A GENERAL ANALYSIS OF THE FIRST AND SECOND LAWS OF THERMODYNAMICS

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By

Jerry D. Griffith

AN ABSTRACT

Submitted to the College of Engineering of Michigan
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ABSTRACT

Thermodynamics is that branch of science which treats of energy transformations. As such it is a very general science. The generality of the First Law of Thermodynamics is well known. Energy must be conserved. Even the student of a high school physics course is familiar with this law. The generality of the Second Law of Thermodynamics, however, is lost in the obscurity of idealized thermal machines and heat power cycles.

It is unfortunate that the generality of the Second Law should be lost by such close association with only heat energy transformations. The Second Law is applicable in all systems just as is the First Law. The Second Law must hold for all processes from the irreversible flow of water down a hill, to the smallest chemical reaction that takes place inside animal and plant life. If the Second Law is to be placed on a level with the First Law, the obscurity with which the Second Law is clothed must be eliminated. This can only be done if the association of the Second Law with heat engine cycles is removed. This can be done.

The First Law for any system may be written as a Pfaffian equation. By utilizing the properties of Pfaffian equations and the directional principles that are observed in natural processes, the Second Law may be derived strictly from mathematical considerations of the First Law. This is what has been done in this thesis.

The procedure described above has been carried out for adiabatic systems of constant composition, systems of constant composition in which no work is done, chemical systems of varying composition, electrical systems, and mechanical systems.

The analysis of these various systems shows conclusively that the entropy cannot decrease in an isolated system. Thus the directional characteristics of processes is found to be the same as predicted by classical thermodynamic methods, but it has been found without the introduction of thermal machines. Thus the Second Law is directly applicable to any process without first reducing the process to an equivalent heat engine cycle. This removes the association of the Second Law with heat energy transfers and the generality of the Second Law is increased.

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INTRODUCTION

Thermodynamics is that branch of science which treats of the laws which govern transformations of energy. It is based on two general laws of nature, the first and second laws of thermodynamics.

The First Law of Thermodynamics may be applied to any system. It states that when any change of state is accomplished, a certain energy balance must hold. This energy balance may be written as follows:

$$dQ = dE + dW$$

Where dQ is the heat transferred to the system during the process, dW is the work transferred from the system during the process, and dE is the change in stored energy of the system during the process.

The First Law written in this form is nothing more than a statement of the law of conservation of energy. Conformance of a given hypothetical process to the law of conservation of energy, however, is no guarantee that this process is possible. There are certain directional laws which have been observed in the physical world. For example, when bodies at different temperatures are placed in contact, the temperatures of the bodies always approach a common value; water always runs down hill; people always grow old; the reverse of these processes is never observed. It would be possible to reverse many of these processes and not violate the law of conservation of energy. Thus conformance to the law of conservation of energy is a necessary but not a sufficient condition to justify the possibility of a change of state.

In thermodynamics the fact that a directional law exists results in a limitation on a change of state other than that imposed by the First Law.

Because the First Law does not completely express the possibility of a change of state, the Second Law of Thermodynamics has been formulated to express the directional limitations imposed upon the First Law. The steam engine had already been invented and was in operation at the time of the first realization of this directional limitation on the First Law. In truth, it was the conception of idealized thermal machines which transform heat into work and vice versa or which pump heat from one resevoir into another that gave the first indications that these directional limitations existed. These limitations were that heat could not be transformed completely into work or raised from a lower to a higher state of temperature without compensation. It was only natural that the engineer use these same idealized thermal machines that indicated the existence of a directional limitation to develop the Second Law, and the classical development of the Second Law proceeded along these lines. It was, however, inevitable that someone would object to the introduction of idealized thermal machines to establish the Second Law, and these objections are not without foundation. It would seem much more desirable to establish the Second Law with sound mathematics thus making the law directly applicable to a general system rather than simply thermal machines.

A mathematical development of the Second Law has been made possible by the principle of Carathéodory. Carathéodory analysed this problem and showed that it was sufficient to know the existence of some impossible processes to derive the Second Law. It must be shown mathematically that there are states in the vicinity of any given state which are inaccessible because of the restrictions placed upon the change of state. This problem can be solved by the differential equations studied by Pfaff.

PROPERTIES OF PFAFFIAN EQUATIONS

Pfaffian equations are expressions of various functions in space. There are two types of Pfaffian equations. One type of Pfaffian equation results in an infinite number of solutions $\phi(x,y,z) = $ constant. This describes parametrically an infinite number of surfaces in space. Other types of Pfaffian equations do not have this property. There are physical examples which describe space distributions of this type. Consider the space distribution which would result if 8 x 11 sheets of paper were placed in an 8 x 11 box. Compare this space distribution to the distribution which would result if 1 x 1 squares of paper were placed at random in the same box. These two space distributions are analogous to the space distributions of two types of Pfaffian equations. The 8 x 11 sheets of paper form surfaces in space. The 1 x 1 squares do not.

Pfaffian equations containing solutions $\phi(x,y,z) = $ constant are mathematical expressions of some of the most common physical processes. It will be shown later that the First Law of Thermodynamics may be written in the form of a Pfaffian equation. Then from considerations of the properties of Pfaffian equations and the use of Carathéodory's principle, which will be stated later, it is possible to derive the Second Law. A knowledge of the properties of Pfaffian equations is necessary before this procedure can be followed.

Consider first a Pfaffian equation of two variables, x and y.

$$dA = Xdx + Ydy \qquad (1)$$

where X and Y are each functions of both x and y.

If the restriction that A be constant is placed on this equation, the ordinary differential equation

$$\frac{dy}{dx} = -\frac{X}{Y} \tag{2}$$

is obtained.

Equation (2) may be integrated and y may be solved for in terms of x or vice versa. Thus if A is constant only one of the variables may be independent. The differential equation (2) has an infinite number of solutions $\phi(x,y)$ equals a constant, representing a set of curves defined implicitly by ϕ in the x-y plane. Now, since the restriction that A be constant has been placed on any change of position in the x-y plane, all those points which do not lie on the curve A equals a constant are not accessible from a point which does lie on this curve. What happens if this restriction is removed? How is the solution of this equation affected by a change in A? It can be shown that if $\phi(x,y)$ equals a constant, then

$$d\phi = \frac{\partial\phi}{\partial x}dx + \frac{\partial\phi}{\partial y}dy = 0 \tag{3}$$

This equation must satisfy the same conditions expressed by the original Pfaffian equation that

$$dA = Xdx + Ydy = 0$$

Thus if the two equations are to be equal

$$X = \lambda\frac{\partial\phi}{\partial x}, \quad Y = \lambda\frac{\partial\phi}{\partial y}$$

or

$$dA = \lambda\frac{\partial\phi}{\partial x}dx + \lambda\frac{\partial\phi}{\partial y}dy$$

$$dA = \lambda d\phi \tag{4}$$

It has been shown then that each Pfaffian equation of two variables has an integrating denominator such that $\frac{dA}{\lambda}$ is a perfect differential.

Examine a Pfaffian equation of three variables,

$$dA = Xdx + Ydy + Zdz \tag{5}$$

where X, Y, and Z are all functions of both x and y. For A equal to a constant, equation (5) defines surfaces in x-y-z space. z is not an independent variable and may be expressed as follows.

$$z = z(x,y)$$

$$dz = \frac{dz}{dx}dx + \frac{dz}{dy}dy \tag{6}$$

Equation (5) may then be expressed as

$$dA = \left[X + Z\frac{dz}{dx}\right]dx + \left[Y + Z\frac{dz}{dy}\right]dy$$

or

$$dA = X'dx + Y'dy \tag{7}$$

where X' and Y' are now each functions of only x and y.

Thus equation (5) reduces to the case previously studied and it can be shown that an integrating denominator, λ, exists such that $\frac{dA}{\lambda}$ is a perfect differential $d\phi$. Therefore, Pfaffian equations of three variables, only two of which are independent, have this integrating denominator and $dA = \lambda d\phi$. These Pfaffian equations define surfaces in space. The resulting Pfaffian equation of two variables which defines a curve in the x-y plane is the curve of intersection of the surface in space and a plane of constant z.

For Pfaffian equations of three or more independent variables this integrating denominator does not exist. Pfaffian equations of this type do not form surfaces in space. That these Pfaffians do not form surfaces in space is easily demonstrated by choosing x,y, and z as the three independent variables in x-y-z space. It is obvious that once x and y are chosen $\phi(x,y,z)$ cannot describe a surface in space if z is allowed to take on any arbitrary value. That these Pfaffians do not have an integrating denominator may be shown mathematically.

Consider the Pfaffian equation

$$dA = -y\,dx + x\,dy + K\,dz \tag{8}$$

where k is a constant. If it were possible to express dA in the form $\lambda d\phi$, where λ and ϕ are functions of x, y, and z, the following equation would result:

$$dA = \lambda\frac{\partial\phi}{\partial x}dx + \lambda\frac{\partial\phi}{\partial y}dy + \lambda\frac{\partial\phi}{\partial z}dz \tag{9}$$

By equating coefficients in equations (8) and (9) it may be shown that

$$\frac{\partial\phi}{\partial x} = -\frac{y}{\lambda}\,,\quad \frac{\partial\phi}{\partial y} = \frac{x}{\lambda}\quad \frac{\partial\phi}{\partial z} = \frac{K}{\lambda}$$

Taking partial derivitives of the above equalities gives:

$$\frac{\partial^2\phi}{\partial y\partial z} = \frac{\partial}{\partial z}\left(\frac{x}{\lambda}\right) = \frac{\partial}{\partial y}\left(\frac{K}{\lambda}\right) \tag{10}$$

$$\frac{\partial^2\phi}{\partial x\partial z} = -\frac{\partial}{\partial z}\left(\frac{y}{\lambda}\right) = \frac{\partial}{\partial x}\left(\frac{K}{\lambda}\right) \tag{11}$$

$$\frac{\partial^2\phi}{\partial x\partial y} = -\frac{\partial}{\partial y}\left(\frac{y}{\lambda}\right) = \frac{\partial}{\partial x}\left(\frac{x}{\lambda}\right) \tag{12}$$

Equation (10) shows that

$$x\frac{\partial}{\partial z}\left(\frac{1}{\lambda}\right) = K\frac{\partial}{\partial y}\left(\frac{1}{\lambda}\right) \tag{13}$$

but $d\frac{1}{\lambda} = -\frac{1}{\lambda^2}\,\partial\lambda$. Hence $x\frac{\partial\lambda}{\partial z} = K\frac{\partial\lambda}{\partial y}$.

In a similar manner equations (11) and (12) give respectively:

$$-y\frac{\partial\lambda}{\partial z} = K\frac{\partial\lambda}{\partial x} \tag{14}$$

$$2\lambda = x\frac{\partial\lambda}{\partial x} + y\frac{\partial\lambda}{\partial y} \tag{15}$$

By substituting $\frac{\partial\lambda}{\partial y}$ and $\frac{\partial\lambda}{\partial x}$ from equations (13) and (14) into equation (15) it is found that $\lambda = 0$. Thus Pfaffian equations of three independent variables do not have an integrating denominator such that $dA = \lambda d\phi$.

This knowledge of Pfaffian equations gives an insight into what needs to be done in any physical application of a Pfaffian equation. If a quantity can be defined by a Pfaffian equation of two independent variables, then any differential change in this quantity may be expressed as $\lambda d\phi$. It remains then only to express $\lambda d\phi$ in terms of known, or if need be, new properties.

MATHEMATICAL ANALYSIS OF THE FIRST LAW FOR CONSTANT COMPOSITION ADIABATIC SYSTEMS

Since the Second Law of Thermodynamics places limitations on the First Law, it would seem logical to derive the Second Law from mathematical considerations of the First Law. Carathéodory's showed that it was sufficient to know of the existence of some impossible processes to derive the Second Law. Moreover, the impossible processes are readily obtainable by examining Joule's experiments. They consist of bringing a system in an adiabatic enclosure from one equilibrium state to another by doing external work. It is an elementary experience that the work cannot be regained by reversing the process. It can therefore be inferred that there exist adiabatically inaccessible states in the vicinity of a given state. This is Carathéodory's principle.

The obvious step now is to construct an adiabatic system in which Q may be expressed as a Pfaffian equation of two independent variables. To do this it is necessary to consider a system in which complete control of the variables of the system is possible. This system must also be isolated from all external effects thereby eliminating any changes of state in the system other than those produced by controlled manipulation of the variables of the system.

To maintain control over all the variables of a system it is necessary to eliminate the use of rigid bodies and incompressible fluids in the system. This leads to the selection of gaseous fluids as the working substance in the desired system.

To isolate this system it would be possible to enclose the gaseous fluids in a container such as a thermos flask and thereby eliminate any external effect on the fluid to a high degree of approximation.

The use of such containers, however, eliminates the desired control over the variables of the system. A new kind of enclosure must be found, and it is necessary to introduce the idea of walls. These walls are to be so thin that they play no part in the physical behavior of the system other than to define the interaction between two neighboring fluids. These walls may also be moved at will to effect changes in the pressure and volume of the fluid. It is necessary to define two types of walls.

An adiabatic wall is defined by the property that equilibrium of a fluid enclosed by it is not disturbed by any external process as long as no part of the wall is moved. This type of wall isolates the system but does not limit the desired control over the variables of the system.

It will be necessary later to allow for the transfer of heat energy from one fluid to another. This cannot be done across an adiabatic wall. Therefore, it is necessary to define another type of wall. This second type of wall is the diathermanous wall, defined by the following property: fluids separated by a diathermanous wall are in equilibrium only if the temperature of the two fluids is the same. The equation of state of a perfect gas then yields the desired relationship between the pressures and volumes of these two fluids. The equation of state of a perfect gas states that:

$$P_1V_1 = n_1R_1T_1$$
$$P_2V_2 = n_2R_2T_2$$

where P, V, n, R, and T have their usual meaning. Now if T_1 equals T_2 and both fluids are composed of the same amount of the same substance then

$$P_1V_1 = P_2V_2 \tag{16}$$

This is the expression of thermal contact. The wall is introduced only to symbolize the impossibility of exchange of material.

It is now possible to apply the properties of Pfaffian equations along with Carathèodory's principle to derive the Second Law of Thermodynamics. Consider two equal masses of the same fluid enclosed by adiabatic walls and separated by a diathermanous wall.

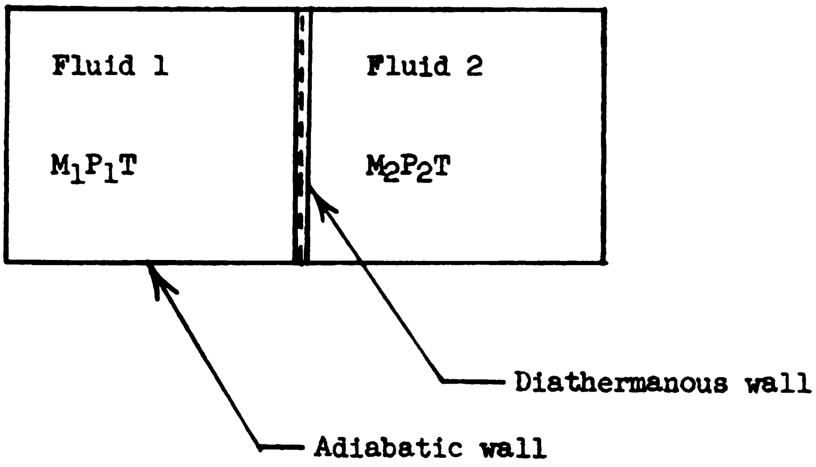

Figure 1.

Either of these two fluids constitute a system and the First Law may be applied.

$$dQ_1 = dE_1 + dW_1$$
$$dQ_2 = dE_2 + dW_2 \tag{17}$$

If movement of the adiabatic walls is restricted to extremely slow "quasi-static" changes the work done on the fluid enclosed by the adiabatic walls is

$$dW = PdV \tag{18}$$

Thus

$$dQ_1 = dE_1 + P_1\, dV_1$$

$$dQ_2 = dE_2 + P_2\, dV_2 \qquad (19)$$

These relationships may be stated in a more convenient form to describe Pfaffian equations of two independent variables in a temperature-volume plane.

Since the internal energy is a function of any two independent variables, V and T may be selected and dE may be expressed as follows:

$$dE = \left(\frac{\partial E}{\partial V}\right)_T dV + \left(\frac{\partial E}{\partial T}\right)_V dT$$

Equations (19) then take the following form:

$$dQ_1 = \left(\frac{dE_1}{\partial T_1}\right)_{V_1} dT_1 + \left[\left(\frac{\partial E_1}{\partial V_1}\right)_{T_1} + P_1\right] dV_1$$

$$dQ_2 = \left(\frac{\partial E_2}{\partial T_2}\right)_{V_2} dT_2 + \left[\left(\frac{\partial E_2}{\partial V_2}\right)_{T_2} + P_2\right] dV_2 . \qquad (20)$$

Now the total heat energy added to the combined system must be the sum of the heat energies added to the two fluids, and this total heat energy must be zero since the combined system is entirely surrounded by adiabatic walls. Therefore,

$$dQ = dQ_1 + dQ_2 = 0$$

or

$$dQ = \left[\left(\frac{\partial E_1}{\partial V_1}\right)_T + P_1\right] dV_1 + \left[\left(\frac{\partial E_2}{\partial V_2}\right)_T + P_2\right] dV_2 + \left[\left(\frac{\partial E_1}{\partial T}\right)_{V_1} + \left(\frac{\partial E_2}{\partial T}\right)_{V_2}\right] dT = 0 \qquad (21)$$

In equation (21), T_1 and T_2 no longer need be distinguished since the diathermanous wall between the two fluids makes $T_1 = T_2 = T$.

Equation (21) describes a Pfaffian equation of two independent variables in V_1-V_2-T space. This may not be immediately obvious, but consider what happens if arbitrary values are assigned to any two of the variables of the two fluids, say V_1 and T_1. The equation of state of a perfect gas establishes P_1. T_2 equals T_1, and the equation of state also establishes the product $P_2 V_2$. Since the system is adiabatic these two properties cannot vary independently in the second fluid (i.e., if P_2 and V_2 can only be varied by manipulation of the adiabatic walls, then a definite value of P_2 corresponds to a value of V_2). Thus only one value of V_2 and a corresponding value of P_2 can possibly maintain the temperature equilibrium required by the diathermanous wall and thermal isolation required by the adiabatic walls, and V_2 is not an independent variable.

Since equation (21) is a Pfaffian equation of two independent variables, it should be possible to construct surfaces in V_1-V_2-T space for $dQ = 0$.

The shape of these surfaces may be determined by examining the lines of intersection of the adiabatic surfaces and the V_1-V_2, V_1-T, and V_2-T planes.

If V_2 is held constant and V_1 is increased, T will decrease. As V_2 approaches infinity, T approaches zero. As V_2 approaches zero, T approaches infinity.

Similarly for V_1 and T. As V_1 approaches infinity, T approaches zero. As V_1 approaches zero, T approaches infinity.

It is then obvious that for a constant temperature plane V_1 approaches zero as V_2 approaches infinity and V_1 approaches infinity as V_2 approaches zero. Thus these surfaces vanish to infinity in the vicinity of the V_1-V_2, V_1-T, and V_2-T planes, but it is possible to construct these surfaces for points not in the vicinity of these three planes. These surfaces have the shape shown in Figure 2.

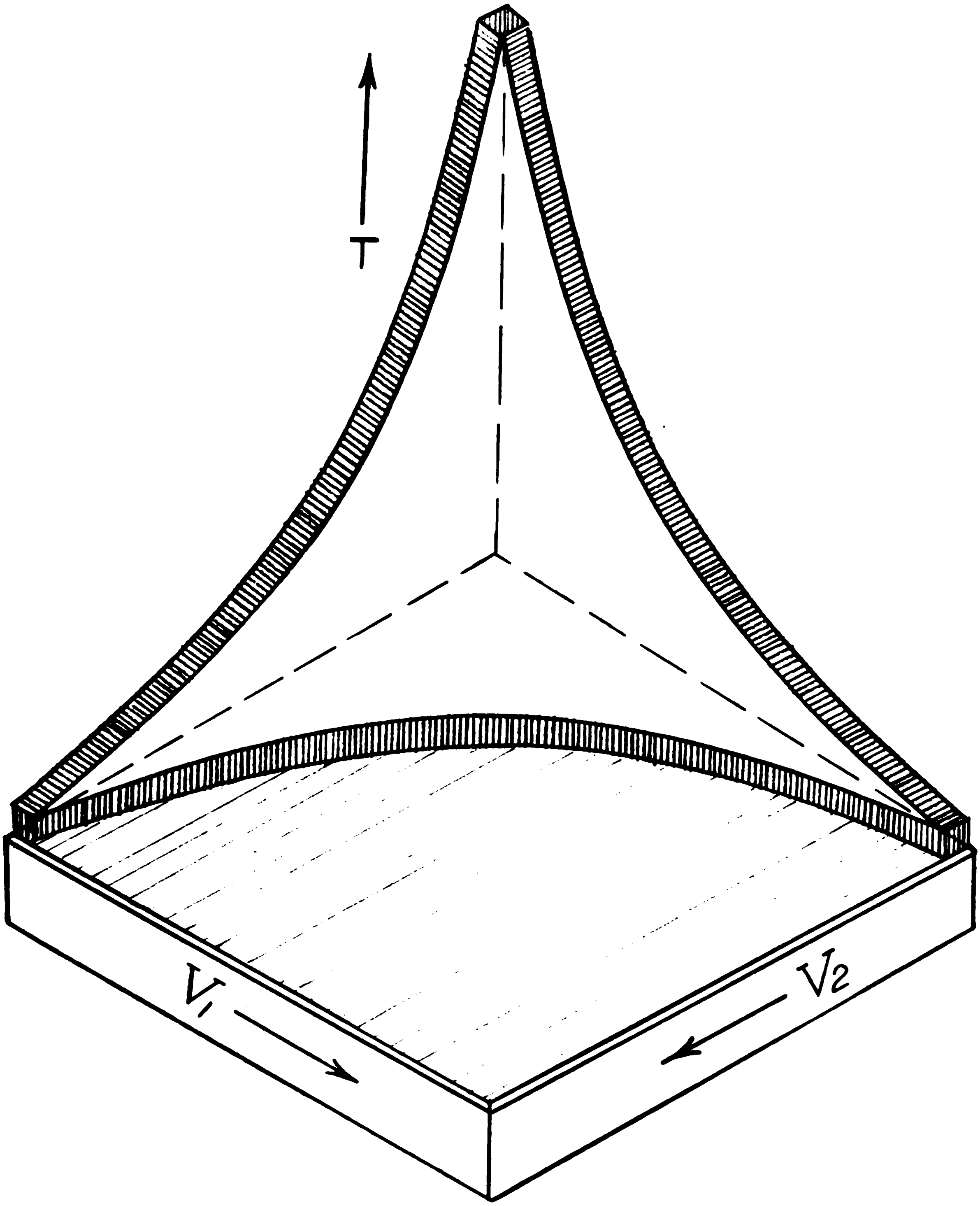

Figure 2.

Adiabatic Surface in V_1-V_2-T Space

Since dQ_1, dQ_2, and dQ have been expressed as Pfaffian equations of two independent variables, it is possible to express each of these quantities in terms of $\lambda d\phi$.

$$dQ_1 = \lambda_1 d\phi_1$$

$$dQ_2 = \lambda_2 d\phi_2$$

$$dQ = \lambda d\phi$$

But

$$dQ = dQ_1 + dQ_2 = 0$$

Hence

$$\lambda d\phi = \lambda_1 d\phi_1 + \lambda_2 d\phi_2 = 0 \tag{22}$$

Equation (22) can hold only if ϕ is a function of ϕ_1 and ϕ_2. Therefore,

$$d\phi = \frac{\partial\phi}{\partial\phi_1} d\phi_1 + \frac{\partial\phi}{\partial\phi_2} d\phi_2$$

Equating coefficients of the exact differential $d\phi$ gives:

$$\frac{\partial\phi}{\partial\phi_1} = \frac{\lambda_1}{\lambda} \; , \; \frac{\partial\phi}{\partial\phi_2} = \frac{\lambda_2}{\lambda}$$

Now ϕ is an independent property of the combined system and ϕ_1 is an independent property of the first fluid. Since λ_1/λ is the partial derivitive of ϕ with respect to ϕ_1, and since ϕ is a function only of ϕ_1 and ϕ_2, λ_1/λ is dependent of the other properties of the system and cannot therefore be a function of the temperature, from which

$$\frac{\partial}{\partial T}\left(\frac{\lambda_1}{\lambda}\right) = 0 \; , \; \frac{\partial}{\partial T}\left(\frac{\lambda_2}{\lambda}\right) = 0 \tag{23}$$

Carrying out the differentiation of equation (23), the following results are obtained:

$$\frac{1}{\lambda_1}\frac{\partial\lambda_1}{\partial T} = \frac{1}{\lambda_2}\frac{\partial\lambda_2}{\partial T} = \frac{1}{\lambda}\frac{\partial\lambda}{\partial T} \tag{24}$$

Now λ_1 is a variable of the first fluid only and is therefore only dependent on the properties of that fluid. Likewise λ_2 is a function only of the properties of the second fluid. The equality of equation (24) holds only if both $\frac{1}{\lambda_1}\frac{\partial\lambda_1}{\partial T}$ and $\frac{1}{\lambda_2}\frac{\partial\lambda_2}{\partial T}$ depend only on T. Hence

$$\frac{1}{\lambda_1}\frac{\partial\lambda_1}{\partial T} = \frac{1}{\lambda_2}\frac{\partial\lambda_2}{\partial T} = \frac{1}{\lambda}\frac{\partial\lambda}{\partial T} = f(T) \qquad (25)$$

It is possible to rewrite equation (25) in the following form:

$$\frac{\partial \ln\lambda_1}{\partial T} = \frac{\partial \ln\lambda_2}{\partial T} = \frac{\partial \ln\lambda}{\partial T} = f(T) \qquad (26)$$

It is now possible to express $\lambda d\phi$ in terms of known properties of the system. From equation (26)

$$\ln\lambda = \int f(T)\,dT + C \qquad (27)$$

λ has now been expressed as a function of temperature and some constant of integration, but it is possible to determine the nature of this constant. Examine a change of state in the λ-ϕ plane. If $dQ=\lambda d\phi$, then the area under the curve represents the heat transferred to or from the system.

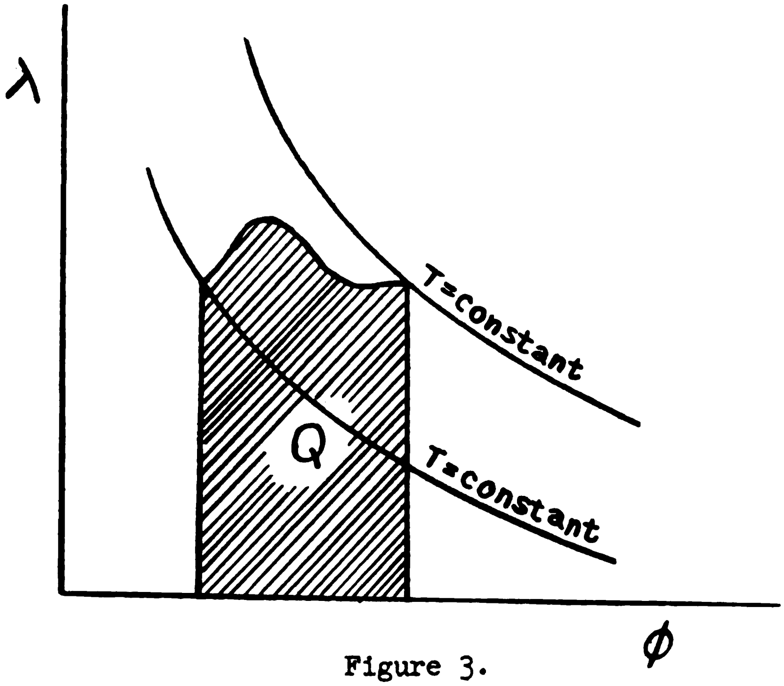

Figure 3.

It is possible to represent constant temperature lines as any general lines in the $\lambda-\phi$ plane. The actual slope and orientation of the constant temperature lines will prove unimportant. It is already known that λ is a function of temperature and the above diagram shows that λ can then be at most a function of one other independent variable. This variable is arbitrary, but it will prove desirable to use ϕ. Thus equation (27) may be expressed as a function of T and ϕ. By re-examining the diagram it is possible to determine what this function of ϕ is. It is evident that λ can be made to vary as a function of ϕ. Then $\ln \lambda$ must be proportional to $\ln f(\phi)$. Therefore equation (27) may be written:

$$\ln \lambda = \int f(T)\,dT + \ln f(\phi)$$

$$\lambda = \Phi e^{\int f(T)dT} \tag{28}$$

where $\Phi = f(\phi)$.

It is now possible to define a thermodynamic temperature as that part of λ which is a function of T.

$$T'(T) = Ce^{\int f(T)dT} \tag{29}$$

where the constant C may be fixed by prescribing the value of $T_1 - T_2$ for two reproducible states of some normal substance (e.g., $T_1 - T_2 = 212°F$ if T_1 corresponds to the boiling point and T_2 the freezing point of water at one atmosphere of pressure).

A new property, entropy, may be defined as follows:

$$S(\phi) = \frac{1}{C}\int \Phi\,d\phi \tag{30}$$

This new property is defined such that

$$dQ = \lambda\,d\phi = T\,dS$$

Similarly

$$dQ_1 = \lambda_1 d\phi_1 = T_1 dS_1$$

$$dQ_2 = \lambda_2 d\phi_2 = T_2 dS_2$$

The above equations refer to "quasi-static" processes which may be represented as sequences of equilibrium states. Ideally all heat transfers can be made by a succession of equilibrium states, and so the above results are quite general and refer to all such reversible heat transfers.

$$dQ_R = TdS \tag{31}$$

To obtain a knowledge of real irreversible phenomena, Carathéodory's principle must be applied considering a finite transition from an initial state (V_o, S_o) to a final state (V,S) where V equals $V_1 + V_2$. It is possible to reach the latter state in two steps: first changing the volume "quasi-statically" and adiabatically from V_o to V the entropy remaining constant, equal to S_o, and then changing the state adiabatically by the addition of external work at constant volume, so that S_o goes over to S. This second change of state could be made by stirring the fluid with a paddle wheel. It should be noted here that work must be added to the system since it is impossible to extract energy from a system during a constant volume adiabatic process. The application of Carathéodory's principle may be more easily understood if these two changes of state are pictured on temperature-volume diagrams.

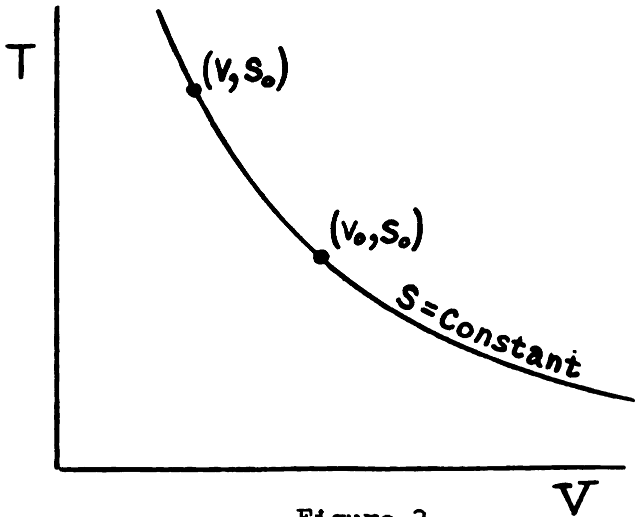

Figure 3

Figure 4 represents step one of the two steps discussed previously. It is obvious that any state (V, S_0) is accessible from any initial state (V_0, S_0) since the volumes of the two fluids are arbitrarily changeable adiabatically by the definition of adiabatic walls. But Carathéodory's principle states that there are adiabatically inaccessible states in the vicinity of any given state. Therefore, step two must provide the desired restriction on the First Law.

Examine step two on a temperature-volume diagram.

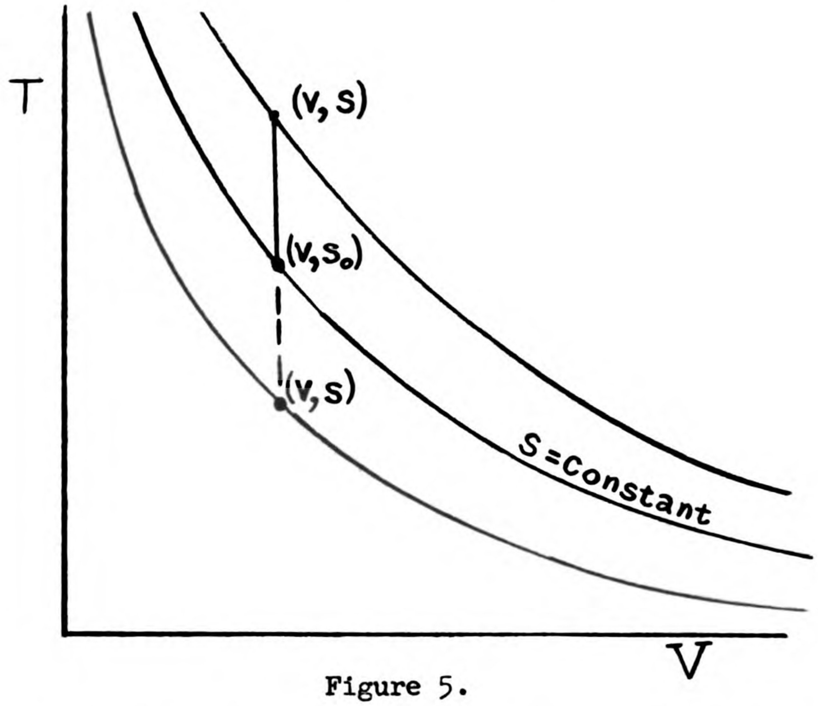

Figure 5.

Figure 5 shows that once the state (V, S_0) has been reached from any initial state by step one, there are two possible relationships between S and S_0, that is $S \geqq S_0$ or $S \leqq S_0$. One of these conditions is then not possible or else all states would be accessible to any given state by adiabatic processes.

The actual choice of sign $\geq$ or $\leq$ depends on the choice of the constant C in equation (29). If this constant is chosen so that T is positive then the relationship $dQ = TdS$ will show that the entropy never decreases in an adiabatic system.

This fact may be seen by considering the process in which S_o was changed to S at constant volume by the addition of paddle wheel work. There is experienced during this process a rise of temperature in the system. Thus the initial temperature is raised to some final temperature T. This temperature T and the volume of the system fix all the other properties of the system including the entropy, S. This value of entropy will be the same at this given volume and temperature regardless of how this state is reached. But it is possible to produce this rise in temperature by the reversible addition of heat to the system at constant volume until the temperature, T, is reached. Since this heat is added to the system, it is a positive quantity. T has already been made a positive quantity by the coice of the constant C in equation (29). Therefore, the relationship $dQ = TdS$ shows that dS must also be a positive quantity, and it has been shown that the entropy never decreases in an adiabatic system.

Consider the relationship $dQ = TdS$ in a different way. Since T is always positive, then the only way the entropy can decrease is to remove heat from a system. Also since the entropy can increase but never decrease in an adiabatic system, $dQ \leq TdS$ for any process. The equality of course holding in reversible processes such as in the hypothetical system used to derive the relationship $dQ = TdS$. Hence for any process $\frac{dQ}{T} \leq dS$. For any cycle, integrating around the cycle,

$$\oint \frac{dQ}{T} \leq \oint dS$$

or

$$\oint \frac{dQ}{T} \leq 0$$

since entropy is a property and has zero change in a cycle. Hence the inequality of Clausius has also been proven without the use of idealized thermal machines.

Thus by the introduction of Pfaffian equations and Carathéodory's principle it is possible to derive the Second Law strictly from mathematical considerations of the First Law. A development similar to the one presented here has been presented by Born.[1]

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[1] Born, Max, Natural Philosophy of Cause and Chance, (New York: Oxford University Press, 1949), pp. 31-45.

MATHEMATICAL ANALYSIS OF THE FIRST LAW FOR CONSTANT COMPOSITION SYSTEMS IN WHICH NO WORK IS DONE

It is surprising that the use of the properties of Pfaffian equations has ended with the previous development since the introduction of Pfaffian principles introduces new areas of thought in other phases of the First Law. The Second Law is directly concerned with irreversibility. Therefore it was natural to examine irreversible phenomena to find the restrictions placed on the First Law. Joule's experiments indicated that there were adiabatically inaccessible states in the vicinity of any given state. This phenomenon was then used to derive the Second Law. But Joule's experiments do not uniquely describe irreversibility. There exist other irreversible phenomena (e.i., a free expansion). It is obvious that if a fluid is allowed to expand freely, it cannot be returned to its initial state solely by the addition or removal of heat. Work must be done to compress the fluid back to its initial volume. Therefore it can be stated that there exist states in the vicinity of any given state which are inaccessible if no work is to be done on the system.

From the First Law

$dW = dQ - dE$

or if all heat transfers are done reversibly and "quasi-statically"

$dW = TdS - dE.$

The work, dW, may be expressed in the form of a Pfaffian equation of two independent variables.

$$dW = \left[T - \left(\frac{\partial E}{\partial S}\right)_P\right] dS - \left(\frac{\partial E}{\partial P}\right)_S dP \tag{32}$$

where P denotes pressure. If the correct system is selected, it should be possible to express dW in terms of $\lambda d\phi$ and make a development similar to the previous one.

To construct the desired system it is necessary to define two new types of walls. The first type of wall is rigid so that no work can be done by deforming the walls, and it is conducting so that heat energy may be added reversibly to the system. The second type of wall requires that the pressures of the two fluids be the same. Once again the equation of state for a perfect gas written for the same amount of the same fluid at the same pressure yields the desired relationship between these variables

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \tag{33}$$

Since there is a possibility that the temperatures of two fluids separated by this wall will be different, it is also necessary that this wall be adiabatic (non-conducting, non-absorbing).

Now examine two fluids enclosed by the first type of wall and separated by the second type of wall.

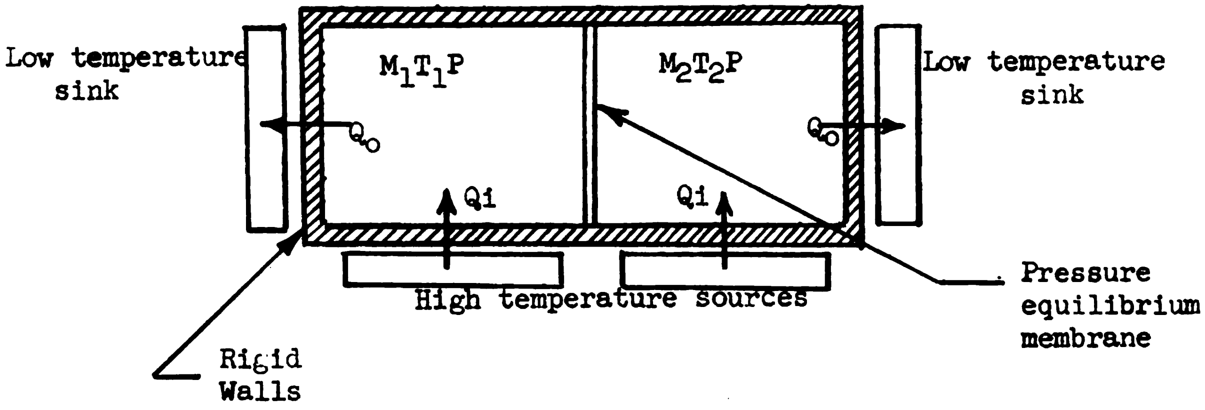

Figure 6.

Either fluid constitutes a system and the First Law may be applied in the form of equation (32)

$$dW_1 = \left[T_1 - \left(\frac{\partial E_1}{\partial S_1}\right)_{P_1}\right] dS_1 - \left(\frac{\partial E_1}{\partial P_1}\right)_{S_1} dP_1$$

$$dW_2 = \left[T_2 - \left(\frac{\partial E_2}{\partial S_2}\right)_{P_2}\right] dS_2 - \left(\frac{\partial E_2}{\partial P_2}\right)_{S_2} dP_2 \qquad (34)$$

These are Pfaffian equations of two independent variables. Thus

$$dW_1 = \lambda_1 d\phi_1$$

$$dW_2 = \lambda_2 d\phi_2$$

The work of the combined system must be equal to the work of the two separate systems, and this sum must be equal to zero since the combined system is entirely surrounded by rigid walls. Hence

$$dW = dW_1 = dW_2 = 0$$

$$dW = \left[T_1 - \left(\frac{\partial E_1}{\partial S_1}\right)_P\right] dS_1 + \left[T_2 - \left(\frac{\partial E_2}{\partial S_2}\right)_P\right] dS_2 - \left[\left(\frac{\partial E_1}{\partial P}\right)_{S_1} + \left(\frac{\partial E_2}{\partial P}\right)_{S_2}\right] dP = 0 \qquad (35)$$

In equation (35) P_1 and P_2 need no longer be distinguished since the wall between the two fluids makes $P_1 = P_2 = P$.

Equation (35) describes a Pfaffian equation of two independent variables in S_1-S_2-P space. That there are only two independent variables in this combined system may be demonstrated by prescribing any two of the variables of this system, say P and S_1. Then all other properties of fluid one are fixed including V_1. This fixes V_2 also since V_2 is equal to the total volume of the combined system minus V_1, and the total volume of the combined system is a constant. P_2 is also fixed by P_1 and the wall separating the two fluids. Therefore, all the properties of fluid two are fixed, and S_2 cannot be an independent variable.

Since equation (35) is a Pfaffian equation of two independent variables it should be possible to construct surfaces in P-S_1-S_2 for space $dW = 0$. These surfaces take the form shown in Figure 7.

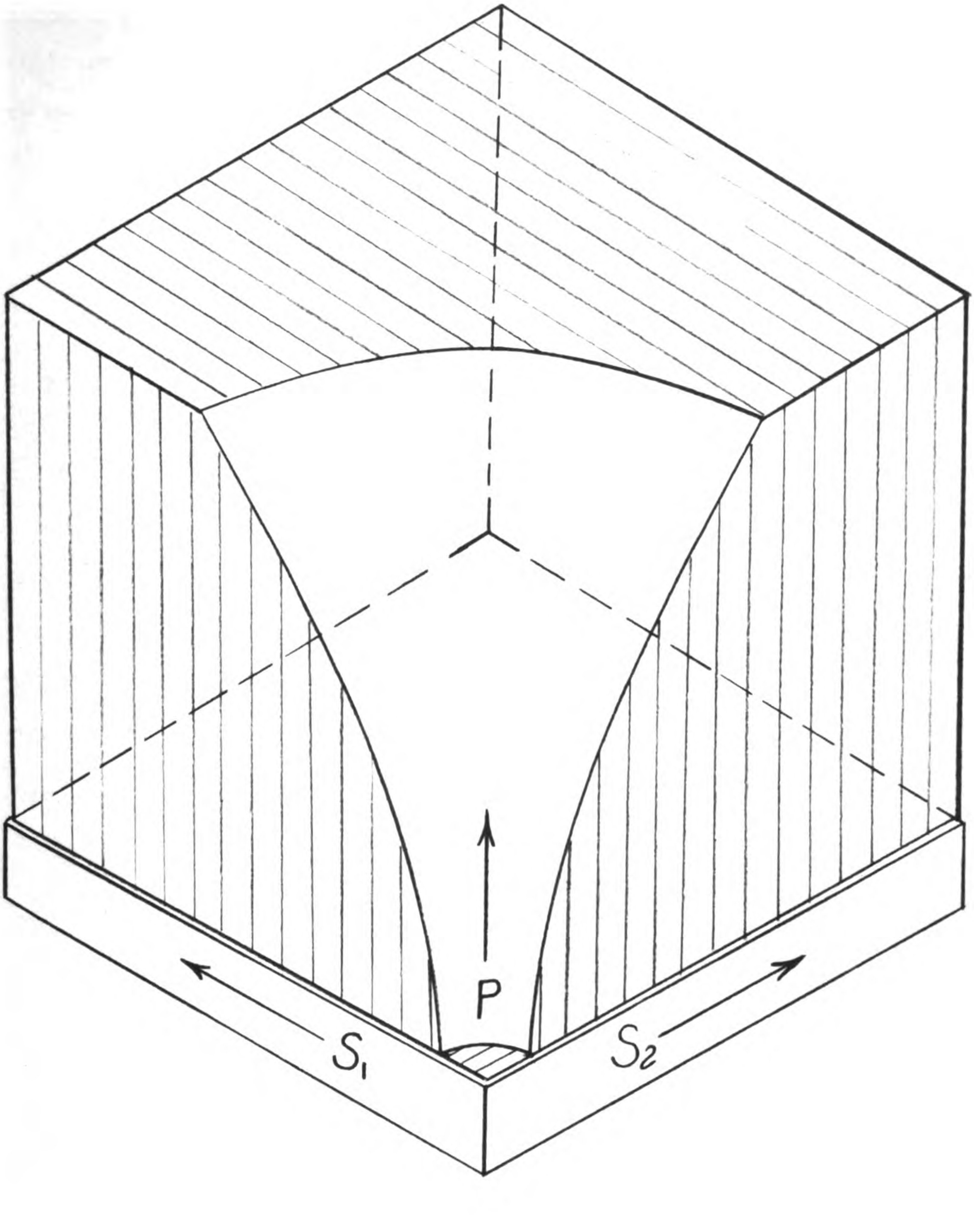

Figure 7.

Surfaces of no work in S_1-S_2-P Space

Note that the variation of S_1 with respect to S_2 in a constant pressure plane may be found by examining the change of S_1 with respect to S_2 at constant pressure.

$$\left(\frac{dS_1}{dS_2}\right)_P = \frac{\left(\frac{\partial S_1}{\partial T_1}\right)_P dT_1}{\left(\frac{\partial S_2}{\partial T_2}\right)_P dT_2} = \frac{\frac{C_P}{T_1} dT_1}{\frac{C_P}{T_2} dT_2} = \frac{T_2 dT_1}{T_1 dT_2}$$

Since constant pressure may be maintained only if heat is added to one system when it is removed from the other and vice versa, dT_1 and dT_2 must have opposite signs and the quantity $\frac{T_2 dT_1}{T_1 dT_2}$ is always a negative quantity. Thus in any $P = \text{constant}$ plane the curve of intersection of the surface of no work and this plane has a slope $\frac{T_2 dT_1}{T_1 dT_2}$ and this is always negative. At a point in a constant pressure plane where S_1 is large and S_2 is small $\frac{T_2}{T_1}$ will be small since heat must be removed from system 2 and added to system 1 to accomplish this state. When S_1 is small and S_2 is large $\frac{T_2}{T_1}$ will be large by similar reasoning. This determines the slopes at these points.

To find the slope of the curve of intersection of the surface of no work and a constant entropy plane, examine the change of S_1 with respect to P when S_2 constant. Consider the case when V_2 is small enough to be negligible compared to V_1. Then V_1 will approximately equal the total volume of the system which is constant. As heat is added to this system dS will increase and may be given by

$$dS_V = C_V \frac{dT}{T}_V + \frac{\beta}{K}\frac{dV}{V}_V$$

Where B is the coefficient of cubical expansion $\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$, K is the coefficient of compressibility $-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$, and C_p is the specific heat at constant volume.

Since dV is zero and $\frac{dT}{T}=\frac{dP}{P}$ at constant volume for a perfect gas

$$dS_V = c_V \frac{dP}{P}_V$$

$$\left(\frac{\partial S}{\partial P}\right)_V = \frac{c_V}{P}$$

The slope of the curve of intersection of the surface of no work and the constant entropy planes decreases with increasing pressure. The surface may now be constructed and takes the form of Figure 7.

Since equation (35) is a Pfaffian equation of two independent variables it is also possible to express dW in terms of $\lambda d\phi$.

$$dW = \lambda d\phi \qquad (36)$$

But

$$dW = dW_1 = dW_2 = 0$$

Thus

$$\lambda d\phi = \lambda_1 d\phi_1 + \lambda_2 d\phi_2 = 0 \qquad (37)$$

Equation (37) can hold only if ϕ is a function of ϕ_1 and ϕ_2. Therefore,

$$d\phi = \frac{\partial \phi}{\partial \phi_1} d\phi_1 + \frac{\partial \phi}{\partial \phi_2} d\phi_2$$

Equating coefficients of the exact differential $d\phi$ gives

$$\frac{\partial \phi}{\partial \phi_1} = \frac{\lambda_1}{\lambda}, \quad \frac{\partial \phi}{\partial \phi_2} = \frac{\lambda_2}{\lambda}$$

ϕ is an independent property of the combined system and ϕ_1 is an independent property of the first fluid. Since λ_1/λ is the partial derivitive of ϕ with respect to ϕ_1, and since ϕ is a function only of ϕ_1 and ϕ_2, λ_1/λ cannot be a function of any other property of the system and is therefore independent of the pressure, P. The partial derivitives of λ_1/λ and λ_2/λ with respect to P must then be equal to zero.

$$\frac{\partial}{\partial P} \frac{\lambda_1}{\lambda} = 0, \quad \frac{\partial}{\partial P} \frac{\lambda_2}{\lambda} = 0$$

By carrying out the differentiation the following equality is obtained:

$$\frac{1}{\lambda_1} \frac{\partial \lambda_1}{\partial P} = \frac{1}{\lambda_2} \frac{\partial \lambda_2}{\partial P} = \frac{1}{\lambda} \frac{\partial \lambda}{\partial P} \qquad (38)$$

This equality can hold only if $\frac{1}{\lambda_1}\frac{\partial \lambda_1}{\partial P}$ and $\frac{1}{\lambda_2}\frac{\partial \lambda_2}{\partial P}$ depend only on P. Therefore,

$$\frac{1}{\lambda_1}\frac{\partial \lambda_1}{\partial P} = \frac{1}{\lambda_2}\frac{\partial \lambda_2}{\partial P} = \frac{1}{\lambda}\frac{\partial \lambda}{\partial P} = f(P) \tag{39}$$

Equation(39) may be rewritten as follows:

$$\frac{\partial \ln \lambda_1}{\partial P} = \frac{\partial \ln \lambda_2}{\partial p} = \frac{\partial \ln \lambda}{\partial p} = f(P) \tag{40}$$

It is now possible to express $\lambda d\phi$ in terms of known properties.

$$\ln \lambda = \int f(P)dP + C$$

This constant can be shown to be a function of at most one other independent variable just as was done in the previous development. This variable is arbitrary but selecting ϕ will give the most desirable results. Then

$$\ln \lambda = \int f(P)dP + \ln \Phi$$

where $\Phi = f(\phi)$.

It is now possible to define a thermodynamic pressure as that part of λ which is a function of P.

$$P'(P) = Ce^{\int f(P)dP} \tag{41}$$

The value of C may be fixed by prescribing the value of $P_2 - P_1$ for two reproducible states of some normal substance.

By defining another property as follows:

$$V(\phi) = \frac{1}{C}\int \Phi d\phi \tag{42}$$

it is seen that

$$dW = \lambda d\phi = PdV = 0$$

Similarly

$$dW_1 = \lambda_1 d\phi_1 = P_1 dV_1$$

$$dW_2 = \lambda_2 d\phi_2 = P_2 dV_2$$

These results are valid for all reversible changes of state and in general

$$dW_R = PdV \tag{43}$$

To obtain knowledge of real phenomena it is necessary to apply a unidirectional principle similar to that of Carathéodory's. This principle is the previously mentioned fact that there exist states in the vicinity of any given state which are inaccessible to the given state if no work is to be done on or by the system.

Examine a finite transition from an initial state (T_0, V_0) to a final state (T,V). It is possible to reach the final state in two steps: first changing the temperature of the system by adding heat to or removing heat from the system reversibly, the total volume of the system remaining constant equal to V_0 and then changing the state with no work being done by allowing a free expansion from V_0 to V, the temperature of the system remaining constant. The first step of this transition may be pictured on a temperature-volume diagram as follows:

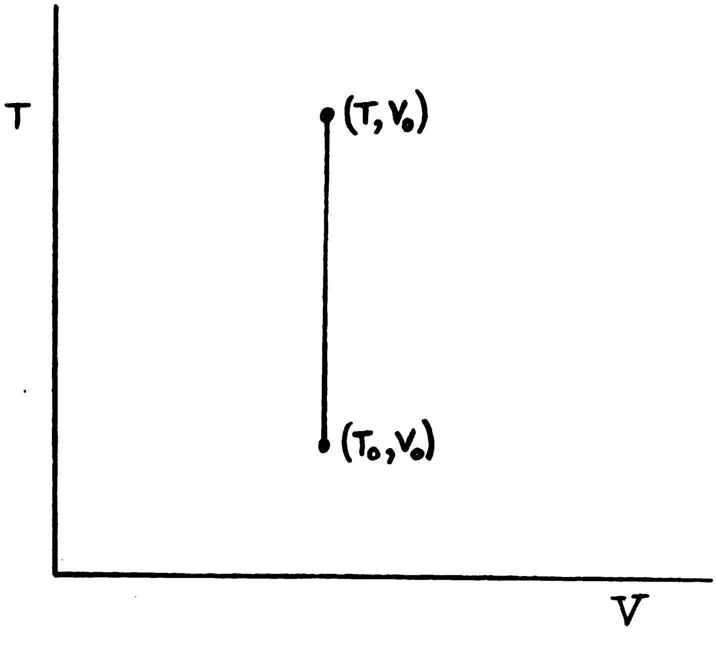

Figure 8.

Figure 8 shows that from any initial state (T_0, V_0), any other state having the same volume, V_0, is accessible by the controlled addition or removal of heat to or from the system. But there are states which are inaccessible in the vicinity of any given state. Therefore step two must provide the restriction on the First Law.

Examine step two on a temperature-volume diagram.

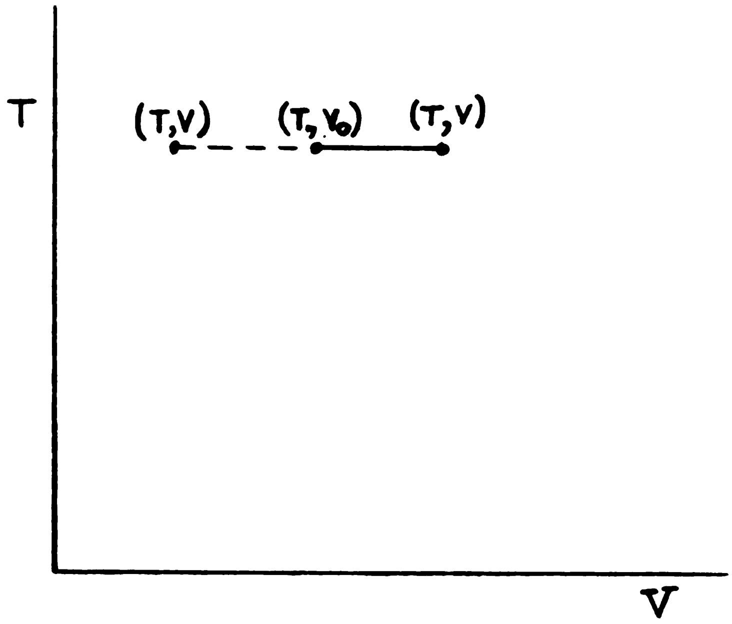

Figure 9.

Figure 9 shows that once the state (T,V_0) is reached by step one, there are two possible relationships between V_0 and V; that is $V_0 \geq V$ or $V_0 \leq V$. One of these conditions is not possible or all states would be accessible to an initial state with no work being done on the system. The actual sign $\geq$ or $\leq$ depends on the choice of the constant C in equation (41). If this constant is chosen so that P is positive, then the relationship $dW = PdV$ may be used to show which sign holds just as was done with $dQ = TdS$ in the previous development.

In systems in which no work is done the only volume change possible is a volume change done against no external forces (i.e., a free expansion).

Consider the process in which V_o was changed to V by allowing a free expansion. There is experienced during this process a decrease of pressure in the system. Thus the initial pressure is decreased to some final pressure P. This pressure, P, and the temperature of the system fix all the other properties of the system, including the volume, V, and the entropy, S. This value of volume will be the same at the given entropy and pressure regardless of how this state is reached. It is possible to reach this state by adding heat to the system reversibly at constant volume until the value of entropy, S, is reached, and then expanding reversibly at constant entropy (thus doing work and decreasing the pressure) until the state (P,S) is reached. This work is a positive quantity. P has already been made a positive quantity by the selection of C in equation (41). Thus the relationship $dW=PdV$ shows that the volume change must also be a positive quantity. Thus $V_o \leq V$ and the volume can never decrease in an isolated system.

Consider the relationship $dW=PdV$ in the same manner as was done for $dQ=TdS$. Since P is always positive, the only way the volume can decrease is to add work to the system in the form of PdV work. Also since the volume can increase but never decrease in an isolated system, $dW \leq PdV$ for any process. The equality of course holding in reversible processes. Hence, for any process $\frac{dW}{P} \leq dV$. For any cycle, integrating around the cycle

$$\oint \frac{dW}{P} \leq \oint dV$$

or

$$\int \frac{dW}{P} \leq 0$$

since volume is a state property and has zero change in a cycle.

The above equation is more often stated that the work of a cycle is less than or equal to the cyclic integral of PdV, but it is interesting to note the analogous form that this equation takes to the previously derived equation

$$\oint \frac{dQ}{T} \leq 0$$

The above results indicated nothing new about systems in general. However, it is observed that application of the properties of Pfaffian equations when applied to one term of the First Law gives different results than the same principles when they are applied to another term. The one result in no way contradicts the other since the relationship between the properties of a system,

$$TdS = dE + PdV$$

results in the following relationship between entropy and volume:

$$S_2 - S_1 = C_v \ln \frac{T_2}{T_1} + \frac{B}{K} (V_2 - V_1)$$

This relationship shows that when volume increases the entropy increases also. However, an increase in entropy is possible without a corresponding increase in volume. Thus the increase in entropy is a more general criterion for irreversibility than the increase in volume, and the statement that the entropy change must be ≥ 0 in any isolated system is not violated.

MATHEMATICAL ANALYSIS OF THE FIRST LAW IN SYSTEMS OF VARYING COMPOSITION WHERE NO WORK IS DONE

Until now only systems involving constant quantities of mass have been considered. There exist, however, systems in which the mass is not constant. It might be possible to examine these systems in the same manner as has been done in the previous systems. It was shown in the previous developments where all the masses were constant

$$TdS = dE + PdV$$

or

$$dE = TdS - PdV. \tag{44}$$

In these systems the internal energy may be expressed as a function of S and V. In a system where the masses of various substances are not constant, E may be expressed as a function of S, V, and the various masses, m_i :

$$E = f(S, V, m_1, m_2, ----- m_n)$$

Hence for small changes of entropy, volume, and composition:

$$dE = \left(\frac{\partial E}{\partial S}\right)_{V,m_1,m_2---} + \left(\frac{\partial E}{\partial V}\right)_{S,m_1,m_2---} + \left(\frac{\partial E}{\partial m_1}\right)_{V,S,m_2---} ---- \tag{45}$$

By comparing coefficients in equations (44) and (45), it is seen that

$$\left(\frac{\partial E}{\partial S}\right)_{V,m_1,m_2---} = T \tag{46}$$

$$\left(\frac{\partial E}{\partial V}\right)_{S,m_1,m_2---} = -P \tag{47}$$

If $\left(\frac{\partial E}{\partial m_1}\right)_{S,V,m_2---}$ is defined as follows:

$$\left(\frac{\partial E}{\partial m_1}\right)_{S,V,m_2---} = \mu_1$$

then equation (45) takes the form

$$dE = TdS - PdV + \sum_{i=1}^{n} \mu_i dm_i \tag{48}$$

The μ in the above equation is called the chemical potential. Its similarity to the potentials temperature and pressure in equation (48) is obvious.

Equation (48) is then the general relationship between properties of a system of varying composition. Consider a system of only one kind of mass. If μdm for this mass is denoted by dM, then equation (48) takes the form

$$dM = dE + PdV - TdS$$

or

$$dM = \left[\left(\frac{\partial E}{\partial V}\right)_S + P\right] dV + \left[\left(\frac{\partial E}{\partial S}\right)_V - T\right] dS \qquad (49)$$

It will later be desirable to construct surfaces of constant M in $T\text{-}V_1\text{-}V_2$ space. These surfaces may be constructed by examining the variation of each of the properties with respect to another when the third is held constant. The above equations do not indicate the variance of one variable with respect to another in T-V space. Therefore, another relationship between the variables must be found. This relationship exists in the form of free and available energies.

By definition, the work done in a reversible isothermal process is equal to the decrease of the maximum work function of the system.

$$dW = -dF$$

From the First Law, for a reversible isothermal process

$$-dW = dE - TdS$$

Thus,

$$dF = dE - TdS.$$

Since the temperature is constant, it follows that

$$dF = d(E - TS)$$

or,

$$F = E - TS. \qquad (50)$$

Thus it is seen that the maximum work function, F, is a property of a system. Equation (50) is sometimes taken to be the definition of the maximum work function.

By definition, the work obtainable in a reversible isothermal process at constant pressure is equal to the decrease in the free energy of the system. It will be shown that the free energy is also a property of a system. The free energy of a system must necessarily be less than the maximum work function of a system since in any process at constant pressure where there is a volume change, part of the total work available must be used in changing the volume at constant pressure. That part of the total available work which may be utilized for other purposes is the free energy, G.

From the definition of free energy

$$dW_{T,P} = -dG.$$

But

$$dW_{T,P} = dW_T - dW_V$$

where dW_V denotes the work done in changing the volume at constant pressure. Therefore,

$$dG = dF + PdV$$

or since pressure is constant

$$dG = d(F+PV)$$

$$dG = d(E-TS+PV)$$

$$G = E-TS+PV. \qquad (51)$$

Equation (51) is the definition of free energy. This free energy is defined such that the work for a constant temperature, constant pressure process is $-dG$. However, equation (51) shows that G is a property of the system, and as such it refers not only to constant temperature, constant pressure processes but all processes in general.

Then for any general process

$$dG = (dE-TdS+PdV)-SdT+VdP \tag{52}$$

If once more systems of varying composition are considered where

$$dE = TdS-PdV + \sum_{i=1}^{n} \mu_i dm_i$$

the expression in parenthesis in equation (52) becomes simply

$$\sum_{i=1}^{n} \mu_i dm_i$$

Thus

$$dG = -SdT+VdP + \sum_{i=1}^{n} \mu_i dm_i \tag{53}$$

Consider equation (53) for a single homogeneous substance.

$$dG = -SdT+VdP + \mu dm \tag{54}$$

Equation (54) expresses the desired relationship between the variables, temperature, pressure, and mass.

$$\left(\frac{\partial G}{\partial T}\right)_{P,m} = -S \qquad \left(\frac{\partial G}{\partial P}\right)_{T,m} = V \qquad \left(\frac{\partial G}{\partial m}\right)_{T,P} = \mu$$

$$\frac{\partial^2 G}{\partial T \partial P} = -\left(\frac{\partial S}{\partial P}\right)_{T,m} = \left(\frac{\partial V}{\partial T}\right)_{P,m} \tag{55}$$

$$\frac{\partial^2 G}{\partial T \partial m} = -\left(\frac{\partial S}{\partial m}\right)_{T,P} = \left(\frac{\partial \mu}{\partial T}\right)_{P,m} \tag{56}$$

$$\frac{\partial^2 G}{\partial P \partial m} = \left(\frac{\partial V}{\partial m}\right)_{P,T} = \left(\frac{\partial \mu}{\partial P}\right)_{T,m} \tag{57}$$

Equation (56) shows that at constant pressure and mass μ varies inversely and linearly with temperature. Equation (57) shows that at constant temperature and mass μ varies directly and linearly with pressure. This information will be utilized later to construct surfaces of constant M in T-V_1-V_2 space.

Consider the following system composed of an initial amount of gaseous fluid contained inside two volumes which are separated by a rigid super-conductive semi-permeable membrane.

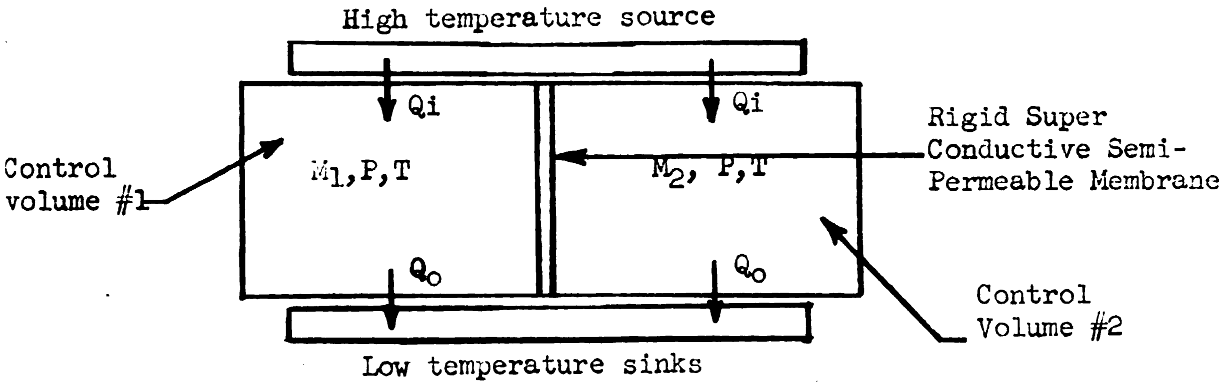

Figure 10.

These two masses of the same fluid are at the same temperature and pressure and have the same μ and therefore also the same $M=m\mu$ It is possible to add heat reversibly to each of the control volumes and to move the walls containing the two fluids at will. In this manner M may be held constant in the combined system by manipulation of the temperature and pressure of the two fluids while mass is allowed to pass from one control volume to the other. For each of the control volumes,

$$dM_1 = \left[\left(\frac{\partial E_1}{\partial V_1}\right)_{S_1} + P_1\right] dV_1 + \left[\left(\frac{\partial E_1}{\partial S_1}\right)_{V_1} - T_1\right] dS_1$$

$$dM_2 = \left[\left(\frac{\partial E_2}{\partial V_2}\right)_{S_2} + P_2\right] dV_2 + \left[\left(\frac{\partial E_2}{\partial S_2}\right)_{V_2} - T_2\right] dS_2$$

or since dM_1 and dM_2 are Pfaffian equations of two independent variables

$$dM_1 = \lambda_1 d\Phi_1$$

$$dM_2 = \lambda_2 d\Phi_2$$

For the combined system,

$$dM = \left[\left(\frac{\partial E_1}{\partial V_1}\right)_{S_1} + P_1\right] dV_1 + \left[\left(\frac{\partial E_2}{\partial V_2}\right)_{S_2} + P_2\right] dV_2 + \left[\left(\frac{\partial E_1}{\partial S_1}\right)_{V_1} - T_1\right] dS_1 + \left[\left(\frac{\partial E_2}{\partial S_2}\right)_{V_2} - T_2\right] dS_2 = 0 \qquad (58)$$

It can be shown that equation (58) is a Pfaffian equation of two independent variables. If T is fixed in the system by adding or removing heat and V_1 is changed an arbitrary amount only one value of V_2 can possibly maintain a constant M for the system and there can be no other independent variable. It is possible to construct surfaces in V_1-V_2-T space by utilizing the information that μ varies inversely and linearly with temperature and directly and linearly with pressure, and that μ must be constant in the system.

$$M = \mu m$$

$$dM = \mu dm + m d\mu$$

Since dm and dM are equal to zero $d\mu$ must equal zero also.

The mass in V_1 may be increased by decreasing V_2 and increasing V_1 at constant temperature. Since the pressure also must remain constant during this process to maintain μ constant, the total volume of the two control volumes must be constant by the equation of state. Thus V_1 varies inversely and linearly with V_2 at constant temperature.

It has already been shown that

$$\left(\frac{\partial\mu}{\partial T}\right)_{P,m} = \text{negative constant,} \qquad \left(\frac{\partial\mu}{\partial P}\right)_{T,m} = \text{positive constant.}$$

To determine the slope of the curve of intersection of the surface of constant M and a constant volume plane, consider the case when $V_2 = \text{constant} = 0$. The total volume of the system is then V_1 and the mass is constant.

The above partials then hold and since μ is a function of T and P at constant mass,

$$d\mu = \left(\frac{\partial\mu}{\partial T}\right)_P dT + \left(\frac{\partial\mu}{\partial P}\right)_T dP = 0$$

$$-A\,dT + B\,dP = 0$$

$$\frac{A}{B}\,dT = dP$$

Since for a perfect gas $\frac{dP}{P} = \frac{dT}{T} - \frac{dV}{V}$

$C_1 dT = \frac{PdT}{T} - \frac{PdV}{V}$; $C_1 = \frac{A}{B}$ and is always a positive constant.

$$\frac{dT}{dV} = -\frac{P}{C_1 V - R}$$

If $C_1V > R$ the slope is negative. If $C_1V < R$ the slope will be positive. When $C_1V = R$ the slope will be infinite. If we consider only those volumes which are small enough to give a positive slope, the slope will increase with increase in temperature and pressure. It is not known if C_1V can ever be greater than R but C_1V can definitely be less than R since the volume may be made arbitarily small. Thus the existence of the surfaces of positive slope is assured. The surfaces of negative slope might not exist and are not included in the construction. The surfaces of constant M then take the form of Figure 11.

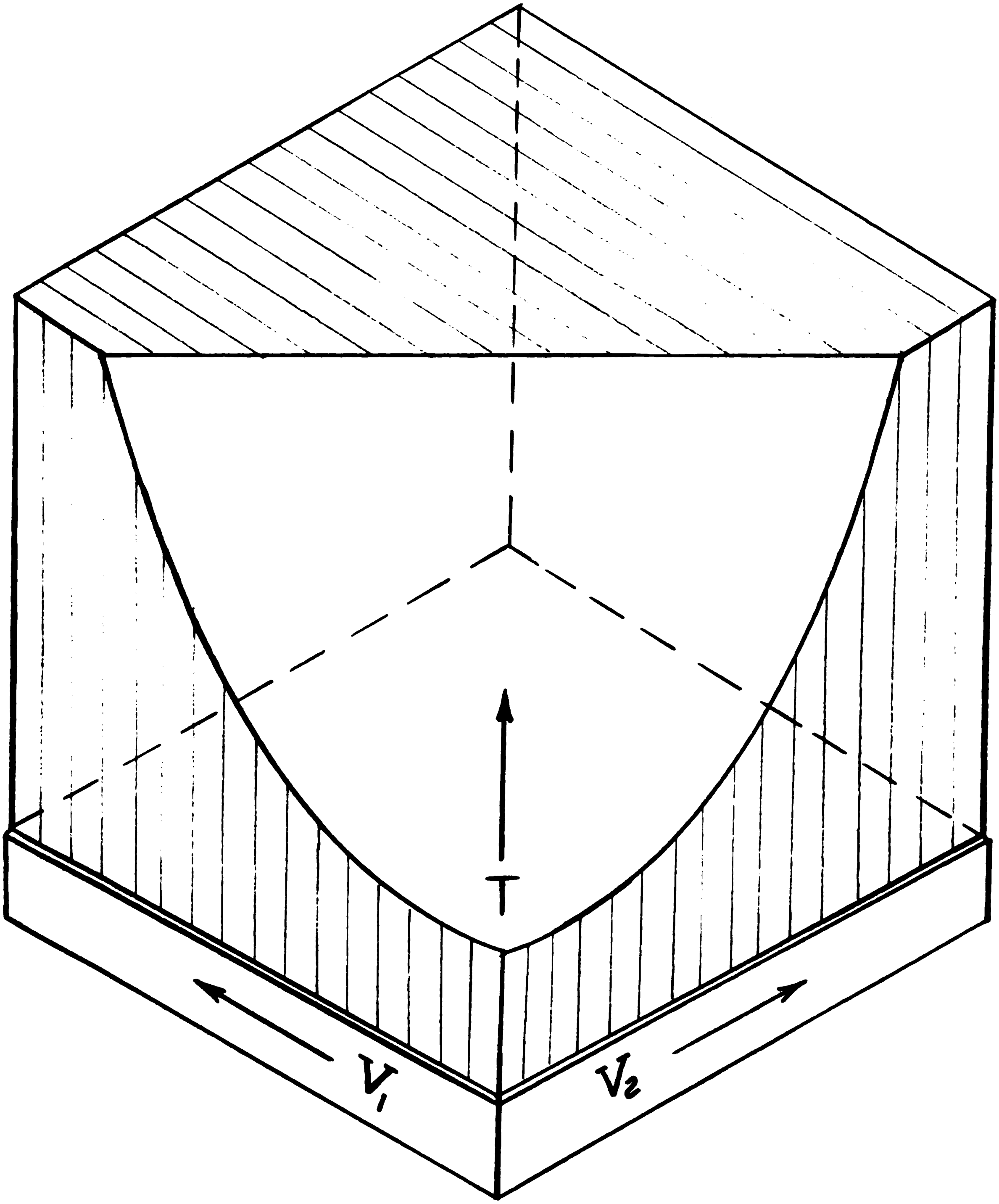

Figure 16.

Surfaces of constant M in V_1-V_2-T space

Since dM is a Pfaffian equation of two independent variables

$$dM=\lambda d\phi$$

But

$$dM = dM_1 = dM_2 = 0$$

Therefore

$$\lambda d\phi=\lambda_1 d\phi_1+\lambda_2 d\phi_2 =0 \qquad (59)$$

Equation (59) can hold only if ϕ is a function of ϕ_1 and ϕ_2. Therefore,

$$d\phi=\frac{\partial\phi}{\delta\phi_1}d\phi_1+\frac{\partial\phi}{\delta\phi_2}d\phi_2$$

Equating coefficients of the exact differential $d\phi$ gives

$$\frac{\partial\phi}{\delta\phi_1}=\frac{\lambda_1}{\lambda} , \frac{\partial\phi}{\delta\phi_2}=\frac{\lambda_2}{\lambda}$$

ϕ is a property of the combined system and ϕ_1 and ϕ_2 are properties of the amount of the fluid on each side of the membrane. Since λ_1/λ and λ_2/λ are the partial derivitives of ϕ with respect to ϕ_1 and ϕ_2 they are independent of the other properties of the system and cannot be a function of the chemical potential, μ. Therefore,

$$\frac{\partial}{\delta\mu}\frac{\lambda_1}{\lambda}=0 , \frac{\partial}{\delta\mu}\frac{\lambda_2}{\lambda}=0$$

It is not necessary to distinguish between the chemical potentials of the two fluids since the semi-permeable membrane maintains pressure and temperature equilibrium in the entire system thereby making $\mu_1=\mu_2=\mu$

By carrying out the differentiation of the above equation

$$\frac{1}{\lambda_1}\frac{\partial\lambda_1}{\delta\mu} = \frac{1}{\lambda}\frac{\partial\lambda}{\delta\mu} = \frac{1}{\lambda}\frac{\partial\lambda}{\delta\mu}$$

The equality of the above equation can hold only if both $\frac{1}{\lambda_1}\frac{\partial\lambda_1}{\delta\mu}$ and $\frac{1}{\lambda_2}\frac{\partial\lambda_2}{\delta\mu}$ depend only on μ.

Hence,

$$\frac{1}{\lambda_1}\frac{\partial\lambda_1}{\delta\mu} = \frac{1}{\lambda_2}\frac{\partial\lambda_2}{\delta\mu} = \frac{1}{\lambda}\frac{\partial\lambda}{\delta\mu} = f(\mu)$$

This equation may be written in the following form:

$$\frac{\partial \ln\lambda_1}{\partial\mu} = \frac{\partial \ln\lambda_2}{\partial\mu} = \frac{\partial \ln\lambda}{\partial\mu} = f(\mu)$$

from which

$$\ln\lambda = \int f(\mu)\,d\mu + \ln f(\phi)$$

$$\lambda = \Phi e^{\int f(\mu)\,d\mu}$$

where $\Phi = f(\phi)$.

The chemical potential may now be defined as that part of λ which is a function of μ.

$$\mu'(\mu) = C e^{\int f(\mu)\,d\mu}$$

Then the mass, m, may be defined as follows:

$$m(\phi) = \frac{1}{C}\int \Phi\,d\phi$$

Thus,

$$dM = \lambda d\phi = \mu dm = 0$$

Similarly,

$$dM_1 = \lambda_1 d\phi_1 = \mu_1 dm_1$$

$$dM_2 = \lambda_2 d\phi_2 = \mu_2 dm_2$$

and in general for all processes in which μ is constant

$$dM = \mu dm$$

If a principle existed such as Carathéodory's, to the effect that there are states in the vicinity of any given state which are inaccessible if M is to remain constant, then the application of this principle to define the directional limitation on the First Law would be possible. There exists, however, no such principle, for all states are accessible in a given control volume simply by adding mass to or removing mass from the volume.

To gain knowledge of the directional limitations imposed on the First Law in systems where the composition of the system is changing, it is necessary to examine the irreversible phenomena involved in these systems. These irreversible phenomena are associated with chemical interactions between two or more elements. In isolated systems these chemical interactions proceed only in one direction.

The introduction of more than one substance in a system, however, results in the inability to express the First Law in the form of a Pfaffian equation of two independent variables, since the second substance obviously introduces another independent variable. This problem may be remedied by lumping the individual μdm's of the system so that equation (48) takes the following form:

$$\sum_{i=1}^{n} \mu_i dm_i = dE - TdS + PdV$$

or

$$\sum_{i=1}^{n} \mu_i dm_i = \left[\left(\frac{\partial E}{\partial S}\right)_V - T\right] dS + \left[\left(\frac{\partial E}{\partial V}\right)_S + P\right] dV \qquad (59)$$

Consider now a system composed initially of hydrogen and oxygen which is allowed to unite chemically to form water.

$$\mu_{H_2O} dm_{H_2O} + (\mu_{O_2} dm_{O_2} + \mu_{H_2} dm_{H_2}) = \left[\left(\frac{\partial E}{\partial S}\right)_V - T\right] dS + \left[\left(\frac{\partial E}{\partial V}\right)_S + P\right] dV$$

where dm_{O_2} and dm_H are negative quantities. If this chemical reaction is carried out at constant volume as in a bomb calorimeter

$$\mu_{H_2O} dm_{H_2O} + (\mu_{O_2} dm_{O_2} + \mu_{H_2} dm_{H_2}) = \left[\left(\frac{\partial E}{\partial S}\right)_V - T\right] dS \qquad (60)$$

Equation (59) indicates that two possible relationships exist for $\Sigma \mu dm$.

$$\mu_{H_2O} dm_{H_2O} + (\mu_{O_2} dm_{O_2} + \mu_{H_2} dm_{H_2}) \geq 0$$

or

$$\mu_{H_2O} dm_{H_2O} + (\mu_{O_2} dm_{O_2} + \mu_{H_2} dm_{H_2}) \leq 0$$

The actual sign $\geqq$ or $\leqq$ depends on the quantity

$$\left(\frac{\partial E}{\partial S}\right)_V - T$$

Since the volume is constant, this quantity may be rewritten as follows:

$dE - TdS$.

By the First Law

$dE - dQ = -dW$

But $dW = 0$ since the process was carried out at constant volume. Therefore

$dE - dQ = 0$

Since $TdS \geqq dQ$

$$dE - Tds \leqq 0 \qquad (61)$$

Thus the quantity $dE-TdS$ is a negative quantity and

$$\mu_{H_2O}\, dm_{H_2O} + (\mu_{O_2} dm_{O_2} + \mu_{H_2} dm_{H_2}) \leqq 0 \qquad (62)$$

Examine the quantity $(\mu_{O_2} dm_{O_2} + \mu_{H_2} dm_{H_2})$. This represents a summation.

For summations of this kind in general

$$\underline{\mu} \sum_{i=1}^{n} dm_i \leqq \sum_{i=1}^{n} \mu_i dm_i \leqq \bar{\mu} \sum_{i=1}^{n} dm_i$$

Where $\underline{\mu}$ denotes the least and $\bar{\mu}$ the maximum of all the possible μ_i's

It is then possible to find a μ' such that

$$\sum_{i=1}^{n} \mu_i dm_i = \mu' \sum_{i=1}^{n} dm_i$$

Where

$$\underline{\mu} \leqq \mu' \leqq \bar{\mu}$$

This μ' represents an equivalent chemical potential of the system for each total infinitesimal change in mass.

For $(\mu_{O_2} dm_{O_2} + \mu_{H_2} dm_{H_2})$ it is possible to construct an equivalent chemical potential, $\mu(H_2, O_2)$, such that when it is multiplied by the total change in mass, $dm_{O_2} + dm_{H_2}$, the amount of energy represented will be the same as that represented by $(\mu_{O_2} dm_{O_2} + \mu_{H_2} dm_{H_2})$.

$$\mu_{O_2} dm_{O_2} + \mu_{H_2} dm_{H_2} = \mu(H_2, O_2)\, dm_{H_2 + O_2}$$

Since

$$\mu_{H_2O}\, dm_{H_2O} + \mu(H_2,O_2)\, dm_{H_2+O_2} \leq 0$$

and

$$dm_{H_2O} = -dm_{H_2+O_2}$$

it is seen that

$$\mu_{H_2O} - \mu(H_2,O_2) \leq 0 \qquad (63)$$

It has been shown then that the chemical potential of an isolated system cannot increase.

Once again these results are consistent with the fact that the entropy cannot decrease in an isolated system since the relationship $dQ \leq TdS$ was used in equation (61) to derive the result that the chemical potential could not increase.

MATHEMATICAL ANALYSIS OF THE FIRST LAW FOR ISOLATED ELECTRICAL SYSTEMS

Energy transformations in electrical systems are made in accordance with the First Law. In electrical systems the same forms of energy are involved that are involved in all other systems, namely heat, work, and some means of storing energy.

It is known that in isolated electrical systems a unidirectional principle exists. This may be demonstrated by examining a charged capacitor in an isolated system with an open switch. When this switch is closed, the observed effect is an increase in the temperature of the system at the expense of the electrical energy stored in the capacitor. The reverse of this process has never been observed. It is not possible for the capacitor to be recharged solely by decreasing the temperature of the system. If this system is to be brought back to its initial state, heat must be removed to restore the system to the original temperature and work must be done by an external source to recharge the capacitor. If this is done, the system is no longer isolated. Therefore, there exist in isolated electrical systems states which are inaccessible from any given state. It should then be possible to determine this directional limitation imposed on the First Law if an isolated system can be constructed in which one of the quantities involved may be expressed as a Pfaffian equation of two independent variables.

Consider first the following electrical system composed of a charged capacitor and an inductance connected by wire of negligible resistance.

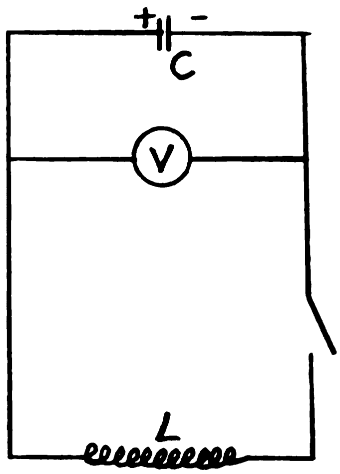

Figure 17.

When the switch is open for the electrical system represented by Figure 17, energy is stored in the capacitor according to the relation $E = \frac{1}{2}CV^2$ where C denotes the capacitance and V denotes the voltage across the capacitor. When the switch is closed a current begins to flow causing a voltage of self induction to be produced by the induction coil. This voltage is not a voltage in an actual sense but is only a tendency to resist the flow of current. The voltage of self induction is equal to the voltage across the coil and is given by

$$e = -L\frac{di}{dt} = V$$

where i denotes the current and L the inductance. This voltage of self inductance will limit the current but will not stop it since the tendency to oppose the flow of current is only present when $\frac{di}{dt} \neq 0$. Thus the current will increase to a maximum value when the voltage across the coil and capacitor is zero. At this time $\frac{di}{dt}$ will be zero also. The energy of the system is stored entirely in the inductance coil in the form

$$E = \frac{1}{2}Li^2$$

The current after having reached its maximum value will continue to flow in the same direction and will begin to recharge the capacitor. This causes a voltage across the coil and capacitor which tends to oppose the flow of current and the current decreases until it is zero, at which time the energy is once again stored in the capacitor. The only change in the system at this time from the initial state is that the capacitor has opposite polarity. This system will continue to oscilate in the above manner as long as the switch is closed.

The First Law for this system could be written as $E = \text{constant}$ or $dE = 0$ since dQ and dW are both zero.

$$E = \tfrac{1}{2}Li^2 + \tfrac{1}{2}CV^2 = \text{constant}$$

If the capacitance and inductance of the system are constant,

$$dE = Li\,di + CV\,dV = 0 \tag{64}$$

The above system serves to show how energy may be stored in an electrical system. It remains to construct an isolated system for which a mathematical analysis of the First Law is possible. The following systems of negligible resistance make this possible.

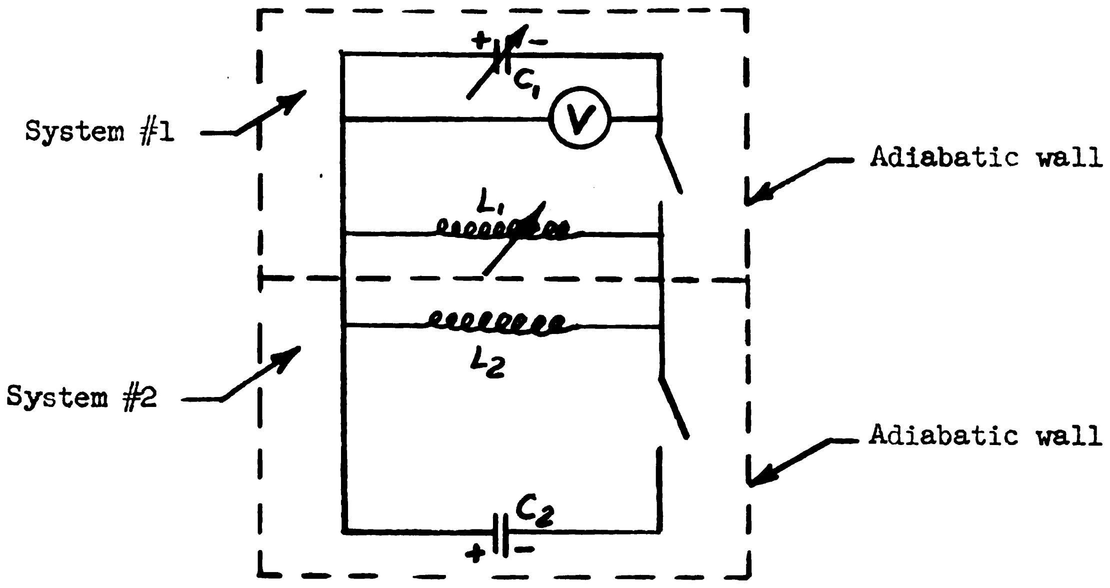

Figure 13.

Both capacitors are originally charged and the voltage across both capacitors is the same. If the switches of Figure 18 are closed simultaneously the system will oscilate as described in the previous example.

If the two capacitors and inductances are initially of equal magnitude, the energy stored in each capacitor at zero current is the same and the energy stored in each inductance coil at maximum current is the same.

Thus there is no change in stored energy in either system. But if both C_1 and L_1 are varied, the energy stored in the two systems is not the same. If C_1 is made less than C_2 the energy stored in C_1 at zero current is less than that stored in C_2 since $E = \frac{1}{2}CV^2$ and the voltage across both capacitances is the same. Likewise if L_1 is made less than L_2 the current will increase more rapidly in L_1 since $V = L\frac{di}{dt}$ and the voltage across both inductance coils is the same. Thus L_1 will have a larger maximum current and the energy stored in L_1 will be greater than that stored in L_2 since $E = \frac{1}{2}Li^2$.

For adiabatic systems the First Law is $-dW = dE$. Thus when there are changes in the stored energy of these systems work must be done reversibly on one of the systems by the other system.

The change in stored energy for a system such as the above two systems has already been found to be if L and C are constant

$$dE = Lidi + CVdV$$

In the above systems this same relationship will hold if C_1 is varied only when the voltage of the system is zero and L_1 is varied only when the current flow is zero. By carrying out the variations of C_1 and L_1 in the above manner, not only are all energy transformations made at constant C_1 and L_1 but also no work is needed from an external source to vary these quantities.

The change in stored energy of each system is thus a function of two independent variables, i and V, and may be expressed as follows:

$$dE = \left(\frac{\partial E}{\partial i}\right)_V di + \left(\frac{\partial E}{\partial V}\right)_i dV \qquad (65)$$

Therefore, dW_1 and dW_2 may be expressed as Pfaffian equations of two independent variables:

$$-dW_1 = \left(\frac{\partial E_1}{\partial i_1}\right)_{V_1} di_1 + \left(\frac{\partial E_1}{\partial V_1}\right)_{i_1} dV_1$$
$$-dW_2 = \left(\frac{\partial E_2}{\partial i_2}\right)_{V_2} di_2 + \left(\frac{\partial E_2}{\partial V_2}\right)_{i_2} dV_2 \qquad (66)$$

The work done by the combined system is equal to the sum of the work of the two separate systems and this sum is equal to zero since no work crosses the boundries of the combined system.

$$dW = dW_1 + dW_2 = 0$$
$$-dW = \left(\frac{\partial E_1}{\partial i_1}\right)_V di_1 + \left(\frac{\partial E_2}{\partial i_2}\right)_V di_2 + \left[\left(\frac{\partial E_1}{\partial V}\right)_{i_1} + \left(\frac{\partial E_2}{\partial V}\right)_i\right] dV = 0 \qquad (67)$$

The voltage of systems one and two need no longer be distinguished since $V_1 = V_2 = V$.

The quantities $-dW_1$ and $-dW_2$ have been expressed as Pfaffian equations of two independent variables. Therefore,

$$-dW_1 = \lambda_1 d\phi_1$$
$$-dW_2 = \lambda_2 d\phi_2 \qquad (68)$$

It can be shown that -dW is also expressed as a Pfaffian equation of two independent variables. This can be shown by constructing the surface for -dW equals zero.

Examine first the intersection of the surface of no work with the V-i planes. Let the voltage be increased and vary L_1 such that i_1 is constant. This could be done by increasing L_1. An equivalent capacitance C for the system may be found. $C = C_1 + C_2$. From energy consideration:

$$\frac{1}{2}CV^2=\frac{1}{2}L_1 i_1^2 \quad \frac{1}{2}L_2 i_2^2$$

But i_1 is constant. Therefore,

$$\frac{1}{2}CV^2-K_1=\frac{1}{2}L_1 i_1^2$$

or

$$V^2-K_2=\frac{L_1}{C}i^2$$

This describes on V-i planes lines of constant i_1 with the following form:

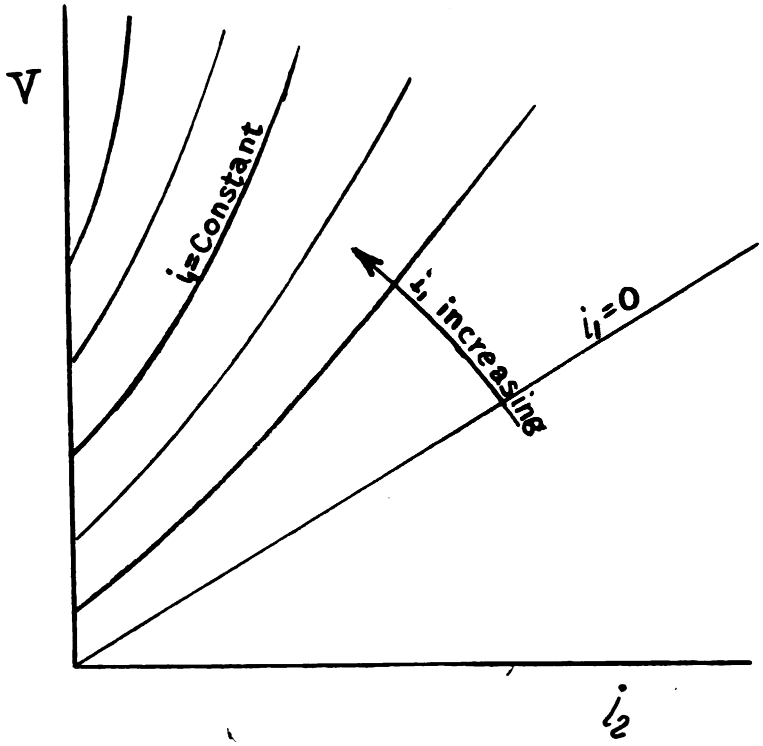

Figure 19.

The shape of the surface is then determined.

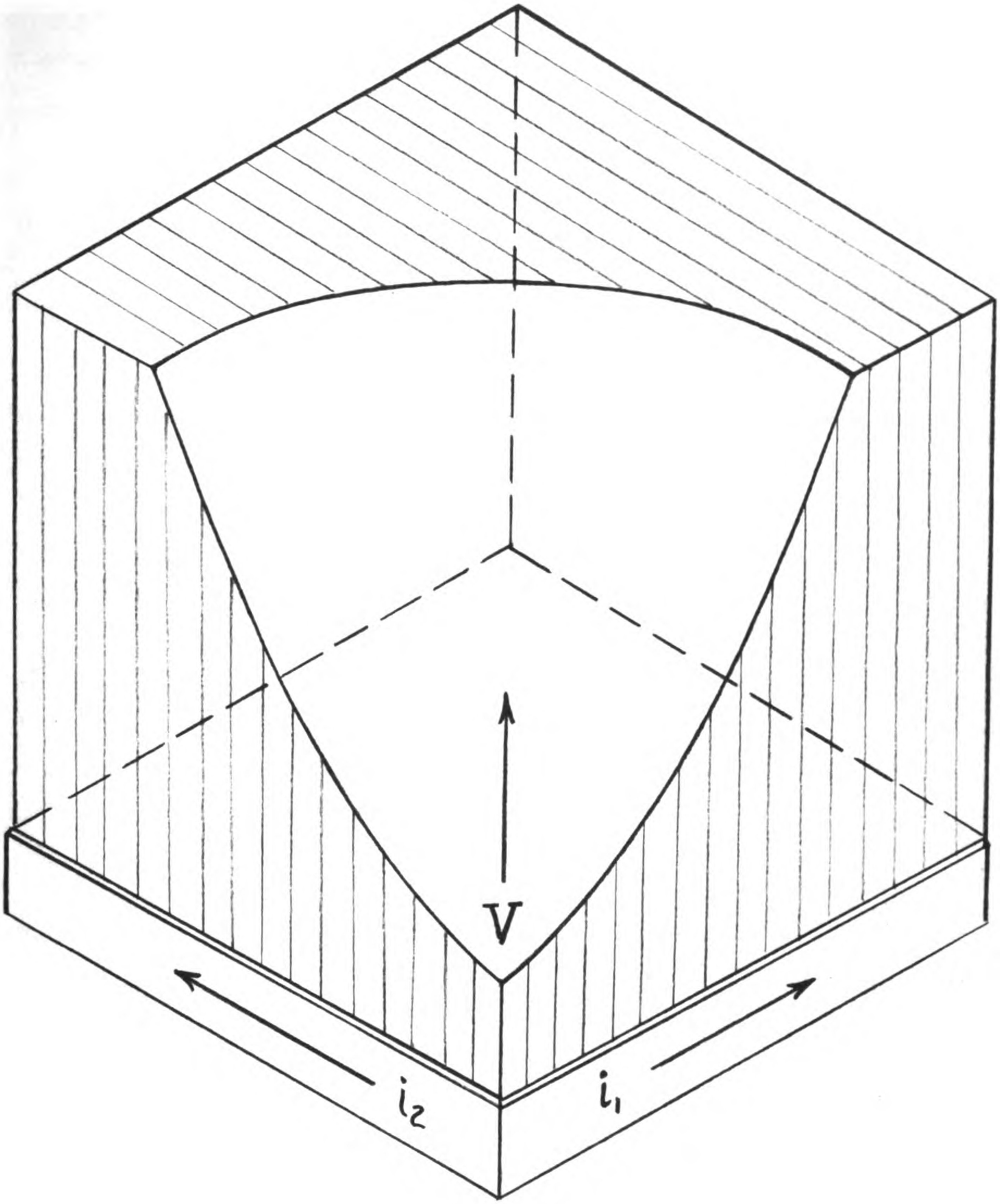

Figure 20.

Surfaces of no work in i_1-i_2-V space

Since -dW is a Pfaffian equation of two independent variables there exists an integrating denominator λ such that $\frac{-dW}{\lambda}$ is an exact differential, $d\phi$.

$$-dW = \lambda d\phi$$

But

$$dW = dW_1 + dW_2$$

Therefore,

$$\lambda d\phi = \lambda_1 d\phi_1 + \lambda_2 d\phi_2 \tag{69}$$

The equality of equation (69) can hold only if ϕ is a function of ϕ_1 and ϕ_2. Therefore,

$$d\phi = \frac{\partial\phi}{\partial\phi_1} d\phi_1 + \frac{\partial\phi}{\partial\phi_2} d\phi_2 \tag{70}$$

Equating coefficients of the exact differential $d\phi$ gives

$$\frac{\partial\phi}{\partial\phi_1} = \frac{\lambda_1}{\lambda}, \quad \frac{\partial\phi}{\partial\phi_2} = \frac{\lambda_2}{\lambda} \tag{71}$$

ϕ is a property of the combined system and ϕ_1 and ϕ_2 are properties of the individual systems. Since $\frac{\lambda_1}{\lambda}$ and $\frac{\lambda_2}{\lambda}$ are the partial derivitives of ϕ with respect to ϕ_1 and ϕ_2, they are independent of the other properties of the system and cannot be a function of the voltage. Therefore,

$$\frac{\partial}{\partial V} \frac{\lambda_1}{\lambda} = 0 \; ; \quad \frac{\partial}{\partial V} \frac{\lambda_2}{\lambda} = 0 \tag{72}$$

It is not necessary to distinguish between the voltages of the two systems since they are equal.

By carrying out the differentiation of equation (72)

$$\frac{1}{\lambda_1} \frac{\partial\lambda_1}{\partial V} = \frac{1}{\lambda_2} \frac{\partial\lambda_2}{\partial V} = \frac{1}{\lambda} \frac{\partial\lambda}{\partial V} \tag{73}$$

The equality of equation (73) can hold only if both $\frac{1}{\lambda_1}\frac{\partial\lambda_1}{\partial V}$ and $\frac{1}{\lambda_2}\frac{\partial\lambda_2}{\partial V}$ depend only on V. Hence,

$$\frac{1}{\lambda_1} \frac{\partial\lambda_1}{\partial V} = \frac{1}{\lambda_2} \frac{\partial\lambda_2}{\partial V} = \frac{1}{\lambda} \frac{\partial\lambda}{\partial V} = f(V) \tag{74}$$

This equation may be rewritten in the following form:

$$\frac{\partial \ln\lambda_1}{\partial V} = \frac{\partial \ln\lambda_2}{\partial V} = \frac{\partial \ln\lambda}{\partial V} = f(V)$$

from which

$$\ln\lambda = \int f(V)dV + \ln f(\phi)$$

$$\lambda = \Phi e^{\int f(V)dV} \qquad (75)$$

where $\Phi = f(\phi)$.

The voltage may now be defined as that part of λ which is a function of the voltage

$$V'(V) = Ce^{\int f(V)dV} \qquad (76)$$

By defining a new property, charge, as follows,

$$Q(\phi) = \frac{1}{C}\int \Phi d\phi \qquad (77)$$

it is seen that

$$-dW = \lambda d\phi = VdQ = 0$$

Similarly,

$$-dW_1 = \lambda_1 dO_1 = V_1 dQ_1$$

$$-dW_2 = \lambda_2 dO_2 = V_2 dQ_2$$

and in general for all such reversible processes

$$-dW = \lambda d\phi = VdQ \qquad (78)$$

To gain a knowledge of the directional limitation imposed on the First Law in electrical systems it is necessary to examine the irreversible phenomena associated with these systems.

Examine the following irreversible system.

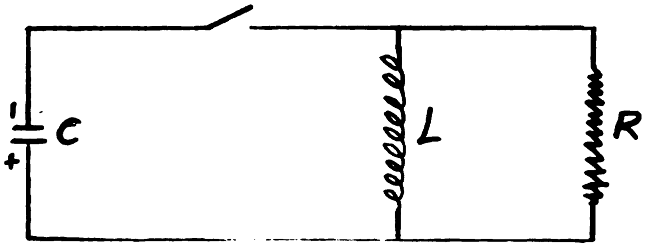

Figure 21.

Consider a finite transition from an initial state (V_0, Q_0) to a final state (V, Q). It is possible to reach state (V, Q) in two steps; first changing the voltage adiabatically by varying the capacitance, the charge remaining constant, equal to Q_0, and then changing the state adiabatically at constant capacitance by closing the switch for a finite length of time until Q_0 goes over to Q.

Examine step one on a capacitance charge diagram.

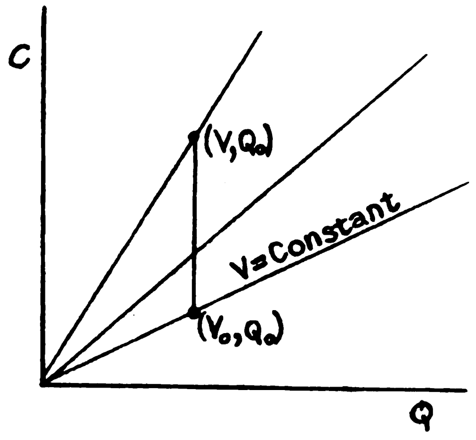

Figure 22.

Figure 22 shows that from any initial state (V_0, Q_0) any other state (V, Q_0) having the same charge may be reached since the capacitance is arbitrarily variable at constant charge. Step two must then give the restriction on the First Law.

Examine step two on a capacitance charge diagram.

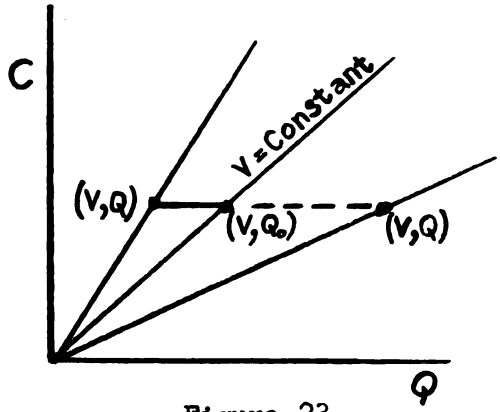

Figure 23.

Figure 23 shows that once state (V,Q) has been reached from any initial state (V,Q_o), there are two possible relationships between Q_o and Q, that is $Q_o \geq Q$ or $Q_o \leq Q$. One of these conditions cannot be possible or else all states would be accessible to any given state in isolated systems.

Consider the process in which Q_o was changed at constant capacitance to Q. There is experienced during this process a decrease in the voltage across the capacitor. This value of voltage and the capacitance determine the charge on the capacitor and this value of charge will be the same regardless of how this state is reached. This state could be reached by allowing this capacitor to reversibly charge another capacitor. If the capacitor does work reversibly in this manner the work done by the system has been shown to be $dW = -VdQ$. This work has been a positive quantity since it was out of the system. If the constant in equation is chosen such that V is positive the relationship $dW = -VdQ$ shows that the charge cannot increase in an isolated system.

Since V is always positive, the only way the charge in a system can increase is to add work to the system in the form of VdQ work. Also since the charge can decrease but never increase in an isolated system, $dW \leq -VdQ$ or $dW \leq |VdQ|$ for any process. The equality holding in reversible processes. Hence, for any process $\frac{dW}{V} \leq |dQ|$. For any cycle integrating around the cycle,

$$\oint \frac{dW}{V} \leq \oint |dQ|$$

$$\oint \frac{dW}{V} \leq 0$$

since charge is a state point and has zero change in a cycle.

This result is not in conflict with the classical statement of the Second Law that the entropy cannot decrease in an isolated system since it can be shown that the entropy increased also during this process.

Consider first the change of state of the capacitor during this process. The capacitor performed an amount of work on the resistor. This work could have been done reversibly and adiabatically on another capacitor. Therefore there was no change of entropy in the capacitor.

Consider next the resistor. If a large source of air at a temperature equal to the initial temperature of the resistor is blown over the resistor so that no change of temperature is caused in the resistor or the air, no change of entropy takes place in the resistor since it is in a steady state condition.

Consider finally the cooling air. There has been an amount of heat energy transferred to the air equal to the work done on the resistor. Therefore the increase in entropy of the air may be calculated by

$$dS = \frac{-VdQ}{T}$$

where T is the temperature of the air and resistor.

Thus the decrease of charge and the increase of entropy in electrical systems indicate the same directional restriction on the First Law.

ANALYSIS OF THE FIRST LAW FOR ISOLATED MECHANICAL SYSTEMS

In the first two constant mass systems, energy could be stored in the system only in the form of molecular activity. In systems of varying composition it was seen that there existed another form of stored energy in the form of the chemical potential. In mechanical systems there exist two other methods by which a system may store energy (i.e., kinetic and potential energy). Thus for mechanical systems in general there exist four ways of storing energy in the system (electricity, magnetism and capillarity being neglected).

If chemical interactions were present in a mechanical system, they could be treated separately by the methods developed for systems of varying composition. Also heat exchanges may be treated separately by the methods developed for adiabatic constant mass systems. This leaves then for reversible adiabatic mechanical systems two forms of energy storage within the system, kinetic and potential energy.

It is known that a directional principle exists for isolated mechanical systems (i.e., if a mass object in an isolated system is allowed to fall a certain distance while doing work on a friction device, the system cannot be returned to its initial state by an adiabatic process). There is experienced during this process a rise in the temperature of the system at the expense of the potential energy of the mass object. The process has never been observed when the potential energy of a mass object has been increased solely by a decrease in the temperature of the system. If the above system is to be returned to its initial state, work must be done by an external source to restore the mass object to its initial state of potential energy, and heat must be removed to restore the temperature of the system to its initial value. When this is done the system is not isolated. Thus in isolated mechanical systems there exist states which are inaccessible from any initial state. It should then be possible to construct an isolated system in which one of the energy quantities envolved may be expressed as a Pfaffian equation of one or two independent variables to determine what this directional principle is.

Consider first the following system.

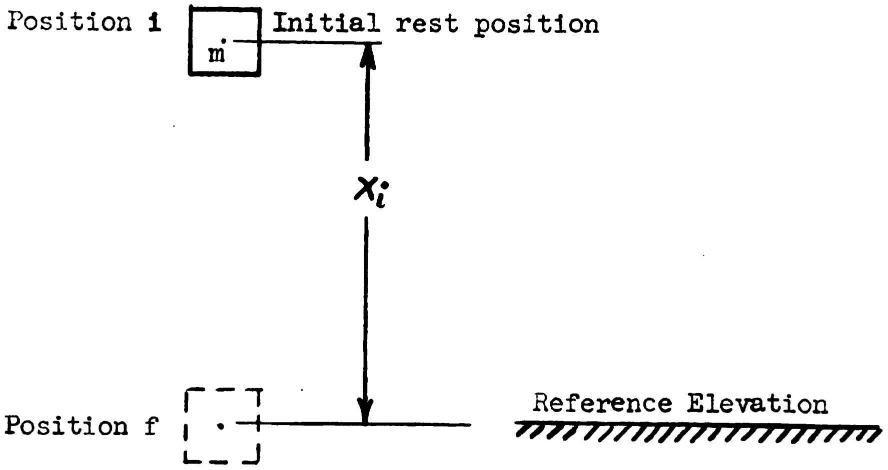

Figure 24.

If the mass in Figure 24 is initially at rest, energy is stored in the system in the form of potential energy.

$$E = \frac{mg}{g_0} X_i$$

Where g is the acceleration due to gravity and g_0 is a dimensional constant $32.17 \frac{ft\ \#_m}{\#_f\ sec^2}$.

If the mass is allowed to fall to position f, it no longer has any potential energy. The energy is totally stored in the system as kinetic energy.

$$E = \frac{1}{2} mV^2$$

where V denotes the velocity of the mass object.

The First Law for this system could be written as $E =$ constant or $dE = 0$ since dQ and dW are both zero. For any position intermediate to the two shown in Figure 24, E will be given by

$$E = \frac{mg}{g_0} x + \frac{1}{2} mV^2 = \text{constant.}$$

For any infinitesimal change in energy

$$dE = \frac{mg}{g_0} dx + mVdV = 0 \tag{79}$$

The above system serves to show how energy may be stored in a mechanical system. It remains to construct an isolated system for which a mathematical analysis of the First Law is possible. Consider the following isolated system of negligible friction which is initially at rest and in which m_1 is greater than m_2.

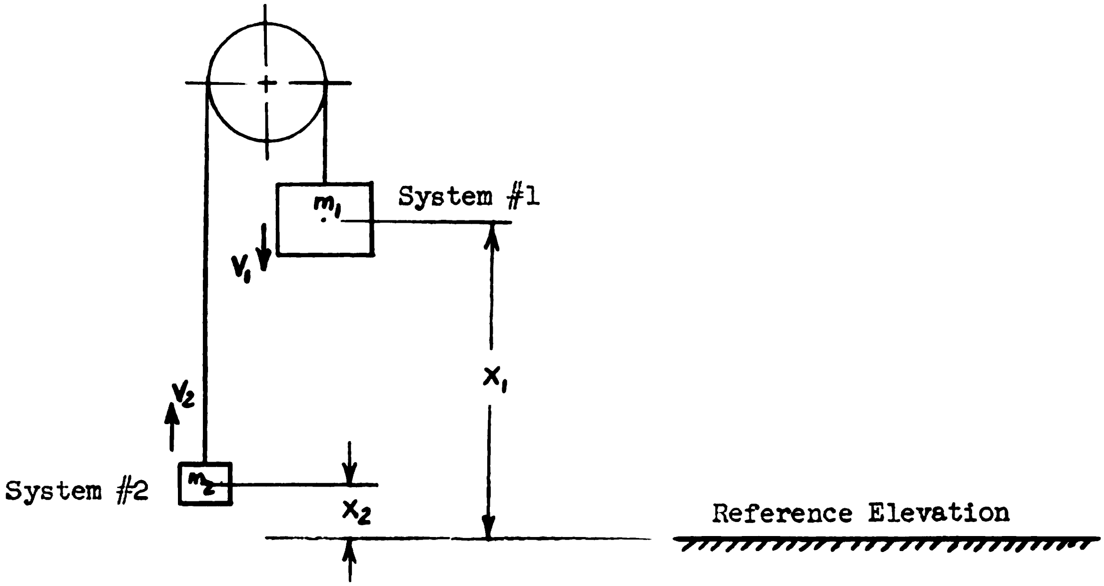

Figure 25.

m_1 and m_2 each constitute separate systems, and the First Law may be applied. For adiabatic systems the First Law is $-dW = dE$. Thus if there is a change in stored energy of either of these systems, work must be done reversibly on or by the other system.

The change in stored energy for a system such as the above two systems has been shown to be

$$dE = \frac{mg}{g_o}dx + mvdV$$

The change in stored energy of each system is thus a function of two variables, x and v, and may be expressed as follows:

$$dE = \left(\frac{\partial E}{\partial x}\right)_V dx + \left(\frac{\partial E}{\partial V}\right)_x dV$$

Therefore $-dW_1$ and $-dW_2$ may be expressed as Pfaffian equations of two variables:

$$-dW_1 = \left(\frac{\partial E_1}{\partial x_1}\right)_{V_1} dx_1 + \left(\frac{\partial E_1}{\partial V_1}\right)_{x_1} dV_1$$

$$-dW_2 = \left(\frac{\partial E_2}{\partial x_2}\right)_{V_2} dx_2 + \left(\frac{\partial E_2}{\partial V_2}\right)_{x_2} dV_2 \qquad (80)$$

The work done by the combined system is equal to the sum of the work of the two separate systems and this sum must be equal to zero since no work crosses the boundries of the combined system.

$$dW = dW_1 + dW_2 = 0$$

$$-dW = \left[\left(\frac{\partial E_1}{\partial x_1}\right)_V + \left(\frac{\partial E_2}{\partial x_2}\right)_V\right]dx + \left[\left(\frac{\partial E_1}{\partial V}\right)_{x_1} + \left(\frac{\partial E_2}{\partial V}\right)_{x_2}\right]dV = 0 \qquad (81)$$

In equation (81) dx_1 and dx_2 need no longer be distinguished since $dx_1 = dx_2$ and v_2 and v_1 need not be distinguished since $V_1 = V_2 = V$.

Equation (81) is a Pfaffian equation with one independent variable since for the system constructed if one variable is known say V_1 all the others are determined. $V_2 = V_1$ and the kinetic energy in the system is determined. Since the total energy in the system is constant the total potential energy is also determined. Thus

$$-\Delta KE = \Delta PE$$

where KE denotes the change in kinetic energy and PE the change in potential energy of the system.

$$-\Delta KE = \frac{m_1 g}{g_0} x_{1i} + \frac{m_2 g}{g_0} x_{2i} + \frac{g \Delta x}{g_0}(m_2 - m_1)$$

where x_{1i} and x_{2i} are the initial rest positions which are known.

The only unknown in equation (81) is Δx and the equation may be solved for Δx.

It has been shown that equation (81) is a Pfaffian equation of one independent variable. It should be possible to construct curves of no work in a v_1-x_1 plane. These curves take the form of Figure 26.

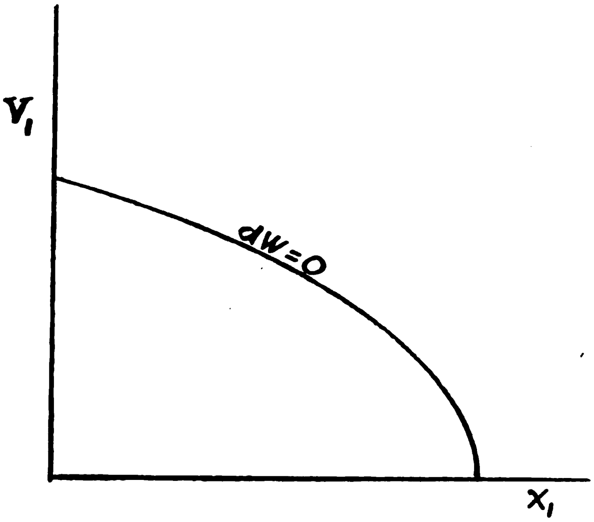

Figure 26.

Curves of No Work in the V_1-x_1 Plane

The slope of the curve in Figure 26 is determined by

$$m_1 V_1 dV_1 + m_2 V_2 dV_2 = -\left[\frac{m_1 g}{g_0} dx_1 - \frac{m_2 g}{g_0} dx_2\right]$$

$$mVdV = -\frac{(m_1 - m_2) g}{g_0} dx$$

$$\frac{dV}{dx} = -\frac{(m_1 - m_2) g}{mV g_0} = -\frac{c}{V}$$

Thus when V is large the slope is small. When V is small the slope is large and the slope is always negative.

Since $-dW_1$, $-dW_2$, and $-dW$ have all been expressed as Pfaffian equations of two variables,

$$-dW_1 = \lambda_1 d\phi_1$$

$$-dW_2 = \lambda_2 d\phi_2$$

$$-dW = \lambda\, d\phi$$

Since $dW = dW_1 + dW_2 = 0$,

$$\lambda d\phi = \lambda_1 d\phi_1 + \lambda_2 d\phi_2 \tag{82}$$

The equality of equation(82)can only hold if ϕ is a function of ϕ_1 and ϕ_2. Therefore,

$$d\phi = \frac{\partial\phi}{\partial\phi_1} d\phi_1 + \frac{\partial\phi}{\partial\phi_2} d\phi_2 \tag{83}$$

Equating coefficients of the exact differential $d\phi$ gives

$$\frac{\partial\phi}{\partial\phi_1} = \frac{\lambda_1}{\lambda}, \quad \frac{\partial\phi}{\partial\phi_2} = \frac{\lambda_2}{\lambda}$$

ϕ is a property of the combined system and ϕ_1 is a property of the first system. Since λ_1/λ is the partial derivitive of ϕ with respect to ϕ_1, and since ϕ is a function only of ϕ_1 and ϕ_2, λ_1/λ cannot be a function of any other property of the system and is therefore independent of the force, F, exerted on system one by the coupling between system one and system two; similarly for λ_2/λ. The partial derivitives of $\frac{\lambda_1}{\lambda}$ and $\frac{\lambda_2}{\lambda}$ with respect to F must then be equal to zero.

$$\frac{\partial}{\partial F}\frac{\lambda_1}{\lambda} = 0 \quad ; \quad \frac{\partial}{\partial F}\frac{\lambda_2}{\lambda} = 0$$

F_1 and F_2 need not be distinguished since $F_1 = F_2 = F$. By carrying out the differentiation, the following equality is obtained.

$$\frac{1}{\lambda_1}\frac{\partial\lambda_1}{\partial F} = \frac{1}{\lambda_2}\frac{\partial\lambda_2}{\partial F} = \frac{1}{\lambda}\frac{\partial\lambda}{\partial F}$$

This equality can hold only if $\frac{1}{\lambda_1}\frac{\partial\lambda_1}{\partial F}$ and $\frac{1}{\lambda_2}\frac{\partial\lambda_2}{\partial F}$ depend only on F. Therefore,

$$\frac{1}{\lambda_1}\frac{\partial\lambda_1}{\partial F} = \frac{1}{\lambda_2}\frac{\partial\lambda_2}{\partial F} = \frac{1}{\lambda}\frac{\partial\lambda}{\partial F} = f(F) \tag{84}$$

Equation (84) may be rewritten as follows:

$$\frac{\partial \ln\lambda_1}{\partial F} = \frac{\partial \ln\lambda_2}{\partial F} = \frac{\partial \ln\lambda}{\partial F} = f(F)$$

from which

$$\ln\lambda = \int f(F)\,dF + C \qquad (85)$$

This constant can be shown to be a function of at most one other variable. Selecting ϕ will give the most desirable results. Equation (85) may then be written

$$\ln\lambda = \int f(F)\,dF + \ln\Phi$$

where $\Phi = f(\phi)$.

$$\lambda = \Phi e^{\int f(F)\,dF}$$

It is now possible to define F as that part of λ which is a function of F.

$$F'(F) = Ce^{\int f(F)\,dF} \qquad (86)$$

The value of C may be fixed by prescribing the value of $F_2 - F_1$ for two reproducible states.

By defining another property x as follows

$$x(\phi) = \frac{1}{C}\int \Phi\,d\phi \qquad (87)$$

it is seen that

$$-dW = \lambda d\phi = F dx = 0$$

Similarly,

$$-dW_1 = \lambda_1 d\phi_1 = F_1 dx_1$$

$$-dW_2 = \lambda_2 d\phi_2 = F_2 dx_2$$

and in general for any reversible process

$$-dW_R = F dx$$

Equation (87) refers only to the reversible processes from which it was derived. To obtain a knowledge of real irreversible phenomena it is necessary to apply the previously mentioned fact that there exist in isolated mechanical systems states which are inaccessible from any given state.

Consider the following system.

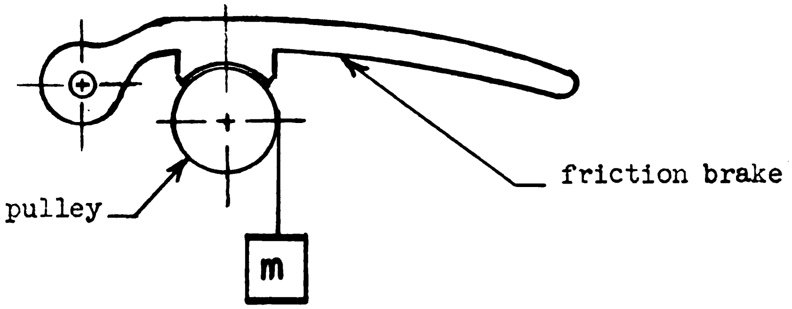

Figure 27.

Examine a finite transition from an initial state $(V_0 - X_0)$ to a final state (V,x). It is possible to reach the final state in one step. Consider the system of Figure 27 in which there is now a frictional device fastened to the pulley. Examine the change on a V-x diagram.

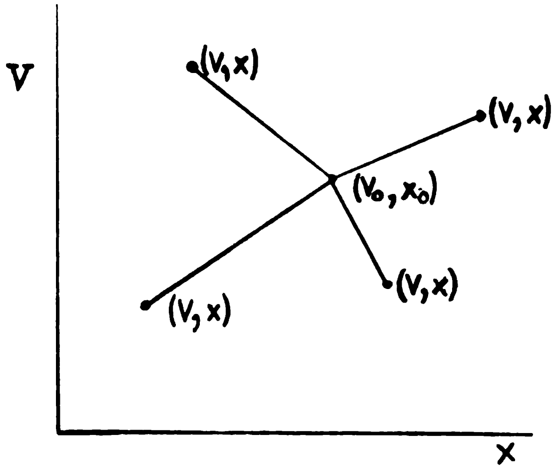

Figure 28.

Figure 28 shows that four possible relationships exist between (V_0, x_0) and (V, x).

$V_0 \geq V$ and $x_0 \geq x$

$V_0 \geq V$ and $x_0 \leq x$

$V_0 \leq V$ and $x_0 \geq x$

$V_0 \leq V$ and $x_0 \leq x$

Any value of velocity is obtainable within the limits of the system simply by varying the friction in the system. Therefore the relationship between x_0 and x must give the restriction on the First Law. Consider what happens when the frictional element is applied. The pulley experiences a force which tends to oppose the direction of rotation. If this force had been exerted by another suspended mass in a way similar to Figure 25 , this force could have been utilized to raise this mass through a distance. If this had been done, work would have been done reversibly by the system. Since this work would have been taken from the system it is a positive quantity and the relationship $-dW = Fdx$ shows that dx is a negative quantity. Therefore $x \leq x_0$ and it can be shown that the potential energy could not increase in this isolated system.

It is obvious that the maximum kinetic energy of the system is also decreased by the friction device, and in general in any mechanical system the sum of the kinetic and potential energies cannot increase.

These results are not in conflict with the classical statement of the Second Law that the entropy cannot decrease in an isolated system since it can be shown that the entropy also increased during this irreversible process.

Consider first the falling mass. There is no change in entropy in the falling mass since the loss in kinetic and potential energies could have been utilized reversibly and adiabatically to do work.

Consider next the pulley and brake. If a large source of air at the original temperature of the pulley and brake is blown over the pulley and brake there is no change in entropy in the pulley and brake since they are in a steady state.

Consider finally the cooling air. There has been an amount of heat added to the air equal to the change in stored energy of the falling mass. The change in entropy may be calculated by

$$S_2 - S_1 = \frac{\Delta E}{T}$$

where T is the temperature of the air.

Thus the increase in entropy and the decrease in potential and kinetic energies indicate the same directional restriction on the First Law in mechanical systems.

CONCLUSION

It is seen that by establishing a method of performing a mathematical analysis of the First Law, the directional characteristic of any process is directly obtainable from the First Law. Thus the association of the Second Law with idealized thermal machines and heat power cycles is removed.

The common conception that thermodynamics is concerned with heat-work relationships in thermal machines is erroneous. The laws of thermodynamics are concerned with energy transformations; as such they are very general. The breadth of the field of thermodynamics is obscured, and the generality of the laws of thermodynamics is frequently lost in the maze of thermal machines classically employed in their proof. The establishment of the Second Law for all systems without the use of idealized thermal machines is at least one step toward making the science more general.

The analysis of various systems shows conclusively that the entropy cannot decrease in an isolated system. However, the mathematical analysis of the various systems did not of itself indicate this direction. Only in adiabatic systems of constant composition did the mathematical analysis show that entropy could not decrease. This resulted in a reduction of the temperature potential.

In systems where no work is done the mathematical analysis of the First Law indicated only that the volume of the system could not decrease. This resulted in a reduction of the pressure potential.

The mathematical analysis of chemical systems showed that in isolated systems the chemical potential could not increase.

In electrical systems it was shown that the charge in the system could not increase if no work were done on the system. This resulted in a reduction of the voltage potential.

Similarly for isolated mechanical systems the total stored energy in the form of potential and kinetic energy cannot increase.

The results of the mathematical analysis of these various systems leave some doubt as to whether the increase in entropy points the direction that an isolated process must take. Possibly the increase in entropy only measures the displacement in this direction during the process as a result of the reduction in the potential of the system. This, however, is irrelevant since both directions are one and the same, and it makes no difference whether it is stated that the entropy cannot decrease or that the potential cannot increase in an isolated system.

If the entropy must increase in isolated systems, then let the Second Law be so stated. It is, however, unnecessary to prove this directional characteristic by the use of thermal machines. There is an obvious gain in generality by being able to analyse any system directly rather than applying a result which was established indirectly by the use of thermal machines.

Consider for example the classical proof that a free expansion is an irreversible process. The Second Law is first stated in one of its classical forms: it is impossible for a heat engine to produce net work in a complete cycle if it exchanges heat only with bodies at a single fixed temperature.

To demonstrate the irreversibility of a free expansion the following procedure is followed. An insulated container, Figure 29, is divided into two regions A and B by a thin diaphragm.

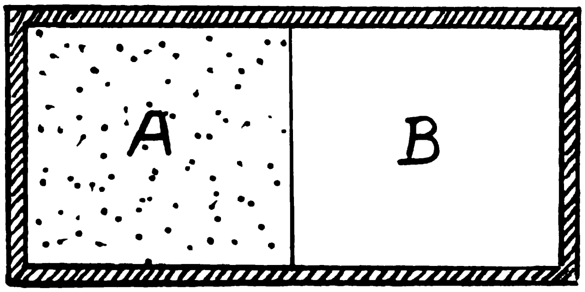

Figure 29.

Region A contains a mass of gas and region B is completely evacuated. If the diaphragm is punctured, the gas will expand into region B until the pressures in A and B become equal, but there will be no effect on the surroundings.

Assume that the free expansion is reversible. Let the reverse process occur, by which the gas in B returns into A with an increase in pressure, without any change in the surroundings. To construct a cycle which shall violate the Second Law, install an engine between A and B, Figure 30, and permit the gas to expand through the engine from A to B instead of using the free expansion.

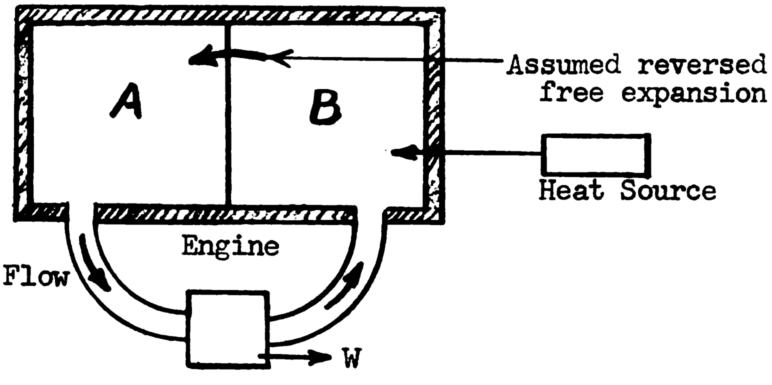

Figure 30.

The engine can obtain work from the system at the expense of the internal energy of the gas as it expands. After the expansion through the engine, the internal energy of the system can be restored to its initial value by heat transfer from a source at a fixed temperature. Thus the system can be brought to the same state as if the free expansion had occurred. Now, by use of the reversed free expansion, the system can be restored to the initial state of high pressure in A and vacuum in B. The result is a cycle which violates the classical statement of the Second Law and is therefore impossible. Since the expansion through the engine and the heat transfer from the fixed temperature source are known to be possible, the reversed free expansion must be impossible; and a free expansion is irreversible.

This proof leaves much to be desired. The very statement of the Second Law used in this proof implies that the Second Law is associated only with heat engines and cycles. This is not the case. The Second Law applies to all processes, not just heat engine processes and not just cycles. The free expansion has been analysed independently of heat engine cycles and the resulting directional characteristic shown.

Other irreversible phenomena may be analysed in a similar way. Only by this removal of the association of the Second Law with heat engine cycles may the generality of the Second Law be elevated to a position consistent with that of the First Law, and the scope of the science of thermodynamics extended beyond the realm of heat-work relationships in thermal machines.

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