one by expressing T_E^* in terms of T_G^* and Δ. Equation (4.3.63), with coefficients of T_G^{*4} and T_G^* collected, then becomes

$$T_G^{*4} + \frac{D + N_c + L_r}{1 + L_o} T_G^*$$
$$- \frac{T_1^{*4} + N_cT_1^* + L_oT_o^{*4} + L_rT_o^* + D(1 + \Delta)}{1 + L_o} = 0 \quad (4.3.64)$$

Although Eq. (4.3.64) is a quartic equation, it is capable of explicit solution because of the absence of second- and third-degree terms (see end of subsection. Trial and error enter, however, because $(\overline{GS_1})_R$ and $\overline{C}_p$ are mild functions of T_G and related T_E, respectively, and a preliminary guess of T_G is necessary. Ambiguity can exist in the interpretation of terms. If part of the enclosure surface consists of screen tubes over the chamber gas exit to a convection section, radiative transfer to those tubes is included in the chamber energy balance but convection is not, because it has no effect on the chamber gas temperature. Although the results must be considered approximations, depending as they do on the empirical Δ, the equation may be used to find the effect of firing rate, excess air, and air preheat on efficiency. With some performance data available, the small effect of various factors on Δ may be found.

For the commonly encountered case of the sink consisting of a row of tubes mounted on a refractory wall, A_1 is the area of the whole plane in which the tubes lie, T_1 is tube surface temperature, and ε_1 is the effective emissivity of the tube-row-refractory-wall combination, as in the earlier numerical example associated with Fig. 4.3.6, where $\varepsilon_1 = 0.702$. A
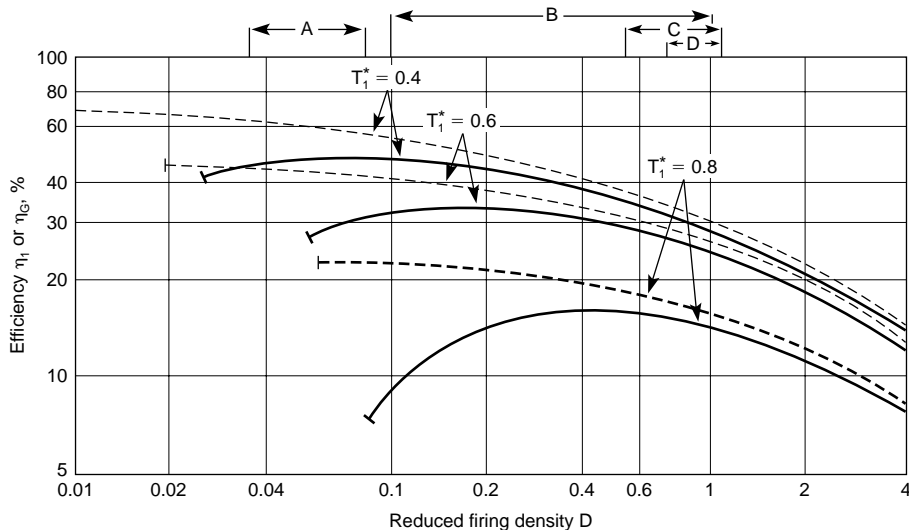

Fig. 4.3.6   The thermal performance of well-stirred furnace chambers. Conditions: $L_R = UA_R/(\overline{GS_1}\sigma T_F^3) = 0.016$; $N_c = hA_1/(\overline{GS_1}\sigma T_F^3) = 0.04$; $L_O = A_OF_O/\overline{GS_1} = 0$; $D = \dot{m}\overline{C}_p/(\overline{GS_1}\sigma T_F^3)$. Dotted lines: $\eta_G = $ (heat flux from gas)/(entering enthalpy in fuel and oxidant). Solid lines: $\eta_1 = $ (heat flux to sink)/(entering enthalpy in fuel and oxidant). Approximate range of D for various furnace classes: A, open hearths, $T_1^* = 0.7$ to 0.8; B, oil processing furnaces, $T_1^* \approx 0.4$; C, domestic boiler combustion chambers, $T_1^* \approx 0.2$; D, soaking pits, $T_1^* \approx 0.6$; gas-turbine combustors, off scale at right.

further simplification is to replace A_1/A_T by C, the ''cold'' fraction of the wall ($A_T \equiv A_1 + A_r$).

With T_G^* known, the chamber efficiency η_G based on heat transfer from the gas is given by

$$\eta_G = \frac{(1 - T_G^* + \Delta)}{1 - T_O^*} \qquad (4.3.65)$$

The efficiency based on energy to the sink is

$$\eta_1 = \eta_G - \frac{L_O(T_G^{*4} - T_O^{*4}) + L_r(T_G^* - T_O^*)}{D(1 - T_O^*)} \qquad (4.3.66)$$

or

$$\eta_1 = \frac{(GS_1)_R \sigma(T_G^4 - T_1^4) + h_1 A_1(T_G - T_1)}{H}$$

All heat transferred to the sink is included in η_1, and losses from its backside to the ambient must be subtracted.

Furnace Chamber Performance—General Although the chamber efficiency η depends on D, N_c, L_r, L_O, T_1^*, and T_O^*, the reduced firing density D is the dominant factor; it makes allowance for such operating variables as fuel type, excess air or air preheat—which affect flame temperature or gas emissivity, for fractional occupancy of the walls by sink surfaces, and for sink emissivity. Variation in the normalized sink temperature T_1^* has little effect until it exceeds 0.3; T_O^* is generally about ⅛; L_O is often negligible; N_c and L_r, though significant, are secondary.

Solution of Eq. (4.3.63) gives the relation between D and T_G^*, and Eqs. (4.3.65) and (4.3.66) give the relation between η_1 and D. As an example, Fig. 4.3.6 gives D versus η_1 (solid lines) and versus η_G (dotted lines), for values of N_c, L_r, L_O, and T_O^* of 0.04, 0.016, 0, and ⅛. Approximate operating regimes of various classes of furnaces are shown at the top of Fig. 4.3.6. Note the significant properties of the functions presented: (1) As firing rate D goes down, η_G rises, and so does η_1 until the losses due to L_O and L_r cause it to decrease. T_G^* approaches T_1^* in the limit as D decreases to $[L_O(T_1^{*4} - T_O^{*4}) + L_r (T_1^* - T_O^*)]/(1 - T_1^*)$, where $\eta_1 = 0$. (2) Changing T_1^* has a large effect only when it exceeds about 0.4. (3) As the furnace walls approach complete coverage by a black sink ($C = \varepsilon_1 = 1$), $\overline{GS_1}$ becomes $\varepsilon_G A_T$ and $D \propto 1/\varepsilon_G$. Thus, at very high firing rates where η_G approaches inverse proportionality to D, the efficiency of heat transfer varies directly as ε_G (gas-turbine chambers), but at low firing rates ε_G has relatively little effect. (4)

When $C\varepsilon_1 \ll 1$ because of a nonblack sink or much refractory surface, the effect of changing flame emissivity is to produce a much less than proportional effect on heat flux.

Equations (4.3.63) to (4.3.66) predict the effects of excess air, air preheat, and fuel quality on performance, through the effect on T_F; through $\overline{GS_1}$ they show the effect of gas and sink emissivity and the fraction of the chamber walls occupied by heat sink; through L_O and L_R they allow for external losses. They serve as a framework for correlating the performance of furnaces with flow patterns—plug flow, parabolic profile, and recirculatory flow—differing from the well-stirred model (Hottel and Sarofim, Chap. 14). As expected, plug-flow furnaces show somewhat higher efficiency, mild recirculation types somewhat lower efficiency, and strong recirculation furnaces an efficiency closely similar to that of the well-stirred model.

Explicit Solution of Limited Quartics Equations like (4.3.64) have the general form $ax^4 + bx = c$, which can be converted to $y^4 + y = B$, with y and B defined by $y \equiv (a/b)^{1/3}x$ and $B \equiv (c/a)(a/b)^{4/3}$.

An explicit solution comes from

$$k = \{[\sqrt{(B/3)^3 + 1/256} + 1/16]^{1/3} - [\sqrt{(B/3)^3 + 1/256} - 1/16]^{1/3}\}/2$$
$$y = \sqrt{\sqrt{4k^2 + B} - k} - \sqrt{k}$$

Refractory Temperature T_r Though the average value of T_r in a combustion chamber is not involved in the evaluation of T_G or η, it is sometimes of interest. It assumes a mean value between T_G and T_1, given by

$$\left(\frac{T_r}{T_G}\right)^4 = \frac{1 + E(T_1/T_G)^4}{1 + E}$$

For the speckled furnace gray gas model

$$E = C\varepsilon_1 \left(\frac{1}{\varepsilon_G} - 1\right)$$

Allowance is made for the difference between emissivity and absorptivity by changing ε_G to $\varepsilon_{G,e}$ in the above equation. For the gray-plus-clear-gas model,

$$E = C\varepsilon_1 \left[\frac{1}{\varepsilon_G} - \frac{1}{a} + \frac{1/a - 1}{C\varepsilon_1 + (1 + C)\varepsilon_R}\right]$$

4.4 TRANSMISSION OF HEAT BY CONDUCTION AND CONVECTION

by Kenneth A. Smith

REFERENCES: McAdams, ''Heat Transmission,'' McGraw-Hill. Eckert and Drake, ''Analysis of Heat and Mass Transfer,'' McGraw-Hill. Carslaw and Jaeger, ''Conduction of Heat in Solids,'' Oxford. Jakob, ''Heat Transfer,'' vols. I and II, Wiley. Kays and Crawford, ''Convective Heat and Mass Transfer,'' 3d ed., McGraw-Hill. Wilkes, ''Heat Insulation,'' Wiley. Kays and London, ''Compact Heat Exchangers,'' McGraw-Hill. ''Thermophysical Properties Data Book,'' Purdue University.

Notation and Units

The units are based on feet, pounds, hours, degrees Fahrenheit, and Btu. Any other consistent set may be used in the dimensionless relations given, but for the dimensional equations the units of this table must be used.

$A =$ area of heat-transfer surface, ft^2
$A_i =$ inside area
$A_o =$ outside area
$A_m =$ average value of A, ft^2
$a =$ empirical constant
$C_p =$ specific heat at constant pressure, Btu/lb · °F
$D =$ diameter, ft
$D_o =$ outside diameter, ft
$D_i =$ inside diameter, ft
$D' =$ diameter, in
$D'_o =$ outside diameter, in
$D'_i =$ inside diameter, in
$G =$ mass velocity, equals w/S, lb/h · ft^2 of cross section occupied by fluid
$G_{max} =$ mass velocity through minimum free area in a row of pipes normal to fluid stream, lb/h · ft^2
$g_c =$ conversion factor, equal to 4.18×10^8 (mass lb)(ft)/(force lb)(h)^2
$g_L =$ local acceleration due to gravity, 4.18×10^8 ft/h^2 at sea level
$h =$ local individual coefficient of heat transfer, equals $dq/dA \Delta t$, Btu/h(ft^2)(°F)diff
$h_c + h_r =$ combined coefficient by conduction, convection, and radiation between surface and surroundings
$h_m =$ mean value of h for entire surface, based on $(\Delta t)_m$
$h_{a.m.} =$ average h, arbitrarily based on arithmetic-mean temperature difference
$h_s =$ heat-transfer coefficient through scale deposits
$J =$ mechanical equivalent of heat, 778 ft · lb/Btu
$K =$ empirical constant
$k =$ thermal conductivity, Btu/h · ft · °F
$$k_m = -\frac{1}{t_1 - t_2} \int_1^2 k\, dt$$
$k_f = k$ at the ''film'' temperature, $t_j = (t + t_w)/2$
$l =$ thickness of material normal to heat flow, ft
$L =$ length of heat-transfer surface, heated length, ft
$N =$ number of rows of tubes
$N_{Gr} =$ Grashof number, $L_c^3 \rho_f^2 g_L \beta_f (\Delta t)_s / \mu_f^2$
$q =$ total rate of heat flow, Btu/h
$\dot{\mathbf{q}} =$ heat-flux vector, Btu/h · ft^2
$\dot{\mathbf{q}}_x = x$ component of heat flux vector
$R =$ thermal resistances, $1/(UA)$, $1/(hA)$, $1/(h_c + h_r)A_0$
$\mathcal{R} =$ recovery factor
$r =$ radius, ft
$S =$ cross section, filled by fluid, in plane normal to direction of fluid flow, ft^2
$T =$ temperature, °R $= t + 460$

$T_1, T_2 =$ inlet and outlet bulk temperatures, respectively, of warmer fluid, °F
$t =$ bulk temperature (based on heat balance), °F
$t_{a.w.} =$ temperature of adiabatic wall
$t_\infty =$ temperature at infinity
$t_w =$ wall temperature, °F
$t_1, t_2 =$ inlet and outlet bulk temperatures of colder fluid, °F
$t_i, t_o =$ temperatures of fluid inside and outside, °F
$t_f = (t + t_w)/2$
$t_{sat} =$ saturation temperature, °F
$U =$ overall coefficient of heat transfer, Btu/h · ft^2 · °F; U_i, U_o based on inside and outside surface, respectively
$V =$ mean velocity, ft/h
$V_s =$ average velocity, volumetric rate divided by cross section filled by fluid, ft/s
$V_{sm} =$ maximum velocity, through minimum cross section, ft/s
$x =$ one of the axes of a Cartesian reference frame, ft
$X = (t_2 - t_1)/(T_1 - t_1)$
$w =$ mass rate of flow per tube, lb/h/tube
$Z = (T_1 - T_2)/(t_2 - t_1)$
$\beta =$ volumetric coefficient of thermal expansion, °F^{-1}
$\Gamma =$ mass rate of flow, lb/(h) (ft of wetted periphery measured on a plane normal to direction of fluid flow); $= w/\pi D$ for a vertical and $w/2L$ for a horizontal tube
$\gamma =$ ratio of specific heats, c_p/c_v; 1.4 for air
$\nabla =$ gradient operator
$\Delta t =$ temperature difference, °F
$(\Delta t)_{ave}, (\Delta t)_{l.m.} =$ arithmetic and logarithmic means of terminal temperature differences, respectively, °F
$(\Delta t)_m =$ true mean value of the terminal temperature differences, °F
$(\Delta t)_o =$ overall temperature difference, °F
$(\Delta t)_s =$ temperature difference between surface and surroundings, °F
$\lambda =$ latent heat (enthalpy) of vaporization, Btu/lb
$\mu =$ viscosity at bulk temperature, lbm/h · ft; equals 2.42 times centipoises; equals 116,000 times viscosity in (lb force)(s)/ft^2
$\mu_f =$ viscosity, lbm/h · ft, at arithmetic mean of wall and fluid temperatures
$\mu_w =$ viscosity at wall temperature, lbm/h · ft
$\rho =$ density, lbm/ft^3
$\sigma =$ surface tension, lb force/ft

Subscripts:

$l =$ liquid
$v =$ vapor

Preliminary Statements The transfer of heat is usually considered to occur by three processes:

1. **Conduction** is the transfer of heat from one part of a body to another part or to another body by short-range interaction of molecules and/or electrons.

2. **Convection** is the transfer of heat by the combined mechanisms of fluid mixing and conduction.

3. **Radiation** is the emission of energy in the form of electromagnetic waves. All bodies above absolute zero temperature radiate. Radiation incident on a body may be absorbed, reflected, and transmitted. (See Sec. 4.3.)

Table 4.4.1   Thermal Conductivities of Metals*

$k = $ Btu/h · ft · °F
$k_t = k_{t_0} - a(t - t_0)$

Substance	Temp range, °F	k_{t_0}	a	Substance	Temp range, °F	k_{t_0}	a
Metals				Tin	60–212	36	0.0135
Aluminum	70–700	130	0.03	Titanium	70–570	9	0.001
Antimony	70–212	10.6	0.006	Tungsten	70–570	92	0.02
Beryllium	70–700	80	0.027	Uranium	70–770	14	−0.007
Cadmium	60–212	53.7	0.01	Vanadium	70	20	—
Cobalt	70	28	—	Zinc	60–212	65	0.007
Copper	70–700	232	0.032	Zirconium	32	11	—
Germanium	70	34	—	Alloys:			
Gold	60–212	196	—	Admiralty metal	68–460	58.1	−0.054
Iron, pure	70–700	41.5	0.025	Brass	−265–360	61.0	−0.066
Iron, wrought	60–212	34.9	0.002	(70% Cu, 30% Zn)	360–810	84.6	0
Steel (1% C)	60–212	26.2	0.002	Bronze, 7.5% Sn	130–460	34.4	−0.042
Lead	32–500	20.3	0.006	7.7% Al	68–392	39.1	−0.038
Magnesium	32–370	99	0.015	Constantan	−350–212	12.7	−0.0076
Mercury	32	4.8	—	(60% Cu, 40% Ni)	212–950	10.1	−0.019
Molybdenum	32–800	79	0.016	Dural 24S (93.6% Al, 4.4% Cu,	−321–550	63.8	−0.083
Nickel	70–560	36	0.0175	1.5% Mg, 0.5% Mn)	550–800	130.	+0.038
Palladium	70	39	—	Inconel X (73% Ni, 15% Cr, 7%	27–1,070	7.62	−0.0068
Platinum	70–800	41	0.0014	Fe, 2.5% Ti)			
Plutonium	70	5	—	Manganin (84% Cu, 12% Mn,	1,070–1,650	3.35	−0.0111
Rhodium	70	88	—	4% Ni)	−256–212	11.5	−0.015
Silver	70–600	242	0.058	Monel (67.1% Ni, 29.2% Cu,	−415–1,470	12.0	−0.008
Tantalum	212	32	—	1.7% Fe, 1.0% Mn)			
Thallium	32	29	—	Nickel silver (64% Cu, 17% Zn,	68–390	18.1	−0.0156
Thorium	70–570	17	−0.0045	18% Ni)			

* For refractories see Sec. 6; for pipe coverings, Sec. 8; for building materials, Sec. 4. Conversion factors for various units are given in Sec. 1. Tables 4.4.3–4.4.7 were revised by G. B. Wilkes.

CONDUCTION

See Tables 4.4.1 to 4.4.7 and 4.4.10

The **basic Fourier conduction law** for an isotropic material is

$$\dot{\mathbf{q}} = -k\nabla t \qquad (4.4.1)$$

In cartesian coordinates, the x component of this equation is $\dot{\mathbf{q}}_x = -k(\partial t/\partial x)$, and if the heat flow is unidimensional, $q = \dot{q}A(x) = -kA(x)(dt/dx)$. This states that the steady-state rate of heat conduction q is proportional to the cross-sectional area $A(x)$ normal to the direction of flow and to the temperature gradient $\partial t/\partial x$ along the conduction path. The proportionality constant k is called the **"true" thermal conductivity** of the material.

The thermal conductivity of a given material varies with temperature, and the mean thermal conductivity is defined by

$$k_m = \frac{1}{t'_0 - t'_i} \int_{t'_0}^{t'_i} k \, dt$$

Over moderate range, k varies linearly with t, and hence k_m is the value of k at the arithmetic mean of t'_i and t'_0.

Thermal Conductivity of Nickel-Chromium Alloys with Iron

$k_t = k_{t0} - a(t - t_0)$

ANSI number	Temp, range, °F	k_{t0}	a
301, 302, 303, 304 (303 Se, 304 L)	95–1,650	8.08	−0.0052
310 (3105)	32–1,650	6.85	−0.0072
314	80–572	10.01	−0.00124
	572–1,650	8.20	−0.0045
316 (316 L)	−60–1,750	7.50	−0.0042
321, 347 (348)	−100–1,650	8.22	−0.0050
403, 410 (416, 416 Se, 420)	−100–1,850	15.0	0
430 [430 F, 430 F (Se)]	122–1,650	12.60	−0.0012
440 C	212–932	12.77	−0.0043
446	32–1,850	12.96	−0.0050
501, 502	80–1,520	21.4	+0.0037

For unidimensional heat flow through a material of thickness l

$$q \int_0^l \frac{dx}{A(x)} = \int_{t'_i}^{t'_0} k \, dt = k_m(t'_i - t'_0) \qquad (4.4.2)$$

with an obvious definition for the mean area:

$$\frac{q}{A_m} = k_m(t'_i - t'_0)$$

For flat plates, $A_m = A_i = A_0$; for hollow cylinders, $A_m = (A_0 - A_i)/\ln (A_0/A_i)$; for hollow spheres, $A_m = \sqrt{A'A_0}$. For more complex shapes, Eq. (4.4.1) must be employed. For other configurations, mean areas may often be found elsewhere, e.g., Kutateladze and Borishanskei, "A Concise Encyclopedia of Heat Transfer," Pergamon Press, pp. 36–44.

CONDUCTION AND CONVECTION

Phenomena of Heat Transmission   In many practical cases of heat transmission—e.g., boilers, condensers, the cooling of engine cylinders—heat is transmitted from one fluid to another through a wall separating the two. The processes occurring in the fluids may be extremely complex. However, to facilitate discussion, it is convenient to imagine that most of the fluid offers no resistance to heat transmission but that a thin film of fluid adjacent to the wall offers considerable resistance. This situation is depicted in Fig. 4.4.1. Then, by definition,

$$q = h_i A_i(t_i - t'_i) = \frac{k}{l} A_m(t'_i - t_0) = h_0 A_0(t'_0 - t_0)$$

The terms h_i and h_0 are the **film coefficients,** or **unit conductances,** of the films f_1 and f_2, respectively, and k is the thermal conductivity of the wall. Since q, A, $t_i - t'_i$, and $t'_0 - t_0$ are susceptible to direct measurement, h_i and h_0 are simply defined quantities and the propriety of the above equation does not rest upon the heuristic film concept. Indeed, for laminar flow, the film concept is a gross misrepresentation, and yet the definition of a film coefficient (or heat-transfer coefficient) remains convenient and valid.

Properties of Molten Metals*

Metal (melting point)	Tempera-ture, °F	k, Btu (h)(ft)(°F)	ρ, lb cu ft	c_p, Btu (lb)(°F)	μ, lb (ft)(h)
Bismuth	600	9.5	625	0.0345	3.92
(520°F)	1,000	9.0	608	0.0369	2.66
	1,400	9.0	591	0.0393	1.91
Lead	700	10.5	658	0.038	5.80
(621°F)	900	11.4	650	0.037	4.65
	1,300	—	633	—	3.31
Mercury	50	4.7	847	0.033	3.85
(− 38°F)	300	6.7	826	0.033	2.66
	600	8.1	802	0.032	2.09
Potassium	300	26.0	50.4	0.19	0.90
(147°F)	800	22.8	46.3	0.18	0.43
	1,300	19.1	42.1	0.18	0.31
Sodium	200	49.8	58.0	0.33	1.69
(208°F)	700	41.8	53.7	0.31	0.68
	1,300	34.5	48.6	0.30	0.43
Na, 56 wt %	200	14.8	55.4	0.270	1.40
K, 44 wt %	700	15.9	51.3	0.252	0.570
(66.2°F)	1,300	16.7	46.2	0.249	0.389
Na, 22 wt %	200	14.1	53.0	0.226	1.19
K, 78 wt %	750	15.4	48.4	0.210	0.500
(12°F)	1,400	—	43.1	0.211	0.353
Pb, 44.5 wt %	300	5.23	657	0.035	
Bi, 55.5 wt %	700	6.85	639	0.035	3.71
(257°F)	1,200	—	614	—	2.78

* Based largely on ''Liquid-Metals Handbook,'' 2d ed., Government Printing Office, Washington.

If t_i' and t_0' are eliminated from the above equation, a relation is obtained for steady flow through several resistances in series:

$$q = \frac{t_i - t_0}{1/(h_i A_i) + 1/(kA_m) + 1/(h_0 A_0)} \quad (4.4.3)$$

Each of the terms in the denominator represents a resistance to heat transfer. There may also be a resistance, $1/(h_s A_s)$, due to the presence of a scale deposit on the surface. Thus, if the overall heat transfer is given by $q = UA(t_i - t_0)$, then the total thermal resistance is given by

$$1/(UA) = 1/(h_i A_i) + 1/(kA_m) + 1/(h_o A_o) + 1/(h_s A_s) \quad (4.4.4)$$

Coefficients for scale deposits are given in Table 4.4.9.

Fig. 4.4.1 Temperature gradients in heat flow through a wall.

Mean Temperature Difference The basic equation for any steadily operated heat exchanger is $dq = U(\Delta t)_o \, dA$, in which U is the overall coefficient [Eq. (4.4.4)], $(\Delta t)_o$ is the overall temperature difference between hot and cold fluids, and dq/dA is the local rate of flow per unit surface. In order to apply this relation to a finite exchanger, it is necessary to integrate it. The assumptions usually made are constant U, constant mass rates of flow, no changes in phase, constant specific heats,

and negligible heat losses. The resulting equation for parallel or countercurrent flow of fluids is

$$q = UA(\Delta t)_m = UA[(\Delta t)_{01} - (\Delta t)_{02}]/\ln [(\Delta t)_{01}/(\Delta t)_{02}] \quad (4.4.5a)$$

in which $(\Delta t)_m$ is the logarithmic mean of the terminal temperature differences, $(\Delta t)_{01}$ and $(\Delta t)_{02}$, between hot and cold fluid. The value of UA is evaluated from the resistance concept of Eq. (4.4.4) and the values of h are obtained from the following pages. For more complicated flow geometries, the logarithmic mean is not appropriate, and the true mean temperature difference may be obtained from Fig. 4.4.2, where

$$Y = \text{ordinate}$$
$$= \frac{\text{true mean temp difference}}{\text{logarithmic mean temp difference for counterflow}}$$

For the other symbols see. p. 4-79. (From *Trans. ASME,* **62,** 1940, pp. 283–294.)

The above discussion focuses on the concepts of an overall coefficient and a mean-temperature difference. An alternative approach focuses on the concepts of effectiveness and the number of transfer units. The alternatives are basically equivalent, but one or the other may enjoy a computational advantage. The latter method is presented in detail by Kays and London and by Mickley and Korchak (*Chem. Eng.,* **69,** 1962, pp. 181–188 and 239–242).

EXAMPLE. Assume an exchanger in which the hot fluid enters at 400°F and leaves at 327°F; the cold fluid enters at 100°F and leaves at 283°F. Assuming U independent of temperature, what will be the true mean temperature difference from hot to cold fluid, (1) for counterflow and (2) for a reversed current apparatus with one well-baffled pass in the shell and two equal passes in the tubes?

1. With counterflow, the terminal differences are $400 - 283 = 117°F$ and $327 - 100 = 227°F$; the logarithmic mean difference is $110/0.662 = 166°F$.

2. $Z = (400 - 327)/(283 - 100) = 0.4$; $X = (283 - 100)/(400 - 100) = 0.61$; from section A of Fig. 4.4.2, $Y = 0.9 = (\Delta t)_m/166$; $(\Delta t)_m = 149°F$.

Table 4.4.2 Thermal Conductivities of Liquids and Gases

Substance	Temp, °F	k	Substance	Temp, °F	k
Liquids:			Gases:		
Acetone	68	0.103	Air (see below)	32	0.0140
Ammonia	45	0.29	Ammonia, vapor	32	0.0126
Aniline	32	0.104	Ammonia	212	0.0192
Benzol	86	0.089	Argon	32	0.00915
Carbon bisulfide	68	0.0931	Carbon dioxide	32	0.0084
Ethyl alcohol	68	0.105		212	0.0128
Ether	68	0.0798	Carbon monoxide	32	0.0135
Glycerin, USP, 95%	68	0.165	Chlorine	32	0.0043
Kerosene	68	0.086	Ethane	32	0.0106
Methyl alcohol	68	0.124	Ethylene	32	0.0101
n-Pentane	68	0.0787	Helium	32	0.0818
Petroleum ether	68	0.0758	n-Hexane	32	0.0072
Toluene	86	0.086	Hydrogen	32	0.0966
Water	32	0.343		212	0.124
	140	0.377	Methane	32	0.0175
Oil, castor	39	0.104	Neon	32	0.0267
Oil, olive	39	0.101	Nitrogen	32	0.0140
Oil, turpentine	54	0.0734	Nitrous oxide	32	0.0088
Vaseline	59	0.106		212	0.0090
			Nitric oxide	32	0.0138
			Oxygen	32	0.0142
			n-Pentane	32	0.0074
			Sulphur dioxide	32	0.005

Thermal Conductivities of Air and Steam

Temperature, °F	32	200	400	600	800	1,000
Air, 1 atm	0.0140	0.0181	0.0225	0.0266	0.0303	0.0337
Steam, 1 lb/in² absolute	—	0.0132	0.0184	0.0238	0.0292	0.0345

SOURCE: F. G. Keyes, *Tech. Rept. 37,* Project Squid (Apr. 1, 1952).
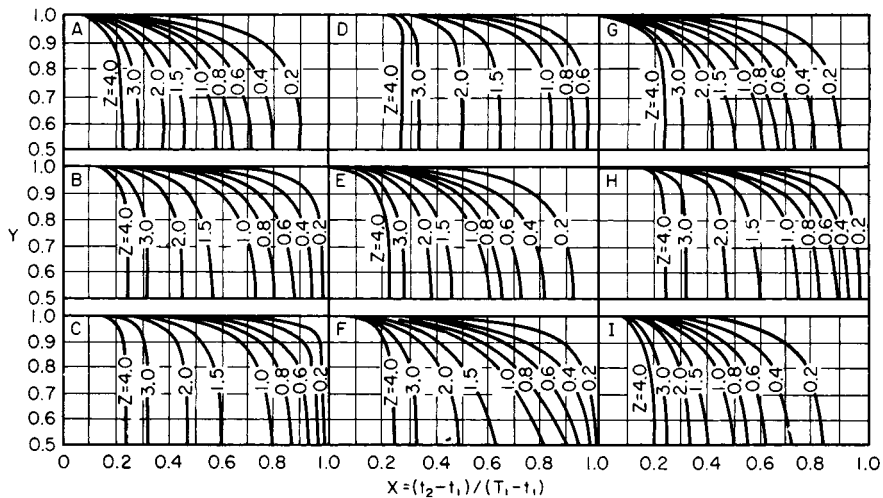
Fig. 4.4.2 (*A*) One shell pass and two tube passes; (*B*) two shell passes and four tube passes; (*C*) three shell passes and six tube passes; (*D*) four shell passes and eight tube passes; (*E*) cross flow, one shell pass and one tube pass, both fluids mixed; (*F*) single-pass cross-flow exchanger, both fluids unmixed; (*G*) single-pass cross-flow exchanger, one fluid mixed, the other unmixed; (*H*) two-pass cross-flow exchanger, shell fluid mixed, tube fluid unmixed, shell fluid first crossing the second tube pass; (*I*) same as (*H*), but shell fluid first crosses the first tube pass.

Table 4.4.3   Thermal Conductivities of Miscellaneous Solid Substances*
Values of k are to be regarded as rough average values for the temperature range indicated

Material	Bulk density, lb/ft³	Temp, °F	k	Material	Bulk density, lb/ft³	Temp, °F	k
Asbestos board, compressed asbestos and cement	123.	86.	0.225	Quartz, crystal, parallel to C axis	. . .	− 300.	25.0
						0.	8.3
						300.	4.2
Asbestos millboard	60.5	86.	0.070	Rubber, hard	74.3	100.	0.092
Asbestos wool	25.	212.	0.058	Rubber, soft, vulcanized	68.6	86.	0.08
Ashes, soft wood	12.5	68.	0.018				
Ashes, volcanic	51.	300.	0.123	Sand, dry	94.8	68.	0.188
Carbon black	12.	133.	0.012	Sawdust, dry	13.4	68.	0.042
Cardboard, corrugated	. . .	. . .	0.037	Silica, fused	. . .	200.	0.83
Celluloid	87.3	86.	0.12	Silica gel, powder	32.5	131.	0.049
Cellulose sponge, du Pont	3.4	82.	0.033	Soil, dry	. . .	68.	0.075
				Soil, dry, including stones	127.	68.	0.30
Concrete, sand, and gravel	142.	75.	1.05	Snow	7–31	32.	0.34–1.3
Concrete, cinder	97.	75.	0.41	Titanium oxide, finely ground	52.	1000.	0.041
Charcoal, powder	11.5	63.	0.029				
Cork, granulated	5.4	23.	0.028	Wool, pure	5.6	86.	0.021
Cotton wool	5.0	100.	0.035	Zirconia grain	113.	600.	0.11
Diamond	151.	70.	320.	Woods, oven dry, across grain†:			
Earth plus 42% water	108.	0.	0.62	Aspen	26.	85.	0.069
Fiber, red	80.5	68.	0.27	Bald cypress	24.	85.	0.063
Flotofoam (U.S. Rubber Co.)	1.6	92.	0.017	Balsa	10.	85.	0.034
				Basswood	24.	85.	0.058
Glass, pyrex	139	200.	0.59	Douglas Fir	29.	85.	0.063
Glass, soda lime	. . .	200.	0.59	Elm, rock	48.	85.	0.097
Graphite, solid	93.5	122.	87.	Fir, white	26.	85.	0.069
Gravel	116.	68.	0.22	Hemlock	29.	85.	0.066
Gypsum board	51.	99.	0.062	Larch, western	36.	85.	0.078
Ice	57.5	. . .	1.26	Maple, sugar	43.	85.	0.094
Kaolin wool	10.6	800.	0.059	Oak, red	42.	85.	0.099
Leather, sole	62.4	. . .	0.092	Pine, southern yellow	35.	85.	0.078
Mica	122.	. . .	0.25				
Pearlite, Arizona, spherical shell of siliceous material	9.1	112.	0.035	Pine, white	25.	85.	0.060
				Red cedar, western	21.	85.	0.053
Polystyrene, expanded ''Styrofoam''	1.7	. . .	0.021	Redwood	25.	85.	0.062
				Spruce	21.	85.	0.052
Pumice, powdered	49.	300.	0.11				
Quartz, crystal, perpendicular to C axis	. . .	− 300.	12.5				
		0.	4.3				
		300.	2.3				

* The thermal conductivity of different materials varies greatly. For metals and alloys k is high, while for certain insulating materials, such as glass wool, cork, and kapok, it is very low. In general, k varies with the temperature, but in the case of metals, the variation is relatively small. With most other substances, k increases with rising temperatures, but in the case of many crystalline materials, the reverse is true.

† With heat flow parallel to the grain, k may be 2 to 3 times that with heat flow perpendicular to the grain, the values for wool are taken chiefly from J. D. MacLean, *Trans. ASHRAE,* **47,** 1941, p. 323.

If one of the temperatures remains constant, as in a condenser or in an evaporative cooler, Eq. (4.4.5a) applies for parallel flow, counterflow, reversed current, and cross flow.

If U varies considerably with temperature, the apparatus should be considered to be divided into stages, in each of which the variation of U with temperature or temperature difference is linear. Then for parallel or counterflow operation, the following relation may be applied to each stage:

$$q = \frac{A[U_2(\Delta t)_{01} - U_1(\Delta t)_{02}]}{\ln [U_2(\Delta t)_{01}/U_1(\Delta t)_{02}]} \qquad (4.4.5b)$$

FILM COEFFICIENTS

The important physical properties which affect film coefficients (see Sec. 4.1) are thermal conductivity, viscosity, density, and specific heat. Factors within the control of the designer include fluid velocity and shape and arrangement of the heating surface. With forced flow of gases or water, under the conditions usually met in practice, the flow is turbulent (see Sec. 3) and under these conditions the film coefficient can be greatly increased by increasing the velocity of the fluid at the expense of a greater power requirement. For a given velocity and fluid, the film coefficient depends upon the direction of flow of fluid relative to the heating surface. With free or natural convection, for a given arrangement of surface, the film coefficient depends on an additional fluid property, the coefficient of thermal expansion, on the temperature difference between surface and fluid, and on the local gravitational acceleration. With forced convection at low rates of flow, particularly with viscous fluids such as oils, laminar motion may prevail and the film coefficient depends on thermal conductivity, specific heat, mass rate of flow per tube, and length and diameter of the tube. In any event, the film coefficients h are correlated in terms of dimensionless groups of the controlling factors.

Turbulent Flow inside Clean Tubes (No Change in Phase), $DG/\mu_f > 7,000$

$$\frac{h_m}{C_p G} \left(\frac{C_p \mu_f}{k_f} \right)^{2/3} = \frac{0.023}{(DG/\mu_f)^{0.2}} \qquad (4.4.6a)$$

Table 4.4.4   Thermal Conductivities for Building Insulation

Material	Bulk density, lb/ft^3	Temp, °F	k
Balsam wool, blanket	3.6	70.	0.021
Cabot's Quilt, eelgrass	15.6	86.	0.027
Glass wool, blanket	3.25	100.	0.022
Hairfelt, blanket	11.0	86.	0.022
Insulating boards, Insu-lite, Celotex, etc.	12–19	100.	0.027–0.031
Kapok, DryZero, blan-ket	1.6	75.	0.019
Redwood bark, loose, shredded, Palco Bark	4.0	100.	0.025
Rock wool, loose	7.	117.	0.024
Sil-O-Cel powder	10.6	86.	0.026
Vermiculite, loose, Zonolite	8.2	60.	0.038

Table 4.4.5   Thermal Conductivities of Material for Refrigeration and Extreme Low Temperatures

Material	Bulk density, lb/ft^3	Temp, °F	k
Corkboard	6.9	100	0.022
		− 100	0.018
		− 300	0.010
Fiberglas with asphalt coating (board)	11.0	100	0.023
		− 100	0.014
		− 300	0.007
Glass blocks, expanded cellular glass	8.5	100	0.033
		− 100	0.024
		− 300	0.016
Mineral wool board, Rockcork	14.3	100	0.024
		− 100	0.017
		− 300	0.008
Silica aerogel, powder, Santocel	5.3	100	0.013
		0	0.012
		− 100	0.010
Vegetable fiberboard, asphalt coating	14.4	100	0.028
		− 100	0.021
		− 300	0.013
Foams:			
Polystyrene*	2.9	− 100	0.015
Polyurethane†	5.0	− 100	0.019

* Test space pressure, 1.0 atm; $k = 0.0047$ at 10^{-5} mmHg.
† Test space pressure, 1.0 atm; $k = 0.007$ at 10^{-3} mmHg.

For L/D less than 60, multiply the right-hand side of Eqs. (4.4.6a), (4.4.6b), and (4.4.6c) by $1 + (D/L)^{0.7}$.

Turbulent Flow of Gases inside Clean Tubes, $DG/\mu_f > 7,000$

$$h_m = 0.024 C_p G^{0.8}/(D_i')^{0.2} \tag{4.4.6b}$$

Turbulent Flow of Water inside Clean Tubes, $DG/\mu_f > 7,000$

$$h_m = 160(1 + 0.012 t_f)V_s^{0.8}/(D_i')^{0.2} \tag{4.4.6c}$$

Turbulent Flow of Liquid Metals inside Clean Tubes, $C_p\mu/k < 0.05$ The equation of Sleicher and Tribus (''Recent Advances in Heat Transfer,'' p. 281, McGraw-Hill, 1961) is recommended for isothermal tube walls:

$$\frac{h_m D}{k} = 6.3 + 0.016 \left(\frac{DGC_p}{k}\right)^{0.91} \left(\frac{C_p\mu}{k}\right)^{0.3} \tag{4.4.6d}$$

Turbulent Flow of Gases or Water in Annull   Use Eq. (4.4.6b) or (4.4.6c), with D' taken as the clearance, inches. If the clearance is comparable to the diameter of the inner tube, see Kays and Crawford.

Water in Coiled Pipes   Multiply h_m for the staight pipe by the term $(1 + 3.5 D_i/D_c)$, where D_i is the inside diameter of the pipe and D_c is that of the coil.

Turbulent Boundary Layer on a Flat Plate, $V_\infty \rho_f x/\mu_f > 4 \times 10^5$, no pressure gradient

$$\frac{h}{\rho_f C_p V_\infty} \left(\frac{C_p\mu}{k}\right)^{2/3} = \frac{0.0148}{(\rho_f V_\infty x/\mu_f)^{0.2}} \tag{4.4.6e}$$

$$\frac{h_m}{\rho_f C_p V_\infty} \left(\frac{C_p\mu}{k}\right)_f^{2/3} = \frac{0.0185}{(\rho_f V_\infty L/\mu_f)^{0.2}} \tag{4.4.6f}$$

Fluid Flow Normal to a Single Tube, $D_o G/\mu_f$ from 1,000 to 50,000

$$\frac{h_m D_o}{k_f} = 0.26 \left(\frac{D_o G}{\mu_f}\right)^{0.6} \left(\frac{C_p\mu}{k}\right)_f^{0.3} \tag{4.4.7}$$

Gas Flow Normal to a Single Tube, $D_o G/u_f$ from 1,000 to 50,000

$$h_m = 0.30 C_p G^{0.6}/(D_o')^{0.4} \tag{4.4.7a}$$

Fluid Flow Normal to a Bank of Staggered Tubes, $D_o G_{max}/\mu_f$ from 2,000 to 40,000

$$\frac{h_m D_o}{k_f} = K \left(\frac{C_p\mu}{k}\right)_f^{1/3} \left(\frac{D_o G_{max}}{\mu_f}\right)^{0.6} \tag{4.4.8}$$

Values of K are given in Table 4.4.8.

Water Flow Normal to a Bank of Staggered Tubes, $D_o G_{max}/\mu_f$ from 2,000 to 40,000

$$h_m = 370(1 + 0.0067 t_f)V_{sm}^{0.6}/(D_o')^{0.4} \tag{4.4.8a}$$

Table 4.4.6   Thermal Conductivities of Insulating Materials for High Temperatures

Material	Bulk density, lb/ft^3	Max temp, °F	100°F	300°F	500°F	1,000°F	1,500°F	2,000°F
Asbestos paper, laminated	22.	400	0.038	0.042				
Asbestos paper, corrugated	16.	300	0.031	0.042				
Diatomaceous earth, silica, powder	18.7	1,500	0.037	0.045	0.053	0.074		
Diatomaceous earth, asbestos and bonding material	18.	1,600	0.045	0.049	0.053	0.065		
Fiberglas block, PF612	2.5	500	0.023	0.039				
Fiberglas block, PF614	4.25	500	0.021	0.033				
Fiberglas block, PF617	9.	500	0.020	0.033				
Fiberglas, metal mesh blanket, #900	. . . . . .	1,000	0.020	0.030	0.040			
Cellular glass blocks, ave. value	8.5	900	0.033	0.045	0.062			
Hydrous calcium silicate, ''Kaylo''	11.	1,200	0.032	0.038	0.045			
85% magnesia	12.	600	0.029	0.035				
Micro-quartz fiber, blanket	3.	3,000	0.021	0.028	0.042	0.075	0.108	0.142
Potassium titanate, fibers	71.5	. . . . .	. . . . .	0.022	0.024	0.030		
Rock wool, loose	8–12	. . . . .	0.027	0.038	0.049	0.078		
Zirconia grain	113.	3,000	. . . . .	. . . . .	0.108	0.129	0.163	0.217

Table 4.4.7   Thermal Conductance across Airspaces
Btu/(h)(ft²)—Reflective insulation

Airspace, in	Direction of heat flow	Temp diff, °F	Mean temp, °F	Aluminum surfaces, $\varepsilon = 0.05$	Ordinary surfaces, nonmetallic, $\varepsilon = 0.90$
Horizontal, ¾–4 across	Upward	20.	80.	0.60	1.35
Vertical, ¾–4 across	Across	20.	80.	0.49	1.19
Horizontal, ¾ across	Downward	20.	75.	0.30	1.08
Horizontal, 4 across	Downward	20.	80.	0.19	0.93

Table 4.4.8   Values of K for N Rows Deep

N	1	2	3	4	5	6	7	10
K	0.24	0.25	0.27	0.29	0.30	0.31	0.32	0.33

Table 4.4.9   Heat-Transfer Coefficients h_s for Scale Deposits from Water*
For use in Eq. (4.4.4)

	Up to 240°F		240 to 400°F	
	125°F or less		Above 125°F	
	3 and less	Over 3	3 and less	Over 3
Distilled	2,000	2,000	2,000	2,000
Sea water	2,000	2,000	1,000	1,000
Treated boiler feedwater	1,000	2,000	500	1,000
Treated makeup for cooling tower	1,000	1,000	500	500
City, well, Great Lakes	1,000	1,000	500	500
Brackish, clean river water	500	1,000	330	500
River water, muddy, silty†	330	500	250	330
Hard (over 15 grains per gal)	330	330	200	200
Chicago Sanitary Canal	130	170	100	130

Headers span: Temp of heating medium (Up to 240°F / 240 to 400°F); Temp of water (125°F or less / Above 125°F); Water velocity, ft/s (3 and less / Over 3 / 3 and less / Over 3).

Miscellaneous cases: Refrigerating liquids, brine clean petroleum distillates, organic vapors, 1,000; refrigerant vapor, 500; vegetable oils, 330; fuel oil (topped crude), 200.
  * From standards of Tubular Exchanger Manufacturers Assoc., 1952.
  † Delaware, East River (NY), Mississippi, Schuylkill, and New York Bay.

For baffled exchangers, to allow for leakage of fluids around the baffles, use 60 percent of the values of h_m from Eq. (4.4.8); for tubes in line, deduct 25 percent from the values of h_m given by Eq. (4.4.8).

Water Flow in Layer Form over Horizontal Tubes, $4\Gamma/\mu < 2{,}100$

$$h_{a.m.} = 150(\Gamma/D_o')^{1/3} \qquad (4.4.9)$$

for Γ ranging from 100 to 1,000 lb of water per h per ft (each side).

Water Flow in Layer down Vertical Tubes, $w/\pi D > 500$

$$h_m = 120\Gamma^{1/3} \qquad (4.4.9a)$$

Heat Transfer to Gases Flowing at Very High Velocities   If a nonreactive gas stream is brought to rest adiabatically, as at the true stagnation point of a blunt body, the temperature rise will be

$$t_s - t_\infty = V^2/(2g_c JC_p) \qquad (4.4.9b)$$

where t_s is the stagnation temperature and t_∞ is the temperature of the free stream moving at velocity V. At every other point on the body, the gas is brought to rest partly by pressure changes and partly by viscous effects in the boundary layer. In general, this process is not adiabatic, even though the body transfers no heat. The thermal conductivity of the gas will transfer heat from one layer of gas to another. At an insulated surface, the gas temperature will therefore be neither the free-stream temperature nor the stagnation temperature. In general, the rise in gas temperature will be given by the equation

$$t_{aw} - t_\infty = \mathcal{R}(t_s - t_\infty) = \mathcal{R}V^2/(2g_c JC_p) \qquad (4.4.9c)$$

where t_{aw} is the gas temperature at the adiabatic wall and $\mathcal{R}$ is the recovery factor.

If a given point on the surface of a body is not at the temperature t_{aw} given by Eq. (4.4.9c) with the proper local value of $\mathcal{R}$ inserted, there will be a transfer of heat to or from the body. This suggests defining the coefficient of heat transfer in the usual way, except that the difference $t_w - t_{aw}$ should be used:

$$q/A = h(t_\infty - t_{aw}) = h\{t_w - [t + \mathcal{R}V^2/(2g_c JC_p)]\} \quad (4.4.9d)$$

where t_w is the surface temperature of the heated wall. With this modification, it is found that the correlations for h are nearly independent of Mach number; e.g., Eq. (4.4.6a) may be used for turbulent, compressible flow in a pipe. Obviously, $\mathcal{R} = 1.0$ at a forward stagnation point. For flows parallel to surfaces which have little or no curvature in the direction of flow, the following are recommended:

Laminar flow $\qquad \mathcal{R} = \left(\dfrac{C_p\mu}{k}\right)^{1/2}$

Turbulent flow $\qquad \mathcal{R} = \left(\dfrac{C_p\mu}{k}\right)^{1/3}$

Very little is presently known about point values of the recovery factor for flow over more complex shapes. Thus, special thermocouples should be used to measure the temperature of high-velocity gas streams (Hottel and Kalitinsky, *Jour. Applied Mechanics,* 1945, pp. A25–A32;

Table 4.4.10   Typical Values of h_m for Heating and Cooling, Forced Convention
$D_0' = 1.31$ ln, $D_i' = 1.05$ in

Fluid and arrangement	t_f, °F	Velocity* ft/s	Velocity* lb/(h · ft²)	Btu/(h · ft² · °F)	Eq. no.
Air inside tubes	.....	$V_S = 31.8$, $G = 8{,}600$		8.0	4.4.6b
Air normal to staggered tubes	170	$V_S = 8.92$, $G_m = 2{,}000$		7.5	4.4.8
Water inside tubes	100	$V_S = 5.0$, $G = 1.12 \times 10^6$		1260	4.4.6c
Water normal to staggered tubes	100	$V_S = 2.0$, $G_m = 0.448 \times 10^6$		800	4.4.8a
Trickle cooler, water	.....	$\Gamma = 100$ lb/(h · ft)		640	4.4.9
Falling water film vertical tube	.....	$\Gamma = 1{,}000$ lb/(h · ft)		1200	4.4.9a

  * Velocity in ft/s at 70°F and 1 atm = $G/3{,}600\rho$.

and Franz, *Jahrb* 1938 *deut. Luftfahrt-Forsch* II, pp. 215–218). Eckert (*Trans. ASME,* **78,** 1956, pp. 1273–1283) recommends that all property values be evaluated at a film temperature defined by

$$t_f = (t_\infty + t_w)/2 + 0.22(t_{aw} - t_\infty) \qquad (4.4.9e)$$

Nielsen (*NACA Wartime Rep.* L-179) gives graphs for predicting the heat transfer and pressure drop for airflow at Mach numbers up to 1.0, in tubes having a uniform wall temperature.

Heat transfer from a reacting gas to a surface is treated by Lees (''Recent Advances in Heat and Mass Transfer,'' p. 161, McGraw-Hill).

LAMINAR FLOW

PIPE FLOW, $DG/\mu < 2{,}100$.   Use the Sieder-tate modification of the Graetz equation for isothermal tube walls and $wC_p/kL > 10$:

$$h_{a.m.}D/k = 2.0(wC_p/kL)^{1/3}(\mu/\mu_w)^{0.14} \qquad (4.4.10)$$

or

$$(h_{a.m.}/C_pG)(C_p\mu/k)^{2/3}(\mu_w/\mu)^{0.14} = 1.85(D/L)^{1/3}(DG/\mu)^{-2/3} \quad (4.4.10a)$$

As shown in Fig. 4.4.3, as DG/μ increases from 2,100 to 7,000, the effect of L/D diminishes and finally becomes negligible for $L/D > 60$.
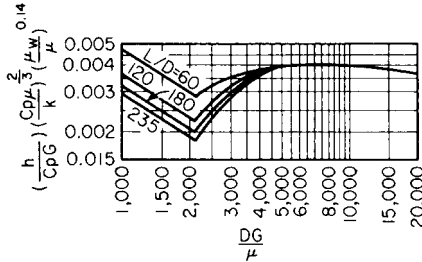
Fig. 4.4.3   Heating and cooling of viscous oils flowing inside tubes. [The curves for DG/μ below 2,100 are based on Eq. (4.4.10).]

LAMINAR BOUNDARY LAYER ON A FLAT PLATE. $\rho V_\infty x/\mu < 4 \times 10^5$, isothermal plate, no pressure gradient

$$\frac{h}{\rho_f C_p V_\infty}\left(\frac{C_p\mu}{k}\right)_f^{2/3} = \frac{0.332}{(\rho_f V_\infty x/\mu_f)^{1/2}} \qquad (4.4.10b)$$

$$\frac{h_m}{\rho_f C_p V_\infty}\left(\frac{C_p\mu}{k}\right)_f^{2/3} = \frac{0.664}{(\rho_f V_\infty L/\mu_f)^{1/2}}$$

Extended Surfaces   Fin efficiency is defined as the ratio of the mean temperature difference from surface to fluid divided by the temperature difference from fin to fluid at the base or root of the fin. Graphs of fin efficiency for extended surfaces of various types are given by Gardner (*Trans. ASME,* **67,** pp. 621–628, 1945) and in numerous texts, e.g., by Eckert and Drake, pp. 92–93. Heat-transfer coefficients for various extended surfaces are given by Kays and London.

Natural Convection   Heat transfer by natural convection is governed by relations of the form

$$\frac{h_m L_c}{k_f} = f[L_c^3\rho_f^2 g_L\beta_f(\Delta t)_s/\mu_f^2, (C_p\mu/k)_f] \qquad (4.4.11)$$

where β_f is defined by the equation $\rho_f = \rho_\infty[1 - \beta_f(\Delta t)_s)]$. For perfect gases, $\beta_f = 1/T_\infty$. The dimensionless group $L_c^3\rho_f^2 g_L\beta_f(\Delta t)_s/\mu_f^2 \equiv N_{Gr}$ represents the ratio of the product (inertial force times buoyant force) to (viscous force squared).

If the flow is of the laminar boundary layer type and if $(C_p\mu/k)_f > 1$, an effective correlation is

$$\frac{h_m L_c}{k_f} = B_1[N_{Gr}(C_p\mu/k)_f]^{0.25} \qquad (4.4.11a)$$

where B_1 is a weak function of $(C_p\mu/k)_f$. Similarly, for $(C_p\mu/k)_f < 1$,

$$\frac{h_m L_c}{k_f} = B_2[N_{Gr}(C_p\mu/k)_f^2]^{0.25} \qquad (4.4.11b)$$

VERTICAL FLAT PLATES.   For this case, $L = L_c$ and the flow of the laminar boundary layer type will be laminar if

$$\begin{array}{ll}(C_p\mu/k)_f > 1 & 10^9 > N_{Gr}(C_p\mu/k)_f > 10^4 \\ (C_p\mu/k)_f < 1 & ? > N_{Gr}(C_p\mu/k)_f^2 > 10^4\end{array}$$

Lefevre (*Rept. Heat* 113, National Engineering Laboratory, Great Britain, Aug. 1956) gives an interpolation formula which contains the proper limiting forms and is in complete agreement with existing numerical results:

$$\frac{h_m L_c}{k_f} = \left[\frac{N_{Gr}(C_p\mu/k)^2}{2.435 + 4.884(C_p\mu/k)_f^{1/2} + 4.953(C_p\mu/k)_f}\right]^{0.25} \quad (4.4.11c)$$

If $(C_p\mu/k)_f$ is in the vicinity of unity and if $N_{Gr} (C_p\mu/k)_f > 10^9$, the boundary layer will be turbulent and

$$\frac{hL}{k_f} = 0.13[N_{Gr}(C_p\mu/k)_f]^{1/3} \qquad (4.4.11d)$$

HORIZONTAL CYLINDERS.   Replace L in the vertical flat plate formulas by $\pi D_o/2$.

HEATED HORIZONTAL PLATES FACING UPWARD OR COOLED HORIZONTAL PLATES FACING DOWNWARD.

$$2 \times 10^7 > N_{Gr}(C_p\mu/k)_f > 10^5$$

$$\frac{h_m L}{k_f} = 0.54[N_{Gr}(C_p\mu/k)_f]^{0.25} \qquad (4.4.11e)$$

$$N_{Gr}(C_p\mu/k)_f > 2 \times 10^7$$

$$\frac{h_m L}{k_f} = 0.14[N_{Gr}(C_p\mu/k)_f]^{1/3} \qquad (4.4.11f)$$

HEATED HORIZONTAL PLATES FACING DOWNWARD OR COOLED HORIZONTAL PLATES FACING UPWARD.

$$3 \times 10^{10} > N_{Gr}(C_p\mu/k)_f > 3 \times 10^5$$

$$\frac{hL}{k_f} = 0.27[N_{Gr}(C_p\mu/k)_f]^{0.25} \qquad (4.4.11g)$$

Equations (4.4.11e) to (4.4.11g) should not be considered reliable if $(C_p\mu/k)_f$ differs greatly from unity.

For more complex systems, it is best to consult plots of experimental data (McAdams).

For any particular fluid, the above equations may be greatly simplified. For air which is at room temperature and atmospheric pressure and is subjected to the gravitational attraction at sea level:

VERTICAL PLATES.

$$10^3 > L^3(\Delta t)_s > 10^{-2}$$
$$h_m = 0.28[(\Delta t)_s/L]^{0.25} \qquad (4.4.12a)$$
$$L^3(\Delta t)_s > 10^3$$
$$h_m = 0.19(\Delta t)_s^{1/3} \qquad (4.4.12b)$$

HORIZONTAL CYLINDERS.

$$10^2 > D^3(\Delta t)_s > 10^{-3}$$
$$h_m = 0.25[(\Delta t)_s/D]^{0.25} \qquad (4.4.12c)$$
$$D^3(\Delta t)_s > 10^2$$
$$h_m = 0.19(\Delta t)_s^{1/3} \qquad (4.4.12d)$$

HEATED HORIZONTAL PLATES FACING UPWARD OR COOLED HORIZONTAL PLATES FACING DOWNWARD.

$$10 > L^3(\Delta t)_s > 0.1$$
$$h_m = 0.27[(\Delta t)_s/L]^{0.25} \qquad (4.4.12e)$$
$$10^4 > L^3(\Delta t)_s > 10$$
$$h_m = 0.22(\Delta t)_s^{1/3} \qquad (4.4.12f)$$

HEATED HORIZONTAL PLATES FACING DOWNWARD OR COOLED HORIZONTAL PLATES FACING UPWARD.

$$10^4 > L^3(\Delta t)_s > 0.1 \qquad (4.4.12g)$$
$$h_m = 0.12[(\Delta t)_s/L]^{0.25}$$

Condensing Vapors   If the condensate of a single pure vapor, saturated or supersaturated, wets the surface, film-type condensation is obtained. The rate of heat transfer equals $h_m(\Delta t)_m$, where $(\Delta t)_m$ is the mean difference between the saturation temperature and the temperature of the surface. As long as the condensate flow is laminar ($4\Gamma/\mu_f < 2{,}100$), the following dimensionless equations may be used:

For **horizontal tubes,**

$$h_m D/k = 0.73[D^3\rho^2\lambda g_L/k\mu_f N(\Delta t)_m]^{0.25}$$
$$= 0.76(D^3\rho^2 g_L/\mu_f\Gamma)^{1/3} \qquad (4.4.13)$$

For **vertical tubes,**

$$h_m L/k = 0.94[L^3\rho^2\lambda g_L/k\mu_f(\Delta t)_m]^{0.25}$$
$$= 0.93(L^3\rho^2 g_L/\mu_f\Gamma)^{1/3} \qquad (4.4.13a)$$

The equations show that a tube of given dimensions, for the usual case where $L/(ND)$ is greater than 2.76, is more effective in a horizontal than in a vertical position. Thus for $L/(ND) = 100$, a horizontal tube gives an average h which is 2.5 times that for a vertical tube. Since there is but little variation in the thermal conductivity or viscosity of the condensate at the condensing temperature at 1 atm, there is little variation in h_m. With horizontal tubes, use h_m from 200 to 400 Btu/h · ft^2 · °F for the following vapors condensing at atmospheric pressure: benzene, carbon tetrachloride, dichlormethane, dichlordifluoromethane, diphenyl ethyl alcohol, heptane, hexane, methyl alcohol, octane, toluene, and xylene. Ammonia gives h_m of 1,000, and mixtures of steam and organic vapors, forming immiscible condensates, give h_m ranging from 250 to 750, increasing with increasing proportion of steam. With film-type condensation of clean steam on horizontal tubes, h_m ranges from 1,000 to 3,000; see Eq. (4.4.13). With vertical tubes 10 to 20 ft long, ripples form in the film; values of h_m from Eq. (4.4.13a) should be increased 20 percent.

For long vertical tubes, $4\Gamma/\mu_f$ may exceed 2,100; in that case:

$$h_m(\mu_f^2/k_f^3\rho_f^2 g_L)^{1/3} = 0.0077(4\Gamma/\mu_f)^{0.4} \qquad (4.4.13b)$$

The presence of **noncondensible gas,** such as air, seriously reduces h, and consequently all vapor-heated apparatus should be well vented.

With steam, small traces of certain promoters (Nagle, U.S. Patent 1,995,361) such as oleic acid and benzyl mercaptan become adsorbed in a very thin layer on the surface of the tubes, preventing the condensate from wetting the metal and inducing dropwise condensation, which gives much higher values of h_m (7,000 to 70,000) than film-type condensation. However, with dirty or corroded surfaces, it is difficult to maintain dropwise condensation. Figure 4.4.4 shows overall coefficients U_o for condensing steam at 1 atm on a vertical 10-ft length of copper tube, ⅝ in OD, 0.049-in wall, at various water velocities.
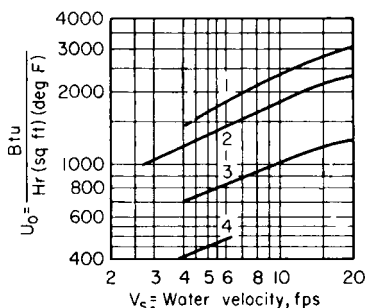

Fig. 4.4.4   Overall coefficients between condensing steam and water. Curve 1, chromium-plated copper, oleic acid; curve 2, copper, benzyl mercaptan; curve 3, copper, oleic acid; curve 4, admiralty metal, no promoter.

Boiling Liquids   The nature of the heat transfer from a submerged heater to a pool of boiling water is shown in Fig. 4.4.5. Other liquids exhibit the same qualitative features. In the range AB, heat transfer to the liquid occurs solely by natural convection, and evaporation occurs at the free surface of the pool. In the range BC, **nucleate boiling** occurs. Bubbles form at active nuclei on the heating surface, detach, and rise to the pool surface. At point C, the heat flux passes through a maximum at
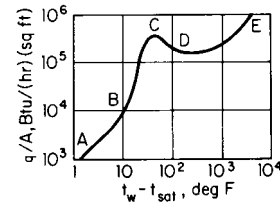

Fig. 4.4.5   Boiling of water at 212°F on a platinum surface.

a temperature difference called the **critical** Δt. In the range CD, transitional boiling occurs. At point D, the transition is complete and the heating surface is completely blanketed by a vapor film. This is the point of minimum heat flux, or the **Leidenfrost point.** In the range DE, the heating surface continues to be blanketed by a vapor film.

The range AB is adequately correlated by the usual natural-convection equations. No truly adequate correlation is available for the range BC because the complex processes of nucleation and interfacial interaction are only partially understood. However, the relation due to Rohsenow (*Trans. ASME,* **74,** 1952, pp. 969–976) is one of the best and can be reliably used for modest extrapolations of existing data.

$$\frac{C_{p,l}(t_w - t_{\text{sat}})}{\lambda} = C_{fs}\left[\frac{q/A}{\mu_l\lambda}\sqrt{\frac{g_c\sigma}{g_L(\rho_l - \rho_v)}}\right]^{1/3}\left(\frac{C_{p,l}\mu_l}{k_l}\right)^{1.7} \qquad (4.4.14a)$$

The value of the constant C_{fs} is intimately dependent on the nature of the particular fluid-solid pair and must be determined by experiment. It usually assumes values in the range $0.003 < C_{fs} < 0.05$ and is not affected by moderate subcooling or the shape of the heating surface.

Zuber (*USAEC Rep.* AECU-4439, June, 1959) has presented a theoretical equation for the maximum heat flux from a flat, horizontal surface. The analysis is based on considerations of hydrodynamic stability. For saturated liquids,

$$(q/A)_{\max} = K_1\rho_v\lambda\left[\frac{\sigma g_L g_c(\rho_l - \rho_v)}{\rho_v^2}\right]^{1/4}\left(\frac{\rho_l}{\rho_l + \rho_v}\right)^{1/2} \qquad (4.4.14b)$$
$$0.12 < K_1 < 0.157 \qquad (\text{theoretical})$$

Berenson (Sc.D. thesis, Mechanical Engineering Department, MIT, 1960) used a similar analysis and obtained a relation which is identical for $\rho_l \gg \rho_v$, but he found that $K_1 = 0.18$ gives better agreement with the data. The theoretical basis of this equation has been subject to attack,

Table 4.4.11   Maximum Flux and Corresponding Overall Temperature Difference for Liquids Boiled at 1 atm with a Submerged Horizontal Steam-Heated Tube

Liquid	Aluminum $\dfrac{q/A}{1{,}000}$	$(\Delta t)_o$	Copper $\dfrac{q/A}{1{,}000}$	$(\Delta t)_o$	Chromium-plated copper $\dfrac{q/A}{1{,}000}$	$(\Delta t)_o$	Steel $\dfrac{q/A}{1{,}000}$	$(\Delta t)_o$
Ethyl acetate	41	70	61	55	77	55		
Benzene	51	80	58	70	73	100	82	100
Ethyl alcohol	55	80	85	65	124	65		
Methyl alcohol	. . . . .	. . . .	100	95	110	110	155	110
Distilled water	. . . . .	. . . .	230	85	350	75	410	150

but the correlation appears to be the best available. Zuber also performed an analysis for subcooled liquids and proposed a modification which is also in excellent agreement with experiment:

$$\left(\frac{q}{A}\right)_{\text{max}} = K_1\rho_v[\lambda + C_{p,l}(t_{\text{sat}} - t_l)]\left[\frac{\sigma g_L g_c(\rho_l - \rho_v)}{\rho_v^2}\right]^{0.25}$$

$$\times \left(\frac{\rho_l}{\rho_l + \rho_v}\right)^{1/2}$$

$$\times \left\{1 + \frac{5.33(\rho_l C_{p,l} k_l)^{1/2}(t_{\text{sat}} - t_l)}{\rho_v[\lambda + C_{p,l}(t_{\text{sat}} - t_l)]}\left[\frac{g_L(\rho_l - \rho_v)\rho_v^2}{\sigma^3 g_c^3}\right]^{1/8}\right\} \quad (4.4.14c)$$

Zuber's hydrodynamic analysis of the Leidenfrost point yields

$$(q/A)_{\text{min}} = K_2\lambda\rho_v\left[\frac{\sigma g_L g_c(\rho_l - \rho_v)}{\rho_l^2}\right]^{1/4}$$

$$0.144 < K_2 < 0.177 \quad (4.4.14d)$$

Berenson finds better agreement with the data if $K_2 = 0.09$. For very small wires, the heat flux will exceed that predicted by this flat-plate formula. A reliable prediction of the critical temperature is not available.

For nucleate boiling accompanied by forced convection, the heat flux may be approximated by the sum of the heat flux for pool boiling alone and the heat flux for forced convection alone. This procedure will not be satisfactory at high qualities, and no satisfactory correlation exists for the maximum heat flux.

For a given liquid and system pressure, the nature of the surface may substantially influence the flux at a given (Δt), Table 4.4.11. These data may be used as rough approximations for a bank of submerged tubes. Film coefficients for scale deposits are given in Table 4.4.9.

For **forced-circulation evaporators,** vapor binding is also encountered. Thus with liquid benzene entering a 4-pass steam-jacketed pipe at 0.9 ft/s, up to the point where 60 percent by weight was vaporized, the maximum flux of 60,000 Btu/h · ft² was obtained at an overall temperature difference of 60°F; beyond this point, the coefficient and flux decreased rapidly, approaching the values obtained in superheating vapor, see Eq. (4.4.6b). For comparison, in a natural convection evaporator, a maximum flux of 73,000 Btu/h · ft² was obtained at $(\Delta t)_v$ of 100°F.

Combined Convection and Radiation Coefficients   In some cases of heat loss, such as that from bare and insulated pipes, where loss is by convection to the air and radiation to the walls of the enclosing space, it is convenient to use a combined convection and radiation coefficient $h_c + h_r$. The rate of heat loss thus becomes

$$q = (h_c + h_r)A(\Delta t)_s \quad (4.4.15)$$

where $(\Delta t)_s$ is the temperature difference, °F, between the surface of the hot body and the walls of the space. In evaluating $(h_c + h_r)$, h_c should be calculated by the appropriate convection formula [see Eqs. (4.4.11c) to (4.4.11g)] and h_r from the equation

$$h_r = 0.00685\varepsilon(T_{\text{av}}/100)^3$$

where ε is the emissivity of the radiating surface (see Sec. 4.3). T_{av} is the average temperature of the surface and the enclosing walls, °R. For oxidized bare steel pipe, the sum $h_c + h_r$ may be taken directly from Table 4.4.12.

Heat Transmission through Pipe Insulation (McMillan, *Trans. ASME,* 1915)   For any number of layers of insulation on any size of pipe, Eqs. (4.4.2), (4.4.4), and (4.4.15) combine to give

$$\frac{q_o}{A_o} = \frac{(\Delta t)_o}{\dfrac{r_o}{k_1}\ln\dfrac{r_2}{r_1} + \dfrac{r_o}{k_2}\ln\dfrac{r_3}{r_2} + \cdots + \dfrac{1}{h_c + h_r}} \quad (4.4.16)$$

where q_o/A_o is the Btu/(h · ft²) of outer surface of the last layer; $(\Delta t)_o$ is the overall temperature difference (°F) between pipe and air; r_o is the radius, feet, of the outer surface; r_1 is the outside radius (ft) of the pipe, $r_2 = r_1 +$ thickness of first layer of insulation, foot; $r_3 = r_2$ plus the thickness of second layer, etc.; and k_1, k_2, k_3, etc., are the conductivities of the respective layers. For average indoor conditions, $h_c + h_r$ is often taken as 2 as an approximation, since a substantial error in $h_c + h_r$ will have but little effect on the overall loss of heat. Figure 4.4.6 shows the variation in U_o with pipe size and thickness of insulation (for $k = 0.042$) for pipe and air temperatures of 375 and 75°F, respectively.
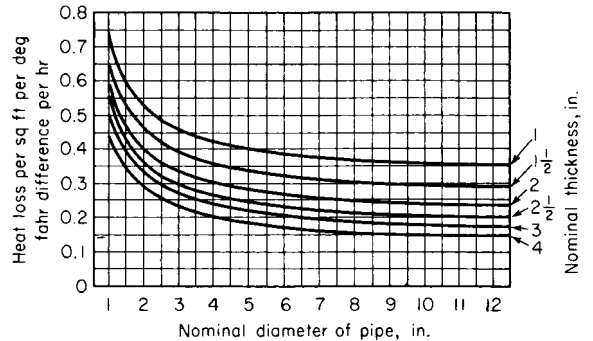

Fig. 4.4.6   Variation with pipe size of overall coefficient U_o for a given thickness of insulation, for $k = 0.042$.

Table 4.4.12   Values of $h_c + h_r$
For horizontal bare or insulated standard steel pipe of various sizes and for flat plates in a room at 80°F

| Nominal pipe diam, in | $(\Delta t)_s$, temperature difference, °F, from surface to room | | | | | | | | | | | | | | |
	50	100	150	200	250	300	400	500	600	700	800	900	1,000	1,100	1,200
½	2.12	2.48	2.76	3.10	3.41	3.75	4.47	5.30	6.21	7.25	8.40	9.73	11.20	12.81	14.65
1	2.03	2.38	2.65	2.98	3.29	3.62	4.33	5.16	6.07	7.11	8.25	9.57	11.04	12.65	14.48
2	1.93	2.27	2.52	2.85	3.14	3.47	4.18	4.99	5.89	6.92	8.07	9.38	10.85	12.46	14.28
4	1.84	2.16	2.41	2.72	3.01	3.33	4.02	4.83	5.72	6.75	7.89	9.21	10.66	12.27	14.09
8	1.76	2.06	2.29	2.60	2.89	3.20	3.88	4.68	5.57	6.60	7.73	9.05	10.50	12.10	13.93
12	1.71	2.01	2.24	2.54	2.82	3.13	3.83	4.61	5.50	6.52	7.65	8.96	10.42	12.03	13.84
24	1.64	1.93	2.15	2.45	2.72	3.03	3.70	4.48	5.37	6.39	7.52	8.83	10.28	11.90	13.70
Flat plates															
Vertical	1.82	2.13	2.40	2.70	2.99	3.30	4.00	4.79	5.70	6.72	7.86	9.18	10.64	12.25	14.06
HFU*	2.00	2.35	2.65	2.97	3.26	3.59	4.31	5.12	6.04	7.07	8.21	9.54	11.01	12.63	14.45
HFD*	1.58	1.85	2.09	2.36	2.63	2.93	3.61	4.38	5.27	6.27	7.40	8.71	10.16	11.76	13.57

* HFU = horizontal facing upward; HFD = horizontal facing downward.