Basic Principles of Classical and Statistical Thermodynamics

By

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In the most general sense thermodynamics is the study of energy -- its transformations and its relationship to the properties of matter. In its engineering applications thermodynamics has two major objectives. One of these is to describe the properties of matter when it exists in what is called an equilibrium state, a condition in which its properties show no tendency to change. The other objective is to describe processes in which the properties of matter undergo changes and to relate these changes to the energy transfers in the form of heat and work which accompany them. These objectives are closely related and a text such as this, which emphasizes primarily the description of equilibrium properties, must include as well a discussion of the basic principles involved in accomplishing these two objectives.

Thermodynamics is unique among scientific disciplines in that no other branch of science deals with subjects which are as commonplace or as familiar. Concepts such as "heat", "work", "energy", and "properties" are all terms in everyone's basic vocabulary. Thermodynamic laws which govern them originate from very ordinary experiences in our daily lives. One might think that this familiarity would simplify the understanding and application of thermodynamics. Unfortunately, quite the opposite is true. In order to

accomplish these objectives, one must almost entirely forget a life-long acquaintance with the terms of thermodynamics and redefine them in a very scientific and analytical manner. We will begin with a discussion of the various properties of matter with which we will be concerned.

1   *Thermodynamic and Non-Thermodynamic Properties*

A property of matter is any characteristic which can distinguish a given quantity of a matter from another. These distinguishing characteristics can be classified in several different ways, but for the purposes of this text it is convenient to divide them into what may be called thermodynamic and non-thermodynamic properties.

The non-thermodynamic properties describe characteristics of what are often called the "ultimate particles" of matter. An ultimate particle from a thermodynamic view point is the smallest subdivision of a quantity of matter which does not undergo any net internal changes during a selected set of processes which alter properties of the entire quantity. The ultimate particles with which we will be concerned are generally considered to be molecules or atoms, or in some cases groups of atoms within a molecule. When the meaning is clear we will some times delete the adjective "ultimate" and refer to them simply as "particles".

Because it has no internal changes an ultimate particle can always be regarded as a rigid mass. Its only alterable distinguishing characteristics which could possibly be detected, if some experimental procedure could do so, are its position and its motion. As a result, the fundamental properties of this particle, which cannot be calculated or derived from any others, consist only of its mass and shape plus the vectors or coordinates needed to describe its position and motion. It is convenient to combine the mass and motion characteristics and represent them as a momentum property. These fundamental characteristics, mass, position, and momentum, are called "microstate" properties and as a group they give a complete description of the actual behavior of an ultimate particle.

Everyone realizes of course, that molecules are not actually inert rigid masses. The forces of attraction and repulsion which we ascribe to them are in reality the consequence of variations in the quantum states of a deformable electron cloud which fills practically all the space occupied by a molecule so that when we represent it as a rigid mass we are constructing a model which allows us to apply classical mechanics to relate its energy changes to changes in its microstate properties. For example, an effective model for a complex molecule is to regard it as a group of rigid spheres of various size and mass held

together by flexible springs. The only justification for this model is that calculations of its energy, when properly averaged, give good agreement with values of energy per molecule obtained from experimental measurements using bulk quantities of the substance. Constructing models is important in all aspects of thermodynamics, not only for individual molecules, but also in describing the behavior of bulk matter.

Values which can be calculated from the microstate properties of an individual particle or of a cluster containing only a few particles represent another group of non-thermodynamic properties. We will refer to these derived values as "molecular" properties. Examples are the translational, vibrational, or rotational energies of an individual molecule, and also the calculated potential energy at various separation distances in a pair of molecules or between other small groups of near neighbors. In some cases we wish to calculate special functions of the potential energy within a group composed of a few neighbors. An important feature of all of these combinations of fundamental microstate properties is that they can produce the same value of a calculated molecular property. For example, assigning values to the microstate properties of a molecule determines its energy but specifying the energy of a molecule does not specify any one particular set of values for its microstate properties.

Whereas the non-thermodynamic properties pertain to a single or to only a few ultimate particles, the characteristics of matter which are called thermodynamic properties are those which result from the collective behavior of a very large number of its ultimate particles. Instead of only one or a few particles, this number is typically on the order of Avogadro's number. In a manner analogous to the way in which molecular properties can be calculated from the fundamental microstate properties of an individual or small group of particles, the various thermodynamic properties likewise depend upon the vastly greater number of all the microstate properties of the very large group. Furthermore, an even larger number of different sets of microstate properties can produce the same overall thermodynamic property value. In contrast to non-thermodynamic properties, thermodynamic properties can always be measured experimentally or calculated from such measurements.

Establishing relationships between non-thermodynamic and thermodynamic properties of matter in equilibrium states is the task of statistical thermodynamics while the study of relationships among the thermodynamic properties alone is generally the topic of classical thermodynamics. In the past it has been customary for textbooks and their readers to make a sharp distinction between the two disciplines. The historical development of

classical thermodynamics and its applications to a wide range of engineering problems took place without any reference at all to ultimate particles or molecular properties. This development is entirely rigorous and has the merit of establishing the validity of general thermodynamic principles to all types of matter regardless of its molecular character. However, the problem of predicting and correlating thermodynamic properties of an increasing diversity of substances both in pure form and in mixtures with the accuracy needed in modern technology requires a combination of the classical and molecular viewpoints. It is this combination which is the objective of this text.

2   *The Selection of a System*

The first concept which must be understood in applying thermodynamics is the necessity to begin with the definition of what is called a "system". In thermodynamics this is any region completely enclosed within a well defined boundary. Everything outside the system is then defined as the surroundings. Although it is possible to speak of the subject matter of thermodynamics in a general sense, the establishment of analytical relationships among heat, work, and thermodynamic properties requires that they be related to a particular system. We must always distinguish clearly between energy changes taking place within a system and energy transferred across the system boundary. We must likewise distinguish between properties of material within a system and properties of its surroundings.

In accordance with their definition, thermodynamic properties apply to systems which must contain a very large number of ultimate particles. Other than this there are no fundamental restrictions on the definition of a system. The boundary may be either rigid or movable. It can be completely impermeable or it can allow energy or mass to be transported through it. In any given situation a system may be defined in several ways; although with some definitions the computations to be performed are quite simple, with others they are difficult or even impossible.

For example, it is often impossible by means of thermodynamic methods alone to make heat transfer calculations if a system is defined so that both heat transfer and diffusional mass transfer occur simultaneously through the same area on the boundary of the system. For processes in which mass transfer takes place only by bulk stream flow this problem can be avoided easily by a proper definition of the system. In a flow process of this type the system is defined so that it is enclosed by moveable boundaries with no stream flows

across them. Heat transfer then always occurs across a boundary not crossed by mass.

3   *Microstates and Thermodynamic States*

The state of a system is an important concept in thermodynamics and is defined as the complete set of all its properties which can change during various specified processes. The properties which comprise this set depend on the kinds of interactions which can take place both within the system and between the system and its surroundings. Any two systems, subject to the same group of processes, which have the same values of all properties in this set are then indistinguishable and we describe them as being in identical states.

A process in thermodynamics is defined as a method of operation in which specific quantities of heat and various types of work are transferred to or from the system to alter its state. As we pointed out, one of the objectives of thermodynamics is to relate these state changes in a system to the quantity of energy in the form of heat and work transferred across its boundaries.

In discussing non-thermodynamic processes, a system may be chosen as a single ultimate particle within a larger quantity of matter. In the absence of chemical reactions the only processes in which it can participate are transfers of kinetic or potential energy to or from the particle. In this case we would like to relate these energy transfers to changes in the microstate of the system. A microstate for this one-particle system is a set of coordinates in a multi-dimensional space indicating its position and its momenta in various vector directions. For example, a simple rigid spherical monatomic molecule would require a total of six such coordinates, three for its position and three for its momentum in order to completely define its microstate.

Now consider a system containing a large number of these ultimate particles. A microstate of this system is a set of all position and momentum values for all the particles. For example, if there were N rigid spherical molecules we would then need 6N coordinates to give a complete set of all the microstate properties and define a microstate for this system. In a multiparticle system a particular microstate exists only for an instant and is then replaced by another so that there is no experimental way to measure the set of positions and motions which comprise one microstate among the vast number of them which occur sequentially.

Because the microstates of a multiparticle system represent exactly what all the particles are doing, all thermodynamic properties of the group are thus determined by them.

With this common origin all the thermodynamic properties are therefore related to each other and we need to develop this relationship. The set of all the thermodynamic properties of a multiparticle system its temperature, pressure, volume, internal energy, etc., is defined as the thermodynamic state of this system.

An important aspect of this relationship between thermodynamic properties is the question of how many different thermodynamic properties of a given equilibrium system are independently variable. The number of these represents the smallest number of properties which must be specified in order to completely determine the entire thermodynamic state of the system. All other thermodynamic properties of this system are then fixed and can be calculated from these specified values. The number of these values which must be specified is called the variance or the degrees of freedom of the system.

4 *The Concept of Energy*

In elementary physics energy is often defined as "the capacity to produce work". At a descriptive level the idea expressed is correct, but for thermodynamics which is to be applied quantitatively this definition is not a good one because the term "work" itself requires a more precise definition than the general idea it ordinarily conveys. A better definition of energy from the viewpoint of thermodynamics would be "the capacity to induce a change in that which inherently resists change". This capacity represents a combination of an effort, expended in overcoming resistance to a particular type of change, with the change it produces. The combination is called energy.

The effort involved is measured quantitatively by what is defined as a "driving force" in thermodynamics. A driving force is a property which both causes and also controls the direction of change in another property. The quantitative value of this change is called a "displacement". The product of a driving force and its associated displacement always represents a quantity of energy, but in thermodynamics this quantity has meaning only in relation to a specifically defined system.

Relative to a particular system there are generally two ways of locating a driving force and the displacement it produces. In one way both the driving force and the displacement are properties of the system and are located entirely within it, so that the energy calculated from their product represents a change in the internal energy of the system. Similarly, both the driving force and its displacement could be located entirely within the surroundings so that the calculated energy is then a change in the total energy of

the surroundings.

In another way, however, the displacement occurs within the system but the driving force producing it is a property of the surroundings and is applied externally at the system boundary. By definition, the boundary of a system is a region of zero thickness containing no matter at all so that the energy calculated in this way is not a property of matter either in the system or in its surroundings but represents a quantity of energy in transition between the two. In any quantitative application of thermodynamics it is always important to make a careful distinction between energy changes within a system or within its surroundings and energy in transition between them.

5   *Microstate Driving Forces*

In order to explain the nature of driving forces, suppose we consider first a system defined as a single ultimate particle of a simple fluid, either a gas or a liquid. The system in this case is a rigid spherical mass with no possibilities for any internal changes and obeying Newtonian mechanics. In its surroundings are similar ultimate particles of this fluid. From a Newtonian point of view the mass of this system resists any change in its condition of motion and a specific change occurs only with the application of an external force to overcome the inertial resistance inherent in the mass. In the presence of mutual attraction and repulsion between this system and neighboring particles it may be considered to resist any displacement from a position in which this attraction and repulsion are balanced. In this situation a force vector directed toward the center of mass must be applied for a fixed time period to produce a change. This force is produced by the environment around the particle chosen as the system. The mechanism for its generation is by the action of neighboring particles in exerting attraction or repulsion or in colliding with the system. The scalar product of the vector force generated in this manner with other vectors which represent the resulting displacements in position and velocity of the system determine the energy added to the system when its velocity is increased, when its position is moved away from attracting neighbors, or when moved toward neighbors which repel it.

Since these displacements represent changes in microstate properties, we define the force vector producing them as a "microstate driving force." According to Newtonian mechanics this applied force is always opposed by an equal and opposite force representing the resistance of the system to change. Although mechanically we could position these two forces anywhere along their line of action, in terms of the system it is convenient to think of

them as opposing one another at the boundary of the system to describe energy in transition across it and then as opposing one another within the system when we describe this quantity of energy as the energy change of the system. An important characteristic of microstate driving forces is that they are true force vectors in the Newtonian sense and there is never a condition of unbalanced driving forces. This is not at all the case for what we will define as "thermodynamic driving forces" which are the agents of change for thermodynamic properties in multiparticle systems.

6   Thermodynamic Driving Forces

In contrast to the one-particle system which we have discussed in section 5, for thermodynamic systems consisting of many particles we are usually as interested in internal energy changes as we are in changes in position or motion of the entire system. In this case we wish to define these internal energy changes in terms of thermodynamic properties, each of which are the collective results of the enormous number of microstates for all the ultimate particles of the system. Because the fundamental agents of change within the system are microstate driving forces, the corresponding agents of change or driving forces in thermodynamic systems are the composite result of all the microstate driving force vectors in the system. However, the only case in which the collective behavior of all these microstate driving force vectors defines a thermodynamic property is the one in which these microstate vectors for all the individual particles are oriented in a completely random manner in every conceivable direction. In this case their overall resultant in the entire system is completely scalar in nature and a thermodynamic property of the system. We define this resultant as a "thermodynamic driving force."

Likewise, the cumulative effect of all the microstate changes induced, which are also vectors, produces in this case a completely scalar thermodynamic property change for the multiparticle system. This overall change is the displacement induced by the thermodynamic driving force.

Because these thermodynamic driving forces are not true vector forces in the Newtonian sense but are scalar properties, the thermodynamic driving forces tending to cause a change are not always balanced by equal and opposite driving forces opposing the change. Changes in internal thermodynamic properties within a system can be controlled as to direction, and in some instances as to their rates, by the degree of difference between the value of a particular thermodynamic driving force property outside the system at its

boundary and a value of this same property somewhere within the system. Between thermodynamic driving forces this difference can be of any magnitude, finite or infinitesimal. When they are exactly equal there is then no net change induced and no energy is transferred.

7   Intensive and Extensive Properties

In discussing microstate driving forces in section 5, we noted that the force to be applied or the force to be overcome in order to make a change in the position or motion of any one particle in a multi-particle system depends both on the nature of the particle and on its environment. When these remain the same then the necessary force to induce a change is also the same, no matter how many other individual particles are present in the system. Because a thermodynamic driving force in a system is the composite result of all the individual particle forces, it likewise should be independent of the number of particles present as long as they all have the same environment and individual characteristics.

Properties of a system which have this type of independence of the number of particles present are called "intensive properties" and all the thermodynamic driving forces are selected from among properties of this type. The test for an intensive property is to observe how it is affected when a given system is combined with some fraction of an exact replica of itself to create a new system differing only in size. Intensive properties are those which are unchanged by this process, whereas those properties whose values are increased/decreased in direct proportion to the enlargement/reduction of the system are called "extensive properties." For example, if we exactly double the size of a system by combining it with an exact replica of itself, all the extensive properties are then exactly double and all intensive properties are unchanged.

As we have explained the displacements in a system induced by thermodynamic driving forces are a summation of all the motion and position changes in all the ultimate particles of the system. Consequently, if we alter the number of particles by changing only the size of the system, we should then alter the overall displacement in exactly the same proportion. This means that the overall change which we call a displacement must be a change in an extensive thermodynamic property of the system.

If the magnitude of a displacement thus varies directly with the size of a system in which it occurs, whereas the driving force is not affected, their product must likewise change directly with the system size so that energy itself is always an extensive property.

8   Identification of Thermodynamic Driving Forces and Displacements

In addition to the differences between thermodynamic driving forces which arise because the thermodynamic forces are scalar properties instead of vectors, another important difference is that they are quite different dimensionally.   This is a consequence of the fact that the thermodynamic driving forces are defined in a quite intuitive manner.

Thermodynamic driving forces are identified empirically as the intensive property whose difference on each side of some part of the boundary between a system and its surroundings control both the direction and the rate of transfer of one specific extensive property displacement across it. For example, consider the volume filled with air within a pump and bicycle tire as a system and the inner surface of the piston of the pump as the boundary across which a volume change is transferred. When the piston is moved the magnitude of the volume change in the surroundings is exactly the magnitude of the volume change of the system and the increase in volume of one is exactly the decrease in volume of the other. We can say, therefore, that volume is an extensive property transferred across this boundary. When only volume and no other extensive property change is transferred, then we find by experiment that the pressure difference is the only intensive property across this boundary that controls both the direction and rate of change of the volume. Then we define pressure as the thermodynamic driving force. It is important that only one extensive property be transferred across this boundary in the experiment. For example, suppose there was a crack in the piston which allowed air to leak through it. We now can have both volume and mass transferred across this same boundary and we observe in this case that lowering the pressure outside the piston may not necessarily cause the volume of the system to expand. To properly identify a driving force we must always examine the transport of only one displacement and one characteristic type of energy.

Although the dimensional and physical nature of each thermodynamic driving force identified in this manner are very different, the product of each with its associated displacement always measures a distinctive type of energy and must have the characteristic energy dimensions of force multiplied by length.

Once a particular type of energy crossing a boundary has been identified, the manner in which it is divided into a driving force and displacement is completely arbitrary as long as the driving force is intensive and the displacement is a change in an extensive property. For example, in this illustration of the transfer of pressure-volume work we could have

equally well called the displacement the distance traveled by the pump piston and the driving force a product of pressure and piston area. We would thus change the dimensions of the driving force and displacement, but this would not affect any thermodynamic computations where only the magnitudes and not the rates of changes in energy and properties are to be determined. In a subject called "non-equilibrium thermodynamics where a description of the rates of various changes is an objective, the definition of driving force and displacement is not at all arbitrary and must be done only in certain ways.[1]

Some of the diversity of driving force-displacement combinations and their dimensions, which represent various types of energy in some important thermodynamic applications is shown in Table I. The product of the two represents a change in the energy of a region in which both the driving force and displacement are properties. It also gives the energy transported between a system and its surroundings when the driving force is located on its outer boundary and the displacement is within the system.

9   The Laws of Thermodynamics

Now that we have discussed the nature of different forms of energy and properties of matter, we must describe the basic principles of thermodynamics which are used to relate them.

Classical thermodynamics is one of the most important examples of the axiomatic form of the scientific method.[2] In this method certain aspects of nature are explained and predicted by deduction from a few basic axioms which are assumed to be always true. The

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[1]H.B. Callen, "Thermodynamics and an Introduction to Thermostatistics," p. 283, New York, NY: John Wiley & Sons, Inc., 1985.

[2]Although thermodynamics is universally regarded as the classic example of an axiomatic science, the rigorous deduction of every concept in thermodynamics from its basic axioms alone is an intricate logical problem which few authors attempt. See for example, P.T. Landsberg, "Thermodynamics," p. 115, Interscience Publishers, New York, 1961 and P.W. Bridgman, "The Nature of Thermodynamics," Harvard University Press, 1943.

axioms themselves need not be proved but they should be sufficiently self-evident to be readily acceptable and certainly without known contradictions. The application of thermodynamics to the prediction of changes in given properties of matter in relation to energy transfers across its boundaries is based on only two fundamental axioms, the First and Second Laws of thermodynamics, although the total field of thermodynamics requires two other axioms. What is called the Zeroth Law considers three bodies in thermal contact, transferring heat between themselves, yet insulated from their external surroundings. If two of these have no net heat flow between them, a condition defined as thermal equilibrium, then thermal equilibrium exists also between each of these and the third body. This is necessary axiom for the development of the concept of temperature, but if one begins with temperature as an already established property of matter, as we will do, the Zeroth Law is not needed. The Third Law states that the limit of the entropy of a substance is zero as its temperature approaches zero, a concept necessary in making absolute entropy calculations and in establishing the relationship between entropy as obtained from the statistical behavior of a multi-particle system, and the entropy of classical thermodynamics. Because in this work we are concerned only with predicting changes in thermodynamic properties, including the entropy, the Third Law also will not be needed or discussed.

10   The Intuitive Perception of the First Law

The First Law of thermodynamics is simply the law of conservation of energy and mass. The ready acceptability of this law is apparent from the fact that the concept of conservation in some form has existed from antiquity, long before any precise demonstration of it could be made. The ancient biblical affirmation, "What so ever a man sows, that shall he also reap" is, in a sense, a conservation law. The Greek philosophers generally considered matter to be indestructible, although its forms--earth, fire, air, or water-- could be interchanged. The situation was confused in the Middle Ages by a feeling that a combustion process actually "destroyed" the matter which burned. This was not set right until 1774 when Lavoisier conclusively demonstrated the conservation of mass in chemical reactions.

It is fortunate that an intuitive feeling for energy conservation is also deep-rooted because its demonstration is experimentally more difficult than that for mass conservation and that which is conserved is more abstract. As discussed in section 4, that which is called energy in classical thermodynamics is a quantity which measures a combination of effort

expended and results produced.

TABLE I

Common Thermodynamic Driving forces and Their Associated Displacements

Driving Force	*Dimensions*	*Symbol*	*Extensive Property Change of Displacement*	*Dimensions*	*Symbol*
Pressure	*(force/area)*	*P*	*volume*	*(length)^3*	*dV*
Temperature	*(^{o} K or ^{o} R)*	*T*	*entropy*	*energy/degree*	*dS*
Surface Tension	*(force/length)*	*γ*	*surface area*	*(length)^2*	*dA*
Various Potentials:					
gravitational	*(energy/unit mass)*	*(h g/g$_c$)*	*mass*	*lbs, kg, etc*	*dm*
chemical	*(energy/mole of species i)*	*μ_i*	*moles of*	*number of species i moles*	*dn$_i$*
electrical	*(volts)*	*v*	*+charges*	*coulombs*	*[v⁻Fdn⁻ + v⁺Fdn⁺]*
electrical	*(volts or emf)*	*$\in$*	*electrons*	*coulombs*	*-[v⁻Fdn⁻ + v⁺Fdn⁺]*

F =	*Faraday's Constant*
v⁻ =	*Valence of a negative ion (a negative number)*
v⁺ =	*Valence of a positive ion (a positive number)*
n⁻ =	*number of moles of a negative ion*
n⁺ =	*number of moles of a positive ion*
h =	*elevation above sea level*
g =	*gravitational acceleration at distance h*
g$_c$ =	*gravitational constant (Newton's law proportionality factor)*

From an intuitive sense of universal justice, we feel that this quantity should be universally conserved, never created from nothing, never destroyed without a trace, but transformable into other forms with the total quantity before and after the transformation remaining the same.

The earliest demonstration of energy conservation is generally credited to Count Rumford in 1797. Fortunately, he made his observations in a cannon factory where the

mechanical work of boring a cannon was converted into heat and transferred to a large amount of cooling water. If this heat transfer had not been very large relative to the heat losses, the correct conclusion could easily have escaped him. The first accurate measurement and indisputable demonstration of the precise equivalence of mechanical work and the total thermal energy obtainable from it did not occur until the experiments of Joule and Kelvin between 1843 and 1848 were done.

At present, when mass and energy can be shown to be mutually interchangeable, conservation of mass and conservation of energy should be combined into a single conservation law which, as far as we know, is universal. At the magnitude of energies involved in thermodynamic state changes the accompanying mass changes are negligible so that mass and energy are always considered to be conserved separately.

11   The Second Law as Common Experience

The Second Law is likewise a concept which is a part of basic human experience. In its intuitive perception the Second Law is a sense of the uniqueness of the direction of the change which results from the action of a particular thermodynamic driving force. For example, no one has to be told that when the earth's gravitational potential is the driving force it will cause water to flow from a tank on top of the hill to one at the bottom, but it alone will never cause the reverse to occur. This direction of water flow is always the same unless we supply some work, as for example with a pump, or unless we allow a change in the properties of some region outside the two tanks, such as the water level in some other reservoir. We identify the earth's gravitational attraction at a given water level as a driving force because when the water levels are the same in each tank there is no further transfer of water and also because the rate of transfer increases with an increase in the difference in elevation.

An analogous example occurs when heat is driven from one system to another by a difference in their temperatures. In our earliest experience temperature is the degree of "hotness to the touch" which in this case is different for each system. We observe that when this temperature difference is large the rate of change of their temperatures is greater than when it is small and when the two have the same temperature we observe no further changes. Consequently we identify temperature as a driving force which causes something called heat to be transferred.

No theoretical knowledge of any kind is required for us to know that if we bring two

objects into close contact and exclude any interaction between them and their surroundings, the cold one will always get hotter and the hot one cooler but never the opposite. This direction is always the same unless we do some work, as with a refrigerator, or allow some energy transfer between the objects and their surroundings.

When expressed more generally to include all types of driving forces and their driven quantities, this uniqueness of direction becomes the Second Law. This is not a concept in any way contained within the First Law, but one involving a completely new requirement. For example, in either the water flow or in the heat flow situations, a flow in the wrong direction would not necessarily violate the conservation of energy or mass.

12   Heat and Thermal Energy

We are familiar with the potential energy changes of water at different elevations, but what is the nature of the energy transferred between objects with a difference in temperature? Before the advent of molecular theory it was also   regarded as a kind of fluid which could flow from one region to another. Although we realize today that heat transfer does not involve any sort of fluid, the idea that heat is something being transferred is essential to modern quantitative applications of thermodynamics.

In thermodynamics heat must always be defined as energy in transition between a system and its surroundings which is caused to flow by a difference in temperature on either side of the boundary between them. By convention heat crossing a boundary in a direction into a system from the surroundings is considered to be a positive quantity while heat crossing a boundary in a direction from the system into the surroundings is always considered a negative quantity. It is essential that this sign convention be followed consistently.

Heat, according to its definition, never exists within a system or within its surroundings and cannot be regarded as a property of either[3]. It exists only at the zero

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[3] Some widespread but unfortunate terminology uses phrases such as "heat content", "specific heat", or "heat capacity" in referring to some properties of a system. This usage is so common that there is no way to change it, but the word "heat" should rigorously be reserved only for the definition given here and not to represent anything contained within a system or any property of it.

thickness boundary between them. This definition shows why it is so important that the system and its boundaries be clearly specified. Without this, heat itself is undefined. The numerical value of a quantity of heat and its sign depend upon how the system and its boundaries are selected. At an interface enclosed within a system there may be thermal energy transfers across it but the heat transferred is zero.

This definition makes an important distinction between heat itself and the effects produced within a system which it enters. These effects within the system are measured by what we define as "thermal energy", which is a part of the total internal energy of the system. In terms of molecular behavior, thermal energy involves the same type of molecular motion and interactions as those at the boundary which accompany heat transfer. It is also energy which is transferred from one region of a system to another if there is a temperature difference between them, but this thermal energy becomes heat only at the boundary of the system.

The reason for this careful distinction is that although heat and thermal energy are qualitatively similar, they are not always quantitatively equal. Thermal energy can be increased in a system not only by heat transfer into it, but also by the energy brought in by different kinds of work done on the system. There is no way to detect any qualitative difference in the thermal energy resulting from any of these sources. For example, applying work in the form of violent agitation can produce an effect in a system which is indistinguishable from that produced by direct heat transfer into it from some source at a higher temperature.

13   Entropy

As indicated in Table I, entropy is the name given to the extensive property whose change when multiplied by temperature gives a quantity of thermal energy. In classical thermodynamics there is no need to give any physical description of this property in terms of molecular behavior. A change in entropy is defined simply as a quantity of thermal energy divided by the temperature driving force which propels it so that it always produces the thermal energy identically when multiplied by the temperature. Because temperature is an intensive property and this product is energy, we know that the entropy must be an extensive property. Furthermore, thermal energy is a part of the total internal energy within a system so that the entropy change computed this way is a change in a property of the system.

Thermal energy crossing a system boundary is defined as heat so that the entropy change transported by it is simply the quantity of heat transported divided by the temperature which transports it. This transporting temperature is the temperature of the external or surroundings side of the system boundary. It is important to realize that this transported entropy change may be only apart of the total entropy change within the system. Because thermal energy can be produced within a system by other means than adding heat to it, a thermal energy increase in the system can be greater than the heat transported into it. In this case the entropy change within the system accompanying its thermal energy increase will be greater than the entropy change transported into the system with the heat flow.

14   Work

Now that we have used the term "work" it is necessary to emphasize that work, like heat, must also be regarded only as a type of energy in transition across a well defined, zero thickness, boundary of a system. Consequently work, like heat, is never a property or any quantity contained within a system. Whereas heat is energy driven across this boundary by a difference in temperature, work is energy driven across by differences in other driving forces on either side of it. Various kinds of work are identified by the kind of driving force involved and the characteristic extensive property change which accompanied it.

Work is measured quantitatively in much the same manner as heat. Any driving force other than temperature, located outside the system on its external boundary, is multiplied by a transported extensive property change within the system which was transferred across the system boundary in response to this force. The result is the numerical value of the work associated with this system and driving force. It is important to emphasize that the extensive property change within the system which is used in this computation must be a transported quantity whose transfer across the system boundary depends on a particular driving force with different values inside and outside the system. This transported extensive property change within the system always occurs with the same magnitude but with opposite sign in the surroundings.

Neither work nor heat results from any part of a change in an extensive property of a system which has not been transported in this manner without alteration in magnitude across the system boundary. A non-transported extensive property change within a system when multiplied by an appropriate driving force property located within the system

measures a form of internal energy change in the system but not work or heat.

Conventionally the quantity of work calculated by this procedure is given a positive sign when work is done by the system on the surroundings and energy crosses the boundary in a direction from the system to the surroundings. An energy transport in the opposite direction, when work is done by the surroundings on the system, is given a negative sign. It is awkward that the sign given to energy transferred as work is opposite to that given to energy transferred as heat in the same direction, but tradition has established the convention and it is important that it be followed consistently. Like heat, both the absolute value and the sign of what is called work depend entirely on how the system is specified.

Several thermodynamic driving forces and their characteristic displacements are listed in Table I. Any of these properties, other than temperature and entropy, can measure various types of work when the driving force is located on the outer side of the system boundary and the displacement is a transported quantity whose change is located within the system. The product, when given the proper sign, is a type of work transfer for this system.

15   Energy Transport by Mass Transfer

For any region with a boundary which is penetrated by mass, a thermodynamic analysis always requires a distinction between mass carried across the boundary by bulk stream flow and mass carried across by diffusion processes resulting from molecular action.

In the case of bulk stream flow with no diffusion mass transport, energy is carried into the region in two distinct ways. Part of the energy added to a region receiving mass by stream flow is the work of a pressure which displaces a quantity of flowing fluid into the region. The remaining part of the energy added is the internal energy content of this quantity of fluid which enters. In a bulk stream flow process these two parts of the total energy transport can be separated and evaluated. This is done most conveniently by defining the system in this case as a fixed mass enclosed by moveable boundaries which are not penetrated by mass at all. In this manner a small contiguous quantity of fluid in an entering conduit becomes a homogeneous sub-region within the system and its energy thus becomes a part of the total internal energy of the entire system. The boundary of this sub-region is acted upon by an external pressure which performs work on the entire system in moving the boundary of the sub-region. When the system is defined in this way, no energy is carried into the system in the form of the internal energy of mass crossing its boundaries.

In a region receiving mass transported by a diffusion process, part of the energy

content of all molecules outside the region is used to propel some of them into the region. In contrast to the situation in a purely bulk stream flow process, there is no way in this case to define a system which excludes the internal energy of transported molecules from the energy crossing the system boundary. There is no way to define a system in which the propelling forces which induce the mass transport are a driving force for all of the energy which crosses the system boundary in the transport process. The diffusion processes these propelling forces result from the behavior of individual molecules and are not scalar thermodynamic properties at all so that we cannot define an intensive thermodynamic driving force property to represent them.

15a   The Chemical Potential

For processes involving diffusion mass transport we can, however, define a thermodynamic intensive driving force responsible specifically for the <u>total</u> energy change accompanying the diffusion mass transfer of molecules from one region to another. This driving force can be defined simply as a partial derivative representing the variation of the total internal energy of a region with respect to an increment in the number of moles of one particular species in the region when no other extensive properties are altered. This partial derivative is an important intensive property called the chemical potential. By reason of its definition the chemical potential is an intensive property because whenever it is multiplied by the extensive property change in moles of a particular molecular species within a system the result is identically the internal energy change of the system resulting only from this change in moles, and not from the change in any other extensive property.

In elementary physics the energy per unit mass, per mole, or per particle involved in moving the mass, mole, or particle from one region to another is generally defined as a potential. Table I lists several types of potentials (driving forces) which are important in thermodynamic applications. A potential therefore can always be regarded as a driving force for a mass change. The chemical potential is a driving force of this type. Physically the driving force represented by the chemical potential results from the same molecular actions which give rise to a partial vapor pressure in a liquid or a partial pressure in a gas. Each of these has the ability to expel molecules of a given type out of a multi-component phase.

The energy change within a system accompanying a change in the number of moles of a given component of the system by molecular processes can now be defined as a type of work which results from a difference in a chemical potential driving force between the

system and its surroundings. As is the case of other types of work, in order to evaluate quantitatively the work of a chemical potential driving force it is first necessary to define a system. In accordance with the principles discussed in section 14, this work is then defined as the product of a chemical potential of a component outside the system on its external boundary and a change in the number of moles of this component inside the system. When the number of moles of a molecular species increases in a system, work must be done on the system to overcome the molecular forces tending to expel molecules of this species. Consequently, in accordance with the sign convention, the work relative to the system receiving this increase in moles within it must be a negative number.

Although we have discussed the chemical potential as a thermodynamic driving force for the diffusion mass transport, its utility is not confined to this particular process alone. Because of its definition the chemical potential is a driving force for changes in moles of a molecular species in a system not only by means of diffusion mass transfer but by any other molecular process as well. The most important example is the role of the chemical potential within a system as the driving force for changes in moles brought about in the system by chemical reactions.

16   The Total Energy Transfer

Because thermodynamic systems are conventionally defined so that no bulk quantities of matter are transported across their boundaries by stream flow, no energy crosses the system boundary in the form of internal energy carried by a flowing fluid. With the system defined in this way the only energy to cross its boundary because of the flow process is that of work measured by the product of the pressure external to a fixed mass system in a stream conduit and the volume change it induces in this system. In the case of diffusion mass transport, as discussed in section 15, the system does not have a fixed mass but the entire change associated with the diffusion mass transport is given by work evaluated by computing the product of an external chemical potential and a specific transported mass change within the system. As a result the combination of heat, work, and any energy transport by non-thermodynamic carriers includes all the energy in transition between a system and its surroundings. Energy by non-thermodynamic carriers is that transported by radiant heat transfer, X-rays, gamma radiation, nuclear particles, cosmic rays, sonic vibration, etc. Energy of this type is not usually considered as either heat or work and must be evaluated separately in system where it is involved. Energy transport by

nuclear particles into a system ultimately appears as an increase in thermal energy within the system and is important in thermodynamic applications to nuclear engineering.

In every application of thermodynamics, however, it is essential that we account for all the energy in transition across the system boundary and it is only when this is done that the laws of thermodynamics can relate this transported energy to changes in properties within the system. In the processes we will discuss, heat and work together include all the transported energy.

17   The Second Law and Molecular Behavior

At the present time we are familiar enough with molecules to formulate the Second Law entirely in relation to an intuitive perception of their behavior. It is easy to see that the Second Law, as expressed in terms of heat flow in section 11, could be violated with some cooperation from molecules.

Consider two systems each consisting of a fixed quantity of gas. At the boundary of each system are rigid, impenetrable, and well insulated walls except for a metal plate made of a good thermal conductor and located between the systems as shown in Figure 1. The gas in one system is at a low temperature T_1 and in the other at a higher temperature T_2. In terms of molecular behavior the
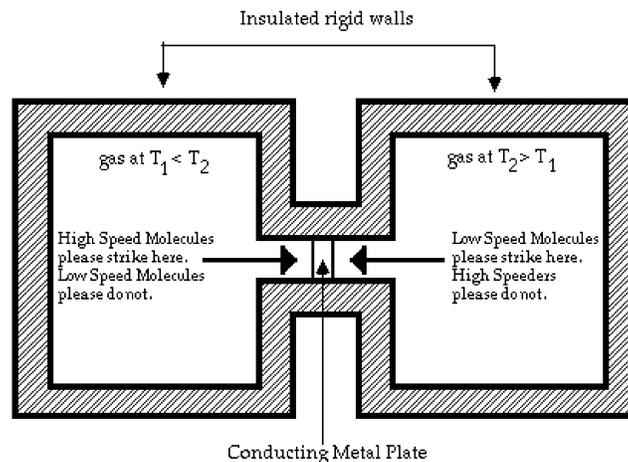

Figure 1: Violation of the Second Law by Molecular Cooperation

temperature difference is produced by different distributions of molecules among the velocities in the molecular states of each system. The number of different velocities, however, is so large that the high temperature system contains some molecules with lower

speeds than some molecules in the low temperature system and vice versa.

Now suppose we prepare some instructions for the molecules in each system as shown on the signs in Figure 1. When following these instructions, only the high speed molecules in the low temperature gas collide with molecules on the surface of the plate, give up energy to them, and thus create on this surface a higher temperature than in the gas. The boundary between the gas and the plate then has a temperature difference across it and, according to our definition, the energy thus transported is heat. In the plate this becomes thermal energy which is conducted through it because the molecules on its other surface are at a lower temperature as a consequence of their energy exchanges only with the low speed molecules in the adjacent high temperature gas system. This constitutes likewise a heat flow into this system. The overall result is then the continuous unaided transfer of heat from a low temperature region to one at a higher temperature, clearly the wrong direction and a Second Law violation. The Second Law therefore, is related to the fact that in completely isolated systems molecules will never of their own accord obey any sort of instructions such as these.

18   Microstates in Isolated Systems

To explain why molecules always behave as though instructions of this type are completely ignored, imagine that we have a fantastic camera capable of making a multidimensional picture which could show at any instant where all the ultimate particles in the system are located and reveal every type of motion taking place, indicating its location, speed, and direction. Every type of distinguishably different action at any moment, the vibration, twisting, or stretching within molecules as well as their translational and rotational movements, would be identified in this manner for every molecule in the system. This picture would thus be a photograph of what we have defined as an instantaneous microstate of the system.

Now, instead of the instructions on the signs in Figure I, suppose we ask the molecules to do everything they can do by themselves in a rigid walled and isolated container where no external arranging or directing operations are possible. We will say, "Molecules, please begin now and arrange yourselves in a sequence of poses for pictures which will show every possible microstate which can exist in your system under the restrictions imposed by your own nature and the conditions of isolation in the container". If we expressed these restrictions as a list of rules to be followed in assigning molecules to

various positions and motions, the list would appear as follows:

1. *In distributing yourselves among the various positions and motions for each microstate picture, do not violate any energy conservation laws. Consequently, because you are in an isolated system the sum of all your individual translational, vibrational, and rotational kinetic energies plus all your intermolecular potential energies must always be the same and equal to the fixed total internal energy of the system.*

2. *Likewise, do not violate any mass conservation laws. There are to be no chemical reactions among you so that the total number of individual molecules assigned must always remain the same.*

3. *All of you must, of course, remain at all times within the container so the total volume in which you distribute yourselves must be constant.*

4. *Do not violate any laws of physics applicable to your particular molecular species. You must remember that no two of you can have all of your microstate position and motion characteristics exactly the same otherwise you would have to occupy the same space at the same time. Furthermore, do not be concerned that there might not be enough different microstates available for each of you to have a different one. Although you are numerous, the number of different possible position and motion values is even more numerous, so that there will never be enough of you to fill all of them and many possible values will be left unoccupied by a molecule in each picture for which you pose.*

19   Distinguishable and Indistinguishable Microstates

With these rules explained, the molecules then arrange themselves for their first microstate picture. Immediately, however, a question arises. The molecules could express this best by saying: "You asked us to show you every different way we could assign ourselves to all possible positions and motions, but there are billions and billions of us which are exactly alike and there is no way that you or your camera can distinguish one individual from another. Also, we are such a disorderly group that you won't be able to identify anyone by observing where he came from. As a result, we could make the very same pose for you again and again by rotating different individuals of the same species among the same particular set of positions and motions of a given overall microstate. If you photographed all of these you would have an enormous number of pictures all exactly alike. Do you want all of these?"

This requires some careful consideration. The reason we want the microstate pictures is to be able to explain the thermodynamic properties and behavior of the group. Any

molecules which have the same mass, size, shape, and the same interaction potential with their neighbors can be individually rotated among the same sets of positions and motions with no change at all in the total energy, volume, or total number of molecules. However, other thermodynamic properties may be affected by this procedure depending on whether or not any of these molecules are in some way distinguishable among themselves. For example, suppose that in one of the containers half the molecules were isotopes of the other half, or were painted a different color, or had some other feature which distinguished them, but otherwise did not alter their identical individual properties and interactions. In this case, one of the thermodynamic properties, the change in the Helmholtz free energy measures the minimum work needed to make an isothermal separation of the molecules of each kind from an initially homogeneous mixture into two subregions of the container. If the molecules are distinguishable, this work exists and a change in Helmholtz free energy occurs. However, if they are not, then every arrangement of them is, according to all possible detection methods, at all times both separated to any degree and also simultaneously mixed to any degree. Consequently there is no work involved in obtaining any degree of separation or mixing and therefore no change in Helmholtz free energy as the molecules are interchanged with each other.

We also note that, since no two molecules can have exactly the same position and motion, the number of permutations of an allowable assignment of N molecules to the same set of positions and motions in a particular molecular state is N! and this number is the same for all other microstates. Consequently no one microstate is given a greater number of ways of being produced than any other merely by permutation of the individual molecules among their assignments. For indistinguishable molecules then, in collecting all possible microstate pictures we shall omit all the duplicates caused by these permutations and consider them as one single state.

20   *Localized and Non-Localized Systems*

The creation of distinguishable microstates when different individuals are assigned to the same positions and motions does not necessarily depend upon the existence of some isotopic difference among them. These assignments can be distinguishable in some cases even when the molecules themselves are identical in every respect. This occurs in a well ordered system such as a crystalline solid where positions in the microstate can be located relative to a superimposed coordinate grid lattice. The assignment patterns made by

rearranging individuals in the same microstate then become distinguishable if one can locate each molecule relative to a particular lattice point. Even if some molecules are moved an appreciable distance from their reference points, the overall assignments created can be distinguished if one can always tell where the displaced molecules came from in the coordinate grid.

In this case all N! permutations of N molecules in the same set of positions and motions are each separate microstates. States which are distinguishable in this fashion are said to belong to a "localized" system. Obviously, this type of distinguishability will be quickly lost if there is even a small amount of disorder in the system. In a gas, where no lattice points of any kind could locate molecules, the term "non-localized" is used to describe the system.

When these concepts are developed quantitatively, we will show that the presence of the N! permutations in localized systems influences only the entropy and those properties, such as the Gibbs and Helmholtz free energies, which change directly with it. Other thermodynamic properties are not affected.

21   The Number of Distinguishable Microstates

Now that it is clearly understood that as a nonlocalized system only one assignment of individual molecules to each set of positions and motions is needed, the molecules then continue to pose for pictures of every distinguishable microstate possible in a rigid walled isolated system. We might at first worry that there could be an infinitely large number of these so that we would never see them all, but as a consequence of an important principle in physics, this number is finite although enormously large.

Because of the uncertainty principle there is a lower limit to the variations which can be detected between any two microstates, even when our camera is capable of the maximum possible resolution. This minimum arises because the product of the smallest difference in a position coordinate of a molecule and the smallest difference in a coordinate representing one of its momentum components forms a tiny area which represents the smallest detectable different detail which can distinguish a microstate from the one it most nearly resembles. This small area lies in a two-dimensional slice of the multi-dimensional picture of all the position and momentum coordinates for all the molecules in the system. According to our camera with the highest possible resolution, two such microstate pictures show no detectable difference unless one coordinate of a molecule's position and one

coordinate of its momentum are altered enough to shift its microstate just outside this small area. Because this area is not zero but a small number, equal to Planck's constant, the difference between any two microstates cannot be made as small as we please. This means that there are then a finite number of different microstates for a system with a fixed total energy, volume, and number of molecules.[4] Thus cheered by the fact that there is indeed an end to the process, we continue until we have photographed all possible different microstates which accompany the assigned total internal energy, volume, and number of molecules in the system.[5] We then count the number of these states and represent it by the symbol Ω.

22   Probability and The Second Law

This total number of distinguishable microstates reveals a great deal about the Second Law and can explain why the instructions in Figure 1, leading to the backward heat transfer, are never obeyed. We recall that each microstate which we counted represents an assignment to positions and motions in accordance with all the restrictions imposed by the nature of the molecules themselves and those imposed by the isolated container, which we listed in section 18. Consequently, there are no remaining factors which could cause any one of these states to be preferred over another and each one is just as likely to occur. We describe this situation by saying that each of these microstates is equally probable.

In determining this number Ω of equally probable microstates we have established an important relationship between molecular properties and thermodynamic properties. The boundary conditions of rigid walls and isolation for this system specify a particular value

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[4]It is remarkable that J. Willard Gibbs, long before the era of modern physics and the uncertainty principle, anticipated that this number is finite. (J.W. Gibbs, "Collected Works," Vol. 2, p. 1, New York, NY: Dover Publication, Inc., 1961.)
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[5]It turns out that this might take a fairly long time. Even with no delays between pictures, if a mole of a perfect gas changed poses with the average molecular velocity corresponding to conditions of one atmosphere and room temperature, we would need a time eons longer than the age of the universe! Fortunately, in a thought experiment, this is only a minor technical detail.

for the total internal energy, a fixed volume, and a constant number of molecules in the multi-molecular system. Consequently this large number of all the equally probable microstates represents the total number of ways the system can produce this value of its internal energy and density, each of which are measurable thermodynamic properties.

It is easy to see why this number of microstates is so large. Because energy is a scalar quantity it depends only on the speed of the molecules and not on their vector directions. This means that the energy of an individual molecule can be produced by a great many different microstates for it. Furthermore, there are an even greater number of ways in which different numbers of molecules can be assigned to the individual energy values which produced the total energy of the multi-molecular system.

We can now compute the probability of any specified behavior in this system which depends on the cooperation of a group of molecules within it while maintaining the same overall system boundary conditions. Since all microstates in this system are equally probable, the number of these which produce the given behavior represents the number of ways in which this behavior can occur. The probability for the behavior is obtained when this number is divided by the total number of all possible ways the system can satisfy its boundary conditions, or the total number of all microstates possible.

If we make this computation for the behavior needed to follow the instructions in Figure 1, we will find out why they are never obeyed. Following these instructions means that only highly restricted microstates can be allowed. A number of possible motion vectors near the plate must not be occupied by a molecule during the time the instructions are in force. It is not that such restricted states never exist. Within the huge collection of all the microstate photographs a sequence which will produce this behavior can surely be found because it is possible for each of them to satisfy the overall system boundary conditions and all the microstates which do so are equally probable. However, the number of microstates which permit obedience to these instructions are insignificant in comparison with the vast number of other equally probably states which do not. The probability of behavior obedient to the instructions is obtained when we divide the relatively small number of properly restricted states by the astronomically immense number of all possible microstates which meet the system's boundary conditions. The result is vanishingly small.

A formulation of the Second Law can now be made in terms of the number of equally probable microstates in the isolated system. As in the previous discussion of this law in section 11, this likewise is an identification of the proper direction for a change. Whereas the previous statements were in terms of the direction of the transfer of a quantity in

response to a specified imbalance in its driving force, this statement concerns the direction of the change in the number of microstates which produce a change in a thermodynamic state of an isolated system. In these terms the Second Law would be stated:

A change in the thermodynamic state of an isolated, rigidly bounded system can occur only if there is an increase in the number of equally probable microstates in the system. In fact, we could completely generalize the Second Law in these probability terms by saying:

In any totally isolated group whose properties result from equally probable actions of many individual things, any change in the state of the group must result in group properties which the individual things can produce in a greater number of ways.

23   Concepts of Order and Disorder

Although these statements of the Second Law in section 22are abstract in their formulation, we apprehend them through ordinary observations. Our intuitive perception of an increase in the number of ways that individual members of an isolated group generate the behavior of the entire group is a recognition of the effect of this increase on the degree of order within the group. There are many more ways of arranging individual things to produce a haphazard or disorderly group than there are ways in which some orderly pattern can be detected. The Second Law then implies that any change occurring in an overall characteristic of an isolated group will always be from an orderly state of the group to a disorderly one, simply because change favors those events which can take place in a greater number of ways.

A simple illustration of this is obtained by filling a transparent box with a layer of white sand and then pouring an equally thick layer of black sand, with identical grain size, on top of the white layer. Then we close the box and shake it in a random fashion which will not give any preferred arrangement to the sand particles. What happens is a demonstration of the Second Law in action.

The well ordered state with which we begin is well ordered because it exists only when there are limitations on the ways in which the individual sand grains can be arranged in the box. Grains of the same color are restricted to position coordinates in only one part of the box. With shaking a more disorderly color pattern occurs. The restrictions on particle location are no longer present in a mixed color state and either color can be anywhere in the box. Consequently there are many more particle arrangements leading to the more

disordered color state and it has a higher probability of appearing. On the other hand, we do not expect the reverse process to occur. We cannot start with mixed up sand and separate the two colors by random shaking, not because it is impossible, but because its probability is negligibly small in comparison with that of producing an even more mixed up state.

This exact same reasoning applies to the gas molecules in Figure 1, microstates capable of causing the overall behavior which does what the signs request are more orderly than those which have no restrictions on the kinds of velocities found near the plate. With continued molecular motion these orderly states vanish in favor of more disorderly ones without these restrictions because the number of them is so much greater.

24   *Equilibrium States*

An important characteristic of a continued growth of disorder in an isolated system, is that eventually it becomes so great that no further change toward disorder can be detected. With continued shaking of the box containing the separated layers of white and black sand the mixing eventually becomes so thorough that no further change can be observed, regardless of the length of time the box is shaken.

Consider a system consisting of a long gas-filled cylinder which is initially heated at the bottom only and then isolated to prevent further heat transfer. If thermocouples were located at various positions in the gas, one could for a time measure different temperatures at each location. Gradually, however, this difference would diminish until eventually no further change could be detected, no matter how much additional time elapsed.

In each of these examples the disorder has increased to a maximum. As we have discussed, the growth of disorder means a growth in the number of microstates in the gas or in the sand so that when the disorder is a maximum these numbers likewise must be at a maximum. This condition in each case is defined as an equilibrium state of the system involved. Because there is no tendency for further change there are no unbalanced driving forces within an equilibrium state so that all equilibrium states free of the effects of external fields consist only of homogeneous regions, either one such region comprising the entire system or separate phases, each homogeneous within themselves. The expression "no unbalanced driving forces" as a description of an equilibrium state frequently means that all driving forces are equal through out the system. However, this is not always the case. The balance in driving forces necessary for an equilibrium state can also occur when two or more driving forces have unequal values in different parts of the system but the change

induced by one driving force inequality is exactly reversed by another so that no net change takes place.

The concept of an equilibrium state is an important one in thermodynamics and it is necessary to develop analytical methods of describing it. These methods always involve maximization of the number of microstates in an isolated system where total energy, volume, and number of particles are all constant. The same condition which accompanies this maximum, however, can exist in systems which are not isolated.

25 Entropy and the Second Law

The particle or molecular behavior which we have described in section 23 as a growth of disorder in an isolated system is qualitatively indistinguishable from the molecular behavior which accompanies an increase in what we have called thermal energy in a system. As we have explained in section 12, thermal energy can be increased in a system in several ways in addition to the direct transfer of heat into the system.

As we have already discussed in section 13, the extensive property which increases with an increase in thermal energy is the entropy. We have shown also that this entropy increase is physically manifested by an increase in the number of equally probable microstates with which the system can satisfy its boundary conditions of isolation. Consequently, there must be a relationship between the entropy increase and the increase in the number of these microstates. This relationship provides a fundamental link between molecular behavior and thermodynamic properties.

The nature of this relationship can be revealed by examining the connection between the number of microstates in a system and the behavior of entropy as an extensive property. For example, suppose that we perform the test we described to detect the existence of an extensive property. In this test we will consider two systems completely alike in every respect so that one system is an exact replica of the other. If the entropy of each system is S, then because entropy is an extensive property, the entropy of a larger system formed by a combination of the two must be S + S = 2S.

The number of microstates however, does not combine in this manner. If Ω represents the total number of all possible microstates in each system before their combination, then the number for the larger combined system is $\Omega \bullet \Omega = \Omega^2$. This is because in counting the number of ways of assigning ultimate particles to position and momentum values for the combined systems we must arrange one system in one of its

microstates and note that there are then Ω microstates in which we can arrange the identical molecules of the other. For the next microstate of the first system there are again Ω microstates for the other which can accompany it, and so on until the first system has been arranged in all of its possible microstates. The total number in the combined system is then obtained when all Ω microstates of the first system have each been multiplied by Ω microstates of the other so that this total number is then the product of the Ω values.

Because of this different behavior for S and Ω, the only way that an increase in entropy can be related to an increase in microstates is for the entropy to be proportional to the logarithm of the number of microstates. In this way the increases in both S and Ω will be described correctly when these increases are produced by altering only the size of the system.

The constant of proportionality can be obtained from any system for which both S and Ω can be calculated. The simplest system for which this can be done is that of a perfect gas and the proportionality constant is found to be the universal gas constant divided by Avogadro's number, a quantity known as Boltzmann's constant.

In this manner the most basic link between molecular behavior and thermodynamic properties is established by the Boltzmann equation:

$$S = k \ln \Omega \ (U,V,N) \tag{1}$$

where S is the entropy, k is Boltzmann's constant, and Ω is the number of equally probable microstates in an isolated system with a fixed total energy U, a fixed volume V, and a fixed total number of particles N.

This relationship means that the Second Law, which we stated in terms of an increase in microstates, can be expressed equally well in terms of an entropy increase. In this manner the Second Law is stated:

Any change in the thermodynamic state of an isolated, rigidly bounded system must be accompanied by an increase in the entropy of the system.

26   *Entropy and Equilibrium State*

Because of Equation 1 the definition of an equilibrium state, given in section 24 in

terms of a maximization of the number of equally probable microstates in an isolated system, can also be expressed in terms of entropy. When the entropy of an isolated system, increasing in accordance with the Second Law, has attained a maximum value, the system is then in an equilibrium state. In this condition there are no longer any detectable sequential changes and all driving forces tending to produce a displacement in one direction are opposed by equal driving forces tending to cause a displacement in the opposite direction.

The description of the approach to an attainment of an equilibrium state is especially important in that it provides a general unifying principle for an extremely wide range of very different physical phenomena. Because the entropy of a system can be calculated analytically from experimentally measurable properties and its maximization in an isolated system can be expressed mathematically, it is possible to obtain quantitative answers to questions of the following type:

In what directions do the various properties of a system change during the approach to equilibrium under various conditions? What are the properties of a system after an equilibrium state has been attained? What variations can be allowed in system properties in order to keep the system always in some equilibrium state? How do the phases change in a multi-phase system during its approach to an equilibrium state?

The distribution of various constituents within an equilibrium system can be determined for a wide variety of different conditions. One can determine equilibrium distributions of:

(a)   various ions between regions differing in electrical potential

(b)   different molecules between reactants and products when chemical reactions take place

(c)   concentrations and other properties between a surface and the bulk interior of a system when surface forces are important

(d)   molecular species in a gravitational or a centrifugal field

(e)   molecular species between different phases

These are examples of some of the very diverse physical situations for which quantitative information can be obtained with the Second Law and the equilibrium concept.

27   *Partial and Complete Equilibrium States*

During the approach to an equilibrium state in many systems, changes in some

properties take place rapidly while others occur much more slowly and it is a common occurrence that a balance is achieved among some thermodynamic driving forces long before it is for others. These remaining unbalanced driving forces may continue to make changes but at a much slower rate. As discussed in section 24, the expression "balance among thermodynamic driving forces" when used to describe equilibrium states refers not necessarily to a condition of uniformity of each driving force throughout the system but to a distribution of driving force values which produces no net changes in the system.

In an isolated system, if one were to make entropy calculations by ignoring these slower changes and their driving forces, it is possible to define a partial equilibrium state which exists when the entropy calculated in this manner reaches a maximum.

The type of partial equilibrium with which we will be concerned occurs when a system attains a state in which it is composed of one or more homogeneous regions. All driving forces resulting from differing values of intensive properties at various locations within any one of these regions have been balanced. However, there may be unbalanced driving forces in the system which can produce further change but do not destroy the regional homogeneity.

An important example of such a partial equilibrium is a system containing homogeneous regions composed of chemically reacting constituents. While chemical reactions are taking place the system can exist in one or more bulk phases which, within detectable limits, remain individually homogeneous. All driving forces tending to create inhomogenieties are balanced but not those changing chemically reactant species into products. Eventually a complete equilibrium may be achieved for the entire system in which driving forces forming the products are balanced by those which reconvert them into the reactants so that no net chemical reaction remains.

Another common example is a system composed of two bulk multi-component phases approaching an equilibrium distribution of various components between them. Outside a small interfacial region, each phase may be regarded as existing always in a homogeneous condition during the process as a consequence of a partial equilibrium state for the system. The complete equilibrium state is attained when there is no unbalanced transfer between phases and no net change.

Partial equilibrium states like these are important because the only systems whose property changes can be described by thermodynamic methods are those which have attained at least a partial equilibrium to insure that the systems consist of one or more homogeneous regions. It is only for these regions that intensive thermodynamic properties can be either

defined in terms of molecular properties, measured experimentally, or predicted by application of thermodynamic procedures. Without the existence of the homogeneity of a partial equilibrium, the microstate driving forces which we defined in section 5 act with directional preferences and produce changes in ordered directions. All thermodynamic intensive properties, however, must be nondirectional scalars resulting from the collective behavior of randomly oriented microstate driving forces. This complete disorder exists only if a system has attained at least the partial equilibrium resulting in homogeneous regions and it is only for these regions that intensive thermodynamic properties can be defined.

In contrast to the situation in regard to intensive properties, all the extensive properties of a system can always be defined in terms of microstate properties regardless of whether a homogeneous equilibrium state exists or not. Furthermore since these extensive properties are additive quantities, their changes in a system not at equilibrium can be determined experimentally by measuring quantities in the surroundings added to the system or received from it. In principle the entropy of a non-equilibrium system can be defined in terms of microstate properties from Equation (1) by deleting from the maximum Ω at a fixed U, V, N the number of configurations which must be excluded to create any desired degree of order in the system. Although this can be expressed in the form of a definition, its numerical evaluation in an actual inhomogeneous system is not usually possible. Analytically manageable relations between entropy and microstate properties depend solely on the maximization of Ω at a constant U,V, N and this requires at least a partial equilibrium state. In this manner the existence of this type of partial equilibrium is important to the prediction of extensive thermodynamic properties by statistical thermodynamics as it is essential to the very existence of the intensive thermodynamic properties.

28   *Misapplication of The Second Law*

Despite the simplicity of the statement in section 25 description of characteristic blunders which are frequently made in applying it is helpful. Although it is probably poor pedagogical technique to discuss how not to apply thermodynamics, these blunders illustrate some important aspects of the Second Law.

Perhaps the most common error is a failure to recognize that the principle of increasing entropy in a region applies only when that region is an <u>isolated</u> system with well-defined rigid boundaries. As an example, the idea has been presented that the evolution

of life on earth in producing highly ordered organisms from simpler life forms is a violation of the Second Law, thereby implying divine intervention or some other non-scientific event for its explanation.[6] However, this is stated without clearly defining an isolated system in which the process could have taken place so that the conclusion is both bad science and bad theology.

Another example of this mistake is to state the Second Law as "The entropy of the universe is always increasing toward a maximum", when one interprets the word "universe" in the cosmological sense. In the equilibrium state of maximized entropy there are no unbalanced driving forces and hence no net changes. Disorder is so complete that there are no detectable events, thus no net changes. Distinguishable past, present, or future from the Second Law is indeed risky since the "universe" in this sense hardly qualifies as a system, with well-defined boundaries. Furthermore, the only reason for unqualified confidence in the Second Law is that no one has ever detected an exception to it. Our experience however is limited to terrestrial systems with much more modest dimensions.

It is indeed possible, and necessary, to describe equilibrium conditions in a non-isolated system, but the description is obtained by making this non-isolated system always a part of and surrounded by a larger system which is totally isolated but with specified forms of energy exchange with the enclosed system.

The second characteristic blunder in applying the Second Law is a failure to recognize that the entropy which increases in an isolated system is the <u>total</u> entropy of the system and not necessarily the entropy of each smaller part of it. During the approach to equilibrium in an isolated system the Second Law in no way prevents a temporary entropy decrease accompanied by the creation of order in one part of the system which is off-set by an entropy increase in some other part so that the total always increases. It is correct to use the Second Law to rule out processes in which this occurs.

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[6]Le Comte Du Nouy, "Human Destiny", p. 40, New York, NY: Longmans, Green and Co., 1947.