nated by subscripts 1 and 2, respectively, and the several terms for the energy term e are enumerated, then:

$$dE = dQ - AdW + \left(\frac{A\omega_1^2}{2g_e} + AZ_1\frac{g}{g_e} + u_1 + AP_1v_1\right)dm_1 - \left(\frac{A\omega_2^2}{2g_e} + AZ_2\frac{g}{g_e} + u_2 + AP_2v_2\right)dm_2 \quad (6)$$

A *steady flow system* is defined as a system in which the mass flows into and out of the system are equal and at a constant rate, and the properties of the system at any point are also constant, with respect to time. An application of the above general equation to the steady flow system ($dE = 0$) gives:

$$Q' - A_1W'_1 = \left\{\left(u_1 + \frac{A\omega_1^2}{2g_e} + AZ_1\frac{g}{g_e} + AP_2v_2\right) - \left(u_1 + \frac{A\omega_1^2}{2g_e} + AZ_1\frac{g}{g_e} + AP_1v_1\right)\right\}m' \quad (7)$$

where

Q' = rate of heat transfer, Btu per hour.
AW' = power (work rate), Btu per hour.
ω = average velocity of stream flow, feet per second.
Z = height of stream above a given datum, feet.
m' = rate of stream flow, pounds per hour.
g_e = acceleration of gravity at sea level.
g = acceleration of gravity at height of stream.

It should be noted that, in Equations 6 and 7, $u + APv = h$, or *enthalpy*.

The energy transfer or *heat* added to the system by conduction, radiation or convection may also be expressed in terms of the properties of the system:

$$dQ = Cdt = mcdt \quad (8)$$

where

$C = mc$ = heat capacity.
c = specific heat capacity of the system.

In applications to systems at moderate pressures, the specific heat capacity may be regarded as a function of temperature only, or as a constant. Empirical equations relating the specific heat capacity as a function of temperature are available in the literature.[11] Where extremes in pressure are encountered, it may be necessary to consider the effect of pressure on the specific heat capacity. However, thermal data on specific heat capacity of high pressures is scarce, and P-v-T data which may be used to calculate the pressure deviations are rarely of sufficient accuracy to permit such calculations. In many cases, sufficient accuracy may be obtained by employing alternate forms of a calculation, in which values of enthalpy and entropy may be used in the appropriate relationships for heat transfer.

SECOND LAW OF THERMODYNAMICS

The *second law of thermodynamics* is a statement to the effect that, if an engine operates continuously receiving energy from a source at a given temperature T_1 and discharging energy to a receiver at a lower temperature T_2, there is a limit to the amount of work that can be obtained from the conversion of heat into work, and this limit depends solely on the temperatures of the source and the receiver. The statement may be adapted to include systems of more than one source or sink.

A number of corollaries follow from this statement:

1. No engine can be more efficient than a reversible engine operating between these same temperatures.
2. The efficiency of all reversible engines (cycles) operating between these temperatures is the same, and:

$$\eta_R = \frac{W_e}{Q_i} = \frac{Q_i - Q_e}{Q_i} = \frac{T_1 - T_2}{T_1}$$

3. The coefficient of performance of all reversible engines (cycles) operating as a refrigerator between the same temperatures is:

$$(\mathrm{CP}) = \frac{T_2}{T_1 - T_2}$$

4. For any engine cycle:

$$\oint \frac{dQ}{T} \leq 0 \text{ (Clausius inequality)}$$

The inequality exists for any but reversible cycles. For a reversible cycle:

$$\oint \left(\frac{dQ}{T}\right)_R = 0$$

and it follows, for a reversible process, that:

$$\int_1^2 \left(\frac{dQ}{T}\right)_R$$

is independent of the path traversed from the initial to the final state, so long as it is reversible. A property *entropy* S is thus defined as:

$$\int_1^2 \left(\frac{dQ}{T}\right)_R = S_2 - S_1$$

From the above inequality it also follows that, for an irreversible adiabatic process, $(S_2 - S_1) > 0$. If an engine receives heat at temperature T_1, the entropy decrease of the reservoir is Q_1/T_1, and, if the engine gives up heat to the receiver at a lower temperature T_2, then the entropy increase of these surroundings is increased by an amount Q_2/T_2.

The net entropy increase of the universe is:

$$\Delta S_{\text{sink}} - \Delta S_{\text{source}} > 0$$

and the net energy made unavailable for doing work due to the irreversibilities is the above quantity multiplied by the temperature T_2 of the receiver, or:

$$Q_u = T_2(\Delta S_{\text{sink}} - \Delta S_{\text{source}})$$

This concept is important in the analysis of irreversible process, as indicated in Part II, Refrigeration Cycles.

EQUATIONS OF STATE

An *equation of state* of a pure substance is a mathematical relation between the pressure, specific volume, and the temperature, when the system is in thermodynamic equilibrium:

$$f(P, v, T) = 0$$

Experimental evidence indicates the above relation to be valid for any pure substance. At present, it is not possible to theoretically develop such an equation of state from mechanics. As a result, empirical equations with varying amounts of theoretical significance have been proposed.

The van der Waals equation is an equation of state having theoretical significance. It qualitatively predicts the behavior of a substance, but with limited accuracy.

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT \quad (9)$$

The virial equation, a power series type of expansion in terms of the density and temperature coefficients, may be used as an equation of state.

$$Pv = A + \frac{B}{v} + \frac{C}{v^2} + \cdots \quad (10)$$

An advantage of this form is that statistical mechanics may be used as means of predicting the second and third coefficients. Thermodynamicists have recently concentrated on the partition or distribution function to determine the virial coefficients.[6] In general, however, experimental values of the second and third coefficients are still preferred. For the more dense fluid, many higher order terms are necessary which can neither be satisfactorily predicted from theory nor be determined from experimental measurements. In general, a truncated virial expansion of three terms is valid for densities less than one-half of the value at the critical point. For higher densities, additional terms may be used which can be determined empirically; as a result, the theoretical implications may be of little value, except for predicting trends.

The van der Waals' equation, expressed in virial form, becomes:

$$Pv = RT + \frac{(RTb - a)}{v} + \frac{RTb^2}{v^2} + \cdots \quad (11)$$

The Beattie-Bridgeman equation is an empirical equation of state that gives excellent results for densities up to approximately one-half of the critical density. Expressed in modified virial form it becomes:

$$Pv = RT(1 - \epsilon)\frac{(v + B)}{v^2} - \frac{A}{v^2} + \cdots \quad (12)$$

where

$A = A_o(1 - a/v)$
$B = B_o(1 - b/v)$
$\epsilon = c/vT^3$
A_o, a, B_o, b, and c are constants.

The coefficients A, B, and C are unique for each substance.[4]

With the use of high speed computers, equations of state that are far more complex have been used with success in predicting P-v-T values, even to high densities. The Benedict-Webb-Rubin equation of state[12] and the Martin-Hou equation[13] have had considerable use, but generally are limited to densities less than the critical value. Strobridge[14] has suggested a modified Benedict-Webb-Rubin relation that gives excellent results at higher densities and may be used for a P-v-T surface that extends into the liquid phase.

A simple relation, the ideal gas equation, is suggested if one plots the product of $P \cdot v$ against P for a real gas at a constant temperature; as the pressure approaches zero, the product becomes independent of the substance of the gas, and the first virial coefficient A in Equation 10 is a function of temperature:

$$\lim_{P \to 0} Pv = A$$

An ideal gas is then defined as:

$$\lim_{P \to 0} \frac{Pv}{T} = R = 1545 \text{ foot pounds per (mol) (Rankine degree).} \quad (13)$$

The virial equation can also be written as:

$$Z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \cdots \quad (14)$$

The ratio Z is the *compressibility factor*.

A useful tool for predicting properties of a fluid in the absence of experimental data is the concept of corresponding states which relate the properties of similar substances by suitable reducing factors, that is, the P-v-T surface of similar fluids in a given region are assumed to be of similar shape. According to van der Waals' principle of corresponding states, the critical point may be used to define the reducing parameters to scale the surface of one fluid to the dimensions of another. Modifications of this principle, as suggested by Kamerlingh Onnes, have been successfully used to improve the correspondence at low pressures.

In practice, the concepts provide useful approximations, and numerous modifications have been reported in the literature. More complex treatments for predicting property values which recognize the similarity of fluids and their P-v-T properties are contained in the literature on generalized equations of state. These equations ordinarily allow for the adjustment of the P-v-T surface by the introduction of parameters. An example of this type of generalized equation, given by Hirschfelder *et al*,[15] allows for departures from the principle of corresponding states by using two additional correlating parameters.

PART II: COMPRESSION REFRIGERATION CYCLES

A refrigeration cycle is one which continually transfers thermal energy from a region of low temperature to a region of higher temperature. The region of higher temperature is usually the ambient atmosphere or a space occupied by economically available water. The two most common methods used to accomplish this transfer of thermal energy are the vapor compression refrigeration cycle, discussed in this section, and the absorption refrigeration cycle, discussed in Part III.

By means of Second-Law analyses, the following will be demonstrated in this section: (1) for a given refrigeration load, the reversed Carnot cycle, having heat transfers through negligible temperature differences, is an ideal standard, and it is the criterion for minimum requirements of work input to a compression refrigeration cycle, (2) departures from this ideal standard, such as fluid friction or heat transfer through a finite temperature difference, will degrade available energy and will cause an increase in entropy of the universe, (3) such departures require that the work input to the refrigeration cycle be greater than the ideal minimum. It will be shown that this increased work input is equal to the product of the absolute temperature of the atmosphere and the increase in entropy of the universe $T_a\Delta S_{\text{univ}}$, which is also equal to the sum of the available energies that are degraded by: (1) irreversibilities that are produced by the refrigerant in its cyclical operation, and (2) heat transfers through finite temperature differences.

THE IDEAL BASIC VAPOR COMPRESSION REFRIGERATION CYCLE

The equipment diagram for this refrigeration cycle is shown in Fig. 1 and the p-h and T-S diagrams are presented in Figs. 2 and 3. At point 1, the refrigerant leaves the evaporator as a low pressure, low temperature, dry, saturated vapor and enters the compressor, where it is compressed reversibly and isentropically. At point 2, it leaves the compressor as a high temperature, high pressure, superheated vapor and enters the condenser, where it is desuperheated and condensed reversibly at constant pressure. At point 3, it leaves the condenser as a high pressure, medium temperature, saturated liquid and enters the expansion valve, where it is expanded irreversibly and adiabatically at constant enthalpy. At point 4, it leaves the expansion valve as a low pressure, low temperature, low quality vapor and enters the evaporator, where it is evaporated reversibly at constant pressure to the dry, saturated state at point 1. Heat transfer to the evaporator and from the condenser both occur with negligible temperature difference between the fluid emitting the heat and the fluid which