

AN INTRODUCTION TO EQUILIBRIUM THERMODYNAMICS

A Rational Approach to Its Teaching

PART 2: Internal Energy, Entropy, and Temperature¹

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In Part 1 of this paper, we introduced notation for functions and their derivatives, and through using this notation, we formulated a purely mathematical background, based on the properties of functions. We shall now show an approach that may be used to introduce the fundamental ideas of thermodynamics.

We start by explaining to the students that the purpose of thermodynamics is to enable us to correlate and predict the behavior of real systems containing matter. In doing this, we shall use the mathematical background which was formulated in Part 1, together with a knowledge of the behavior of matter (which is studied in such subjects as physics and applied mathematics).

Additionally, we will need to make some basic

assumptions or axioms, which we have labeled below as "postulates." There can be no *a priori* justification or "proof" of such postulates, and some of them may seem at the time to be rather peculiar. The only reason for using these assumptions rather than others is that the equations which result seem, from experience, to be useful in our stated purpose of predicting the behavior of matter-containing systems.

This state of affairs is similar to the exposition of Euclidean geometry, where we first had to accept a number of axioms (such as "parallel lines never meet," and "vertically opposite angles are equal"). We could then develop a succession of theorems (many of which have results which now seem second nature to us) which have proved to be useful in many areas of the science of measurement. Alternative sets of axioms (such as, for example, "parallel lines *do* meet") lead to the development of alternative (non-Euclidean) geometries, some of which are, in fact, found to have uses in other areas.

Physical Background

We should agree, before we begin, that we have an understanding from physics of the concepts of *length, time, and mass*, to which we shall add the chemical concept of the measurement of amount of material in number of *moles* rather than mass.

The concept of length extends readily to give us *area* and *volume*. Combined with time, it gives us the concepts of *velocity* and *acceleration*. From mass and acceleration (or from momentum, obtainable from mass and velocity) we may obtain the concept of *force*. From force and area we obtain *pressure*, and from force and length we obtain *work*. We therefore assume that we have a common agreed-upon understanding of these ideas, which we shall not bother to



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define more fully at this point.

We shall need to consider a number of "thought experiments" involving these concepts. Some of these we could actually perform; others are somewhat idealized, so that it might be difficult to set them up exactly in practice. But we should have no difficulty in envisaging the outcome of these procedures. In some of them we shall need the concept of *temperature*. It is more difficult to agree upon an exact quantitative definition of temperature at this point, but we should be able to agree that we have common concepts of "hotter" (= higher temperature) and "colder" (= lower temperature).

Conservation of Energy

Our basic primary axiom is that energy is conserved. We can no more prove this than we can any of the other postulates which we shall make below, although we may perhaps take comfort in the successful description of the behavior of matter in the vast amount of science (in addition to thermodynamics) which has as its basis the Principle of Conservation of Energy.

We now need to develop a quantitative mathematical expression of this principle. We might start by saying that if energy is conserved, the energy of a body or system in state 2 must be the same as it was in state 1, which we might express as

$$E_1 = E_2 \quad (42)$$

Now, what terms go to make up the energy E ? If we consider experiments which we might make with falling stones or moving projectiles, experiment would lead us to conclude (in an idealized situation) that the energy of these bodies was made up of the sum of the two separately identifiable forms of energy which we call kinetic and potential energies. Thus, we could re-write Eq. (42) as

$$E_{K1} + E_{P1} = E_{K2} + E_{P2} \quad (43a)$$

or

$$\Delta E_K + \Delta E_P = 0 \quad (43b)$$

where we are assuming the usual definitions that $E_K = \frac{1}{2}mv^2$ and $E_P = mgh$.

Consideration of the state of affairs when we raise our stones by hand (increasing their E_P without changing E_K) or proceed to throw them (increasing their E_K without decreasing E_P) shows that this formulation is inadequate. We need to invent a concept of the transfer of energy *to* the body (or system) under consideration from an external source. Giving this concept the symbol w , we may extend Eq. (43b) to

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$$\Delta E_K + \Delta E_P = w \quad (44)$$

(Of course, the Principle of Conservation of Energy still applies overall since the corresponding equation for our hand or other source of the energy term w will be $\Delta E - w = 0$.) We find that Eq. (44) is now an adequate description of these cases if we use a w value calculated from

$$w = \int \mathbf{f} \cdot d\mathbf{x} \quad (45)$$

(where \mathbf{f} is the force applied over distance \mathbf{x}). We may thus identify w with our prior concept of *work*.

But now consider what happens when our flying objects hit the ground, or an immovable wall, losing their E_K and E_P without any w being apparent. We are forced either to abandon the Principle of Conservation of Energy, or (noting in passing that bodies in such situations are observed to get hotter) to conclude that the energy which is "missing" from the terms of Eq. (44) must still be present in another form. We invent the concept of "energy of state" or "internal energy" to account for this energy. Giving this new concept the symbol U and extending Eq. (44) to account for it, we obtain

$$\Delta E_K + \Delta E_P + \Delta U = w \quad (46)$$

We shall not continue the argument further at this point, but will merely note that further additions to the left-hand side of Eq. (45) may be necessary in situations where energy is present in forms which we have not accounted for. Terms such as magnetic, electrostatic, or surface energies may need to be introduced (or these may be regarded as an extension of the concept of potential energy).

We find by experiment that if we put a fixed amount of some specific material (such as oxygen gas) into a well-insulated enclosure, we can totally define the properties of the material if we know two of the variables, such as the values of the pressure and volume. That is, whatever happened before, if we know the "state of the system" (*i.e.*, the values of the pressure and volume), then we know that the values of other variables (such as density, refractive index, and thermal conductivity) will be uniquely determined. In other words, we know that these

other variables are a function of pressure and (specific) volume only.

It turns out in practice that not all pairs of variables are equally good for *uniquely* determining the state of the system. For example, pressure and volume will not uniquely determine the state of liquid water close to 4°C, where the density goes through a maximum. Thus, our postulates will later be made in terms of specific pairs of variables which do not have such problems associated with them.

Now consider an experiment such as the one shown in Figure 1a. Material contained in a well-insulated enclosure may be agitated by the stirrer or acted upon by the piston. The movements of the piston and the stirrer shaft both involve work which we may measure in terms of our accepted concepts of force-times-distance (or the straightforward extension to torque-times-rotation). The pressure and volume of the material in the container are also measurable quantities.

Now consider the changes in P and V which we may obtain in this apparatus. (For this purpose it may be easier to first consider the contents to be a gas—but similar, more complex, apparatus could at least be envisaged for other materials.) By pushing or pulling on the piston we may change the P and V of our gas along curved lines such as those shown in Figure 1b. (If we had an ideal gas, these would be the lines $PV^\gamma = \text{constant}$.) By rotating the stirrer with the piston held fixed, we find that we increase the temperature, and hence the pressure, at a fixed volume.

By utilizing suitable portions of such paths, we find that not only can we move (in one direction, anyway) between any pair of points, but we can also, in fact, do so by a variety of different paths. Figure 1b shows two of the infinitely many paths from point 1 to point 2. For each path, we may measure the sum of the work done by the stirrer and the piston. We find that, for fixed final and initial points, the total work required is a constant, irrespective of the path taken.

Now consider the energy conservation equation, Eq. (46). Since there are no changes in the kinetic or potential energies of our stationary apparatus, the equation in this case reduces to

$$\Delta U = w \quad (47)$$

Thus, it appears that our concept of "internal energy" U is a useful one, in that U turns out to be a "state function"; that is, ΔU depends only on the

initial and final states, not on the path. By choosing some arbitrary reference state (say, P_0, V_0) and assigning it a value of U (say, $U_0 = 0$), we may by a suitable experiment measure the value of U at any other (P,V) point. Therefore we need have no further "understanding" of the nature of our quantity U; it is sufficient that we can measure it (and that it will prove in due course to be a useful concept for our purpose).

However, if we perform these experiments in an apparatus that is not well insulated, all our carefully thought-out theory appears to collapse. Indeed, in some cases an apparatus left in state 2 may return to another state without the performance of any work w. Rather than abandon the Principle of Conservation of Energy, we conclude that there must be other ways than work of transferring energy to the system. We give this means of transferring energy the symbol q, and Eq. (46) becomes

$$\Delta E_K + \Delta E_P + \Delta U = w + q \quad (48)$$

We may obtain quantitative values of q from experiments in an apparatus such as the one shown in Figure 2. From experiments performed as in Figure 1, we may obtain the ΔU value for any change. Thus (theoretically at least) we know the dependence of U on P and V, which is the function U^{PV} . The energy balance for experiments conducted as in Figure 2 may be rearranged to give

$$q = \Delta E_K + \Delta E_P + \Delta U - w \quad (49)$$

Experiments (or processes) for which Eq. (46) (or Eq. 47) is an adequate description are termed *adiabatic* processes and need to be surrounded by perfectly insulating or adiabatic surfaces. Those in which it is necessary to allow for the energy transfer term q are said to be *non-adiabatic*, and the surfaces which permit energy to be transported through them

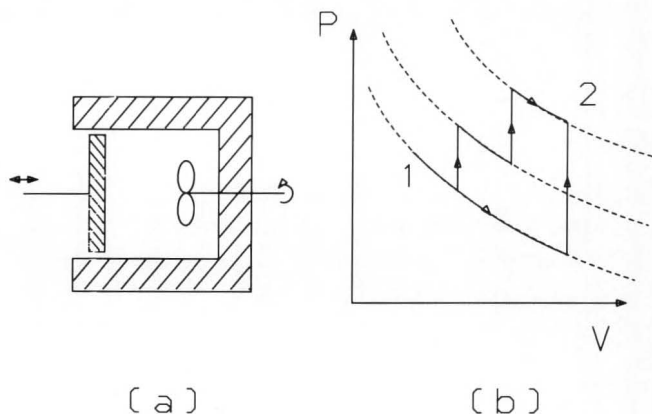


FIGURE 1. System with work terms.

in this fashion are called *diathermal*.

We note from experience that the energy transfer term q occurs when our (non-adiabatic, or un-insulated) system and its surroundings are at different temperatures, and we give q the name *heat*. One should be careful about the fact that heat q is an energy *transfer* mechanism, not a form of energy itself. Once energy has entered a system in this fashion, it is indistinguishable from energy that entered as work. It is incorrect to expect to be able to find the "heat" inside the system. Terms such as "heat content" or "conversion of heat into work" are misleading; they are based upon a misunderstanding of the equivalent roles of heat and work as energy transfer mechanisms. Because of the fact that both q and w refer to energy transfer processes rather than to quantities of some substance (caloric!), it is convenient to emphasize this by calling q "heating" and w "working." This has the advantage of being related to the words used by other authors, but emphasizing the process aspect.

Neither q nor w is, of course, confined to adding energy to the system. Both are also possible ways for energy to leave the system. Thus, if the piston in Figure 1 or 2 moves so as to increase the volume, it actually has work done on it by the contents of the apparatus, the energy of which therefore decreases. We also know that if the non-adiabatic apparatus is hotter than its surroundings, it will lose energy as heat to the surroundings.

If we use different amounts of substance in our experiments in order to determine U^{PV} , we will obtain different relations (or surfaces in U - P - V space). We find, however, that we may reduce these all to one surface by considering not volume V , but *molar volume*, given by $\hat{V} = V/N$, where N is the number of

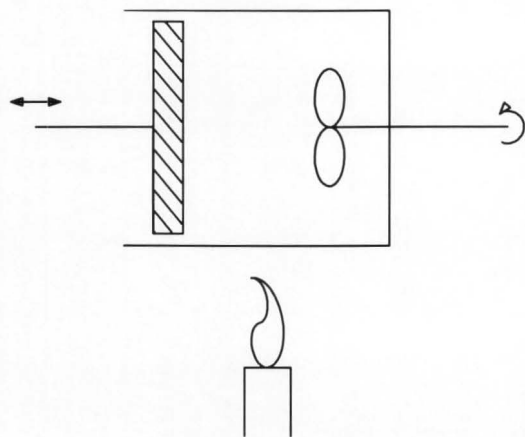


FIGURE 2. Apparatus for measuring q .

moles of material involved. This gives us values of *specific internal energy*, or *molar internal energy*, i.e.

$$\hat{U} = \hat{U}^{PV} \quad (50)$$

We say that U is an *extensive* property, which depends on the amount of material present, while \hat{U} is an *intensive* property, which depends only on the state (or condition) of the matter, not on how much there is.

In Part 1 of this paper, we assumed a function U^{SV} and showed that this leads to Eq. (28)

$$(\Delta U)_1 = \int TdS - \int PdV = Q + W \quad (28)$$

From our experiments, we have now obtained (for processes where $\Delta E_k = \Delta E_p = 0$) the relationship

$$(\Delta U)_2 = q + w \quad (51)$$

Here we have used the subscript 1 to identify the value from the equations of Part 1, and the subscript 2 to identify the physical values from our experiment. The work term w results from the displacement of the point of action of a force, or $w = \int \mathbf{f} \cdot d\mathbf{x}$. Suppose the process under consideration changes under the influence of driving forces which are so small that it is effectively in equilibrium at each stage (such a process is termed *reversible*). It is then easy to show from physical considerations that this (force-times-distance) term may be expressed (in the absence of work terms such as that for the stirrer in Figure 1) as $-\int PdV$.

We now choose to equate $(\Delta U)_1$ and $(\Delta U)_2$; that is, we regard our internal energy U as the function U^{SV} of Part 1. This is in line with our experimental finding that the state of a system depends only on two independent variables. The ones we used before were P and V , but once we have any two we can easily change them to any other two with which there is a monotonic relationship. (The reader need not be disturbed by the fact that we have not yet identified the variable S .) We may choose to identify the V terms of both Part 1 and Part 2. Now consider a series of experiments performed in the apparatus of Figure 1, but *without* using the stirrer to increase the internal energy. As we discussed in the previous paragraph, the work done by (or on) the moving piston is $-\int PdV$. Thus the energy balance becomes

$$(\Delta U)_2 = -\int P_2 dV_2 \quad (52)$$

In these experiments, if dV_2 is zero, it follows that ΔU_2 is zero. From Eq. (28), however, when dV_1 is zero, we have

$$(\Delta U)_1 = -\int T_1 dS_1 \quad (53)$$

It seems then, that whatever S represents is constant during the experiments we are considering, since $(\Delta U)_1$ must be zero as long as V is constant. Thus we have, for these experiments,

$$(\Delta U)_1 = -\int P_1 dV_1 \quad (54)$$

Since we have equated the U and the V terms, Eqs. (52) and (54) will only yield the required results for all possible experiments if the P terms represent the same quantity. We thus identify the variable P which we defined in Eq. (16) by $P = -U^{SV}$ with our physical concept of *pressure*.

It then follows that we may put

$$w = W = -\int PdV \quad (55)$$

and hence

$$q = Q = \int TdS \quad (56)$$

If the process is not at equilibrium at each stage (that is, it is not a reversible process), then $w \neq -\int PdV$. Thus for this type of process, $w \neq W$ and so $q \neq Q$. In practice, we seem to find that

$$w \geq W = -\int PdV \quad (57)$$

so that

$$q \leq Q = \int TdS \quad (58)$$

Predicting the Behavior of a System

Figure 3 shows an example of what we may regard as the basic problem of thermodynamics; if we can find a method for solving problems of this nature, we shall in fact be well on the way to our desired objectives. The diagram shows a container constructed of walls which are

- **rigid** so that the volume of the material which they contain cannot change
- **adiabatic** so that the transfer of energy to the contents of the container by the " q " process is not possible
- **impermeable** so that the material in the container cannot penetrate the walls, nor can additional matter enter through the walls

The container is divided into two sections by a barrier, the material of which is also rigid, adiabatic, and impermeable. The volumes on each side of the divider contain material at specified conditions (nature of the matter, amount of matter, temperature, pressure, etc.). These conditions need not be the same for each side.

We assume that each side of the apparatus is in an *equilibrium state*, by which we mean that there

are no observable macroscopic changes in the state of the matter in the system with time ("observable" using whatever senses or methods of measurement we might apply.) We shall further assume that we are concerned with *simple systems*, which are chemically inert and homogeneous.

The problem which we wish to solve is this: Suppose that one (or more) of the constraints imposed by the barrier is removed. If we remove the rigidity constraint, for example, we allow the barrier to move. Removing the adiabatic constraint permits energy to transfer as q through the barrier while maintaining the other constraints. Removing the impermeability constraint would permit material to pass through the barrier, which would still be rigid and adiabatic. (It is less easy to think of how this might be achieved directly in practice, but that is no reason for not considering the problem.) When any of the constraints are removed, we can see that in general some (at least) of the conditions in the two sections of the apparatus will change. We wish to predict the new equilibrium states that will result.

We know from experiments that if we release the constraints, certain things will happen, but not the reverse. For example, pressure, temperature, and concentrations tend to equalize, while the reverse does not happen. These statements in no way violate anything we have said before, but neither do they give us any information as to which states the system will proceed to at equilibrium. In order to describe these experiments it is necessary to have further postulates. Furthermore, while we have agreed that we have some idea of what constitutes a constant S experiment, we have not really defined either S or T . Thus, what follows addresses the definition of these quantities, and gives us results which are in accordance with our knowledge of the real world.

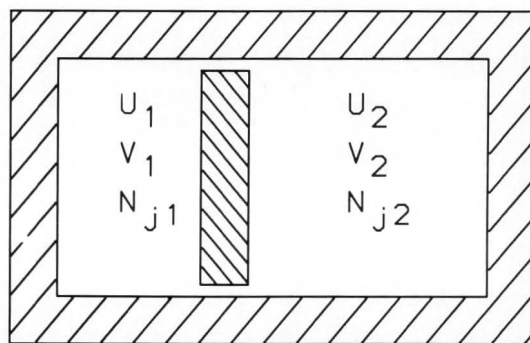


FIGURE 3. Apparatus with internal partition.

Solving the Problem: The Postulates

We shall accept that matter contained in a system in an equilibrium state has an internal energy U , and that this is an extensive property (so that it is proportional to the amount of material present) and an additive property (so that the total internal energy of the apparatus is the sum of the internal energy of the two portions). We shall then make our first postulate:

POSTULATE 1: Equilibrium states are completely characterized by the values of U , V , and N_j —that is, by their internal energy, volume, and number of moles of various materials which they contain.

Note that this is entirely consistent with our experimental knowledge that (for a fixed amount of a given substance) the equilibrium properties are a function of two variables. The two variables that are chosen are a pair which do not give rise to the problems with uniqueness discussed earlier.

We now consider how to predict the state to which our system will move when we relax (as discussed above) one of the internal constraints. Will it, for example, move to the state of lowest energy? This idea might sound attractive; unfortunately, a little further thought shows that the rigid, adiabatic nature of the external walls (which constraints are *not* going to be relaxed) means that both q and w will be zero. Hence $\Delta U = q + w = 0$; that is, the total internal energy of the system is going to remain constant. Thus, this suggestion is not correct. We need some further postulates:

POSTULATE 2: Each equilibrium state of a simple system has a property S , to which we shall give the name *entropy*. This can be modeled mathematically by

$$S = S^{U,V,[N_j]}(U,V,[N_j]) \quad \text{where } S^{U,V,[N_j]} > 0 \quad (59)$$

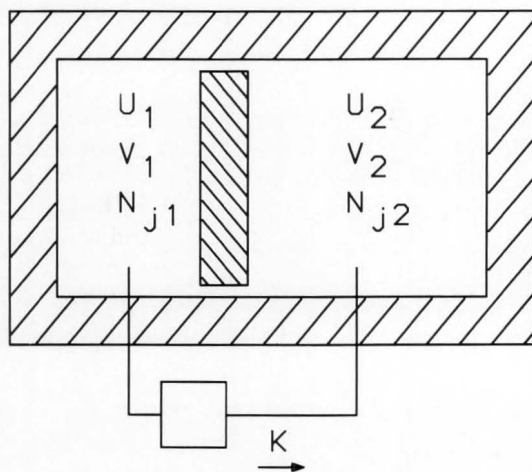


FIGURE 4. Alternative form of experiment.

POSTULATE 3: Entropy S is *extensive*. That is, $S = N\hat{S}$, and for a composite system of n equilibrium states of simple systems, the total entropy is additive; that is

$$S = \sum_{k=1}^n S_k \quad (60)$$

Now let us consider the apparatus of Figure 3. Suppose that we have the apparatus in an initial state, with the contents of the two sides at different conditions. The material in each side is in an equilibrium state. Suppose that for each side we know the function $S = S^{U,V,N_j}$. We may therefore calculate the entropies S_1 and S_2 of the two sides of the apparatus, and from Postulate 3, the total entropy, which is given by $S_{\text{tot}} = S_1 + S_2$.

We now relax the adiabatic constraint imposed on the internal partition. This means that energy may move (as q) between the two sides of the apparatus. We want to be able to predict the conditions on each side of the partition when the apparatus reaches its new equilibrium state (we shall call this Experiment 1). The energy balance for either side of the apparatus is of the form $\Delta U = q + w$, but $w = 0$ since the barrier is rigid ($\Delta V = 0$). Thus after energy q has moved from one side to the other, the internal energies will be $U_1 - q$ and $U_2 + q$, respectively. V_1 , V_2 , N_{1j} , and N_{2j} remain unchanged. We may therefore calculate new values for S_1 , S_2 , and S_{tot} .

Consider now the alternative form of the experiment shown in Figure 4 (which we shall call Experiment 2). Here the adiabatic nature of the partition is maintained, but some form of "energy exchange machine" removes energy k from side 1 and adds the same quantity of energy to side 2. Again, we may calculate the total entropy S_{tot}^k , which by Postulate 3 equals $S_1 + S_2$ for any value k of the energy transferred.

We now postulate that the equilibrium state that will be reached in Experiment 1 is the same as the state of Experiment 2, at which S_{tot}^k has its maximum value. Notice that at each stage of Experiment 2, after transferring energy k , we have to wait for the two parts of the apparatus to reach equilibrium states before we can calculate S_1 and S_2 , since Postulates 1 and 2 both apply only to equilibrium states. It would therefore be wrong to say that in Experiment 1 conditions change so that S goes to a maximum. While conditions in the apparatus are changing, it is obviously not in an equilibrium state, and S is not defined. We therefore state our new postulate as follows:

POSTULATE 4: The equilibrium state resulting after the removal of an internal constraint is that possible constrained state with maximum entropy. (We assume that there is only one such constrained maximum.)

Let us now apply the theory we have stated to the solution of the problem of Experiments 1 and 2. We have

$$dU = TdS - PdV + \sum \mu_i dN_i \quad (61)$$

If we consider only small values of the differentials dU , dS , dV , and dN_i , then these small values on the tangent plane will correspond to small changes in the physical system. (If the changes are not small, the values of the [derivatives] T , P , and μ_i of the real system will change, so that the differentials [which all lie on the tangent plane at a particular point] no longer represent possible states of the real system.) Identifying these small values by the symbol δ , we may write

$$\delta U = T\delta S - P\delta V + \sum \mu_i \delta N_i \quad (62)$$

Since the partition retains its rigid and impermeable nature, we know that

$$\delta V_1 = \delta V_2 = 0 \quad (63)$$

and

$$\delta N_{1j} = \delta N_{2j} = 0 \quad (64)$$

Thus

$$\delta U_1 = T_1 \delta S_1 \quad \text{and} \quad \delta U_2 = T_2 \delta S_2 \quad (65)$$

or

$$\delta S_1 = \frac{1}{T_1} \delta U_1 \quad \text{and} \quad \delta S_2 = \frac{1}{T_2} \delta U_2 \quad (66)$$

Now

$$\delta S_{\text{tot}} = \delta S_1 + \delta S_2 \quad (67)$$

$$= \frac{1}{T_1} \delta U_1 + \frac{1}{T_2} \delta U_2 \quad (68)$$

For the whole apparatus, the energy is the sum of that in the two portions; hence

$$U_{\text{tot}} = U_1 + U_2 \quad (69)$$

Since the exterior walls are rigid, impermeable, and adiabatic, the total energy of the apparatus is constant ($q = w = 0$), i.e.,

$$\delta U_{\text{tot}} = \delta U_1 + \delta U_2 = 0 \quad (70)$$

Hence

$$\delta U_1 = -\delta U_2 \quad (71)$$

Thus

$$\delta S_{\text{tot}} = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \delta U_1 \quad (72)$$

From which

$$\frac{\partial S_{\text{tot}}^{U_1}}{\partial U_1} = \frac{1}{T_1} - \frac{1}{T_2} \quad (73)$$

Equation (73) follows from Eq. (9); although the δ values are small, they are still differentials, since they came from Eq. (61).

For a maximum of S^{U_1} , this derivative will be zero. Thus, Postulate 4 tells us that at the new equilibrium state we will have

$$\frac{1}{T_1} - \frac{1}{T_2} = 0 \quad \text{or} \quad T_1 = T_2 \quad (74)$$

Temperature

We may also consider what happens if we do not allow the system to go all the way to this final equilibrium state; that is, if we relax the adiabatic constraint on the barrier for only a short time and then reimpose it. This is the same as operating the apparatus in Figure 4, but using the energy-transfer machine to transfer a lesser amount of energy than would maximize S .

Suppose that the initial state of the system is such that when we relax the adiabatic constraint on the internal partition, energy moves as heat from compartment 1 into compartment 2. It follows that U_1 will decrease (and U_2 will increase by the same amount). These changes in U_1 and U_2 will cause a change in S_{tot} (as in Eq. 68) which must be positive, since S must change towards its maximum. Consider the graph of S_{tot} versus U_1 , as shown in Figure 5. Since we have $\Delta U_1 < 0$ and $\Delta S_{\text{tot}} > 0$, we have moved from a point such as A towards a point such as B, and along this curve

$$\frac{\partial S_{\text{tot}}^{U_1}}{\partial U_1} < 0 \quad (75)$$

thus

$$\frac{1}{T_1} - \frac{1}{T_2} < 0 \quad \text{or} \quad T_1 > T_2 \quad (76)$$

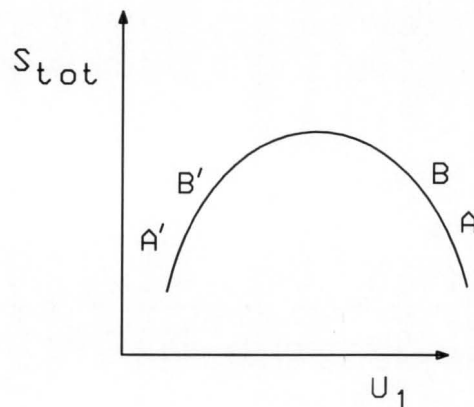


FIGURE 5. Maximum of S^{U_1}

By a similar argument, we can see that if the heat flow is from compartment 2 to compartment 1, ΔU_1 will be positive, and we will be moving from a point such as A' towards B'. Thus the derivative of Eq. (75) will be positive, and we will conclude that $T_1 < T_2$.

Finally, we note that in Eq. (16) (or Eq. 75) we defined T by

$$T = U^{S'V} \quad (16)$$

which is exactly equivalent to the definition

$$T = \hat{U}^{\hat{S}'\hat{V}} \quad (77)$$

It follows that T is *intensive*, i.e., independent of the amount of material we are considering.

We thus have for the quantity represented by our symbol T that

- it is intensive
- at equilibrium, in the absence of any adiabatic constraint, we find that $T_1 = T_2$
- prior to equilibrium, q moves from 1 to 2 when $T_1 > T_2$ and from 2 to 1 when $T_1 < T_2$

We thus see that T fulfills all our intuitive notions of the concept of *temperature*, and we shall in the future identify T with temperature. We may further note that it was part of Postulate 2 that

$$S^{U'VN_j} > 0$$

hence

$$U^{S'VN_j} = \frac{1}{S^{U'VN_j}} > 0 \quad (78a)$$

i.e.,

$$T > 0 \quad (78b)$$

Equations of State

Postulate 2 (Eq. 59) tells us that we may write the entropy of a simple system in an equilibrium state as a function of the internal energy U, the volume V, and the number of moles of various materials:

$$S = S^{U,V,N_j} \quad (59)$$

Now recall the definitions of T and P

$$T = U^{S'V} = T^{SV} \quad (18)$$

and

$$P = -U^{SV'} = P^{SV} \quad (16)$$

We may substitute for S in these equations from Eq. (59) and then eliminate S between the resulting equations to obtain a relationship between V, T, P, and N_j . As an example, suppose that for a particular

system

$$S = K(NVU)^{1/3} \quad (79)$$

where N is the total number of moles involved. From this expression

$$T = \frac{\partial U^{SV}}{\partial S} = \frac{3S^2}{NVK^3} \quad (80)$$

and

$$P = -\frac{\partial U^{SV}}{\partial V} = \frac{S^3}{NV^2K^3} \quad (81)$$

from which

$$P^2V = \frac{N}{27} T^3 K^3 \quad (82)$$

These relationships between P, V, T, and N are the form of equation of state to which we are accustomed in physics and chemistry. Notice that, unfortunately, it is not in general possible to reconstruct Eq. (79) or its equivalent from Eq. (82), the equation of state, without further information. From Eq. (82) we have

$$\left(\frac{\partial U^{SV}}{\partial V} \right)^2 V = \frac{NK^3}{27} \left(\frac{\partial U^{SV}}{\partial S} \right)^3 \quad (83)$$

and we cannot obtain a solution to this partial differential equation without boundary conditions.

Units and Value for Temperature

If we consider our definition $T = U^{SV}$, we see that the units and value of T will depend upon those which we ascribe to S. Working in the other direction, we may choose to give T arbitrary units of degrees Kelvin. Since U must have energy units, this means that we are assuming units of J/K for S, or J/mol K for \hat{S} .

For historical reasons, we are probably stuck with this system. If we were free to start from scratch it might be more logical to let \hat{S} be dimensionless, which would result in measuring temperature in Joules per mole. In particular, it would be possible to choose a temperature scale such that the ubiquitous "gas constant" $R = 8,314 \text{ J/mol K}$ (and many other possible equivalent values) had a dimensionless value of 1. The time saved by chemists and chemical engineers in units conversions involving R would surely be enormous!

Other Versions of the Problem

We have considered only one version of the problem posed above. The reader should be able to provide the solution to other versions and show, for example, that

- relaxation of the rigidity constraint on the partition leads to a final equilibrium state in which the pressures in the two compartments are equal

- removal of both the adiabatic and rigidity constraints results in a final equilibrium state in which both the temperatures and the pressures in the two compartments are equal
- removal of the adiabatic and impermeability constraints gives a final equilibrium state in which the temperatures are equal and $\mu_{i1} = \mu_{i2}$ for all i .

We may regard T as a "thermal potential," in that a difference in T tends (in the absence of constraints) to cause energy to transfer as q . Similarly, P is a "mechanical potential," tending to cause work to be done (as an $\int PdV$ term). In the light of the third result above, we name μ the *chemical potential*, since a difference in μ_i produces a potential for the movement of component i .

We note that in this approach it is not necessary to "define" S by way of equations such as $\delta S = \delta q/T$, where the value of δq is so circumscribed that the equation really has no meaning, and the student ends up learning the subject (if at all) by a hierarchical process of learning what is or is not permissible. The difficulty of trying to understand the "meaning" of entropy is obviated by having a perfectly formal way of defining it. Thus we only need to calculate its value, not to understand it.

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The two parts of this paper lean heavily on the approach of our former colleague, W. F. Harris. He introduced the thermodynamics course in this form at our university, but unfortunately his interests turned elsewhere before he could produce the definitive write-up we were always promised. It is therefore true to say that the felicities of the approach are his, and any faults in the detailed development are ours. □

REVIEW: Introduction to Rheology

Continued from page 131.

phenomena, to material functions, and to the importance of rheology in industrial processes. The text is complemented by numerous tables and figures that illustrate the behavior of a wide range of materials. Theoretical and empirical relationships among material functions are discussed in these chapters, and well-known models for non-Newtonian viscosity (*e.g.*, power law, Carreau, Bingham) and for linear viscoelasticity (*e.g.*, Kelvin, Maxwell, Jeffreys) are presented.

Each of the chapters mentioned above includes a

section describing the experimental measurement of the material functions discussed in the chapter. This emphasis on rheometry will be interesting and useful to many readers, especially those involved with rheological characterization of materials. Measurement techniques and configurations of commercial rheometers and research instruments are surveyed, and the suitability of particular types of instruments for particular tasks is discussed. Theoretical principles of measurements in various rheometer geometries are presented, and excellent introductory discussions of the factors limiting the range and accuracy of measurements are provided.

While the first part of the book is concerned with general aspects of rheology, the sixth and seventh chapters are devoted, respectively, to the rheology of polymeric liquids and the rheology of suspensions. These chapters provide an overview of two important areas of rheology, and also include introductions to topics of current research interest such as liquid crystal polymers, reptation models, and numerical simulations of suspension rheology.

The final chapter returns to continuum mechanics, a topic no doubt dreaded by many of the intended readers. But those who persevere are rewarded by a concise statement, mostly in words rather than equations, of the principles of continuum mechanics that govern the formulation of constitutive equations. A highly condensed survey of the mathematical forms and rheological predictions of constitutive models is also included. This brief chapter refers interested readers to many excellent references for more detailed treatments of the subject.

Throughout the book, the authors guide the reader toward more comprehensive sources of information, and the reference list is excellent and up-to-date. Although the treatment of many topics is necessarily brief, it is authoritative, and beginning rheologists will not need to relearn the material as they advance in their sophistication. The text is well written, and it is infused with explanations of the history and development of rheology, which enhance the reader's pleasure as well as his or her understanding. The book is very suitable as a textbook for an introductory course in rheology. However, the material is not presented in a problem-oriented style, and some instructors may feel that the absence of example and homework problems is a drawback. The book is certainly well suited for individual study, and I would recommend it highly to anyone seeking a sound, but accessible, introduction to rheology. □