by applying a small modulating signal or by switching, using an electromagnetic field or plasma injection.

FUTURE POSSIBILITIES

In large power applications for space (above 1,000 kWe), the nuclear thermionic system appears to have advantages over a vapour cycle turbine system, partly because of its inherent compactness.

In terrestrial nuclear power systems thermionic conversion is superior to either the magnetohydrodynamic (MHD) generator or the thermoelectric system for power plant topping. With fossil power, however, the MHD system may be a more attractive topping technique.

Extensive undersea applications, both small power and large power, still await development. For this use the thermionic converter is substantially more efficient than the thermoelectric system.

BIBLIOGRAPHY. S.L. SOO, *Direct Energy Conversion* (1968), a modern text dealing with all aspects of direct energy conversion, devices, comparison, and long-range prospects, including an extensive bibliography; S.N. LEVINE (ed.) *Selected Papers on New Techniques for Energy Conversion* (1961), an overall survey and collection of important papers on progress made to 1960; E. BLUE and J.H. INGOLD, "Thermionic Energy Conversion," in O.W. SUTTON (ed.), *Direct Energy Conversion*, pp. 239–335 (1969), a discussion of recent surveys, emphasizing basic theories of plasma physics and solid-state physics; and G.C. SZEGO and J.E. TAYLOR (eds.), *Space Power System Engineering* (1966), a general survey including comparison of various devices, selection and range of application, and costs for space emissions.
For information on recent developments, see the *Proceedings of the Intersociety Energy Conversion Engineering Conference* (annual).

(S.L.S.)

Thermodynamics, Principles of

Thermodynamics is that part of physical science that is concerned with the conditions that material systems may assume and the changes in conditions that may occur either spontaneously or as a result of interactions between systems, including interactions such as heat, which cannot be described in terms of mechanics. It is basic to the distinction between mechanics and thermodynamics that according to mechanics all the energy of a system in any state is convertible to work, whereas according to thermodynamics only a fraction of the energy of a system in most states is convertible to work without other effects. The scope of thermodynamics has been steadily broadening since early in the 19th century as a result of a better understanding that has grown up of its underlying principles.

The word thermodynamics was derived from the Greek words *thermē* ("heat") and *dynamis* ("force"). The beginnings of the study of thermodynamics are found in the early 19th century in the study of the motive power of heat; that is, the capability of hot bodies to produce mechanical work. These early studies revealed several underlying principles, the most important of which are the first and second laws of thermodynamics. The discovery and clear enunciation in 1850 of the two laws by Rudolf Julius Clausius, a German mathematician and physicist, broadened greatly the scope of the subject. Throughout the rest of the 19th century it developed into a science, now known as classical thermodynamics, concerned primarily with physical systems in or passing through stable equilibrium states (the terms system and state are defined below). More recently thermodynamics has been extended to include physical systems in non-equilibrium states.

Although the development of thermodynamics, in contrast to other aspects of the study of physics, has progressed without regard to the details of the microscopic structures of physical systems, many scientists, beginning with Ludwig Eduard Boltzmann, Austrian physicist, have felt that the laws of thermodynamics might be justified and explained by means of detailed microscopic descriptions of matter and the laws of mechanics (classical or quantum) and statistics. Work in this direction has resulted in the development of the branch of

thermodynamics known as statistical thermodynamics, which, though it plays an important role in the evaluation of properties of systems, has not achieved one of its original goals, namely, the derivation of the laws of thermodynamics from the laws of mechanics. In particular, it now appears that the second law of thermodynamics is an independent law of nature. This particular point will be clarified below.

This article is divided into two parts. In the first part, the general principles of thermodynamics that apply to any physical system in any state—and the corollaries of these principles—are presented without reference to the detailed microscopic structure of matter. The presentation, therefore, encompasses both classical and nonequilibrium thermodynamics. In the second part, the detailed microscopic structures of physical systems are considered, and the states of such systems are discussed in the light of the laws of both quantum mechanics and thermodynamics. Quantum mechanics and thermodynamics are shown to be complementary parts of physical science, and they are neither separable nor are they derivable one from the other.

This article is divided into the following sections:

I. Brief history of classical thermodynamics

Temperature is probably the earliest thermodynamic concept to attain operational status. Early in the 17th century Galileo, an Italian astronomer and physicist, devised a thermoscope that was a rudimentary thermometer. Soon thereafter a liquid-expansion thermometer with bulb and stem, open at the top, was devised in France by Jean Ray. In 1640 the grand duke Ferdinand II of Tuscany, one of the founders of the Florentine Academy of Experiment, invented the sealed-stem alcohol thermometer. Such devices were put to clinical (determining degrees of fever), agricultural (incubation), and meteorological uses.

The purpose of these instruments was to measure a quantity, that had as yet been undefined, that was more objective in nature than the physiological sensations of hotness and coldness. An equilibrium concept was probably involved; namely, that all bodies exposed to the same atmosphere would ultimately attain the same degree of hotness or coldness, despite any contrary evidence of the senses. An associated concept of the equilibrium concept was that temperature is a driving potential that causes some influence to pass from one body to another of unequal hotness or coldness. Thus, when a body is taken from a warm room to the cold outdoors, its length begins immediately to decrease.

What was it that passed from one body to another at different temperatures? Was it temperature itself that was

transmitted? The English philosopher and scientist Francis Bacon as early as 1620, and the Florentine Academy a few years later, began to make this distinction between this influence and temperature; but it was more than a century before Joseph Black, a chemist at the University of Glasgow, in 1770 made the distinction sharply. He showed by mixing equal masses of pairs of liquids of different temperatures that the temperatures of the two substances often changed by radically different amounts. Indeed, a large change in temperature of a solid body produced no change at all in the temperature of a mixture of ice and water or of water and steam. Temperature was not necessarily conserved or even transmitted in the process.

Black established the science of calorimetry, which led to the establishment of the caloric theory, based upon the following postulates: (1) Caloric is an all-pervading elastic fluid, the particles of which repel one another strongly. (2) Particles of caloric are attracted by particles of matter. (3) Caloric is conserved. (4) Caloric is either sensible (i.e., change in caloric is associated with change in temperature) or latent. (5) Caloric has weight. These postulates were intended to account for expansion and contraction upon heating and cooling, variations in heat capacity, calorimetry, latent heat, and gain in weight of certain metals when heated in air (calcined). Frictional heating was subsequently accounted for by postulating that friction reduced the attraction between caloric and matter.

Toward the end of the 18th century, Count Rumford (Benjamin Thompson), an expatriate American colonial engineer and physicist, attacked the validity of the caloric theory on the basis of experiments intended to show that caloric could be created and, therefore, was not conserved. More refined measurements on the generation of heat by frictional work were made nearly a half century later by an English physicist, James Prescott Joule.

In 1824 Sadi Carnot, a French military engineer, introduced the concept of the heat-engine cycle, a concept that permitted a sharp distinction to be made between interactions of systems and changes in their states. Carnot then proved from conservation of caloric and the impossibility of the production of work without compensating changes in the environment that (1) a reversible cyclic engine is the most efficient possible means of producing work from heat, and (2) all reversible cyclic engines operating between the same pair of heat reservoirs must have the same efficiency. Although the proof, as it turned out, was invalid, Clausius asserted in 1850 that Carnot's principle is itself a basic postulate and is, in effect, what came to be known as the second law of thermodynamics.

In the decade of the 1840s Joule laid the foundations of the first law of thermodynamics by showing that the amount of work required to bring about a given change of state is independent of the kind of work (whether mechanical, electric, or magnetic), the rate of doing work, or the method of delivering it. Joule concluded that work can be converted into heat, with a fixed ratio of one to the other, and that heat can be converted into work. In 1844 Julius Robert von Mayer, a German physicist, postulated that in a work-producing cycle the heat introduced must exceed the heat rejected by an amount proportional to the work. He deduced the value of the proportionality constant from calculation of cycles in a gaseous system.

In 1849 Lord Kelvin (William Thomson), an engineer of Glasgow, pointed out the conflict between the caloric basis of Carnot's arguments and the conclusions reached by Joule. In 1850 Clausius resolved the difficulty by stating explicitly the first and second laws of thermodynamics. Within a few years Clausius defined and named the property entropy that is conserved in all reversible processes, and derived from the second law the principle of increase of entropy.

The first law was stated by Clausius as follows: In all cases in which work is produced by the agency of heat, a quantity of heat is consumed that is proportional to the work done; and, conversely, by the expenditure of an equal quantity of work, an equal quantity of heat is produced. He applied this statement to a cyclic process in a system (a concept with which he credits Carnot) in order to obtain a statement of the first law in terms of work and heat without reference to alteration in the state of the system. This led naturally to a definition of the property energy—called mechanical energy by Kelvin and contracted to energy by J. Willard Gibbs, an American mathematician and physicist. Clausius stated the second law in the following terms: A passage of heat from a colder to a hotter body cannot take place without compensation.

Clausius' paper of 1850 marked the birth of the science of thermodynamics. Immediately thereafter, Kelvin, who had previously displayed an interest in the theory of temperature, proposed and discussed various definitions for thermodynamic temperature scales, including the one that now bears his name. James Clerk Maxwell, a physicist of Edinburgh and Cambridge, averred that two bodies each equal in temperature to a third body are equal in temperature to each other. This statement, which is sometimes called the zeroth law of thermodynamics, is an incomplete version of a condition for equilibrium, subsequently derived by Gibbs and others, that is a corollary of the second law. Maxwell also devised a number of mathematical relations that now bear his name. Kelvin and Max Planck, a German physicist, later restated the second law, so as to avoid the undefined term compensation used by Clausius, in terms of the impossibility of a perpetual-motion machine of the second kind (see below).

In the years 1873–78 Gibbs published three papers that proved to be definitive as regards the conditions for equilibrium. These papers provided a mathematical method so orderly and systematic that they have served as the foundations of physical chemistry and many subsequent applications of classical thermodynamics.

At the turn of the century, the French mathematician Henri Poincaré addressed the problem of definition of temperature and heat and the statement of the first and second laws. In 1909 Constantin Carathéodory, a Greek mathematician teaching in Germany, presented an alternative logical structure in which he shunned use of the term heat. It is closest in method and spirit to that used here. He states the two laws as follows: First, an extensive property exists the increment in which is the work received by the system while surrounded by an adiabatic wall (an adiabatic wall being one that permits only work interactions between the system and its surroundings). Second, in the neighbourhood of any prescribed initial state are states that cannot be reached by an adiabatic process.

In 1918 Walther Nernst, a Nobel-Prize winning chemist of Germany, stated the Nernst heat theorem, treated below, which is essentially the third law of thermodynamics, which rounds out the exposition of classical thermodynamics by providing a common base for values of entropy for all atoms or molecules that can be formed from simpler species.

II. Basic concepts and laws of thermodynamics

SYSTEMS, STATES, AND PROPERTIES

The description of physical phenomena is based on the concept of state of a system and the changes of state that occur either spontaneously or because of interactions with other systems. Knowledge of the states of a system is equivalent to knowledge of the outcomes of all possible observations on the system; namely, observations of all its properties.

The term system means any identifiable collection of matter that can be separated from everything else by a well-defined surface so that changes in everything else need not affect the condition of the collection. Examples of systems are a number of water molecules confined within a watertight container, a thermonuclear plasma (a special collection of charged particles) confined by a suitably designed magnetic field, and the vapour of a solid within a cavity in the solid.

The particles of a system may have a finite rest mass, as do molecules, atoms, or electrons, or zero rest mass, as do photons. The number of particles of a system can be large, as in a cubic centimetre of tungsten, or small, as in a hydrogen atom.

At any instant of time a system is in a condition called a state, which encompasses all that can be said about the results of any measurements or observations that can be performed on the system at that time. The state at a given instant of time determines the properties of the system. A property is any quantity the value of which depends upon the state but not the history of the system. For a given state the value of a property can be determined by some type of measurement (some physical operation or test). When the values of all properties of two states are identical, the two states are identical; otherwise they are different.

Because of unavoidable quantum mechanical considerations, a simple measurement, no matter how nearly perfect, will not yield the precise value for a property. In general, a very large number of measurements of the same kind is required to yield the precise value, each measurement performed on a duplicate of the system in the given state and each yielding a different result. The value of a property is defined, therefore, as the sum of all the results of the measurements of the property divided by the number of measurements (in other words, the arithmetic average or expectation value of all the results of the measurements of the property). It will be shown below that a state can be described by a set of weighting factors, or probabilities, that enter into the evaluation of all properties.

Although an indefinite number of properties can be associated with a state, the values of these properties are not all independent of each other. The number of independent properties is finite and is either small or large, depending on the type of state in question; that is, on whether or not it is a stable equilibrium state. The meaning of the terms that define the various types of states will be given below.

WORK AND NONWORK

An interaction between two systems such that whatever happens in each of the interacting systems could have been brought about while the sole effect external to each system was the change in level of a mass in a gravity field will be defined as work; that is, work is an interaction that must satisfy a test: each of the interacting systems is separately required to experience the same changes as in the actual interaction, but, through alteration of circumstances external to that system, the effect outside of it is solely the rise or fall of a mass. If this test can be satisfied in the case of both systems, then the original interaction is work.

It can be shown from experimental evidence that the following interactions conform to the definition just cited and are, therefore, work interactions: (1) the displacement of a point on the boundary of a system at which point a force is exerted in the direction of the displacement by another system (this is essentially the definition of work in mechanics, which is less general than the one given here, which covers interactions other than those considered in mechanics; the present definition implies that the force applied on a body by a stationary force field, such as gravity or an electrostatic field, results in no work, even though the body is in motion—for example, freely falling); (2) the electromagnetic interactions between primary and secondary coils of a transformer; and (3) the exchange of radiation emitted by lasers. Such radiation consists of wave particles, which are in order relative to each other as contrasted with those, for example, from an incandescent lamp, which are randomly arranged. On the other hand, it can be shown by virtue of the second law that the exchange of radiation between a hot system and a cold system (such as blackbody radiation) does not conform to the requirement stated in the definition of work and is not, therefore, a work interaction.

Work is one of several distinguishable types of interaction that can occur between two systems. Any interaction that is not work will be hereinafter called nonwork. A special type of nonwork interaction that will be treated below in detail is a heat interaction. In general, an interaction is fully specified if the exact sequence of states, called the path, of each of the interacting systems is specified. In turn, the path of one of the systems and the interactions that occur specify the process experienced by the system. In an interaction that satisfies the definition of work, each system is said to be experiencing an adiabatic process.

The state and, therefore, the values of the properties of a system can change either spontaneously or as a result of interactions with other systems. During changes of state the values of certain properties are subject to limitations imposed by the laws of physics. The limitations imposed by thermodynamics are consequences of the first and second laws, which will be stated here in an unusually general way.

FIRST LAW

The first law is a statement of existence of a property called energy. It is based on the concept of work and can be stated as follows: For any process involving no effects external to the system except displacement of a mass between specified levels in a gravity field, the magnitude of that mass is fixed by the end states of the system and is independent of the details of the process. This law has many implications or corollaries, some of which are as follows.

1. *Uniqueness of work values.* By virtue of the first law a unique number can be assigned to a work interaction between two systems. This number is n when n arbitrarily selected units of mass are displaced between two arbitrarily specified levels in a gravity field. The sign of work is selected positive when work is done by a system—that is, when the sole external effect would be the rise of a weight.

2. *Definition of energy.* By virtue of the first law, the work in an adiabatic process depends on the initial and final, or end, states only. It follows that a property of a system can be defined, called energy, such that its change of value between states A_1 and A_2 is equal to the work W_{12}^a involved in an adiabatic process that has A_1 and A_2 as end states. In terms of symbols, if E_1 and E_2 denote the energies of states A_1 and A_2, respectively, and W_{12}^a the work done in any adiabatic process connecting A_1 and A_2, the difference $E_2 - E_1$ is equal to the negative of W_{12}^a; i.e.,

$$E_2 - E_1 = -W_{12}^a. \qquad (1)$$

Energy is only partially defined by equation (1) because the difference between E_1 and E_2 does not specify the values of E_1 and E_2. An arbitrary value such as zero, however, can be assigned to E_0 of some reference state A_0, so that the energies of all other states are fixed by equation (1).

It will be shown below that by virtue of the second law of thermodynamics certain interactions that cause change of energy cannot be described as work. The corresponding process is, by definition, a nonadiabatic process. Because energy is a property, the energy change associated with any nonadiabatic process will equal numerically the work in any adiabatic process between the same end states.

Because work values are additive, energy is an additive or extensive property; that is, the energy of a whole is equal to the sum of the energies of its parts.

3. *Conservation of energy.* The magnitude of the work in an adiabatic process can be positive, negative, or zero, depending on the end states of the process, but zero adiabatic work does not necessarily imply identical end states. An adiabatic zero-work change of state may occur spontaneously in a system, as, for example, when an electrical capacitor discharges through an internal resistor. During such a process, equation (1) requires that the energy of the system remain invariant. This is the so-called law of conservation of energy, which is a consequence of the first law of thermodynamics. The

first law, on the other hand, cannot be deduced from the law of conservation of energy.

A system that experiences an adiabatic, zero-work process is said to be isolated from all other systems in the environment.

4. *Impossibility of perpetual-motion machine of the first kind.* A perpetual-motion machine of the first kind (PMM1) is any system that undergoes a cycle and has no external effect except the rise of a weight. The term cycle (or cyclic process) is defined as a process in which the initial and final states of the system are identical.

By virtue of the first law, the work of an adiabatic cycle must be equal to zero and, therefore, a PMM1 is impossible.

5. *The first law and relativity.* According to the general theory of relativity, the energy E of a system is equal to the product of its mass m and the square of the speed of light c in a vacuum, namely,

$$E = mc^2. \tag{2}$$

By virtue of the first law, the energy E of an isolated system is conserved. Therefore, equation (2) requires that the mass m of the system is also conserved, regardless of the processes occurring within the system (such as chemical reactions, nuclear reactions, and creation and annihilation of particles). Moreover, if the energy of a system is altered by virtue of an adiabatic or nonadiabatic interaction, the mass of the system must also be altered in accordance with equation (2). In most applications the energy transferred to or from a system is so much smaller than the total energy mc^2 of the system that the change in mass is negligible.

SECOND LAW

The second law is a statement of existence of stable equilibrium states and of special processes that connect these states to others. More than the first law, the second law distinguishes thermodynamics from other parts of physics. Because it has far-reaching implications concerning the properties and behaviour of matter, it is frequently invoked in discussions of philosophy as well as in discussions of physics.

Of the many statements of the second law, those of Clausius, Planck, and Carathéodory are the most notable. All of these statements imply the existence of a stable equilibrium state for given values of energy, the number of particles, and the constraints (see below)—an implication that is here taken to be the essential element of the second law.

The term equilibrium state means a state that does not change with time while the system is isolated from all other systems in the environment. Equilibrium state is sometimes confused with steady state: a steady state does not change with time even though the system, rather than being isolated, is interacting with other systems.

If a system is in an equilibrium state, a finite change of state may be caused by interactions with the environment, including those that leave no finite net effects in the environment. Several types of equilibrium states can be distinguished. Among these is the stable equilibrium state for which a finite change of state cannot occur, regardless of interactions that leave no net effects in the environment.

Consistent with its nature, a system might assume any one of a set of possible states, but some of the possible states may be prohibited by restrictions imposed by the environment. These restrictions are called constraints. For example, a given amount of gas may assume any of a large number of states. The same amount of gas, however, confined in a gas-tight container of fixed volume is restricted to states with volumes smaller than or equal to the volume inside the container. The possible states of the system that are consistent with the constraints will be called allowed states.

The second law can now be stated as follows: Among all the allowed states of a system with given values of energy, numbers of particles, and constraints, one and only one is a stable equilibrium state. Such a state can be reached from any other allowed state of the same energy,

numbers of particles, and constraints and leave no effects on the state of the environment.

The second law cannot be derived from the laws of mechanics (either classical or quantum). The second law asserts that a stable equilibrium state exists for each value of the energy, whereas in mechanics the only stable state is that of minimum energy, what is known as the ground state.

Some corollaries of the second law are as follows.

1. *State principle.* By virtue of the second law, stable equilibrium states exist, and a unique stable equilibrium state corresponds to each set of values of energy, numbers of particles, and constraints. The uniqueness implies the following corollary: the value of any property of a system in a stable equilibrium state may be expressed as a function of the values of the energy, numbers of particles, and constraints only. This corollary is known as the state principle.

2. *Reversible and irreversible processes.* A process is reversible if the system and its environment can be restored to their initial states, except for differences of smaller order of magnitude than the maximum changes that occur during the process.

According to the second law, a system may start from any allowed state and reach the corresponding stable equilibrium state with no net effect on the environment. Such a process could not be reversible. For if it were, the system, starting from the stable equilibrium state, could undergo a process that ends at another state with no net effect on the environment. This conclusion, however, violates the definition of a stable equilibrium state. It follows that irreversible processes exist.

3. *Impossibility of perpetual-motion machine of the second kind.* It can be shown from the definition of a stable equilibrium state that a system in such a state can receive but cannot produce work. The plausibility of this corollary will be evident from the observation that work can always be used to change from any state to a nonequilibrium state by creating relative velocity of parts or compression to a smaller volume. If a system in a stable equilibrium state were to produce work, that work could be used to cause the system itself to end in a nonequilibrium state with no net effects on the environment—contrary to the definition of its initial state.

This corollary applies strictly only to systems of which the energy can be increased indefinitely, such as any system with particles free to move from one place to another or any system with translational degrees of freedom. Most practical systems satisfy this requirement. The generalization to systems that do not satisfy the requirement, such as a nuclear-spin system, is discussed below under *Negative temperature.*

A perpetual-motion machine of the second kind (PMM2) is any device that would deliver net work; i.e., raise an external weight, while undergoing a cycle and interacting with a single system in a stable equilibrium state. A perpetual-motion machine of the second kind is a device that permits a system to violate the corollary stated above and is, therefore, impossible.

Prior to the discussion of the fourth corollary, it is necessary to define the terms mutual stable equilibrium and reservoir. Two systems A and B are said to be in mutual stable equilibrium if the combined system AB is in a stable equilibrium state. It can be readily verified that if two systems are in mutual stable equilibrium, each system must be in a stable equilibrium state. Moreover, if the two systems are brought into communication so that interactions are not prohibited, no interactions will occur unless the allowed states of at least one of the systems are altered.

A reservoir R is a special kind of a system that provides useful reference states for applications of the second law and satisfies the following conditions: (1) it is closed to the transfer of rest mass—i.e., its boundaries cannot be crossed by material particles; (2) its constraints are invariant with time—for example, its volume has the same value at all times; (3) it passes through stable equilibrium states only; and (4) in the course of finite interactions it remains in mutual stable equilibrium with a dupli-

Reservoirs as systems

cate of itself that experiences no such interactions. An example of a reservoir is a mixture of solid, liquid, and vapour water in mutual stable equilibrium while enclosed in a container.
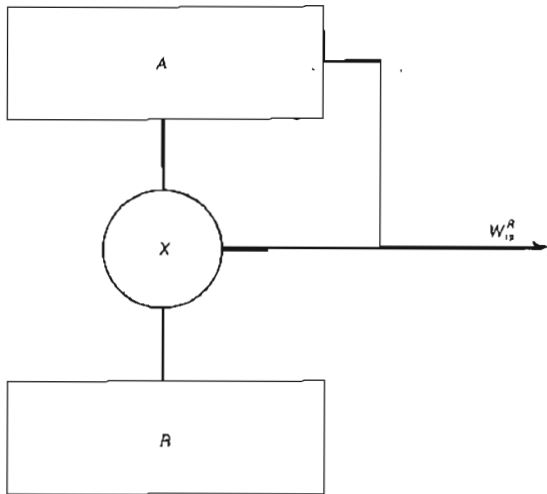

Figure 1: Production of work by a system A interacting with a reservoir R through an intermediate device X (see text).

4. *Work done reversibly by a system in combination with a reservoir.* A system A in combination with a reservoir R can experience a work interaction with other systems either directly or through an intermediate device X, or both, while X is undergoing a cyclic process (Figure 1). During this work interaction no rest mass is exchanged between A and R while the state of A changes from A_1 to A_2. The work done is denoted by W_{12}^R for processes in general and by $(W_{12}^R)_{rev}$ for processes that are reversible.

By virtue of the second law it can be shown that for a given change of state from A_1 to A_2, the work $(W_{12}^R)_{rev}$ is the same for all reversible processes and for all reservoirs in mutual stable equilibrium with each other; that is, $(W_{12}^R)_{rev}$ is fixed by the end states A_1 and A_2. Moreover, W_{12}^R cannot exceed $(W_{12}^R)_{rev}$ when both correspond to the same change of state from A_1 to A_2.

ENTROPY

The two laws of thermodynamics imply the existence of a property called entropy that is conserved in all reversible processes. Its definition is based on another property called available work.

Available work. Because for a given system and reservoir $(W_{12}^R)_{rev}$ depends on the end states of the system only, a property can be defined called available work (symbolized Ω, omega), such that its change of value between states A_1 and A_2 is equal to the work $(W_{12}^R)_{rev}$; that is (using the symbol $\equiv$ to imply definition),

$$(\Omega_2 - \Omega_1) \equiv -(W_{12}^R)_{rev}. \qquad (3)$$

It can be easily verified that available work is an additive or extensive property.

Definition of entropy. Because both energy and available work are extensive properties, the difference between them is also an extensive property. Entropy will be defined as the extensive property S the change of which, DS, in a change of state is equal to a positive constant c_R times the difference between the corresponding changes of energy DE and available work $D\Omega$ evaluated with respect to a standard reservoir. This definition can be written in the form of an equation; *i.e.*,

$$DS \equiv c_R (DE - D\Omega). \qquad (4)$$

The symbol D denotes a change, finite or infinitesimal, in magnitude of the property the symbol of which it precedes.

The standard reservoir may be chosen to be a mixture of solid, liquid, and vapour water in mutual stable equilibrium, and an arbitrary value, as explained below, may be assigned to the constant c_R. Subject to subsequent considerations, an arbitrary value may be assigned to the entro-

py of an arbitrarily selected reference state of the system. Thereafter, by means of equation (4), a value may be found for any state, equilibrium or nonequilibrium, once values for E and Ω have been determined by appropriate measurements.

Entropy changes in adiabatic processes. If the process from state A_1 to state A_2 in system A is adiabatic—that is, system A experiences only work interactions—then the work done by A must, by equation (1), equal the decrease in the energy of A. For a reversible adiabatic process the work done must, by equation (3), also equal the decrease in available work, so that the difference between the decrease in energy and the decrease in available work must be equal to zero. It follows from equation (4) that for a reversible adiabatic process the entropy change of the system is equal to zero; that is, the entropy is invariant. Moreover, because the fourth corollary states that the work for any adiabatic process cannot exceed that for the reversible adiabatic process, it follows that for an adiabatic process in general the entropy change must be greater than or at least equal to zero. In terms of symbols these conclusions can be written as

$$(DS)_{rev}^a = 0, \text{ for reversible adiabatic processes,} \quad (5)$$

and

$$(DS)^a \geq 0, \text{ for adiabatic processes} \qquad (6)$$

(the symbol $>$ means "greater than," and $\geq$ means "greater than or equal to").

Principle of increase of entropy. When equation (6) is applied to any process in an isolated system—*i.e.*, to an adiabatic process for which the work is zero—it becomes

$$DS \text{ (isolated)} \geq 0. \qquad (7)$$

Thus, the entropy of an isolated system may remain constant or may increase, but a decrease of entropy in an isolated system is impossible. Because any process in any system may be conceptually changed to a process in an isolated system by including in the isolated system all systems with which the original system interacts, the conclusion represented by equation (7) is of great generality. Equation (7) is known as the principle of increase of entropy, although it may be more strictly said to be the principle of the impossibility of a decrease of entropy. According to this principle, whenever any process occurs in nature, the total entropy of all systems involved in the process must either increase or, if the process is reversible, remain constant.

STABLE EQUILIBRIUM

Criterion for stable equilibrium. Changes of state in an isolated system can occur only until the system reaches the unique stable equilibrium state consistent with the given values of energy, numbers of particles, and constraints. It follows from equation (7) that the entropy of the stable equilibrium state must be larger than that of any equilibrium or nonequilibrium state with the same values of energy, numbers of different particles, and constraints. By the same token, a criterion for stable equilibrium is that the entropy should be at its maximum value for fixed values of energy, numbers of particles, and constraints.

Equations relating properties for stable equilibrium states. By virtue of the state principle, the simplest illustrations of the laws of thermodynamics are provided by applications to systems in or passing through stable equilibrium states. For the properties and the relations between properties of systems in such states can be expressed by means of relatively simple mathematical forms.

The term numbers of particles, as used in the state principle, implies certain species of particles. The set of species selected must be a minimum set in terms of which the composition of all allowed states may be described. Such a minimum set of species, which will be unique in the number of its members for a given system regardless of the choice of species to make up the set, is called a set of components.

For a system A with given fixed values E of energy,

$n_1, n_2, \ldots, n_k$ of the numbers of particles of components 1, 2, ..., k of the set of k components, and $\beta_1, \beta_2, \ldots, \beta_s$ of constraints 1, 2, ..., s of the set of s constraints, the uniqueness of the corresponding stable equilibrium state implies that the value of any property of A in that state must be fully and uniquely determined by the given fixed values. Moreover, for all stable equilibrium states, the values of a property F may be expressed as a mathematical function having a single value for each single set of values $E, n_1, n_2, \ldots, n_k, \beta_1, \beta_2, \ldots, \beta_s$,

$$F = F(E, n_1, n_2, \ldots, n_k, \beta_1, \beta_2, \ldots, \beta_s). \quad (8)$$

Several relations like equation (8) for several properties may be manipulated mathematically to express the values of any property as a function of the values of any set of independent properties of stable equilibrium states. A set of independent properties is such that the value of each property in the set can be varied without affecting the values of the remaining properties in the set.

Two functions of interest to subsequent considerations are those that relate the values of entropy S to the values of $E, n_1, n_2, \ldots, n_k, \beta_1, \beta_2, \ldots, \beta_s$, and the values of energy E to the values of $S, n_1, n_2, \ldots, n_k, \beta_1, \beta_2, \ldots, \beta_s$. These functions are denoted as

$$S = S(E, n_1, n_2, \ldots, n_k, \beta_1, \beta_2, \ldots, \beta_s) \quad (9)$$

and

$$E = E(S, n_1, n_2, \ldots, n_k, \beta_1, \beta_2, \ldots, \beta_s). \quad (10)$$

In general, the change of entropy per unit change of energy, or of any of the numbers of particles, or of any of the constraints can be evaluated with the help of equation (9). The same remark applies to energy and equation (10). Such changes are called partial derivatives and are used to define a number of useful properties that have meaning for stable equilibrium states only.

Mutual stable equilibrium of closed systems. If two systems A and B that are closed to the transfer of rest mass taken together constitute a system in a stable equilibrium state, then the entropy of that system must be at a maximum for the value of its energy. One of the consequences of this requirement will be seen from a possible variation—a conceptual alteration of state consistent with the description of the system and the constraints imposed on it and its parts A and B by the environment —in which the energy of A is increased by a small amount denoted by dE_A, and that of B is decreased by the same amount, while both A and B pass through stable equilibrium states without changes of values of their constraints. The entropy of part A is correspondingly altered by the amount dS_A. This amount can be expressed as

$$dS_A = \left(\frac{\partial S_A}{\partial E_A}\right)_{n,\beta} dE_A,$$

in which $(\partial S_A/\partial E_A)_{n,\beta}$ denotes the rate of change of S_A per unit change of E_A as A passes through stable equilibrium states while its numbers of particles (n) and its constraints (β) are held constant, namely, the partial derivative of S_A with respect to E_A. A similar expression can be written for the entropy change dS_B of B, so that the alteration dS of combined system AB is given by the expression

$$dS = \left(\frac{\partial S_A}{\partial E_A}\right)_{n,\beta} dE_A + \left(\frac{\partial S_B}{\partial E_B}\right)_{n,\beta} dE_B. \quad (11)$$

It can be shown that if the entropy S is to be at a maximum for the given fixed value of energy $E_A + E_B$ of the combined system AB and for both positive and negative variations dE_A, then it is necessary that the two partial derivatives $(\partial S_A/\partial E_A)_{n,\beta}$ and $(\partial S_B/\partial E_B)_{n,\beta}$ be equal to each other, namely,

$$\left(\frac{\partial S_A}{\partial E_A}\right)_{n,\beta} = \left(\frac{\partial S_B}{\partial E_B}\right)_{n,\beta}. \quad (12)$$

The quantity $(\partial S/\partial E)_{n,\beta}$ of a system may be thought of as a potential that governs the tendency of energy to pass from one system to another. It can be shown that

it is a "capturing tendency" in that if

$$\left(\frac{\partial S_A}{\partial E_A}\right)_{n,\beta} > \left(\frac{\partial S_B}{\partial E_B}\right)_{n,\beta},$$

then dE_A may be greater than zero (energy may pass from system B to system A) in an actual process but not less than zero (because less than zero would be contrary to the principle of increase of entropy). Conversely, the reciprocal quantity $(\partial E/\partial S)_{n,\beta}$ may be thought of as an "escaping tendency."

"Capturing" and "escaping" tendencies

Temperature. The potential that governs the flow of energy is called temperature. A scale of temperature may be defined in terms of any function of $(\partial S/\partial E)_{n,\beta}$ or $(\partial E/\partial S)_{n,\beta}$ that continuously increases or decreases with either. The scale commonly used in thermodynamics is the Kelvin scale of temperature. It is denoted by T and defined as

$$T \equiv \left(\frac{\partial E}{\partial S}\right)_{n,\beta}, \quad (13)$$

so that T becomes a measure of the escaping tendency of energy. The necessary condition, equation (12), for mutual stable equilibrium between two systems A and B is equivalent to an equality between the temperatures T_A and T_B of A and B, namely,

$$T_A = T_B. \quad (14)$$

From the observations that the work produced by the combination of systems A, X, and R used in the definition of entropy change is the decrease in energy of the combination AR and that for a reversible process the entropy of that combination is conserved, it is readily shown that the constant c_R in equation (4) is equal to the partial rate or derivative $(\partial S_R/\partial E_R)_{n,\beta}$ of the entropy of the reservoir R or the inverse of the temperature T_R of the reservoir. Because the magnitude of constant c_R is arbitrary, a selection of a value for it for a simple reservoir fixes not only the scale of entropy but also that of the Kelvin temperature. By international agreement the value of T for solid, liquid, and vapour water in mutual stable equilibrium is 273.16° K. Among the reasons for the selection of this five-digit figure is that it causes the temperature interval between the freezing and boiling points of water under a pressure of one atmosphere to be almost exactly 100 degrees. If any other reservoir R' is used with X and A, the change in entropy found from equation (4) for a change in state of system A from A_1 to A_2 will be the same as that found using R if constant c_R' is taken equal to the inverse temperature of the reservoir R'.

Entropy constant

When the number 273.15 is subtracted from the value of any given Kelvin temperature T, the result will be the Celsius temperature t, or t (degrees Celsius) $\equiv T - 273.15$.

Heat. An argument will now be outlined to prove that certain nonwork interactions are entirely distinguishable from work in that no fraction of any one such interaction will satisfy the definition of work.

If two systems A and B are in stable equilibrium states and each is under constant constraints, but they are not in mutual stable equilibrium, then an interaction could occur between them. By virtue of the third corollary of the second law, any such interaction must be a nonwork interaction; that is, its effects on at least one system, say A, could not have been produced while the sole external effect was the rise of a weight. In general, however, the effects on A could be produced while weights external to A are raised and, in addition, a change of state of B takes place. It can be shown that maximum work will be delivered to the weights if the process is carried out reversibly and each system passes through stable equilibrium states. A reversible cyclic device X (Figure 2) interposed between systems A and B will permit these conditions to be fulfilled. The device X may produce work, but the reversible interactions experienced by A with X and X with B cannot be work by virtue of corollary 3 of the second law.

For the reversible process just described it can be shown from the functions that relate energy to entropy and other independent properties that the work δW that will

be delivered to the weights is equal to the negative of the energy change dE_A of system A times the ratio $(T_A - T_B)/T_A$. This conclusion can be written as an equation; i.e.,

$$\delta W = - \frac{T_A - T_B}{T_A} dE_A. \qquad (15)$$

In equation (15), the symbol d denotes an infinitesimal change of the value of a property, whereas δ denotes an
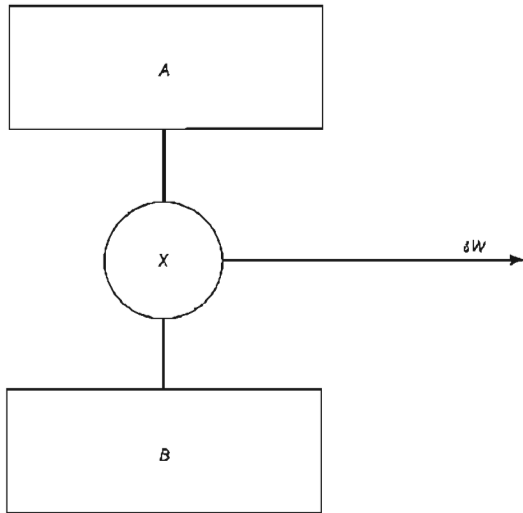

Figure 2: Production of work by a reversible cyclic device X that undergoes reversible nonwork interactions with systems A and B (see text).

infinitesimal amount of a quantity that is not a property or state function. Work is not a property of any system, and therefore δW is the appropriate way to indicate an infinitesimal amount of W.

Because dE_A is a measure of the magnitude of the interaction experienced by A with X, equation (15) expresses the work produced as a fraction of the magnitude of that interaction. As systems A and B approach mutual stable equilibrium, temperatures T_A and T_B approach equality, a necessary condition, and the fraction that represents the ratio of δW over dE_A approaches zero; that is, the work that can be obtained from the interaction between A and B through X becomes a vanishingly small fraction of the magnitude of the interaction. Moreover, it can be shown that then the interactions between A and X and between X and B are exactly equal, and each may be expressed as a product of temperature and entropy change $T_A \, dS_A$ and $T_B \, dS_B$.

In the limit, therefore, as T_A approaches T_B, the cyclic device X is no longer required, and the nature of the interaction approaches something completely distinguishable from work. It is this special kind of interaction that is called heat and denoted by the symbol Q. Moreover, for any process for which a system passes only through stable equilibrium states of fixed constraints and for a change of state corresponding to changes dS in entropy and dE in energy, the infinitesimal amount of heat $(\delta Q)_{rev}$ received by the system is given by the relations

$$(\delta Q)_{rev} = TdS = dE. \qquad (16)$$

If the interacting systems pass only through stable equilibrium states, then the process will be reversible.

Heat is not a property of a system. Accordingly, the symbol δQ is used to denote an infinitesimal amount of heat but not the change in value of a property. Nor is heat contained within a system. Being an interaction, its magnitude depends upon the arbitrary selection of boundaries between systems.

Meaning of heat

The term heat is used here in a special sense that is quite foreign to the popular conception of its meaning. A different term might have been used were it not for the historical association of the word heat with thermodynamics. It will be observed from the context that the word heat is reserved here for a very special kind of interaction between systems, which only by virtue of the second law

is entirely distinguishable from all other kinds of interactions, including the special kind called work. If a less restrictive definition had been used, then some of the relations between heat and entropy given here would not always hold.

Heat and flow of entropy. When a heat interaction occurs between two systems A and B that pass through stable equilibrium states, the process is reversible. For the combined system AB the process may be considered an adiabatic process for which the work is zero, so that, in accordance with equations (5) and (7) expressed in terms of subsystems A and B, $DS_A + DS_B = 0$. Because, from equation (16), DS_A is equal to $(\delta Q_A/T)_{rev}$ and different from zero, the heat interaction is associated with a flow of entropy from A to B if heat flows from A to B and conversely. By way of contrast, work in a reversible process leaves the entropies of the interacting systems unaltered.

To system B may be added a part that is not in a stable equilibrium state and that may experience an irreversible process without affecting the state of the other part or the interaction between A and B. Although the process as a whole is no longer reversible, the interaction is the same as before and could appropriately be called heat. A flow of entropy from A to B is still associated with the flow of heat from A to B, but the increase of entropy in B exceeds the amount that has flowed from A; that is, the statement $dS > \delta Q/T$ may be written for the irreversible process, and

$$dS \geq \frac{\delta Q}{T} \qquad (17)$$

for processes in general.

For an adiabatic process equation (17) reduces to equation (6). For other processes equation (17) will apply provided that the only nonwork interactions are heat; that is, at least locally where the interaction occurs, the behaviour on each side of the boundary is the same as if both systems were passing through stable equilibrium states, with identifiable temperatures, and the process was reversible. It can readily be shown that certain nonwork interactions when used in place of δQ will not satisfy equation (17).

Inequality of Clausius. An inequality that was first stated by Clausius bears his name. It is as follows: For an irreversible cycle the sum of ratios, each of which is a heat δQ received by the system divided by the temperature T at which the heat is received, is always less than zero. When each amount of heat δQ is very small, the sum of the ratios $\delta Q/T$ can be represented by a cyclic integral, and the inequality of Clausius is given by the relation

$$\left(\oint \frac{\delta Q}{T} \right)_{Irrev} < 0. \qquad (18)$$

(The symbol $\oint$ means to integrate over a closed path, the complete cycle.) The inequality of Clausius follows directly when the inequality of equation (17) is applied to each step of an irreversible cycle and summed up for all the steps, because dS, being the change in a property, sums up to zero. Application of the inequality of Clausius is restricted, of course, to processes for which all nonwork interactions are heat.

Work, heat, and change of energy. If work and heat interactions occur successively, then the total energy change dE will be the sum of the work effect $(-\delta W)$ and the heat effect δQ; or, by equations (1) and (16),

$$dE = \delta Q - \delta W, \qquad (19)$$

the minus sign resulting from the conventions regarding the signs for heat and work.

In practice it is not always necessary that work and heat should be successive in time. For example, if simply by shifting a boundary between systems a process can be made either adiabatic or heat only, then simultaneous heat and work are identifiable and may be used together in equation (19).

Expression (19) for change of energy is applicable, of course, only to those processes for which the interactions are identifiable as heat and work. Because heat and work are limiting cases of actual processes, equation (19) is strictly applicable only where all interactions have been carried to these limits.

Reversible cyclic engine.   By reference to the definition of heat, it will be observed that the reversible interactions between A and X and between X and B in Figure 2 are heat interactions in which one part of X is in equilibrium with A and another part with B, whether or not A and B are close to mutual stable equilibrium. Because the process for the combined system AXB is adiabatic, it can be shown that the heat δQ_B received by B is equal to the heat δQ_A received by A times the negative of the ratio T_B/T_A; namely,

$$\delta Q_B = -\frac{T_B}{T_A}\delta Q_A. \qquad (20)$$

The work produced by cyclic device X is, by equation (19), equal to the negative of the sum $\delta Q_A + \delta Q_B$, and, because of equation (20),

$$\delta W = -\delta Q_A - \delta Q_B = \frac{T_A - T_B}{T_A}(-\delta Q_A). \qquad (21)$$

It is seen from equation (21) that X will produce positive work if $T_A > T_B$ and $\delta Q_A < 0$; that is, if heat flows from the hotter system to X and from X to the cooler system. The efficiency η with which X converts to work the heat it receives from the hotter system is thus

$$\eta = \frac{T_A - T_B}{T_A}. \qquad (22)$$

This quantity is called the Carnot efficiency after Carnot, who, before the discovery of the first and second laws of thermodynamics, made the following statements concerning the efficiency of engines working between reservoirs at specified levels of temperature: The efficiency of a reversible engine has a fixed value that is the same for all reversible engines and is greater than that of any irreversible engine.

An example of a reversible cycle in which a system receives all heat at one temperature and rejects all heat at another with reversible adiabatic changes between the two temperatures is the Carnot cycle, devised by Carnot. Its efficiency is given by equation (22).

Work-producing systems and devices.   A problem of economic and social importance in heat engineering is the production of work to be used for practical purposes such as lifting weights, driving electric generators, propelling vehicles, or operating cutting tools. Work can be obtained from any system that is not in a stable equilibrium state as it changes toward a stable equilibrium state without changes in constraints. For example, work may be obtained by lowering a weight inside a closed system while causing—through appropriate levers, belts, and pulleys—a weight to rise outside. The production of work need not end until the internal weight has reached the lowest position in the gravity field that the configuration of the system permits. Similarly, an electric storage battery may produce work until it is completely discharged. The maximum work that can be produced by the system adiabatically will be obtained if the process is executed reversibly—that is, at constant entropy. By virtue of the second law the maximum work is only a fraction of the energy of the system. This fraction is larger the farther the system is initially from stable equilibrium; *i.e.,* the larger the difference between the maximum entropy corresponding to the initial energy and the entropy of the initial nonstable state. The fraction is equal to zero when the difference in entropy just described is equal to zero— namely, when the system is initially in a stable equilibrium state.

On the other hand, a system in any state, including a stable equilibrium state, can produce work when combined with a system in the environment that passes through stable equilibrium states but is not in mutual stable equilibrium with the first. The maximum work that can be obtained is the maximum possible decrease in the available work when the system in the environment acts as a reservoir, or it is the maximum possible decrease of one of the other availability functions discussed below when other conditions are imposed by the environment. In order to obtain this maximum, the work-producing process must be completely reversible. For example, if the system with the elevated weight described in the preceding paragraph is at a higher or lower temperature than the atmosphere, then further work may be obtained by interposing a Carnot heat engine between the system and the atmosphere, so that the system is gradually cooled or heated to the temperature of the atmosphere as heat flows to the engine and produces work. If the whole process is executed reversibly, then the maximum possible work will be produced.

The greatest sources of work are fuels found in nature that are either not themselves in stable equilibrium states —for example, uranium in a reactor—or are not in mutual stable equilibrium with the atmosphere from which they have been isolated in the course of geologic history—for example, the fossil fuels coal and petroleum. In either case, the maximum work can be obtained only by a reversible approach to stable equilibrium or mutual stable equilibrium.

In the case of uranium, a reversible nuclear reaction is required; for the fossil fuels, a reversible chemical reaction. A close approximation to a reversible chemical reaction is found in lead storage batteries used in automobiles for starting and for lighting. No close approximation to a reversible nuclear reaction has yet been realized in practice, although in principle such a reaction is possible.

Because the cost of work includes not only fuel costs but also capital costs that usually increase as irreversibility in the process is reduced, the economical means of producing work may in some respects depart radically from the reversible means. For example, in fossil-fueled central power stations, fuel and oxygen in the air enter into an irreversible chemical reaction that raises the temperature of the resulting products by about 2,000 degrees on the Kelvin scale and reduces the work available by about one quarter. Energy from these hot products is then transferred irreversibly across a large temperature difference to appear as heat added to liquid and vapour water that is the working fluid of a heat engine. The loss in work available is again about one quarter of that of the original fuel and air. Irreversibility in the heat-engine cycle accounts for another 10 percent, so that about 40 percent is actually realized as work delivered to the electrical distribution system.

A Carnot cycle is an obvious but usually impractical means to produce work from heat interactions with hot products of chemical or nuclear reactions. Most commonly used is the Rankine cycle, in which heat is used to generate vapour from a liquid; the vapour is expanded through a work-producing engine, condensed to liquid as it rejects heat to the environment, and pumped back into the vapour generator. The Stirling cycle, which has had only limited application, passes through gaseous states only.

III. Simple systems

STABLE EQUILIBRIUM STATES

A closed simple system is one in which the numbers of particles of the various components are fixed and the only constraint provided by the environment is an upper value for the volume of the system. By virtue of the state principle, volume (regardless of shape) and energy become sufficient to determine a stable equilibrium state, and the number of independent properties is two. A system that is not influenced by capillarity and external force fields is a simple system. These conditions may be satisfied despite capillarity and gravity fields if homogeneous parts of the system are large, so as to have small surface-to-volume ratio, yet shallow in the vertical direction of the gravity field and free of electric and magnetic fields created by external bodies.

For stable equilibrium states of a closed simple system, entropy S or any other property can be regarded as fixed by the two independent properties volume V and energy

Economical production of work

Definition of a simple system

U; therefore, S can be expressed as a function of V and U of the form

$$S = S(V,U). \qquad (23)$$

For a number of reasons the energy E of a simple system is denoted by a different symbol U and is called the internal energy. Alternatively, equation (23) may be solved for U in terms of S and V to give

$$U = U(S,V). \qquad (24)$$

The energy change dU between two neighbouring stable equilibrium states can be expressed in terms of the corresponding entropy and volume changes, dS and dV, respectively, by means of the relation

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV. \qquad (25)$$

The first partial differential coefficient has already been identified (by equation 13) as the Kelvin temperature. The second is the rate of energy change (the rate of receiving work) with change in volume in reversible adiabatic compression or expansion. It can be shown to be the negative of the pressure p that the system exerts on constraining walls. Substitution of the temperature T and the pressure p in equation (25) results in the equation

$$dU = TdS - pdV, \qquad (26)$$

in which the first term in the right-hand member represents the heat and the second the work of a reversible process. It may be observed, however, that equation (26) holds for any change between neighbouring stable equilibrium states regardless of the nature of the process, because it is a relation between properties and changes in values of properties. But for the general process, the terms (TdS) and $(-pdV)$ are not in general equal to the respective heat and work that may be involved in the process.

By means of the criterion of stable equilibrium and equation (26), it can be shown that not only the temperature but also the pressure must be uniform throughout a simple system in a stable equilibrium state.

Representation of states on diagrams. Because a stable equilibrium state in a simple system is determined by two independent properties, all such states may be represented by points on a surface in a space in which two of the three coordinates represent independent properties and the third the dependent property. Alternatively, the traces
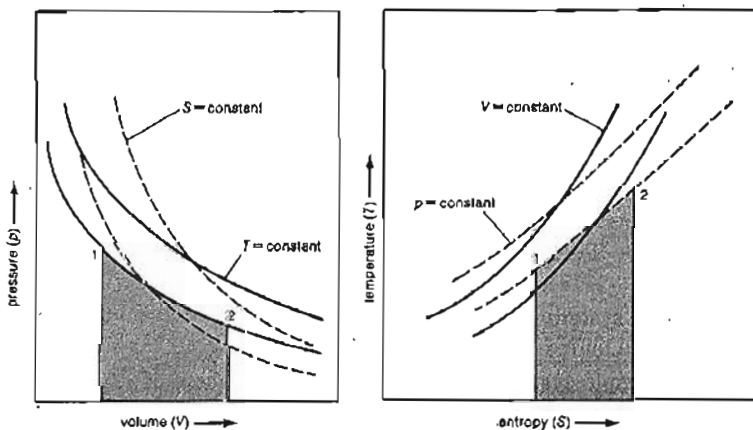

Figure 3: *Relationships between thermodynamic properties of systems.*
(Left) Relationships of pressure and volume of systems maintained at fixed temperature *(T)* or at fixed entropy *(S).*
(Right) Relationships between temperature and entropy of systems maintained at fixed pressure *(p)* or at fixed volume *(V).*

of planes of constant value of one property may be shown on a two-dimensional chart in which the coordinates represent the other two properties. Two common choices of the latter class are pressure–volume $(p-V)$ and temperature–entropy $(T-S)$ charts. An example of the former is shown in Figure 3 (left), with traces of planes of constant temperature from the pressure–volume–temperature space and of planes of constant en-

tropy from the pressure–volume–entropy space. On the $p-V$ chart the area under a curve of states represents the work done on a slowly moving piston that confines the fluid in a cylinder. On the $T-S$ chart (Figure 3 [right]) the area under the curve represents the heat received by the system in a reversible process passing through the states represented by the curve. Because the change of energy of a system undergoing a cycle is equal to zero, it is seen from equation (19) that the cyclic integral $\oint \delta Q$ must be equal to the cyclic integral $\oint \delta W$. For a reversible cycle, TdS may be substituted for δQ and pdV for δW so that

$$\oint TdS = \oint pdV. \qquad (27)$$

For any cycle, therefore, the area enclosed by the representation on the $T-S$ chart is equal to that on the $p-V$ chart; for example, the areas enclosed by the representations of the Carnot cycle in the $p-V$ and $T-S$ charts (Figure 4 [left] and 4 [right]) are equal.
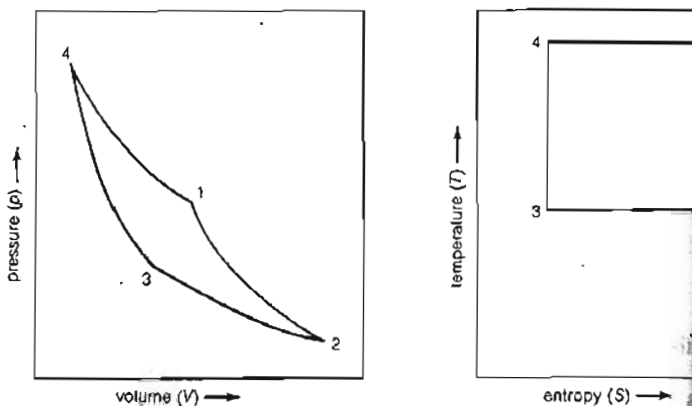

Figure 4: *Relationship between work done and heat received by a fluid undergoing a Carnot cycle.*
The lines from state 1 to state 2 represent reversible and adiabatic expansion of the fluid; from 2 to 3, reversible compression at fixed temperature accompanied by heat rejection; from 3 to 4, reversible and adiabatic compression; from 4 to 1, reversible expansion at fixed temperature accompanied by heat reception. The enclosed area (left) represents the net work done by the fluid during the complete cycle; it is exactly equal to the enclosed area (right) that represents the net heat flow to the fluid.

Reversible constant-pressure process. The reversible process at constant pressure, because of its practical importance, warrants special consideration. Because for constant pressure the change in the product pV is also p times the change in V, pdV, it can be shown that the expression for the heat $(\delta Q)_p$ received by the system is equal to the change of an extensive property called enthalpy, which is defined by the relation $H \equiv U + pV$; that is,

$$(\delta Q)_p = dH. \qquad (28)$$

Thus, in any heating of a simple system in such a way (for example, under a piston loaded by a weight) that its boundary expands slowly as it maintains constant pressure, the enthalpy of the system increases by the amount of heat added.

MAXWELL RELATIONS

For a closed simple system that assumes only stable equilibrium states, it can be shown that the partial derivative $(\partial T/\partial V)_S$ is equal to the negative of the partial derivative $(\partial p/\partial S)_V$, thus,

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V.$$

This relation is one of the Maxwell relations, named for the man who first stated them.

Enthalpy, Helmholtz free energy, and Gibbs free energy are, respectively, defined as follows:

$$H \equiv U + pV, \qquad (29)$$
$$\Psi \equiv U - TS, \qquad (30)$$
$$Z \equiv H - TS. \qquad (31)$$

These properties can be manipulated mathematically to obtain the following equations:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V, \tag{32}$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p, \tag{33}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V, \tag{34}$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p. \tag{35}$$

These equations are Maxwell relations. They relate the entropy to the relatively easily measured properties pressure, volume, and temperature.

PHASE RULE

An intensive property of system A is defined as a property of which the value at a spatial point in a part of A approaches a limit independent of the size of the part as the size is reduced until it can no longer be identified as a system. As a system is subdivided into smaller and smaller parts, at some point a part becomes so small as compared with the extent of force fields between the parts that it is no longer isolatable and may not, therefore, be considered a system.

For certain stable equilibrium states of a simple system, parts of the system may assume different values of intensive properties; for example, liquid and vapour water may coexist in mutual stable equilibrium for which liquid and vapour parts have the same pressure and temperature but radically different densities. Each such part is called a phase. More generally, a phase of a system is the collection of all homogeneous parts open to the transfer of rest mass and having identical values of their intensive properties.

In the absence of chemical reactions and membranes that are permeable to one substance and not to another, the number of components of a phase of a multiphase system will be identical with the number of molecular species present in the whole system. As soon, however, as a chemical reaction is permitted in which some of these species may be formed from others, then the number of components is reduced by one.

A closed simple system has two independent properties; a simple system open to the transfer of rest mass will have these same two plus the number n of components for the system, because the quantity of each component may be independently varied. On the other hand, the number of independent properties of the same simple open system is also equal to the sum $F + r$, in which F denotes the number of independent intensive phase properties and r the number of phases, because the F intensive properties fix the intensive states of the phases, and the r masses of the r phases fix the size of the system. From these remarks it follows that F is given by the relation

$$F = n + 2 - r. \tag{36}$$

This is the phase rule of Gibbs. It reveals, for example, that for a single-component open system, such as water, the number of independent intensive properties may be 2, 1, or 0 if the number of phases present is 1, 2, or 3, respectively. Thus, for water vapour, temperature and pressure are independent properties; i.e., after the value of one is arbitrarily selected, the value of the other may be arbitrarily selected. For coexisting liquid and vapour, either pressure or temperature may be considered the independent property; for coexisting solid, liquid, and vapour (the triple point), the values of all intensive phase properties are fixed by the nature of the substance, and the value of none may be arbitrarily selected.

SIMPLE ONE-COMPONENT SYSTEMS

Phases. All systems that consist of a single pure molecular species, such as argon, oxygen, or water, exhibit largely common patterns of coexisting phases. A closed system of this kind, being a simple system, has two independent properties and the relationships between proper-

ties for stable equilibrium states may therefore be shown as a surface in three-dimensional space. The projection of one such surface onto the pressure–temperature plane is shown in Figure 5 (top) and onto a pressure–volume plane in Figure 5 (bottom). It will be evident from these
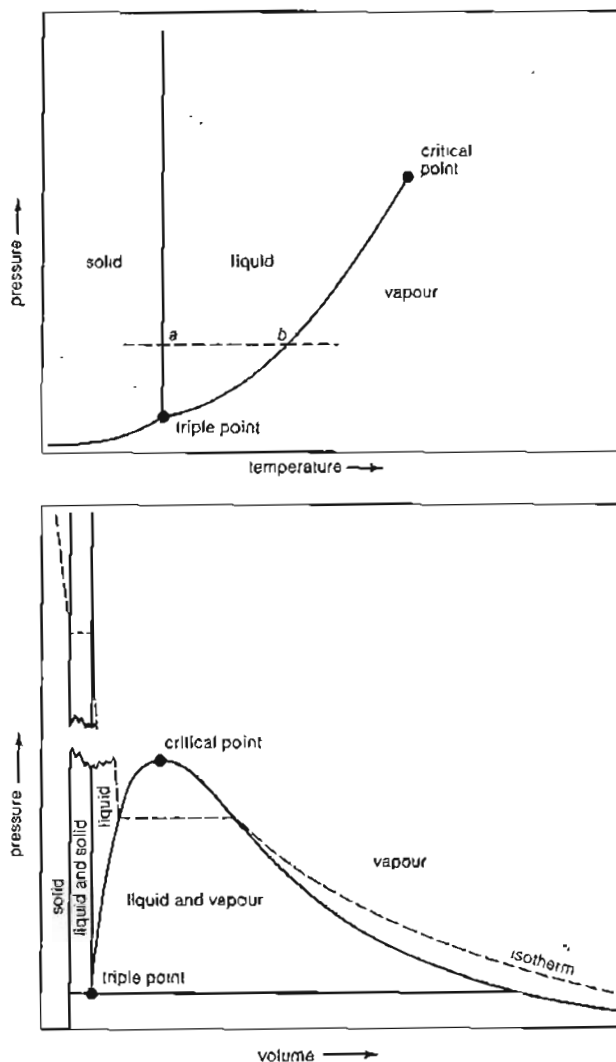

Figure 5: *Relationships between phases of a pure substance.* (Top) The horizontal broken line through a and b represents the effects of absorption of heat by a substance at a constant pressure. (Bottom) The broken line from lower right to upper left represents the effects of compressing a substance, initially entirely vaporous, while keeping the temperature fixed (an isothermal process).

figures that the solid may be heated under constant pressure until some liquid appears. Further heating increases the proportion of liquid present at constant temperature until the solid vanishes, leaving only liquid. Further heating increases the temperature of the liquid until vaporization begins, provided that the pressure is less than the critical pressure. Continued heating increases the proportion of vapour present at constant temperature until the liquid vanishes, leaving only vapour. The vapour may then be raised in temperature indefinitely or until chemical dissociation destroys the assumed purity of the molecular species.

At the critical pressure the coexisting liquid and vapour states are identical, and the vaporization process contracts to an infinitesimal process. At higher pressures no vaporization occurs. It becomes clear, then, that liquid and vapour states differ in degree rather than in kind, because any liquid state can be transformed to any vapour state by a process for which the system remains in a single-phase condition throughout. The same cannot be said of the transition from solid states to either liquid or vapour states.

Processes at constant volume and at constant pressure. When a simple system is heated at constant volume, no work occurs at the boundaries, so that the heat, according to equation (23), is equal to the increase in energy as

Heat capacities

well as to the product of temperature and increase in entropy:

$$(\delta Q)_V = dU = T\,dS.$$

The heat of a constant-volume process is therefore equal to the area under the curve on a temperature–entropy chart. The constant-volume heat capacity is defined in terms of the partial derivatives of energy and entropy as follows:

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V; \qquad (37)$$

and the constant-volume specific-heat capacity is defined similarly as

$$c_v \equiv \left(\frac{\partial u}{\partial T}\right)_v = T\left(\frac{\partial s}{\partial T}\right)_v, \qquad (38)$$

in which lowercase letters denote values per unit of mass or per mole. By reference to equation (28) it will be seen by analogy that the corresponding definitions of heat capacities at constant pressure are as follows:

$$C_p \equiv \left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p \qquad (39)$$

and

$$c_p \equiv \left(\frac{\partial h}{\partial T}\right)_p = T\left(\frac{\partial s}{\partial T}\right)_p. \qquad (40)$$

By means of Maxwell relations it can be shown that the difference between the two heat capacities is given by the product of two partial derivatives, both of which are fixed entirely by the relation between p, V, and T:

$$C_p - C_V = T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p. \qquad (41)$$

When a phase change occurs during constant-pressure heating or cooling, the temperature is unchanged by the heating or cooling as long as both phases are present. The heat required in such a process to change a unit mass from one phase to the other is equal, according to equation (28), to an increase in enthalpy. It is called the latent heat of that phase change. Thus, a latent heat of fusion h_{jl}, a latent heat of vaporization h_{fg}, and a latent heat of sublimation h_{ik} can be defined by means of the relations

$$h_{jl} = h_l - h_j = T(s_l - s_j), \qquad (42)$$
$$h_{fg} = h_g - h_f = T(s_g - s_f), \qquad (43)$$
$$h_{ik} = h_k - h_i = T(s_k - s_i), \qquad (44)$$

in which subscripts j, l, f, g, i, and k refer, respectively, to solid in equilibrium with liquid, liquid in equilibrium with solid, liquid in equilibrium with vapour, vapour in equilibrium with liquid, solid in equilibrium with vapour, and vapour in equilibrium with solid.

In a two-phase region the change in any extensive property is directly proportional to the corresponding change in any other for a fixed value of temperature, and the pressure is a function of temperature only. From these observations and Maxwell relations (33) or (34), it follows that the rate of change of pressure with temperature change for a two-phase mixture is equal to the ratio of the entropy change to the volume change when a fixed quantity of the substance is changed from one phase to the other—e.g., from liquid state to vapour state. Alternatively, the ratio of enthalpy change to volume change gives the rate of change of pressure with change in the natural logarithm (ln) of temperature:

The Clapeyron relation

$$\frac{dp}{dT} = \frac{s_2 - s_1}{v_2 - v_1} \qquad (45)$$

$$\frac{dp}{d(\ln T)} = T\frac{dp}{dT} = \frac{h_2 - h_1}{v_2 - v_1}. \qquad (46)$$

These equations are used to express the Clapeyron relation.

Equation of state. The mathematical relation between the pressure, volume, and temperature for stable equilibrium states of a closed simple system is called its equation of state. Although it will be subsequently shown to be a relation that does not completely specify the nature of the system, the mathematical relation is an important

one because the three properties it relates are relatively easily measured.

Experimentally it is found that the relation between the pressure, volume, and temperature of a system is extremely complicated. No explicit mathematical expression has ever been devised that represents all the stable equilibrium states of any one simple system. Instead, equations have been proposed, each of which represents some limited range of states of a particular system. The complexity of equations of state ranges from that for a perfect gas with a single constant to those for liquid and vapour states, of which that for water is an example, which often have between 10 and 100 constants, the values of which must be determined so as to fit experimental data.

For the range of liquid and vapour states of a pure molecular species, the general pattern of the p-v-T relation is best shown by drawing a graph of the quantity pv/RT versus the ratio of pressure to critical pressure. If v is taken to be the specific volume (the volume per unit mass) and R is chosen so that pv/RT becomes unity at zero pressure and infinite specific volume for any temperature, then a coincidence occurs: pv/RT is unity for every temperature for that substance, provided only that the specific volume is infinitely large. The constant R is called the gas constant of the molecular species.

The molecular weight of oxygen is 32 and the molecular weight M for any species is inversely proportional to the gas constant R of the molecular species. Thus, the molecular weight M of any species can be defined as 32 times the ratio of the gas constant of oxygen and the gas constant of the species:

$$M \equiv 32\frac{R \text{ (for } O_2)}{R}. \qquad (47)$$

It follows that the volume occupied by a molecular weight of a gas at very low pressure is the same for all gases for any selected pair of values of p and T. Moreover it is directly proportional to T and inversely proportional to p.

The product of molecular weight M and gas constant R is the same for all gases and is called the universal gas constant (denoted by R). The result is an equation, called the perfect-gas equation of state, that appears frequently in the literature of thermodynamics; that is,

$$pv/RT = 1, \qquad (48)$$

in which v is the volume occupied by one molecular weight, or one mole, of gas.

The equation of state (48) applies, therefore, to any pure molecular species in states for which the specific volume is extremely large and the pressure, at finite temperature, is therefore extremely small. It holds within 2 percent for water vapour at a pressure of one atmosphere and with correspondingly better precision as the pressure is lowered. A gas that conforms to equation (48) is called a semiperfect gas.

By means of Maxwell relations and equation (23) it can be shown in the case of a semiperfect gas that internal energy, enthalpy, and both heat capacities are functions of temperature only and are independent of the effects of volume or pressure. Moreover, the difference $c_p - c_v$ between the specific-heat capacities is equal to the gas constant R when all three quantities are defined in terms of unit mass or, alternatively, in terms of molecular weight.

When quantum effects are not important, an approximate expression for the specific-heat capacity may be obtained from statistical thermodynamics. It is

$$c_v = \frac{f}{2}R, \qquad (49)$$

in which f denotes the number of active degrees of freedom of the molecule (the number of independent ways in which the space configuration of the molecule may change). For a mass concentrated in a point, f would be three (corresponding to the three directions of translation), and c_v would be $3R/2$. With spatial distribution of the mass, additional degrees of freedom appear by

The universal gas con

virtue of rotation and vibration of the molecule. The number of such degrees of freedom active in a molecule depends, in accordance with quantum theory, on the temperature. In Table 1 are shown the molal heat capac-

Table 1: Molal Specific Heat Capacities of Gases at Room Temperature

	c_v	c_p	$c_v/(\frac{1}{2}R)$	$c_p/(\frac{1}{2}R)$	$k = c_p/c_v$
He*	2.979	4.965	3.000	5.000	1.667
H$_2$	4.88	6.87	4.92	6.91	1.406
O$_2$	5.02	7.00	5.05	7.04	1.406
N$_2$	4.97	6.96	5.01	7.00	1.400
CO	4.97	6.96	5.01	7.00	1.400
H$_2$O	6.02	8.01	6.07	8.06	1.330
CO$_2$	6.81	8.80	6.86	8.85	1.292

*And all other monatomic gases.

ities of several gases at room temperature along with the corresponding number of degrees of freedom $c_v/(\frac{1}{2}R)$. For a monatomic gas this number of degrees of freedom proves to be three almost exactly; for diatomic gases it is nearly five (corresponding to two degrees of rotational freedom); and for more complex molecules, a number in excess of five, which implies vibrational degrees of freedom. For all except the monatomic molecule, the value of c_v increases with temperature as new degrees of freedom become active.

The expressions for energy, enthalpy, and entropy of a semiperfect gas are as follows:

$$u = \int_{T_0}^{T} c_v dT + u(T_0), \tag{50}$$

$$h = \int_{T_0}^{T} c_p dT + u(T_0) + RT_0, \tag{51}$$

$$s = \int_{T_0}^{T} c_v \frac{dT}{T} + R \ln \frac{v}{v_0} + s(T_0, v_0)$$

$$= \int_{T_0}^{T} c_p \frac{dT}{T} - R \ln \frac{p}{p_0} + s(T_0, p_0); \tag{52}$$

in these equations the subscript 0 refers to an arbitrarily selected state.

The perfect gas is a special case of the semiperfect gas —namely, that for which the heat capacities are independent of temperature. The integrals of the previous expressions can now be resolved to give the following:

$$u = c_v(T - T_0), \tag{53}$$

$$h = c_p T - c_v T_0, \tag{54}$$

$$s = c_v \ln \frac{T}{T_0} + R \ln \frac{v}{v_0} + s_0$$

$$= c_p \ln \frac{T}{T_0} - R \ln \frac{p}{p_0} + s_0, \tag{55}$$

in which s_0 denotes the arbitrary value of s at T_0 (for which u is zero) and at p_0.

For a reversible adiabatic process in a perfect gas, the following relations hold: $pv^k = $ constant, $Tv^{k-1} = $ constant, and $pT^{-k/(k-1)} = $ constant, and k is the ratio c_p/c_v.

In 1873 the Dutch physicist Johannes van der Waals proposed the following equation, which in a qualitative way describes the liquid and vapour states of a pure species:

$$p = \frac{RT}{v - b} - \frac{a}{v^2}, \tag{56}$$

in which a and b are constants for any one species. Not only does this equation approach that of the semiperfect gas as v goes to infinity, but the equation also provides for a region of coexisting states that is capped by a critical state, as in actual substances. Below the temperature T_c (equal to $8a/27Rb$), three values of v correspond to each value of p. Pairs of high-volume and low-volume states, such as P and R (Figure 6), may be found at each pressure–temperature combination. The one pair for which the areas $PQbP$ and $QaRQ$ are equal can be shown

to be the pair that can coexist in mutual stable equilibrium.

An approximate justification of the van der Waals equation can be made based in part on the Newtonian equation of motion for a collection of particles having the following characteristics: (1) the particles are uniform rigid spheres; (2) their diameters are appreciable fractions of the mean distances between them, except at infinite specific volume; and (3) they exert finite attractive forces, which vary with the distance between them, as well as infinite repulsive forces upon contact.
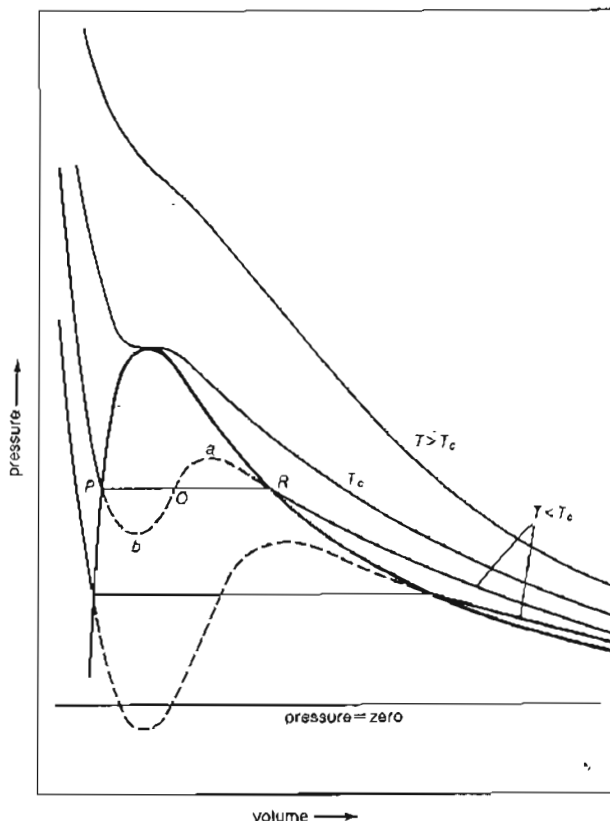
Figure 6: Relations between pressure (p) and volume (v) of liquid and vapour states of a pure molecular species at different temperatures according to the van der Waals equation (see text).

Equations of state, by proper assignment of values of constants, can be made to represent quantitatively (as contrasted with qualitatively for the van der Waals equation) the properties of many molecular species with fair precision. An equation has been developed that represents the properties of water within the precision of virtually all experimental measurements on liquid and vapour water.

A general type of equation of state, which can be made to fit almost any range of gaseous states at the expense of indefinite increase in the number of constants, is the virial form. It may be written as

$$\frac{pv}{RT} = 1 + B\rho + C\rho^2 + D\rho^3 + \dots, \tag{57}$$

Virial equations of state

in which ρ denotes the density, and the coefficients B, C, D, . . . , called the second, third, fourth, . . . virial coefficients, are functions of temperature only. Substantial progress has been made in determining the forms of the functions B and C for the simpler molecular structures by means of models of the structure and force fields between them.

Critical point. In recent decades the relationships between the various properties of a pure molecular species at and near the critical point have been the subject of many studies. It appears from these that certain mathematical singularities occur at the critical point, including an infinite value for the heat capacity at constant volume, which indicate that no continuous equation (such as the van der Waals equation) relating pressure, volume, and temperature can represent the actual variation in these

properties for states closer than a few degrees in temperature to the critical point. A so-called scaling law has been devised to cope with the mathematics of this region.

Fundamental equations. As was implied above by the development of the equation of state for a semiperfect gas, such an equation alone is not adequate to yield the values of energy u, enthalpy h, and entropy s. It must be supplemented by a knowledge of the variation of heat capacity with temperature.

A type of equation for which any of the properties p, T, u, v, s (or any algebraic combination of these) not explicit in it are found by differentiation is called a fundamental equation, and the corresponding function has been called a characteristic function. For a simple system, the four characteristic functions—specific energy u, specific enthalpy h, specific Helmholtz free energy ψ, and specific Gibbs free energy ζ—are expressed in terms of fundamental equations as follows:

$$u = u(v,s), \quad T = \left(\frac{\partial u}{\partial s}\right)_v, \quad p = -\left(\frac{\partial u}{\partial v}\right)_s, \qquad (58)$$

$$h = h(p,s), \quad T = \left(\frac{\partial h}{\partial s}\right)_p, \quad v = \left(\frac{\partial h}{\partial p}\right)_s, \qquad (59)$$

$$\psi = \psi(v,T), \quad p = \left(\frac{\partial \psi}{\partial v}\right)_T, \quad s = -\left(\frac{\partial \psi}{\partial T}\right)_v, \qquad (60)$$

$$\zeta = \zeta(p,T), \quad v = \left(\frac{\partial \zeta}{\partial p}\right)_T, \quad s = -\left(\frac{\partial \zeta}{\partial T}\right)_p, \qquad (61)$$

where the specific Helmholtz free energy ψ and the specific Gibbs free energy ζ are defined by

$$\psi \equiv u - Ts \text{ and } \zeta \equiv h - Ts. \qquad (62)$$

SIMPLE MULTICOMPONENT SYSTEMS

Gibbs equation. The change of entropy dS between neighbouring stable equilibrium states of a simple system open to the transfer of rest mass can be expressed in terms of the corresponding change of energy dU, volume dV, and number of particles dn_i ($i = 1, 2, \ldots, k$) of the k components in the system. By use of equation (9) it can be shown that the expression for dS involves partial derivatives as coefficients that multiply the changes in the independent properties $U, V, n_1, n_2, \ldots, n_k$:

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,n} dU + \left(\frac{\partial S}{\partial V}\right)_{U,n} dV + \left(\frac{\partial S}{\partial n_1}\right)_{U,V,n} dn_1 +$$
$$\ldots + \left(\frac{\partial S}{\partial n_k}\right)_{U,V,n} dn_k, \qquad (63)$$

in which subscript n denotes all of $n_1, n_2, \ldots, n_k$ that can be held constant. Upon identifying, as in equation (23), the first two partial derivatives in terms of pressure p and temperature T and introducing a new quality μ_i to be defined shortly, equation (63) becomes what is called the Gibbs equation:

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu_1}{T} dn_1 - \ldots - \frac{\mu_k}{T} dn_k. \qquad (64)$$

Chemical potential The quantity μ_i, which is called the chemical potential of component i in the system, is defined as follows:

$$\mu_i \equiv -T\left(\frac{\partial S}{\partial n_i}\right)_{U,V,n} \quad \text{for } i = 1, 2, \ldots k. \qquad (65)$$

Mutual stable equilibrium. Upon seeking the conditions that must be satisfied in order that two or more phases should be in mutual stable equilibrium while open to transfer of rest mass between them, it is unnecessary to consider any states for which any one phase would be in a nonequilibrium state if it were suddenly isolated. It is unnecessary because any change of state that could occur spontaneously while the phase was isolated would be one of many allowed changes of state when it was not isolated and would, therefore, serve as an indication that at least one spontaneous change is possible and that equilibrium does not exist.

It is sufficient, therefore, to consider only those states for which the individual phases are in stable equilibrium states when isolated. The Gibbs equation provides a general statement of the change of entropy of a simple phase that may exchange component substances with neighbouring phases as it passes through stable equilibrium states. If the formation of any new part unlike the existing parts is prohibited by the definition of the phase, then a set of stable equilibrium states is prescribed for which the Gibbs equation expresses changes in entropy between states in the set.

A heterogeneous system may be considered to be made up of several homogeneous phases, within each of which the formation of a new part is prohibited as proposed above. The states that these phases may assume consistent with mutual stable equilibrium may now be found by seeking out the state of maximum entropy of the whole system for a given volume and energy. This kind of procedure was used above to show that the phases of such a system must have equal temperatures. By similar reasoning it can now be shown that the phases must have equal pressures and equal values of the chemical potential μ_i of each component i present in all the phases. That is, among the necessary conditions for stable equilibrium of a multiphase simple system (i.e., in the absence of force fields and capillarity) is uniformity throughout the multiphase system of temperature, pressure, and chemical potential of each component present in all the phases.

Of these conditions the one most open to exception is equality of pressure. In order for it to apply, an encroachment of the volume of each phase upon every other, for constant energy and composition of each phase, must be an allowed variation in state of the system. Wherever phases are separated by a rigid boundary, which may be permeable to one or more components, then equality of pressure between such phases is not necessary to mutual stable equilibrium.

If two phases are separated by a wall that is permeable to some components but not permeable to others, then equality of chemical potential of those other components across the wall is not necessary. An exception can be made as regards the potentials T, p, and μ_i in cases in which a transfer of energy, volume, and component i can occur at stable equilibrium in one direction but not in the other direction. Then a condition for mutual stable equilibrium becomes, because entropy is to be maximized, that the temperature in the phase that can receive energy but cannot supply it may be greater than or equal to the temperature in phases that can both receive and supply energy. Similar statements can be made in regard to pressure and the transfer of volume and in regard to chemical potential of component i and the transfer of that component.

These statements imply that potentials T, p, and μ_i are escaping tendencies for energy, volume, and component i, respectively. For equilibrium each escaping tendency must be balanced as between phases, unless the escape of one flux has reached its upper limit for a phase so that no further escape is possible. For such a phase it is necessary for equilibrium that the escaping tendency be not less than in other phases, but it may be more. This consideration is relevant for certain quantum effects at low temperature, for two phases separated by a movable solid boundary that has come up against a stop and behind which the pressure may be greater than in front (but not less), and for exhaustion of a phase as regards one component.

From the definitions of enthalpy H (29), Helmholtz free energy Ψ (30), and Gibbs free energy Z (31), it is readily shown that the chemical potential can be expressed in alternative forms; that is,

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{V,S,n} = \left(\frac{\partial H}{\partial n_i}\right)_{p,S,n}$$
$$= \left(\frac{\partial \Psi}{\partial n_i}\right)_{V,T,n} = \left(\frac{\partial Z}{\partial n_i}\right)_{p,T,n} \qquad (66)$$

The last of these is known as the partial Gibbs free energy ζ_i of component i in the phase. In view of the definition of Z, μ_i may also be expressed in terms of the partial enthalpy h_i and the partial entropy s_i; thus,

$$\mu_i = \left(\frac{\partial Z}{\partial n_i}\right)_{p,T,n} = \left(\frac{\partial H}{\partial n_i}\right)_{p,T,n} - T\left(\frac{\partial S}{\partial n_i}\right)_{p,T,n}$$

$$= \zeta_i = h_i - Ts_i. \qquad (67)$$

In general, lowercase symbols with subscript i denote the partial property. For a phase of pure component i, any partial property is identical with the corresponding specific property—that is, the value of the property per unit mass, which is here taken to be the mole. The chemical potential of a component i in a mixture containing i is equal to the specific Gibbs free energy of i in a phase of pure i in equilibrium with the mixture through a membrane permeable to i alone.

A semipermeable membrane such as the one just proposed is one across which the pressure need not be balanced for equilibrium. By definition of the membrane, encroachment of the mixture phase into the volume of the pure phase cannot occur, but the reverse encroachment can occur. The membrane must, of course, have sufficient structural strength to support the pressure difference.

The expression for the chemical potential of a semiperfect gas in terms of temperature and pressure is found from equations (67), (51), and (52). It proves to be the sum of a simple function of pressure p and temperature T plus a relatively complicated function $f_i(T)$ of temperature as follows:

$$\mu_i = RT \ln p + f_i(T), \qquad (68)$$

in which the function $f_i(T)$ is different for different semiperfect gases i. For a given temperature, however, equation 68 indicates that the chemical potential increases with increase in pressure. That is, temperature being fixed, the escaping tendency increases as the pressure increases.

Three equations will be recorded here but not derived.

1. The Gibbs equation as an expression for the change in Gibbs free energy of a phase between neighbouring stable equilibrium states:

$$d\mathbb{Z} = V dp - S dT + \sum_i \mu_i \, dn_i. \qquad (69)$$

In the equation the short notation $\sum_i \mu_i \, dn_i$ has been used to denote $\mu_1 dn_1 + \mu_2 dn_2 + \cdots + \mu_k dn_k$, in which subscript $i = 1, 2, \ldots, k$ denotes a component substance.

2. The Gibbs free energy as a summation of products of chemical potentials and numbers of moles of component substances i of a phase:

$$\mathbb{Z} = \sum_i \mu_i \, n_i. \qquad (70)$$

3. The Gibbs–Duhem equation, which relates for a phase the changes between stable equilibrium states in temperature, pressure, and numbers of moles of components:

$$S dT - V dp + \sum_i n_i \, d\mu_i = 0. \qquad (71)$$

Mixtures of gases. *Gibbs–Dalton rule for mixtures.* Gibbs revised the earlier rule of the 18th- and 19th-century English physicist John Dalton for determining the properties of a mixture of gases from the properties of the pure components. Two equivalent statements of the Gibbs–Dalton rule for mixtures are as follows: (1) The pressure in a mixture of different gases is equal to the sum of the pressures of the different gases as existing each by itself at the temperature of the mixture and with the same value of the chemical potential as it has in the mixture. (2) The pressure of a mixture of different gases is equal to the sum of the pressures of the pure components each existing as a phase in equilibrium with the mixture through a membrane permeable to the component.

Using single subscripts to refer to components in the mixture and double subscripts to refer to pure component phases, the Gibbs–Dalton rule takes the form

$$p = p_{11} + p_{22} + p_{33} + \cdots \qquad (72)$$

for

$$T = T_{11} = T_{22} = \ldots, \qquad (73)$$

and

$$\mu_1 = \mu_{11}, \mu_2 = \mu_{22}, \ldots. \qquad (74)$$

In this notation p_1 would have no "operational" meaning because no instrument has been devised that can measure the pressure of component 1 when it is part of a mixture.

It can now be shown from the Gibbs–Dalton rule and the Gibbs–Duhem equation that the number c_i of mass units of component i in unit volume of the mixture (the concentration c_i of i in the mixture) is equal to the density ρ_{ii} or the inverse of the specific volume v_{ii} of i in the pure phase in mutual stable equilibrium with the mixture. The concentration c_i denotes the ratio of mass n_i of i in the mixture to the volume v of the mixture. It follows immediately that the density ρ (or $1/v$) of the mixture is the sum of the densities ρ_{ii} (or $1/v_{ii}$) of the pure phases.

Further application of the Gibbs–Duhem equation yields the following expressions for extensive properties:

$$U = nu = \sum_i n_i \, u_{ii},$$

$$H = nh = \sum_i n_i \, h_{ii},$$

$$S = ns = \sum_i n_i \, s_{ii},$$

$$\Psi = n\psi = \sum_i n_i \, \psi_{ii}, \text{ and}$$

$$\mathbb{Z} = n\zeta = \sum_i n_i \, \zeta_{ii} = \sum_i n_i \, \mu_{ii} = \sum_i n_i \, \mu_i. \qquad (75)$$

In these equations the mass n_i of component i in the mixture will be identical with n_{ii} the mass of i in the pure phase if the volume of the pure phase ii that is in mutual stable equilibrium with the mixture is made equal to the volume of the mixture. The result is in accord with Dalton's concept that each component behaves as if it were present alone.

A further conclusion that can be reached is that a Gibbs–Dalton mixture of semiperfect gases is itself a semiperfect gas. That is, for the mixture the ratio pv/RT is equal to unity if v is the volume per mole of all components and R the universal gas constant. If a specific gas constant is used and v is the volume per unit mass, then the mixture behaves as a semiperfect gas with a molecular weight M that is the mass m of the mixture divided by the total number n of moles of all components. It is also the average of the molecular weights M_i of the components, each weighted proportionately to the mole fraction y_i of that component in the mixture:

$$M = \frac{m}{n} = \sum_i y_i \, M_i.$$

Mixing gases. Some further results of the Gibbs–Dalton rule will be given here without proof. If a number of pure species are confined by thin partitions in separate parts of an insulated volume V in such quantities that their pressures are equal when their temperatures are equal, then when the partitions are removed (or destroyed), the gases will mix irreversibly without change in temperature, pressure, energy, or enthalpy. The change of entropy ΔS is greater than zero, as is appropriate for an adiabatic irreversible process. It is given by the negative of the product of the number n of moles of all components multiplied by the gas constant R and a mean logarithmic mole fraction:

$$\Delta S = -nR \sum_i y_i \ln y_i, \qquad (76)$$

in which y_i denotes the mole fraction of the species i in the final mixture. Both the Helmholtz free energy and the Gibbs free energy decrease in the mixing process.

The Gibbs–Dalton rule holds in regions of state in which the pressure is low relative to the critical pressure of every component. Outside these regions an equation of state for a mixture may be devised from the equations of state of its components, with varying degrees of precision, by means of certain combining rules. One of these rules, proposed by the 19th- and 20th-century French physicist Émile-Hilaire Amagat, states that the volume of a mix-

ture is the sum of the volumes of the pure components—each at the pressure and temperature of the mixture. A 20th-century U.S. chemist, James Alexander Beattie, later proposed a rule of more general application that prescribes how the coefficients in the Beattie–Bridgman equations for the pure components may be combined in order to obtain the corresponding coefficients for the mixture.

Vapour pressures of pure liquids. The vapour of a pure species may be in mutual stable equilibrium with its liquid at a flat interface at the normal or saturation vapour pressure corresponding to its temperature. The vapour may also, however, be in mutual stable equilibrium at a nonwetting porous wall that is permeable to vapour but not to liquid or at a curved interface, either of which can support a pressure difference between liquid and vapour. The effect of change in pressure of the liquid on the corresponding vapour pressure is called the Poynting effect. It is found by equating chemical potentials of liquid and vapour. For an incompressible liquid and a semiperfect vapour, the Poynting effect proves to be approximately proportional to the change in pressure on the liquid. For water at 40° C (104° F) the equilibrium pressure of the vapour increases by 1 percent when the pressure on the liquid is increased by a factor of 200.
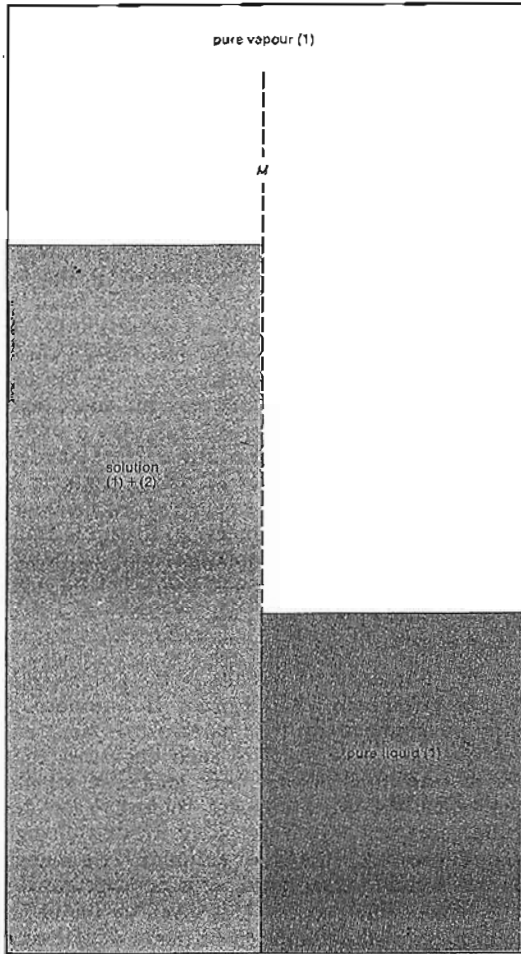
The Poynting effect

Figure 7: Equilibrium between a pure volatile liquid (1), a solution of nonvolatile substance (2) in liquid (1), and the vapour of substance (1). Substance (1) can pass through the membrane (M), but substance (2) cannot. The difference in the vapour pressures of solvent and solution causes the liquid levels to be unequal. The difference in pressure between pure liquid and solution is called the osmotic pressure (see text).

Ideal solutions. When a solute is added to a volatile solvent, the volatility of the solvent is reduced. The effect is to reduce the pressure of solvent vapour that is in equilibrium with the liquid in proportion to the reduction in the mole fraction of solvent in the solution. Thus the effect on the volatility is the same for equal numbers of moles of different solutes in solution, the mole being measured as described by equation (47). This observation, which holds only for dilute or ideal solutions, is

expressed in Raoult's rule. The rule states that at given pressure p and temperature T the pressure p_1^v of pure solvent vapour in equilibrium with the solution is equal to the product of the mole fraction x_1 of solvent in the solution and the vapour pressure p_1^0 of pure liquid solvent at the pressure and temperature of the solution. By ignoring the small Poynting effect on the vapour pressure of the solvent, the rule of boiling-point raising may be derived from Raoult's rule by mathematical deduction. It is that the rate of change of boiling temperature T with mole fraction x_2 of solute 2, as solute is added to a dilute solution, is equal to the rate of change of boiling temperature of pure solvent 1 with the logarithm of the pressure p_1^0 on the pure solvent. The mathematical statement of the rule of boiling-point raising is given by the relation

$$\left(\frac{\partial T}{\partial x_2}\right)_{x_2 \to 0} = \left[\frac{dT}{d(\ln p_1^0)}\right]_{x_1 \to 0}. \qquad (77)$$

For water at 25° C (77° F) the value of $(\partial T/\partial x_2)$ is about 17° C (31° F) or, more practically, 0.17° C for each mole percent of solute regardless of the nature of the solute.

Figure 7 depicts a container in which volatile solvent liquid 1 is separated from a solution containing nonvolatile solute 2 by a wall M permeable to 1 only. The wall extends only part way to the top, leaving a vapour space with free access of vapour 1 from one liquid surface to the other. Because the pressure of vapour in mutual stable equilibrium with the solution is less, by Raoult's rule, than that in equilibrium with the pure solvent, the height of the solution surface must be greater than that of the pure liquid by enough to provide the appropriate hydrostatic head of vapour between them. The corresponding hydrostatic head of liquid, of course, is much greater and accounts, except for the head of vapour, for a substantial difference between the pressure of the solution and the pressure of the solvent with which it is in equilibrium through the semipermeable wall. This difference in pressure, which is required to prevent migration of solvent into the solution, is called osmotic pressure. With the usual approximations for a dilute solution and a perfect vapour, it can be shown by equating chemical potentials of solvent across the wall that the osmotic pressure P is approximately equal to the product of gas constant R, temperature T, and number of moles c_2 of solute per unit volume of solution.

By means of the Gibbs–Duhem equation (71) and the assumption of perfect vapours for the two components of a binary solution, it can be shown that Raoult's rule requires that the pressure p_2^v of solute vapour in equilibrium with a solution is proportional to the mole fraction x_2 of solute in the solution; that is, p_2^v is equal to
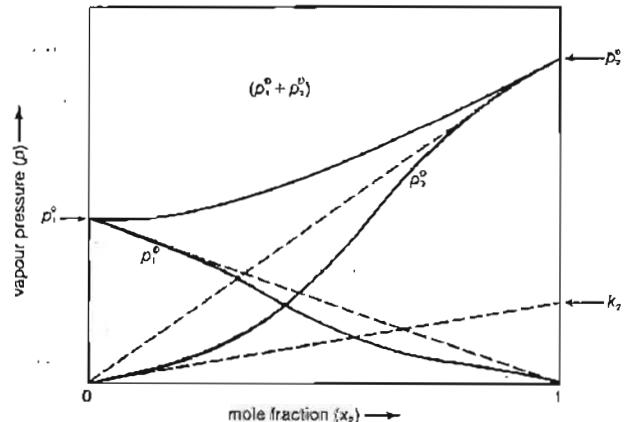

Figure 8: Variation of vapour pressure above solutions of two completely miscible volatile substances, 1 and 2, from pure 1 ($x_2 = 0$, $P_1^v = p_1^0$) to pure substance 2 ($x_2 = 1$, $P_2^v = p_2^0$). The Henry's rule constant, k_2, is shown as the tangent to the graph of p_2^v at $x_2 = 0$.

$k_2 x_2$, k_2 being a constant of proportionality. This relation is known as Henry's rule. Unlike Raoult's rule, in which the coefficient of x_1 is the vapour pressure of the pure solvent, the proportionality constant k_2 bears no simple relation to the properties of the components. Of course, if Raoult's and Henry's rules were to hold over the whole range of x_2 from 0 to 1, then k_2 would be the vapour pressure of pure solute. In general, however, the laws hold only for dilute solutions; that is, for x_2 nearly zero. An example of the variation of vapour pressures of a binary mixture of two completely miscible volatile species is shown in Figure 8, in which the distinction between

Henry's rule constant k_2 and the vapour pressure p_2^o of pure solute is made evident.

Equation (68) for the chemical potential of a semiperfect gas can be used in combination with Raoult's and Henry's rules to show that any change in chemical potential of solvent in a solution between two states at the same temperature is proportional to the change in $RT \ln x_1$. Similarly, the change in chemical potential of solute is proportional to change in $RT \ln x_2$. Expressions for the chemical potentials, therefore, are

$$\mu_1 = RT \ln x_1 + \mu_1^o \qquad (78)$$

$$\mu_2 = RT \ln x_2 + \mu_2^o, \qquad (79)$$

in which μ_1^o is the chemical potential of pure solvent ($x_1 = 1$) at the pressure and temperature of the solution. The quantity μ_2^o is the chemical potential of pure solute in a hypothetical ideal-solution state for which x_2 is unity. Equations (78) and (79) indicate that the logarithm of the mole fraction of a component is the measure of the escaping tendency of that component.

When to an ideal solution at a given pressure and temperature is added some pure solvent starting from the same pressure and temperature, it can be shown that the total volume occupied by solution and solvent remains unchanged by the process of dissolving. Similar statements may be made concerning the total energy and total enthalpy. One consequence is that no heat flows to or from the fluids during this process of solution; thus, the heat of solution is zero, and the process is adiabatic. The total entropy, on the other hand, increases during the process of solution, as would be expected from equation (6) for an irreversible adiabatic process. In general, a similar addition of pure solute to an ideal solution will result in change in total volume, energy, and enthalpy, and the heat of solution will not be zero. The change in volume, energy, and enthalpy per unit of solute added will be independent of the composition of the solution over the range of ideality.

BULK FLOW

A kind of transfer of matter in which each elementary piece of the flowing fluid can be considered to be a closed and separable system bounded by a prescribed surface is called bulk flow. Contrasting with this definition is transfer of material by molecular diffusion, in which the flowing molecules cannot be considered to be closed and separable systems.

Figure 9 shows a system A enclosed within a fixed boundary σ and an infinitesimal adjacent mass dm separated from A by a part of σ that is penetrable by A. The mass dm may be pushed across σ to join the larger mass inside. The work done by the surroundings on the combined system comprising A and dm will be equal to the product $pv\,dm$—namely, the pressure p multiplied by the specific volume v and the mass dm. This statement must be qualified by limiting it to slow motion of the boundary of dm and to zero shear effects in the fluid.

It can now be shown from equation (19) that the change in energy found within the boundary σ is the initial value of $E + pV$ for the mass dm, or $(e + pv)\,dm$, e denoting energy per unit mass. To this must be added any heat δQ that crosses the boundary of the combined system, and from it must be subtracted any work δW_s, called shaft work, that crosses boundary σ by virtue of
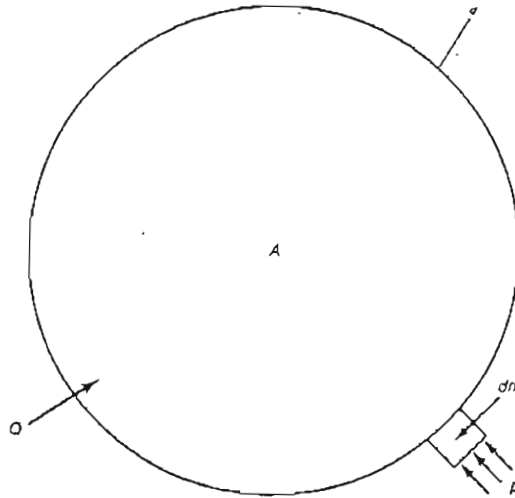
Figure 9: Schematic calculation of the change in energy of system resulting from the introduction of additional mass (see text).

torque in a rotating shaft or the equivalent. The corresponding statement for the energy change dE within σ when an infinitesimal mass of fluid dm crosses σ is

$$dE = (e + pv)\,dm + \delta Q - \delta W_s. \qquad (80)$$

Equation (80) is sufficiently general to apply to otherwise simple systems that may change level in a gravity field and that depart from equilibrium to the extent that elementary parts acquire the uniform velocity ϕ. Then it may be shown by consideration of work in adiabatic processes that the energy e of unit mass is the sum of the internal energy u, the kinetic energy $\phi^2/2$, and the gravity potential energy gz for height z above a datum level $z = 0$, g denoting the gravity constant, which has the dimensions of acceleration:

$$e = u + \frac{\phi^2}{2} + gz. \qquad (81)$$

Equation (80) may now be repeated after substituting the enthalpy symbol h for $u + pv$:

$$dE = \left(h + \frac{\phi^2}{2} + gz\right) dm + \delta Q - \delta W_x. \qquad (82)$$

A special case of the problem of bulk flow is one for which inward flow and outward flow occur, each in one or more channels, and the state of the fluid within the control volume is the same at all times. The state of the control volume for which this assumption holds is called a steady state, and the flow condition is called steady flow. A simple example with single entry and single exit is shown in Figure 10. It would apply to a boiler, for which W_s is zero, and to a steam turbine, for which Q is nearly zero, as well as to many other engineering devices.
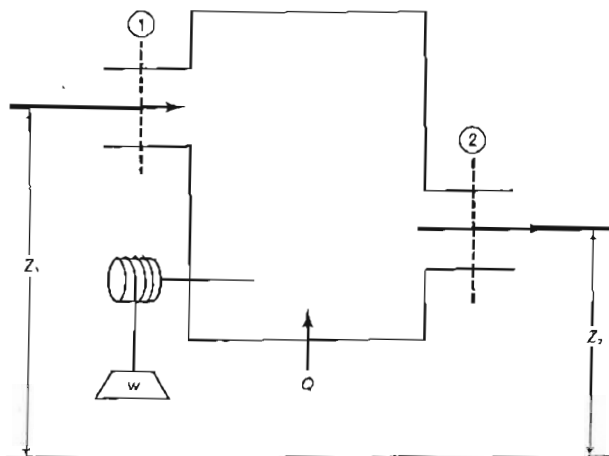
Steady flow

Figure 10: A system in a steady state in which the state of the fluid between boundaries 1 and 2 is the same at all times. The net mass flux across the entire boundary of the system must be zero. The heights of boundaries 1 and 2 above a datum are denoted Z_1 and Z_2 (see text).

The condition of steady state requires that dE be zero. The value of $(h + \frac{\phi^2}{2} + gz)dm$ is then summed up over all entry and exit conditions. For the simple example of Figure 10, equation (82) indicates that the difference between $(h + \frac{\phi^2}{2} + gz)$ at entry and exit when added to the heat Q' and shaft work W_x' passing inward across σ for each unit of mass entering must equal zero:

$$(h + \frac{\phi^2}{2} + gz)_1 - (h + \frac{\phi^2}{2} + gz)_2 + Q' - W_x' = 0. \quad (83)$$

CHEMICAL REACTIONS

Stable equilibrium states. An isolated closed simple system in which chemical reactions occur will attain a stable equilibrium state if the reactions are left uninhibited to proceed as far as they will. Such a state is fixed by two independent properties such as energy and volume or temperature and volume, and it is called a state of chemical equilibrium. Among the properties of the chemical equilibrium state fixed by the two independent properties are the proportions of the molecular species present.

When a chemical reaction proceeds at such a rate that chemical equilibrium is not achieved, each state passed through may be considered, for the purposes of analysis, to be a stable equilibrium state for which an anticatalyst has prevented chemical reaction. Between these states the system may experience chemical reaction in such degree as to produce a certain chemical aggregation in a second state different from that in the first. These states may be considered to have been achieved by successively removing and replacing an agent, such as an anticatalyst, that prohibits a chemical reaction. In the presence of such an agent each stable equilibrium state would correspond to a different set of proportions of species that would constitute a system with its own set of allowed states. To identify the state, therefore, it is necessary to add to the two independent properties required by the state principle an additional property that identifies the system. For example, for a mixture of molecules of nitrogen (N_2), hydrogen (H_2), and ammonia (NH_3) and the chemical reaction of formation of ammonia from the elements N_2 and H_2,

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftarrows NH_3,$$
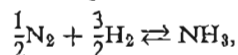
the energy, volume, and some measure of the degree to which this reaction has proceeded in one direction or the other would be required to identify the system and its stable equilibrium state.

Heat in chemical reactions. For any chemical reaction in a simple system, for which heat Q and work W are the only interactions, the energy change ΔE is given, according to equation (19), by the difference between heat and work: $\Delta E = Q - W$. For a chemical reaction in a system held at constant volume, the heat $(Q)_V$, in the absence of other interactions, is given by the increment in energy:

$$(Q)_V = \Delta E. \quad (84)$$

For a chemical reaction in a system held at constant pressure, the heat $(Q)_p$ is given by the increment in enthalpy:

$$(Q)_p = \Delta H. \quad (85)$$

For steady flow between entry section 1 and exit section 2, the heat interaction, in view of equation (83), is the increase in enthalpy $H_2 - H_1$ between the two sections plus any shaft work W_x:

$$Q = H_2 - H_1 + W_x.$$

For a chemical reaction at constant volume in an isolated system, no change in energy occurs despite the large change in temperature that is usually observed, as may be seen from equation (84) in which $(Q)_V$ (and therefore ΔE) is equal to zero for an isolated system.

When values are sought in the literature for the properties E and H for use in the preceding equations or for S and Z for use in other equations, it is found that for different molecular species they are not available on a common base—that is, an arbitrarily selected zero state is used for each separate species independently of that for any other. It is necessary, therefore, to supplement data for the molecular species with data on change in values of properties when each species is formed from the chemical elements without change in pressure or temperature.

Equilibrium between chemically reacting species. Included in the description of a system is the set of possible states that the system may assume. The choice of this set is often arbitrary and may be made to suit convenience in approximating a real system and its behaviour. For example, a system consisting of a mixture of hydrogen and oxygen gases may or may not have included among its possible states those in which water has been formed by chemical reaction.

The description of a multicomponent system may or may not permit a certain chemical reaction in which some species are formed from others. Whenever a reaction is permitted that was not permitted before, the number of components, each of which must be independently variable, decreases by one. Moreover, one new kind of change of state is introduced—namely, a variation in which certain species leave phases in which they are actual components to form other species in phases in which these others are actual components.

From O.A. Hougen, K.M. Watson, and R.A. Ragatz, *Chemical Process Principles*, 2nd ed. (1957), used with permission of John Wiley and Sons, Inc.
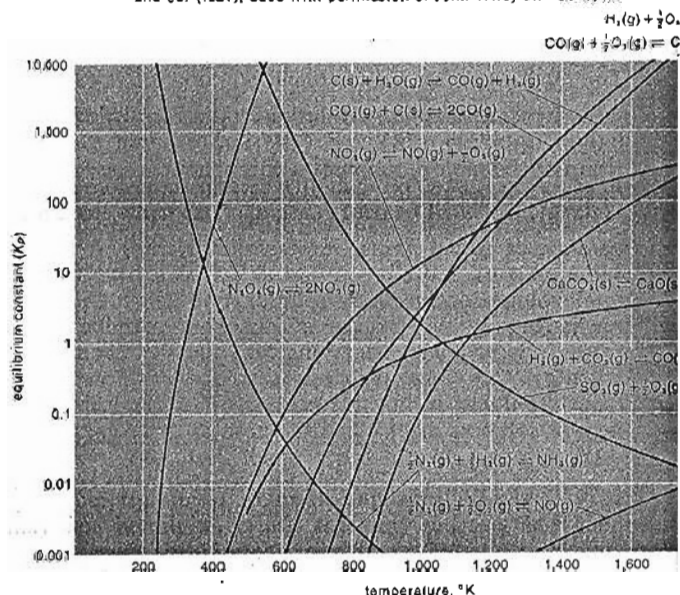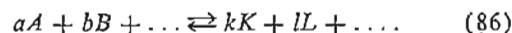

Figure 11: Variation in equilibrium constant, K_p, with variation in temperature for several chemical reactions (see text).

For a reaction such that a moles of A combine with b moles of B, etc., to form k moles of K plus l moles of L, etc., the stoichiometric (chemical-reaction) statement is

$$aA + bB + \ldots \rightleftarrows kK + lL + \ldots \quad (86)$$

This statement implies that the change Δn_A in number of moles of species A resulting from the reaction, when divided by the coefficient a, is numerically identical with similar quotients for the other species; i.e.,

$$\frac{\Delta n_A}{a} = \frac{\Delta n_B}{b} = \ldots = -\frac{\Delta n_K}{k} = -\frac{\Delta n_L}{l} = \ldots = -\Delta\xi. \quad (87)$$

The common value of the ratios, sometimes called the degree of reaction, is denoted by $\Delta\xi$. The stable equilibrium state in a system for which reaction (86) is allowed must be the state for which the entropy is at a maximum for all the states having given values of energy and volume of each phase. By reference to the Gibbs equation (64), it can be shown that this maximum is attained when the chemical potentials μ_A, μ_B, $\ldots$, μ_K, μ_L, $\ldots$ of species A, B, $\ldots K$, L, $\ldots$ are related as in the following equation, which is called the equation of chemical equilibrium:

$$a\mu_A + b\mu_B + \ldots - k\mu_K - l\mu_L - \ldots = 0. \quad (88)$$

Because for each component of a Gibbs–Dalton mixture

of semiperfect gases the chemical potential may be simply expressed, as in equation (68), in terms of the logarithm of the partial pressure of the species in the mixture, the condition for stable equilibrium becomes such that a product of powers of the partial pressures p_A, p_B, . . . , p_K, p_L, . . . is the same for a given temperature regardless of the proportions of the components that make up the mixture. This product is called the equilibrium constant in terms of pressure. For reaction (86) it is given by

$$\frac{p_K^k p_L^l \cdots}{p_A^a p_B^b \cdots} = K_p(T). \qquad (89)$$

The variation of K_p with variation in temperature for a number of familiar reactions is shown in Figure 11.

For a chemical reaction among the components of an ideal solution, a similar equilibrium constant is found for which the mole fraction x_I of component I is substituted in equation (89) for the partial pressure of component I:

$$\frac{x_K^k x_L^l \cdots}{x_A^a x_B^b \cdots} = K_x(T). \qquad (90)$$

When a gas mixture is not a Gibbs–Dalton mixture or a solution is not ideal, then a property called the fugacity takes the place of pressure in equation (89), and one called activity takes the place of mole fraction in (90). (For the definitions of these properties, see SOLUTIONS AND SOLUBILITY.)

Because each of these so-called equilibrium constants changes with change in temperature, some knowledge of the rate of change of the value of K with temperature is of great value. This rate is expressed most simply as the rate of change of ln K with temperature, and it proves to be equal to the quotient of the change in enthalpy when the reaction occurs at constant pressure and temperature and the product RT^2. In non-ideal mixtures (or solutions) the change in enthalpy must be measured between a reactants state for which the fugacity (or activity) of each reactant species is unity and a product state for which the fugacity (or activity) of each product is unity:

$$[d(\ln K_\alpha)/dT]_p = \frac{\Delta H^\circ}{RT^2}. \qquad (91)$$

AVAILABILITY FUNCTIONS

The economic and engineering importance of a system in a given state is often determined by its available work Ω_R with reference to ambient systems as a reservoir. The function Ω_R, which was used above to introduce and define entropy, proves to be one of a number of availability functions (all of which were stated or implied by Gibbs in his papers of 1873 and 1877–78).

The decrease in Ω_R between two states of a system is the maximum work that can be obtained from the system and a reservoir at T_0, no net changes of state occurring in any other systems aside from, for example, the rise of an external weight. The maximum work is also the value of the work produced by system and reservoir in a reversible process and is a value common to all reversible processes joining the two prescribed states of the system. In view of equation (4) and the definition of the entropy constant c_R, the decrease in available work Ω_R may now be identified as the decrease in the quantity $(E - T_0 S)$, in which the subscript 0 is introduced to refer to the reservoir. The value of Ω_R itself may be taken to be the maximum possible decrease in $(E - T_0 S)$, which is also the decrease when the system changes to a state of mutual stable equilibrium with the reservoir.

If the system is surrounded by an atmosphere at temperature T_0 that applies a constant pressure p_0 at all interfaces with other systems, then some of the work discussed in the previous paragraph is associated with change in volume of the atmosphere. The net maximum useful work, $(W_u)_{max}$, that can be delivered by system and atmosphere to other things for a change from state 1 of the system to state 2, no net changes in state occurring in any other things aside from the rise of a weight, is given by the decrease in an availability function Φ defined as $E + P_0 V - T_0 S$:

$$(W_u)_{max} = \Phi_1 - \Phi_2.$$

The function Φ is useful in evaluating the performance of a work-producing device that changes volume as it uses up its capacity for doing work.

A less well known availability function is that for a system exposed as before to a large reservoir at fixed pressure p_0 and temperature T_0 with which the system can exchange (through permeable or semipermeable membranes) component species; that is, transfer of these species can occur until the chemical potential of each in the system equals that in the reservoir. This availability function, denoted by Ξ, has a minimum value of zero. It is given by the relation

$$\Xi \equiv E + p_0 V - T_0 S - \sum_t \mu_{t0} n_t, \qquad (92)$$

μ_{t0} denoting the chemical potential of component i in the reservoir.

NEGATIVE TEMPERATURE

In the interest of simplicity, the third corollary of the second law was stated above as follows: A system in a stable equilibrium state can receive but cannot produce work. Although this statement is satisfactory for all ordinary systems, which are also called normal systems, recent developments in the theory of nuclear spins—the spinning of neutrons and protons of the atomic nucleus that contributes to both the angular momentum and the magnetic moment of the atom—have shown that some systems, which will be called special systems, in stable equilibrium states can produce work but cannot receive work.

A special system requires the following characteristics: (1) the energy of its allowed states has a finite upper limit; and (2) it must be coextensive in space with another system that shields it from work interactions that would change its volume or the velocity of its parts. For example, a lithium fluoride crystal may be considered to contain two distinct systems occupying the same space. The first, a special system, consists of the nuclear spins of the atoms of the crystal and has the energy of these spins. The second, a normal system, consists of the same atoms in the crystal, but its energy does not include that of the nuclear spins of the atoms. The stable equilibrium states of the two systems can be identified and distinguished because each comes to equilibrium in itself much more rapidly than they together approach mutual stable equilibrium.

It can be shown by reference to the second law of thermodynamics that for a closed special system the entropy–energy diagram is as shown in Figure 12. The

Characteristics of special systems
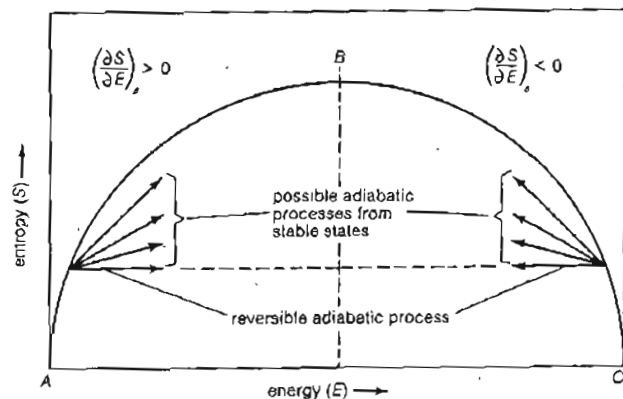
Figure 12: Entropy-energy diagram for a closed special system, for which negative absolute temperatures exist (see text).

curve ABC represents stable equilibrium states as well as the upper boundary for the region of all allowed states for given values of constraints β. Normal stable equilibrium states, which a special system may assume, are those on the AB part of the curve. Special stable equilibrium states are those on the BC part of the curve, and for these special equilibrium states the energy decreases with increase of entropy. In view of the definition of tempera-

ture (equation [13]), the temperature is therefore represented by a negative number.

The significance of negative temperatures on the scale of hotness and coldness can best be described in terms of the reciprocal Kelvin scale τ, in which $\tau \equiv 1/T$. The possible range of values of τ is from minus infinity to plus infinity, with the hottest temperature possible at minus infinity and the coldest temperature possible at plus infinity. Thus, negative temperatures correspond to hotter levels (the direction of heat flow being from hot to cold) than plus infinity on the Kelvin scale. The so-called absolute zero on the Kelvin scale becomes plus infinity on the τ scale of temperature.

THIRD LAW

Valid calorimetric experiments at temperatures near zero on the Kelvin scale invariably are in accord with the following postulate, which is the third law of classical thermodynamics: The entropy of any finite system approaches a noninfinite value as the temperature on the Kelvin scale approaches zero.

States to which the third law is applied

The third law applies only to stable equilibrium states and implies that the heat capacity at constant constraints must go to zero at zero temperature. It follows that a substance cannot be treated as a perfect gas at temperatures near zero, because for a perfect gas the specific heat capacity at constant volume is constant, and the entropy, as given by equation (55), approaches minus infinity. For crystalline substances near zero temperature, the variation of heat capacity is often found to be proportional to T^n, n being greater than unity.

From the third law in combination with the second law, it can be shown that for any finite system all paths of stable equilibrium states for fixed values of constraints β_i must converge on a single value of entropy as they approach zero temperature, as shown in Figure 13.
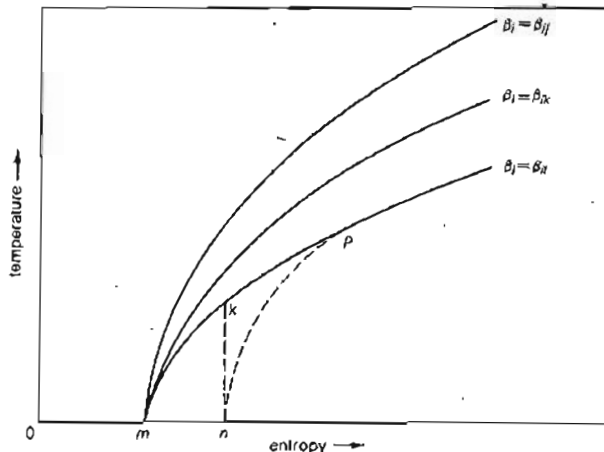

Figure 13: Convergence of values of entropy of stable equilibrium states of a system upon a single value at very low temperatures, as postulated by the third law of thermodynamics. For a given value β_{II} of constraint β_i, Pm represents stable equilibrium states and Pn metastable states (see text).

From the curve of stable equilibrium states for constant values β_{II} of constraints β_i, a branching may occur, as shown by Pn of Figure 13, but the states along Pn cannot be stable equilibrium states. They may be metastable or unstable, and the constant-entropy process nk from one of these states to the corresponding stable equilibrium state can be neither reversible nor adiabatic. Moreover, the change at zero temperature from n to m may be a spontaneous irreversible change to a stable equilibrium state. It follows that, as the temperature approaches zero, the magnitude of the entropy change in any isothermal reversible process approaches zero. This is the Nernst heat theorem, named for the Nobel-Prize winning German chemist, which is a corollary of the third law as stated above. An equivalent statement is that, as the temperature approaches zero, the magnitude of the entropy change between any pair of stable equilibrium states at the same temperature approaches zero.

Because the change between stable equilibrium states

Nernst heat theorem

may involve a change in value of a constraint, such as the volume, all states that can coexist in stable equilibrium at zero temperature must have the same minimum value of the entropy for the same mass. Moreover, if a system consisting of chemically reacting species can be brought into a stable equilibrium state by imposing appropriate electrostatic forces in an electrolytic cell, then the system must have the same minimum value of entropy whether in the reactants state or the products state.

It is appropriate now to assign the value zero to the minimum value of the entropy for a given system. The energy at any finite temperature for given values of constraints β may be found from the experimentally determined relation between the heat capacity C_β and temperature by integrating the product $C_\beta dT$ from temperature zero to temperature T:

$$[E - E_{(T=0)}]_\beta = \int_{T=0}^{T=T} C_\beta dT.$$

Similarly, the entropy at any finite temperature may be found by integrating the product $(C_\beta/T)dT$:

$$S_\beta = \int_{T=0}^{T=T} \frac{C_\beta}{T} dT.$$

It is possible, therefore, to determine the values of Gibbs free energy $(E + pV - TS)$ for chemically reacting species at some standard pressure and temperature and, from these values, the conditions for chemical equilibrium, including the equilibrium constants—all without experimental values for the chemical reaction as such between the species.

IV. Force fields

NONRELATIVISTIC EFFECTS

When to the conditions for a simple system, gravitational, electrical, and magnetic constraints in the form of applied force fields are added, an additional term appears in the Gibbs equation for each additional constraint. Each added term is a product similar to the product pdV in that it represents the work done in a reversible process in which the value of a constraint is varied.

When a gravity field is applied to a system of mass small enough so that the field is affected by it only negligibly, a gravity potential γ may be defined as the increase in energy per unit mass of an elementary system as it is moved from a reference level ($\gamma = 0$) to the given level while entropy, number of particles, and volume constraint are held constant. The Gibbs equation (64) for a system of mass m then becomes

$$dS = \frac{1}{T}[dE + pdV - \sum_i \mu_i dn_i - md\gamma]. \tag{93}$$

A simple and familiar condition for stable equilibrium that can be deduced from the Gibbs equation in form (93) is that for an otherwise simple fluid system in a gravity field, the rate of change of pressure with vertical distance is proportional to the density of the fluid. The proportionality factor proves to be g, the so-called acceleration of gravity.

A modification of the Gibbs equation similar to but more complicated than that given above for a gravity field has been devised to apply to a dielectric material, a material of which the electrically charged component species cannot move from one position in the material to another as it changes between neighbouring stable equilibrium states in an electric field between the plates of a capacitor. Another has been devised for a magnetic material in a magnetic field. (They will not be given here.)

RELATIVISTIC EFFECTS IN A GRAVITY FIELD

In an extremely intense gravity field, relativistic effects cannot be ignored. By combining the Einstein relation between energy and mass ($E = mc^2$) with the first and second laws, the following two conclusions are reached: (1) For stable equilibrium in a vertical column, it is necessary, as in nonrelativistic systems, that the temperature, $(\partial E/\partial S)_{n,\beta}$, be uniform. (2) If a system is held at

constant volume and lifted reversibly and adiabatically —that is, at constant entropy S—the pressure and temperature of the system both increase. More specifically, the increase in the natural logarithm of the pressure when the system is lifted from the level at which the gravity potential γ is arbitrarily assigned the value zero to a level at which it has the value γ is equal to the quotient of γ and the square of the speed of light c. A similar statement holds for temperature. Since the square of the speed of light c is a very large number, the effect on pressure and temperature will be small except in very intense gravitational fields.

The relation between temperature and gravity potential may be derived by consideration of a cycle in which a pure molecular species in a triple-point state (for example, solid, liquid, and vapour in mutual stable equilibrium) is lifted reversibly, adiabatically, and at constant volume from the reference level $\gamma = 0$ to the level γ, heated reversibly at constant temperature, lowered reversibly and adiabatically to $\gamma = 0$, and cooled to the original state. Because of the increase in mass in the heating process, the work of descent will exceed the work of ascent. The efficiency of this cycle may then be equated to that of a Carnot cycle in terms of temperature, as in equation (22), to obtain the desired relation.

V. Steady rate processes

Many applications of thermodynamics involve interactions between systems some or all of which are passing through nonequilibrium states. For example, chemical and nuclear reactions and flow of energy and matter are processes occurring in systems passing through nonequilibrium states.

The analysis of nonequilibrium states is more difficult, both conceptually and numerically, than that of stable equilibrium states. For example, because the number of properties required for the description of nonequilibrium states is larger than that for stable equilibrium states, the mathematical relations between properties are correspondingly more complicated.

In the interest of simplicity, the following applications are restricted to systems in steady states having fixed time rates of change of extensive properties. These applications will be called steady rate processes.

APPROACH TO MUTUAL STABLE EQUILIBRIUM

If two systems I and II are each in a stable equilibrium state but not in mutual stable equilibrium, a process in which they change toward mutual stable equilibrium will occur if they are connected by an intermediate system M. Depending upon the nature of the three systems and their states, the process that occurs may be caused by the transfer through M of energy alone or of matter with energy. The rate at which such transfer occurs will depend upon the initial departure from mutual stable equilibrium of systems I and II. By means of the first and second laws of thermodynamics and one additional postulate to them, a number of useful relationships between rates and potential differences or gradients may be determined for a substantial variety of rate processes, most of which are irreversible.

Generally it is possible to conceive of the process in M as being caused by two systems I and II, each of which would immediately assume a stable equilibrium state if the communication with M were suddenly stopped. To meet this requirement, the conductivity of matter or energy in I and II must be very great, so that whatever the influence on I of interaction through M with II, that influence will be felt uniformly through I and similarly with II. If the region is fluid, this result could be attained by minimal stirring of the fluid.

Under these circumstances, values of properties may be assigned to I and II. Region M, on the other hand, is in a nonequilibrium state. Nevertheless, values of intensive properties such as temperature and chemical potential of component i can be assigned to a point A in the region M by the method of local isolation. This method consists of isolating a region comprising point A and measuring the intensive property for this region when it reaches a stable equilibrium state. The value of the property in the limit as the size of the region is reduced to the smallest consistent with isolation may be taken to be the value at point A.

Region M will be assumed to be in a steady state; that is, the rate of change of any intensive property of I, II, or M is negligible. Extensive properties of I and II, on the other hand, may change at a finite rate, and any such rate is called a flux. Thus, an energy flux J_u is defined as the negative of the change of energy of I per unit time and, because of steady state in M, the change of energy of II per unit time:

$$J_u \equiv -\frac{dU_I}{dt} = \frac{dU_{II}}{dt}. \tag{94}$$

Similarly a flux of component i is denoted by J_i and is given by

$$J_i \equiv -\frac{dn_{iI}}{dt} = \frac{dn_{iII}}{dt}. \tag{95}$$

Under the steady-state conditions assumed and with I and II each held at constant volume, any one flux must depend upon those differences in intensive properties between I and II that measure the departure from stable equilibrium. Among these may be differences in temperature, pressure, mole fraction of component i, potential of component i, etc. The choice of differences that is made is governed by the postulate to be employed. It is made by expressing the rate of entropy generation in the process in terms of the Gibbs equation and using the resulting expression to define conjugate pairs of fluxes and forces. Each flux is then expressed in terms of all the forces so defined.

The region M between I and II may be subdivided into vertical laminas dM, over any face of which, for interaction in one direction only, the values of all intensive properties are uniform. For any one lamina, therefore, constant-volume stable equilibrium regions I and II may be substituted for material adjoining M without altering the process in the lamina (Figure 14).
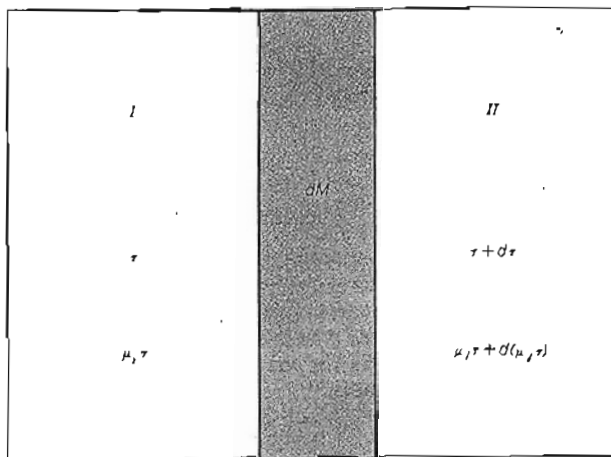

Figure 14: Two systems, I and II, each in stable equilibrium but not in mutual stable equilibrium, interacting through a thin intermediate system dM, which is in a nonequilibrium state. The symbol τ represents the quantity $1/T$, the reciprocal of the absolute temperature (see text).

For steady state in dM the rate of entropy generation in the process will be wholly accounted for by changes of entropy in I and II. Because the Gibbs equation (64) states the entropy change of a phase such as I or II in terms of the temperature, chemical potentials of components, change in energy, and change in masses of components, it will yield an expression for the rate of entropy change in terms of temperature, chemical potentials, and rates of change of energy and masses. These rates of change are the fluxes, J_u and J_i, of energy and of component, as indicated above. Because of the steady-state condition these fluxes may prove to be identical for regions I and II, but they will differ at most only infinitesimally for an infinitesimal thickness of the lamina dM.

The rate of entropy generation in the whole process is

found by summing for regions *I* and *II* the rates of entropy change, one of which will be negative and the other positive, to get an infinitesimal difference between two finite rates. This rate of entropy generation will then be the sum of products of fluxes and differences between *I* and *II* of potentials. These products are $J_u d(1/T)$ and $J_i d(-\mu_i/T)$, symbol *d* denoting the difference between the value in *II* and the value in *I* of the potential in parentheses. Thus the expression for the rate of entropy generation $d\dot{S}$ is

$$d\dot{S} = J_u \, d\left(\frac{1}{T}\right) + \sum_i J_i \, d\left(-\frac{\mu_i}{T}\right), \qquad (96)$$

in which $\sum_i$ denotes summation over all component substances $i = 1, 2, \ldots k$.

This last expression serves the purpose of identifying conjugate fluxes and forces; that is, for energy flux J_u the difference $d(1/T)$ is the conjugate force, etc.

Each flux J_u, J_i of equation (96) is a function of the state of one of the stable equilibrium regions *I* or *II* and of the forces $d(1/T)$, $d(-\mu_i/T)$, with the further condition that, whatever the state, the flux will be zero when all forces are zero—that is, for mutual stable equilibrium. Purely mathematical considerations indicate that the functional relation between a flux such as J_u and the forces $d(1/T)$, $d(-\mu_i/T)$ is a very simple one, provided that the fluxes are small; *i.e.*, provided that the departure from mutual stable equilibrium is small. This functional relation is that the flux is equal to the sum of terms each consisting of a force multiplied by a coefficient *L*. From thermodynamic considerations it can be shown that the magnitudes of the coefficients *L* are fixed once the nature and states of regions *I* and *M* are fixed. They are independent of the magnitudes of the forces $d(1/T)$ and $d(-\mu_i/T)$. The functional relation is thus given by

$$J_u = L_{uu} \, d\left(\frac{1}{T}\right) + \sum_i L_{ui} \, d\left(-\frac{\mu_i}{T}\right) \qquad (97)$$

$$J_i = L_{iu} \, d\left(\frac{1}{T}\right) + \sum_i L_{ii} \, d\left(-\frac{\mu_i}{T}\right), \qquad (98)$$

in which the first subscript on an *L* refers to the flux and the second to the force term in which it appears. Although exceptions to them may doubtless be found, these equations are of general application to rate processes and become increasingly valid the more nearly all the fluxes approach zero. They are known as phenomenological equations, and the coefficients *L* are known as conductivities.

The Onsager reciprocal relation The Onsager reciprocal relation, the additional postulate referred to above, is as follows: The matrix of coefficients *L* of a set of equations such as (97) and (98), in which conjugate pairs of fluxes and forces are identified through expression (96) for the rate of entropy production, is symmetrical; that is,

$$L_{ij} = L_{ji} \text{ for } i, j = u, 1, 2 \ldots . \qquad (99)$$

Lars Onsager, a Norwegian–American theoretical chemist, stated this new law in 1931 in an argument based on a principle of statistical mechanics called the principle of microscopic reversibility and a postulate that is closely related to the second law of thermodynamics. The new law was subsequently shown to be of general application in irreversible processes and was extended to a wide variety of phenomena.

Phenomenological equations The phenomenological equations reduce to special forms for various special systems and force conditions and are known under different names. For example, Fourier's law of heat conduction (for the 19th-century French mathematician and physicist Jean-Baptiste Fourier), Ohm's law of electric current flow (for the 19th-century German physicist Georg Simon Ohm), Fick's law of neutral particle diffusion (for the 19th-century German physiologist Adolf Eugen Fick), and the law of ambipolar diffusion of positive and negative charges are all special cases of the linear phenomenological equations. The constants appearing in the laws just cited, such as

electric resistance in Ohm's law, may be expressed easily in terms of the conductivities *L* of the phenomenological equations.

FLOW OF A SUBSTANCE THROUGH A BARRIER

A relatively simple application of the thermodynamics of rate processes is to the flow of a single-component substance through a barrier *M* under conditions such that the phenomenological equations (97) and (98) are valid. An example would be the flow of helium through a rubber membrane between two stable equilibrium regions *I* and *II*. The Onsager reciprocal relation is simply that $L_{u1} = L_{1u}$, subscript 1 referring to helium.

The two forces are the differences across the membrane $d(1/T)$ and $d(\mu_1/T)$. When the flux of helium is zero, then the difference $d(1/T)$ causes its conjugate energy to flow downgrade in temperature and upgrade in $1/T$. When the temperature difference and $d(1/T)$ are zero, then its conjugate helium will flow downgrade in chemical potential and in μ_1/T. Each of these forces, however, tends to cause its nonconjugate flux, as well as its conjugate flux, in one or the other direction. This behaviour is called coupling. In the absence of coupling, the coefficients L_{u1} and L_{1u} would both be zero.

By virtue of coupling, the two forces may be set in relation to each other so as to stop the flow of helium because of a balance between the opposing influences of the two forces. Such a steady state will be attained spontaneously if a temperature difference is maintained between *I* and *II* for a long enough period of time while the volumes of *I* and *II* are held constant. The flow of helium will eventually cease—or at least approach zero as a limit as time proceeds. A flow of energy will persist, however, in the steady-state condition by virtue of the temperature difference.

It can be seen from the second phenomenological equation (98) that the ratio L_{1u}/L_{11} is equal to the ratio of forces $d(\mu_1/T)/d(1/T)$ when J_1 is zero. From the two equations (97) and (98) taken together it can be seen that the ratio L_{u1}/L_{11} is equal to the ratio of fluxes J_u/J_1 when $d(1/T)$ is zero. Because the Onsager reciprocal relation requires that L_{1u} be equal to L_{u1}, it follows that the ratio of forces when J_1 is zero must equal the ratio of fluxes when the temperatures of *I* and *II* are equal.

By means of a simple thermodynamic analysis, the ratio of forces $d(\mu_1/T)/d(1/T)$ may be expressed in terms of the ratio of pressure difference to temperature difference dp/dT, which then proves to be proportional to the excess of J_u/J_1 for dT equal to zero over the enthalpy h_1 of helium in region *I*. The actual relation is

$$\left(\frac{dp}{dT}\right)_{J_1 = 0} = -\frac{1}{v_1 T}\left[\left(\frac{J_u}{J_1}\right)_{dT=0} - h_1\right]. \qquad (100)$$

This relation gives the ratio of the pressure gradient to the temperature gradient for which the particle flow is stopped. Because it can be shown that for simple bulk flow J_u/J_1 is h_1 for fluid crossing any section in which the temperature is uniform in the direction of flow, it follows from equation (100) that bulk flow may be stopped even in a temperature gradient by zero pressure gradient. Whenever the energy flux per unit particle flux differs from h_1 in constant-temperature flow, then a pressure gradient is necessary to stop flow in a temperature gradient.

Application of equation (100) to the flow of a perfect gas may be made for a porous plug with pore sizes very small compared with the mean distance travelled by gas molecules between collisions or compared to flow between emitting and receiving surfaces separated by a distance that is very small compared with the mean distance between collisions. For both of these the result is the same and can be shown to be

$$\left(\frac{dp}{dT}\right)_{J_1 = 0} = \frac{1}{2}\frac{p}{T} \qquad (101)$$

or, for a finite length,

$$\left[\frac{p^I}{p^{II}} = \sqrt{\frac{T^I}{T^{II}}}\right]_{J_1 = 0}. \qquad (102)$$

These relations describe what is known as the Knudsen effect.

The excess over the enthalpy flux of the energy flux across the barrier per unit of matter flowing when dT is zero is called the heat of transport and is denoted by q_1^*:

$$q_1^* \equiv \left(\frac{J_u}{J_1}\right)_{dT=0} - h_1. \qquad (103)$$

It is the direct heat interaction that must be provided between regions II and I (Figure 14) when one unit of mass flows from I to II through M if the temperatures of I and II are to be maintained equal. Its magnitude can be found, in accordance with (100), by a measurement of the ratio dp/dT that corresponds to a flux J_1 of zero. The value found in this way for the heat of transport through a rubber membrane for nitrogen is -260 calories per gram mole and for hydrogen $+100$.

VI. Statistical thermodynamics

The mechanical theory of heat was developed concurrently with thermodynamics. It relates heat to changes in the motion of the atoms and molecules of matter. The history of the theory can be traced back to the Greek philosophers Democritus (*c.* 400 BC) and Epicurus (*c.* 300 BC). The French philosopher Pierre Gassendi developed in the 17th century a theory in which all material phenomena are attributable to the indestructible motion of atoms. Although the English philosopher Robert Hooke, the German philosopher and mathematician Gottfried Wilhelm Leibniz, and the Swiss mathematician and physicist Daniel Bernoulli improved upon it in the 17th and 18th centuries the theory was not firmly established until Joule demonstrated experimentally in the 19th century, that a quantitative relation exists between heat and work when they produce identical effects.

After Joule's demonstration the theory developed rapidly into a science of major importance that became known as statistical mechanics or statistical thermodynamics. Its subject is the relation between the laws of thermodynamics and the details of the structure of matter. Its development, which can be traced through Hermann Ludwig Ferdinand von Helmholtz, a German physicist and anatomist; Clausius; Maxwell; and Boltzmann, culminated in the work of Gibbs, who in 1901 presented an exposition of statistical thermodynamics that excels in completeness, rigour, and generality. Although the exposition of Gibbs is stated in terms of classical mechanics, it is better adapted to quantum mechanics, which in some ways it anticipates.

Perhaps because Gibbs's contribution was not fully understood, a less general and less rigorous molecular statistics prevailed in the literature, with few exceptions, until after World War II.

GIBBSIAN STATISTICS

According to classical mechanics, the state of a system having N degrees of freedom (independent ways in which the space configuration of the system may change) is fully specified by the values of N position coordinates $q_1, q_2, \ldots, q_N$, and N momentum coordinates $p_1, p_2, \ldots, p_N$. For example, the state of a system consisting of n point particles (particles without internal structure and therefore without internal degrees of freedom) is specified if the position coordinates along three Cartesian axes x, y, and z and the corresponding momentum coordinates along these same axes for each of the particles are specified. For such a system the number N of the degrees of freedom is equal to three times the number n of the particles of the system.

The position of a particle in space may be represented geometrically by a point in three-dimensional space having coordinates x, y, and z. The state of the particle involves not only the values of the coordinates x, y, and z but also the values of momentum component (which fixes the velocity component) p_x in the x direction, p_y in the y direction, and p_z in the z direction. These considerations suggest a mental extension of the concept of space to six dimensions, having coordinates x, y, z, p_x, p_y, and p_z. The state of the particle could then be completely described by a point in the six-dimensional space for which the values of x, y, z, p_x, p_y, and p_z are appropriately fixed.

The particle just discussed is said to have three degrees of freedom, and its state can be represented by a point in a six-dimensional space. A collection of two such particles might have six degrees of freedom, and the representation of its state would call for a 12-dimensional space. The number of degrees of freedom of a more complex system is the number of independent kinds of displacement to which it is subject. The state of such a system having N degrees of freedom may be represented geometrically in classical mechanics by a point in $2N$-dimensional space having as coordinates $q_1, q_2, \ldots, q_N$, $p_1, p_2, \ldots, p_N$. This $2N$-dimensional space was called by Gibbs phase space.

Phase space

According to Gibbs, the term thermodynamic state of a system with N degrees of freedom does not necessarily correspond to a unique point in phase space, but to a set of probabilities of the system being in any one of the allowed points consistent with the constraints imposed on the system. Because any set of allowed states in classical mechanics forms a continuum, Gibbs introduced a probability density or distribution P, which he called the coefficient of probability, such that the product $P dq_1 dq_2 \ldots dq_N dp_1 dp_2 \ldots dp_N$ is equal to the probability of the system being in states having values of coordinates between q_1 and $q_1 + dq_1$, q_2 and $q_2 + dq_2$, $\ldots$, q_N and $q_N + dq_N$ and values of momenta between p_1 and $p_1 + dp_1$, p_2 and $p_2 + dp_2$, $\ldots$, and p_N and $p_N + dp_N$. For a given thermodynamic state, the distribution P will be a corresponding function of q's and p's. Furthermore, because a system must be at some one of the allowed states, the sum of all the probabilities must always be equal to unity or, by the same token, the integral of the distribution P over all q's and p's must be always equal to unity.

Various types of thermodynamic states correspond to particular mathematical forms of the distribution P. For example, Gibbs assumed without proof that, for the stable equilibrium states of a system with N degrees of freedom, the coefficient of probability P corresponding to the state $q_1, q_2, \ldots, q_N, p_1, p_2 \ldots, p_N$ of energy ε is equal to the number 2.718282 (the base of natural logarithms) raised to the $(\Psi - \varepsilon)/\Theta$ power, in which Ψ and Θ are constants; in other words, P is given by the exponential relation

$$P = \exp\left(\frac{\Psi - \varepsilon}{\Theta}\right). \qquad (104)$$

He called this distribution of probabilities a canonical distribution. Further discussion of Gibbsian statistics will be omitted because the quantum statistical thermodynamics discussed below, though based on Gibbsian ideas, is more complete.

QUANTUM STATISTICAL THERMODYNAMICS

Definition of state. In contrast to classical mechanics, a fundamental premise of quantum mechanics is that at a given time the most that can be said about results of measurements on a system is the probability of finding particular values of properties, such as coordinates and momenta, rather than the particular values that will be observed. This premise reflects the principle of indeterminacy first introduced by the German physicist Werner Heisenberg. It requires a description of the state of a system in terms of probabilities.

The principles of quantum mechanics may be stated by means of a number of mathematical formulations. Among these, the best known are the wave formulation by the German physicist Erwin Schrödinger, the vector formulation by the English physicist P.A.M. Dirac, and the matrix formulation by Heisenberg. The matrix formulation is especially suited to the exposition of quantum statistical thermodynamics and is adopted below (for a discussion of matrices in general, see the article ALGEBRA, LINEAR AND MULTILINEAR).

Any property of a system that in classical mechanics

may be expressed as a function of position and momentum coordinates is expressed in quantum mechanics by a matrix. For example, the Hamiltonian function of classical mechanics, which is the energy of the system, is represented by the Hamiltonian matrix. Matrix representations are used also for properties (such as spin) that have no classical analogue. The method of calculation of elements of matrices is specified by the principles of quantum mechanics.

Each matrix possesses eigenvalues; that is, a set of numbers that can be found by solving the characteristic equation of the matrix. The eigenvalues of the matrix of a property are real, as distinguished from complex, in the mathematical sense. Each one corresponds to a possible outcome of a measurement of the property performed on the system. For example, a measurement of the energy of a system in a given condition will yield any one of the real eigenvalues of the Hamiltonian matrix of the system. The number of eigenvalues of a property may be either finite, as with spin, or infinite, as with energy for most systems.

According to quantum mechanics, it is impossible to predict from knowledge of the condition of a system which eigenvalue a measurement will yield. Instead, the most that can be said at any instant of time is the probability that a measurement will yield a given eigenvalue.

The state of a system is defined as the set of all probabilities for the outcomes of all measurements that may be performed at a given instant of time. That is, the state of a system is represented by Table 2, in which $\bar{F}$, $\bar{G}$,

Table 2: State of a System

property	$\bar{F}$	$\bar{G}$	$\bar{H}$	
Probabilities	$W(F_1)$	$W(G_1)$	$W(H_1)$	...
	$W(F_2)$	$W(G_2)$	$W(H_2)$	...
	•	•	•	
	•	•	•	
	•	•	•	

$\bar{H}$, . . . denote observable properties and in which $W(F_1)$ denotes the probability that any one measurement of property $\bar{F}$ will yield the eigenvalue F_1, . . . , $W(G_1)$ denotes the probability that any one measurement of property $\bar{G}$ will yield the eigenvalue G_1, . . . and so forth. It can be shown that these probabilities can be combined to form a matrix $[\rho]$, called the density matrix or statistical matrix. Conversely, a systematic procedure exists for determining from a given density matrix $[\rho]$ the probability $W(E_n)$ that a measurement of energy corresponding to the Hamiltonian matrix $[E]$ will yield the energy eigenvalue E_n of $[E]$. Again, the procedure yields the probability $W(F_m)$ that a measurement of property $\bar{F}$ corresponding to matrix $[F]$ will yield the eigenvalue F_m of $[F]$.

Expectation values of properties. Because measurements of a property $\bar{F}$ of a system in a given state yield different eigenvalues F_m, each with a probability $W(F_m)$ specified by the density matrix $[\rho]$ that represents the state, an expectation value or simply a value of the property corresponding to the given state is defined as the weighted average of the various possible eigenvalues, each eigenvalue being weighted by the probability that it will be observed. Symbolically, the value F of a property $\bar{F}$ may be represented as a sum over many terms, each of which is the product of a probability $W(F_m)$ and the eigenvalue F_m; that is,

$$F = \sum_m W(F_m)F_m, \tag{105}$$

in which the symbol $\sum_m$ denotes summation over all eigenvalues, and each eigenvalue is represented by a different symbol (different value of the subscript m) even when two or more eigenvalues have the same value. (For some matrices several distinct eigenvalues may have identical numerical values. The eigenvalues are then called degenerate.)

Reversible equation of motion. Quantum mechanics provides an equation, called the equation of motion, from which can be found the rate of change of the density matrix $[\rho]$ with time for each of the numerous processes that are reversible and adiabatic. The equation will not be given here.

Conditions for equilibrium are found from the equation of motion. If the eigenvalues of the density matrix $[\rho]$ for an equilibrium state are denoted by x_1, x_2, . . . , x_m, . . . and the eigenvalues of the Hamiltonian matrix $[E]$ by E_1, E_2, . . . , E_m, . . . , it can be shown that, in the absence of irreversibilities, a necessary and sufficient condition for equilibrium is that the first eigenvalue x_1 be equal to the probability $W(E_1)$, that a measurement of the energy will yield the first eigenvalue E_1, the second eigenvalue x_2 be equal to $W(E_2)$, etc. Moreover, for equilibrium states the expectation value of the energy E can be expressed as a sum of terms each of which is the product of x_m and E_m; that is,

$$E = \sum_m x_m E_m. \tag{106}$$

General expression for entropy. According to the first and second laws of thermodynamics, entropy is a property or state function of a system. Moreover, it must be invariant in any reversible adiabatic process. From these two conditions and the requirement that it is an extensive property, the expectation value S of entropy can be shown to be proportional to a mean of the natural logarithms of the eigenvalues of the density matrix. When y_1, y_2, . . . , y_m, . . . denote the eigenvalues of the density matrix $[\rho]$ (corresponding to an arbitrary state, which is not necessarily equilibrium or stable equilibrium), the mean is calculated by weighting each $\ln y_m$ with the value y_m. In mathematical form this statement is expressed

$$S = -k \sum_m y_m \ln y_m, \tag{107}$$

in which k is a universal constant that proves to be the Boltzmann constant.

Pure states. A pure state is defined as one for which the eigenvalues of the density matrix $[\rho]$ are all equal to zero, except for one that is equal to unity. It follows from equation (107) that the entropy of a pure state is equal to zero.

It can be shown that any pure state may be described also by means of a wave function of quantum mechanics; and, conversely, states that can be described by wave functions correspond to zero entropy. In general, however, the entropy of a system is not equal to zero, and the state of the system cannot in general, therefore, be described by a wave function.

Stable equilibrium states. In the language of quantum statistical thermodynamics, the criterion for stable equilibrium (see above *Stable equilibrium*) implies that the density matrix for a stable equilibrium state be such that the entropy (equation [107]) is at its maximum for given expectation values of energy and numbers of particles. When this criterion is applied to a system of which the numbers of particles are known without uncertainty (the probability of the value for the number of particles of a given kind that is found by a measurement is unity), it yields the eigenvalues x_1^o, x_2^o, . . . , x_m^o, . . . for the stable equilibrium states as functions of the energy eigenvalues E_1, E_2, . . . , E_m, . . . of the Hamiltonian matrix of the system and the temperature of the stable equilibrium state in question. The various mathematical functions are as follows:

$$x_1^o = \frac{\exp(-E_1/kT)}{\sum_m \exp(-E_m/kT)}; x_2^o = \frac{\exp(-E_2/kT)}{\sum_m \exp(-E_m/kT)}; \cdots \tag{108}$$

$$T = \left(\frac{\partial E}{\partial S}\right)_\beta, \tag{109}$$

$$E = \sum_m x_m^o E_m = \frac{\sum_m E_m \exp(-E_m/kT)}{\sum_m \exp(-E_m/kT)}, \tag{110}$$

and

$$S = -k \sum_m x_m^o \ln x_m^o$$
$$= k \ln \left[\sum_m \exp(-E_m/kT) \right] + \frac{E}{T}. \quad (111)$$

Because the eigenvalues $x_1, x_2, \ldots, x_m, \ldots$ of the density matrix for any equilibrium state and, therefore, the eigenvalues $x_1^o, x_2^o, \ldots, x_m^o, \ldots$ of the density matrix for any stable equilibrium state represent probabilities that measurements of energy will yield eigenvalues $E_1, E_2, \ldots, E_m, \ldots$, respectively, equation (108) can be thought of as analogous to the canonical distribution postulated by Gibbs, provided that the two constants Θ and Ψ in equation (104) are expressed in terms of the temperature T and the energy eigenvalues $E_1, E_2, \ldots, E_m, \ldots$. It can be shown that Θ and Ψ are given by the relations

$$\Theta = kT \quad (112)$$

and

$$\Psi = kT \ln \left[\sum_m \exp(-E_m/kT) \right]. \quad (113)$$

It can be readily verified from equations (111) and (113) that the function Ψ is equal to the Helmholtz free energy of the system; i.e., equal to $E - TS$. Moreover, because the energy eigenvalues $E_1, E_2, \ldots, E_m, \ldots$ are in general functions of the values of the constraints, the Helmholtz free energy Ψ is a function of temperature and the constraints and, therefore, a characteristic function. This means that in quantum statistical thermodynamics the problem of evaluating the properties of any system with numbers of particles that are known without uncertainty and in a stable equilibrium state reduces to the problem of evaluating the energy eigenvalues as functions of the constraints. The evaluation of the energy eigenvalues is a difficult mathematical task that has been carried out for only a very few systems. The difficulty, however, is in the calculation rather than in the conception of the evaluation.

The quantity Q_c, called the canonical partition function, is defined as the sum of $\exp(-E_1/kT)$, $\exp(-E_2/kT)$, $\exp(-E_3/kT)$, etc. It appears in the expressions for many properties of systems in stable equilibrium states. For example, because

$$Q_c \equiv \sum_m \exp(-E_m/kT), \quad (114)$$

it follows that the probability x_m^o of observing an energy eigenvalue E_m is the quotient of $\exp(-E_m/kT)$ and Q_c, that the Helmholtz free energy per mole is the product of (kT) and the logarithm of Q_c, and that the entropy is the sum of the product $k \ln Q_c$ of k and logarithm of Q_c and the quotient E/T of the expectation value of the energy and the temperature:

$$x_m^o = \frac{\exp(-E_m/kT)}{Q_c}; \quad \Psi = kT \ln Q_c; \text{ and } S = k \ln Q_c + \frac{E}{T}.$$

STATISTICS OF GRAND SYSTEMS

Stable equilibrium states. In many systems the numbers of particles may be uncertain either because the system is open to the transfer of rest mass or because particles can be created and annihilated within the system. The terminology of Gibbs suggests that such systems be called grand systems.

By definition, uncertainty in the numbers of particles means that measurements of these numbers for a grand system in a given state yield different particle-number eigenvalues. This uncertainty is analogous to that associated in general with the energy. It follows that an expectation value rather than a dispersion-free value (that is, rather than a unique value that is observed as a result of every measurement) is assigned to the number of particles of each component of a state of a grand system. Without discussion of the matrix formalism for grand systems, some results applicable to stable equilibrium states will be given.

A stable equilibrium state of a grand system is fully described by the set of eigenvalues $x_1^o, x_2^o, \ldots, x_m^o, \ldots$

of the density matrix that maximizes the entropy of the system at given expectation values of energy, numbers of particles of the components, and constraints. The mth eigenvalue x_m^o is equal to the probability that a suitable measurement will yield the mth energy eigenvalue E_m and the mth number-of-particle eigenvalues $n_{1m}, n_{2m}, \ldots, n_{km}$ for the set of k components of the system. It can be expressed as a function of the energy eigenvalues $E_1, E_2, \ldots, E_m, \ldots$ of the Hamiltonian matrix of the system, the eigenvalues $n_{11}, n_{12}, \ldots, n_{1m}, \ldots$ of the number of particles of component number one, the eigenvalues $n_{21}, n_{22}, \ldots, n_{2m}, \ldots$ of the number of particles of component number two, $\ldots$, the total potential $\mu_1, \mu_2, \ldots, \mu_k$ of the k components $1, 2, \ldots k$, and the temperature T of the stable equilibrium state in question. It is given by the relation

$$x_m^o = \frac{\exp[(n_{1m}\mu_1 + n_{2m}\mu_2 + \ldots + n_{km}\mu_k - E_m)/kT]}{\sum_m \exp[(n_{1m}\mu_1 + n_{2m}\mu_2 + \ldots + n_{km}\mu_k - E_m)/kT]}. \quad (115)$$

The sum in the denominator of (115) is called the grand partition function Q_g; i.e.,

$$Q_g \equiv \sum_m \exp[(n_{1m}\mu_1 + n_{2m}\mu_2 + \ldots + n_{km}\mu_k - E_m)/kT]. \quad (116)$$

It appears in many relations between properties for grand systems in stable equilibrium states. For example, for a grand system with volume V as the only independent constraint, the equation of state is given by the relation

$$pV/kT = \ln Q_g. \quad (117)$$

Equation (117) applies to grand systems in gaseous, liquid, or solid states.

The one-particle approximation for one-component systems. Because of mathematical difficulties, the energy eigenvalues of most systems can be computed only approximately. A class of approximations that consists in expressing each energy eigenvalue of the system as a sum of energy eigenvalues of suitably defined subsystems, each having one particle only, is called the one-particle approximation. It is valid for some crystals and for dilute gases at such low densities that short-range interparticle forces (forces between two particles that act only when the two particles are very near each other) can be neglected, and long-range forces on each particle are independent of the positions of other particles. Some results of the analysis applicable to dilute gases will be given below.

In the context of the one-particle approximation, each of the energy eigenvalues $E_1, E_2, \ldots, E_m, \ldots$ of a dilute gas having one component only (namely, consisting of a number of particles of a single type) is expressed as a sum of terms such that each term is a positive integer multiplied by an energy eigenvalue of a system that has one particle only and for which the eigenvalues can be evaluated. For example, if $\nu_{m1}, \nu_{m2}, \ldots, \nu_{mj}, \ldots$ denote the positive integers that appear in the sum for the mth eigenvalue E_m and $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_j, \ldots$, the energy eigenvalues of the system with the one particle, then E_m is given by the relation

$$E_m = \nu_{m1}\varepsilon_1 + \nu_{m2}\varepsilon_2 + \ldots + \nu_{mj}\varepsilon_j + \ldots$$
$$= \sum_j \nu_{mj}\varepsilon_j \text{ for all values of } m. \quad (118)$$

Equation (118) is interpreted as meaning that of the n_m particles associated with the energy eigenvalue E_m, ν_{m1} have energy ε_1, ν_{m2} have energy ε_2, $\ldots$, ν_{mj} have energy $\varepsilon_j, \ldots$. From this interpretation it follows that the sum of all the positive integers $\nu_{m1}, \nu_{m2}, \ldots, \nu_{mj}, \ldots$ must be equal to n_m; i.e.,

$$\nu_{m1} + \nu_{m2} + \ldots + \nu_{mj} + \ldots = \sum_j \nu_{mj} = n_m. \quad (119)$$

The values that each integer ν_{mj} can assume are restricted by the nature of the particles in question. For certain particles, called fermions, each ν_{mj} may be either zero or unity for all values of the subscripts m and j; i.e., for any energy eigenvalue E_m of the overall system and any energy eigenvalue ε_j of the auxiliary one-particle sys-

Fermions and bosons

tem. For example, because electrons are fermions a grand system consisting of electrons has, for a state with an energy eigenvalue E_m, at most one electron of one-particle energy eigenvalue ε_j. (This restriction is equivalent to Pauli's exclusion principle of atomic physics.) On the other hand, for certain particles called bosons, each of the integers ν_{mj} may have any positive integral value as well as the value zero. In a grand system consisting of photons—which are bosons—in a state with energy eigenvalue E_m, any number of photons from zero to n_m may have a particular energy ε_j.

When the allowed numerical values of the integers ν_{mj} are considered, the properties of a dilute gas in a stable equilibrium state can be expressed as functions of the one-particle energy eigenvalues $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_j, \ldots$ rather than the eigenvalues $E_1, E_2, \ldots, E_m, \ldots$ of the overall system.

For example, the expectation or average value ν_j of the number of particles that can be thought of as having one-particle energy ε_j—namely, the expectation value ν_j of the integers $\nu_{1j}, \nu_{2j}, \ldots, \nu_{mj}, \ldots$—is defined as the sum of terms each being an integer ν_{mj} multiplied by the probability x_m^0 that a suitable measurement will yield the energy eigenvalue E_m.

It can be shown that, if μ denotes the total potential of the single component of the grand system, then ν_j is given by the relations

$$\nu_j = \sum_m x_m^0 \nu_{jm} = \frac{1}{\exp[(\varepsilon_j - \mu)/kT] + 1} \text{ for fermions} \quad (120)$$

and

$$\nu_j = \sum_m x_m^0 \nu_{jm} = \frac{1}{\exp[(\varepsilon_j - \mu)/kT] - 1} \text{ for bosons.} \quad (121)$$

Relation (120) is called the Fermi–Dirac distribution, and the corresponding dilute gas is said to obey Fermi–Dirac statistics. Relation (121) is called the Bose–Einstein distribution, and the corresponding dilute gas is said to obey Bose–Einstein statistics.

Again, for a system with volume V as the only constraint, it can be shown that the equation of state, (117), and the expectation value n of the number of particles are given by the relations

$$\frac{pV}{kT} = \sum_j \ln \{1 \pm \exp[(\mu - \varepsilon_j)/kT]\}^{\pm 1} \quad (122)$$

and

$$n = \sum_j \{[\exp(\varepsilon_j - \mu)/kT] \pm 1\}^{-1}, \quad (123)$$

in which the plus sign in $\pm$ applies to fermions and the minus sign to bosons.

Fundamental equation for one-component simple systems. For a system for which both sets of eigenvalues $E_1, E_2, \ldots, E_m, \ldots$ and $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_j, \ldots$ are functions of volume V only, equations (122) and (123) indicate that p and n are functions of volume V, temperature T, and potential μ only. In principle, the p and n functions can be combined so as to eliminate volume V and obtain a fundamental equation that gives the total potential as a function of n, p, and T. But because equations (122) and (123) are transcendental, the derivation of such a fundamental equation is a difficult mathematical task. Under certain conditions it can be done with the aid of some approximations that are additional to the one-particle approximation.

For example, for a dilute gas in which the molecules have three translational degrees of freedom and of which the temperature is sufficiently high and pressure sufficiently low, it can be shown that the potential μ can be approximated by the expression

$$\mu = kT\ln p - \frac{5}{2}kT\ln T - kT\ln q_s - kT\ln \frac{k(2\pi mk)^{3/2}}{\hbar^3}, \quad (124)$$

in which m denotes the mass of each particle of the system; $\hbar$, an alternate form of Planck's constant; and q_s, the partition function associated with the energy eigenvalues $\bar{\varepsilon}_i$ for the internal structure of each molecule:

$$q_s = \sum_i \exp(-\bar{\varepsilon}_i/kT).$$

Such a gas is called a semiperfect gas. Consistent with the relations found for a semiperfect gas above without reference to the detailed structure of the molecules of the system, its fundamental equation is independent of n. This result reflects conformity with the definition of a simple system, which excludes capillarity. In contrast with equation (68), equation (124) gives the chemical potential per particle instead of per mole. It includes, therefore, the Boltzmann constant k, which is related to a single molecule and which is equal to the universal gas constant R divided by the number of molecules contained in a mole.

As indicated earlier, the heat capacities of a semiperfect gas are functions of temperature. From equation (124) may be found the following expressions for specific heat capacities per molecule:

$$c_p = \frac{5}{2}k + 2kT\frac{\partial \ln q_s}{\partial T} + kT^2\frac{\partial^2 \ln q_s}{\partial T^2}$$

and

$$c_v = \frac{3}{2}k + 2kT\frac{\partial \ln q_s}{\partial T} + kT^2\frac{\partial^2 \ln q_s}{\partial T^2},$$

in which $\partial^2 \ln q_s/\partial T^2$ denotes the partial derivative of $\partial \ln q_s/\partial T$ with respect to T. Because q_s is a function of T, both specific heat capacities are functions of T.

A particular semiperfect gas is one for which c_p and c_v are independent of temperature. As stated above, such a gas is called a perfect gas. A gas behaves as a perfect gas either when the molecules have no internal structure, so that q_s is unity, or when q_s can be approximated by the product $g \exp(-\overline{\varepsilon_0}/kT)$, in which g and $\overline{\varepsilon_0}$ are constants.

Electronegativity of atoms and molecules. An atom or a molecule may be regarded as a grand system with electrons as its only component particles because it can exchange energy and electrons while reacting chemically with other atoms and molecules.

An atom A of atomic number z contains z units of positive electric charge in addition to its electrons. It has all the energy eigenvalues of the neutral atom and of each of the multiply (positively) charged ionized atoms. Consideration will be limited to atoms having energy eigenvalues corresponding to a singly charged negative ion; i.e., an ion with $z + 1$ electrons.

The eigenvalues n_i of the number of electrons in atom A are such that

$$n_i = i = 0, 1, 2, \ldots, z, z + 1;$$

that is, the atom can be fully ionized ($i = 0$), partially ionized ($i < z$), neutral ($i = z$), or singly negatively charged ($i = z + 1$).

For each n_i a number g_{i0} of energy eigenvalues will have the minimum numerical value E_{i0}, in which g_{i0} may be one or greater than one. Each of the g_{i0} identical eigenvalues E_{i0} represents the energy of the so-called ground state of A with exactly n_i electrons. Moreover, an infinite number of energy eigenvalues E_{ij} ($j = 1, 2, \ldots$), each with a multiplicity or degeneracy g_{ij}, correspond to the excited states for each n_i.

For a stable equilibrium state at temperature T, the expectation value n of the number of electrons of the atom is given in terms of the above notation by the relation

$$n = \frac{\sum\limits_{i,j} n_i g_{ij} \exp[(n_i\mu - E_{ij})/kT]}{\sum\limits_{i,j} g_{ij} \exp[(n_i\mu - E_{ij})/kT]}, \quad (125)$$

in which the symbol $\sum\limits_{i,j}$ denotes a double summation, one over all values of i from zero to $z + 1$ and the other over all values of j from zero to infinity. The number n may assume any value between 0 and $z + 1$, although n_i can assume only integral values.

For given n and T values equation (125) can be solved for the value of the potential μ. Although the solution is numerically tedious, some general results are readily established: (1) For a fully ionized state (that is, for the minimum value $n = 0$) μ is minus infinity, and for a singly charged negative-ion state (that is, for the maximum value $n = z + 1$) μ is plus infinity, both for all

values of T. Such extreme values of μ are always obtained when the value of the number of particles of the grand system is either minimum or maximum. They are consistent with the interpretation of the potential μ as an escaping tendency. (2) For values of n in the range between z and $z + 1$, the potential μ is positive. For all other values the potential μ is negative. (3) For a neutral atom state (that is, for $n = z$), in the limit as T approaches zero, μ is equal to one-half the difference between the energy eigenvalues of the ground states of the singly charged negative ion and the singly charged positive ion. It can also be written in the form

$$\mu = -\frac{I_1 + A_1}{2}, \qquad (126)$$

in which I_1 and A_1 are, respectively, the first ionization energy and the electron affinity of the atom. For example, for the hydrogen atom the first (and only) ionization energy is equal to 13.6, the electron affinity is 0.7, and, therefore, the potential μ is -7.15, all in electron-volt units.

Since μ is a measure of the escaping tendency, $-\mu$ is a measure of a capturing tendency or power to attract. The power of an atom to attract electrons is called the electronegativity of the atom. The preceding analysis indicates that electronegativity can be identified with the potential $-\mu$ of electrons in an atom, and its value can be computed by means of statistical thermodynamics. Similar results can be obtained for molecules and for solid surfaces.

VII. Concluding remarks

The concepts of a system and states of a system adopted throughout this article are more general than are usually adopted in the science of thermodynamics. In the first part of the article, in which the microscopic structure of the particles that constitute the. system is ignored, the many relations for systems in stable equilibrium states that are well-known to classical thermodynamics are derived. The method, however, lends itself well to the treatment of states other than stable equilibrium inasmuch as the values of entropy may be found for such states.

In the second part, the microscopic structure is brought into consideration but without loss of the concept of an unambiguous stable equilibrium state. This result is achieved through the quantum-mechanical interpretation of measurement as an operation that yields definite eigenvalues with certain probabilities. The results are, first, many relations familiar to statistical mechanics that permit evaluation of properties of a system from the known structure of the particles and, secondly, a means of applying the laws of thermodynamics to systems that are large or small, simple or complex. The limitation of thermodynamics, frequently applied in the past, to macroscopic systems no longer applies. To illustrate this generality, thermodynamic ideas are applied above to a single atom in order to discover the meaning of the previously recognized quantity electronegativity.

BIBLIOGRAPHY. E. MENDOZA (ed.), *Reflections on the Motive Power of Fire by Sadi Carnot; and Other Papers on the Second Law of Thermodynamics, by É. Clapeyron and R. Clausius* (1960), on the original theoretical development of the first and second laws; J.R. MAYER, "Bemerkungen über die Kräfte der unbelebten Natur," *Annln. Chemie Pharmacie*, 42:233–240 (1842), perhaps the first attempt to demonstrate the conversion of heat into work; *The Scientific Papers of J.P. Joule*, vol. 1 (1884), on the experimental foundations of the first law; W.D. NIVEN (ed.), *The Scientific Papers of J.C. Maxwell* (1890), includes the development of the Maxwell relations; *The Collected Works of J. Willard Gibbs*, 2 vol. (1928), the definitive treatment of equilibrium statistical mechanics in terms of classical mechanics; MAX PLANCK, *Vorlesungen über Thermodynamik*, 7th ed. (1921; Eng. trans., *Treatise on Thermodynamics*, 3rd ed., 1927), on the connection between the second law and the concept of reversibility and statement of impossibility of perpetual motion of the second kind; HENRI POINCARE, *Thermodynamique* (1892), definitions of temperature and heat and statements of the first and second law; C. CARATHEODORY, "Untersuchungen über die Grundlagen der Thermodynamik," *Math.*

Annln., 67:355–386 (1909), a rigorous mathematical exposition marked by avoidance of undefined terms such as heat and temperature; G.N. LEWIS and MERLE RANDALL, *Thermodynamics*, rev. ed. by K.S. PITZER and LEO BREWER, 2nd ed. (1961), extensive application of the Gibbsian conditions of equilibrium to heterogeneous systems; W.M. LATIMER, *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, 2nd ed. (1952), experimental data on chemical reactions; N.F. RAMSEY, "Thermodynamics and Statistical Mechanics at Negative Absolute Temperatures," *Phys. Rev.*, 103:20-28 (1956), on special systems that can assume negative temperatures on the Kelvin scale; A.B. PIPPARD, *The Elements of Classical Thermodynamics for Advanced Students of Physics* (1957), a concise and consistent application of principles to systems in equilibrium; G.N. HATSOPOULOS and J.H. KEENAN, *Principles of General Thermodynamics* (1965), a broad, rigorous, and logically complete exposition of classical thermodynamics, including the application of entropy to nonequilibrium systems, the combination of the postulates of thermodynamics, and of statistical mechanics through the use of information theory; S.R. DEGROOT, *Thermodynamics of Irreversible Processes* (1951), general and extensive application of the Onsager reciprocal relations and the theory of rate processes; R.C. TOLMAN, *The Principles of Statistical Mechanics* (1938), a scholarly exposition of classical and quantum statistical mechanics, including the density matrix; R.H. FOWLER, *Statistical Mechanics*, 2nd ed. (1936, reprinted 1955), written from the viewpoint of molecular statistics, and with E.A. GUGGENHEIM, *Statistical Thermodynamics* (1939, reprinted 1956), extensive applications to terrestrial physics and chemistry.

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Thermoelectric Devices

Thermoelectric devices are devices that either convert heat directly into electricity—in the case of thermoelectric generators—or provide cooling by passing an electric current through appropriate materials—in the case of thermoelectric refrigerators. Both devices are based on thermoelectric effects involving interactions between the flow of heat and of electricity through solid bodies. Although the effects themselves were discovered in the first half of the 19th century, it is only in recent years that the devices based on them have begun to compete with conventional generators and refrigerators. The growing knowledge of solid-state physics in general, and semiconducting materials in particular, has made possible such applications as a refrigerator the size of a thimble and a nuclear-powered generator on the Moon to provide electrical power for equipment that sends moonquake information back to the Earth.

The two most important thermoelectric effects are the Seebeck effect and the Peltier effect. In the Seebeck effect, an electrical current or voltage is produced in a circuit made of two different conducting materials if the two junctions (points of contact) are held at different temperatures. The flow of heat from the hot to the cold junction gives rise to an electrical current; this effect is the basis for thermoelectric generation of electricity from heat. In the Peltier effect, when a direct electric current flows through a circuit made of two different conductors, one junction between the two materials is cooled while the other is heated, depending on the direction of current flow. This effect, which may be considered the inverse of the Seebeck effect, is the basis for thermoelectric refrigeration.

A major advantage of thermoelectric devices is that they involve only the motion of heat and electricity, rather than the motion of mechanical parts as in rotating machinery such as turbines, dynamos, motors, or compressors used in more familiar generators and refrigerators. The major disadvantages of thermoelectric devices are that they are often less efficient to operate and more expensive to produce than conventional machines and so are usually used in specialized applications rather than as replacements for large-scale power generating plants or air-conditioning equipment.

HISTORY

Thomas Johann Seebeck, a German physicist, discovered the effect which bears his name in 1821. He found

The Seebeck and Peltier effects