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L.C. Woods

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L. C. Woods
School of Mechanical Engineering

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THE FOUNDATIONS of CLASSICAL THERMODYNAMICS

by

L. C. WOODS
(Nuffield Research Professor of Mechanical Engineering in the University of New South Wales, Australia.)

A course of lectures given in 1957.
1. Temperature

1.1 Thermodynamic Systems

As thermodynamics is a branch of physics, it is concerned with certain characteristics of a particular domain of space and matter, a domain of interest which we call a system. Everything outside a system which could have a direct influence on the behaviour of the system is termed the surroundings. A system can be defined by stating its various physical and chemical properties in full, but for many purposes it is found sufficient to define a system by only a few large-scale physical characteristics. These are termed macroscopic coordinates, and have the two important characteristics of (1) involving no special assumptions concerning the structure of matter, and (2) being capable, in general, of direct measurement. Simple examples are the pressure and volume of a gas in a container, and the tension and length of a stretched wire.

In the microscopic description of a system, assumptions are made about the structure of matter, i.e. a molecular structure is assumed, and the microscopic coordinates are the velocities and positions of a very large number of molecules. This approach yields the branch of physics known as statistical mechanics, and offers an alternative, or rather complementary treatment of thermodynamics. Classical or macroscopic thermodynamics gives results which apply to averages over a period of time of the behaviour of a very large number of molecules, and this provides a means of checking one theory against the other. Classical thermodynamics has the advantage of being based on fewer and more directly verifiable assumptions than statistical thermodynamics, its conclusions are unaffected by the changes and refinements found necessary from time to time in molecular theory, and it thus provides a reference datum for the basic assumptions of the statistical approach. Of course the more detailed basic assumptions of statistical thermodynamics mean that it yields many results quite beyond the reach of classical theory, and the study of it forms a natural sequel after a course along classical lines.
Classical thermodynamics is concerned with the internal state of a system, and those macroscopic coordinates found (by experiment) to be necessary and sufficient to define this state for a given purpose are termed thermodynamic coordinates. Systems which can be described by such coordinates are called thermodynamic systems. Examples of thermodynamic systems are steam, surface films, electric cells, thermocouples and magnetic substances.

1.2 Equilibrium States: Quasi-static Changes

An equilibrium state of a system is one in which the coordinates defining it remain constant in time. Classical thermodynamics deals only with equilibrium states of thermodynamic systems, and it is especially concerned with the comparison of different equilibrium states of the same or of different systems. "Thermostatics" might be a more apt description of the subject. In the sequel by "state" we shall mean "equilibrium state".

Suppose that for a given system n independent thermodynamic coordinates $x_1, x_2, \ldots, x_n$ are found to be necessary and sufficient to uniquely define the state, then the possible states of the system can be regarded as forming a connected set* of points in an $n$-dimensional domain, which we may describe as being the "state-space" for the system. Any two distinct states $A$ and $B$ of the system can be joined by a path $AB$ lying in the state space, and we may conceive the system to pass successively from $A$, through all the (equilibrium) states on $AB$ and ending at $B$. Such changes are purely theoretical concepts, and can never occur naturally. There is no restriction on their direction, so they are sometimes called reversible changes, or alternatively, quasi-static changes. The natural process by which a system changes from one state to another is quite different. In this, the system passes out of state $A$, finally to end up in state $B$, through conditions which are not equilibrium states. Although the coordinates take, in

* In any two-phase chemical system a number of thermodynamical variables range only over certain discrete domains -- we exclude these cases here.
sequence, sets of values which denote points in state-space, the non-equilibrium states themselves are not represented in state-space at all. The conditions of the system during the transition from A to B are outside the scope of thermodynamics, although, as we shall see later, thermodynamics does have one fundamental statement to make regarding these natural changes.

A system in thermodynamic equilibrium must satisfy the following requirements:

1. Mechanical Equilibrium. The forces on each element of the system must be in equilibrium, or balanced by external forces.
2. Chemical Equilibrium. The molecular structure and chemical composition must remain constant (except metastable systems).
3. Thermal Equilibrium. The energy content of the system must remain fixed. The significance of 1. and 2. is clear, but 3. introduces a new thermodynamic concept and needs amplification.

1.3 Thermal Equilibrium.

At this stage it is helpful to introduce the concept of "walls", which serve to separate systems from each other, and from their surroundings. These walls are not essential to the argument, but they aid the physical description and help to fix ideas. They are assumed to be so thin that they play no part in the behaviour of the system, except to define the thermodynamic interaction between the systems they separate.

Walls can be one of two distinct types. If they isolate a system completely from surrounding systems, they are said to be adiabatic while if they do no more than simply physically separate a system from the surroundings, they are called diathermic walls. To simplify the discussion we shall consider thermodynamic systems of constant mass and composition, whose states are completely defined by just two independent coordinates. No essential loss in generality will arise from this choice, as is easily verified a posteriori. A familiar system suiting our purpose is a gas in a container, and whose
state is defined by the independent variables \( v \), the volume and \( p \), the pressure. We can now express the definitions of rigid adiabatic and diathermic walls in mathematical terms as follows.

An adiabatic wall between two systems is defined by the property that a state \(( p_1, v_1)\) for the first system, and a state \(( p_2, v_2)\) for the second may coexist as equilibrium states for any attainable values of the four variables. (More generally if system 1 is defined by \( n \) variables, and system 2 by \( m \) variables, then these systems are separated by an adiabatic wall if it requires \( n+m \) variables to define the composite system 1 plus 2 completely).

On the other hand if the two systems are separated by a diathermic wall they are not in equilibrium states for arbitrary values of \( p_1, v_1 \) and \( p_2, v_2 \), but only when a definite relation

\[
F(p_1, v_1, p_2, v_2) = 0
\]

is satisfied. This means that in the composite system 1 plus 2 only three of \( p_1, v_1, p_2, \) and \( v_2 \) are independent variables. (More generally \( m+n-1 \) variables define the composite system). In this case systems 1 and 2 are said to be in thermal contact, and equation (1) is the condition of thermal contact. (We exclude flexible adiabatical walls, which would equalize pressures but not temperatures.)

Suppose at first that systems 1 and 2 are in equilibrium separated by an adiabatic wall as shown in figure 1 (a). Then if this wall is replaced by a diathermic wall the systems will, in general, move out of equilibrium, and some time later achieve new equilibrium states subject to a restriction like (1). The systems can now be described as being in thermal equilibrium with each other.

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**FIGURE 1. Composite Systems.**

(a) Isolated Systems

(b) Systems in thermal contact
1.4 The Zeroth Law of Thermodynamics

We can now introduce the first of the four fundamental laws of thermodynamics. This states:

"Two systems in thermal equilibrium with a third are in thermal equilibrium with each other." R. H. Fowler (see Fowler & Guggenheim 1939, p. 56) has termed this the Zeroth Law of Thermodynamics. Its main significance is that it enables us to establish the existence of a function of state, $\theta$, which is called the empirical temperature. This can be done as follows.

Suppose systems 1 and 2 are in thermal equilibrium, i.e. by (1)

$$ F(p_1, V_1, p_2, V_2) = 0, $$

and suppose a third system is also in thermal equilibrium with the second, then a relation

$$ f(p_2, V_2, p_3, V_3) = 0, $$

holds. The zeroth law now tells us that 1 and 3 are in thermal equilibrium, i.e. that there exists a relation of the form

$$ \psi(p_1, V_1, p_3, V_3) = 0. $$

Equation (4) shows that $F$ and $f$ must be of such a form that it is possible to eliminate $p_2$ and $V_2$ simultaneously from equations (2) and (3).

Similarly it must also be possible to eliminate $p_1$, $V_1$ from (2) and (4), and $p_3$, $V_3$ from (3) and (4).

Now solve (3) and (4) for $V_3$, and then eliminate $V_3$ from the resulting equations. The result is

$$ \phi(p_1, V_1, p_3) - \kappa(p_2, V_2, p_3) = 0, $$

but by the argument just given, it should be possible to eliminate $p_3$ at the same time. A little reflection shows that this is possible only if we can split the functions $\phi$ and $\kappa$ in the following way:

$$ \phi(p_1, V_1, p_3) = G_1(p_3) \{F_1(p_1, V_1) - G_2(p_3)\} $$

$$ \kappa(p_2, V_2, p_3) = G_1(p_3) \{F_2(p_2, V_2) - G_2(p_3)\}. $$

In this case (5) reduces to

$$ F_1(p_1, V_1) = F_2(p_2, V_2). $$

Thus the zeroth law restricts the condition of thermal contact.
(2) to be of the form given in (6), and a similar result holds for (3) and (4).

1.5 The Empirical Temperature, and The Equation of State

Let $\bar{p}_2, \bar{V}_2$ indicate fixed values of $p_2, v_2$, and let a number $\theta$ be defined by the equation

$$\theta = F_2(\bar{p}_2, \bar{V}_2)$$  \hspace{1cm} (7)

Then the condition of thermal equilibrium is now that $p_1, v_1$ lie on the curve

$$F_1(p_1, v_1) = \theta = \text{const.}$$  \hspace{1cm} (8)

in the $p_1, v_1$ plane. This curve is called an isotherm of system 1.

Changing the values of $p_2, \bar{V}_2$ will change the value of the constant in (8), and in this way a family of isotherms can be generated.

Thus an isotherm is the locus of all points representing states at which a system is in thermal equilibrium with one state of another system.

Similarly, by again using system 2 as a reference system we can obtain a corresponding family of curves $\theta = \text{constant}$ in the $p_3, v_3$ diagram for system 3. By the zeroth law all states of system 1 lying on the isotherm $\theta = k$ in the $p_1, v_1$ diagram, where $k$ is a given constant, will be in thermal equilibrium with all states of system 3 lying on the isotherm $\theta = k$ in the $p_3, v_3$ diagram. The systems themselves, in these states, may be said to possess a property called the temperature. Thus the temperature of a system is a property that determines whether or not a system is in thermal equilibrium with other systems.

The temperature of all systems in thermal equilibrium can be represented by a number, and an obvious choice is the number $\theta$ defined by (7). Thus we shall call this number $\theta$ the empirical temperature.
System 2, on which the numerical value of $\theta$ closely depends, and which was used as an intermediary for the comparison of systems 1 and 3, is called a thermometer. The variety of systems that have been found suitable, for practical reasons, to be thermometers, and the selection of a suitable empirical temperature scale, lie outside the scope of these lectures.

Equation (8), viz.,

$$F_1(p_1, V_1) = \theta,$$

in which $\theta$ is now the variable we have named the empirical temperature, is termed the equation of state. In the form given $p_1$ and $V_1$ are the independent variables, while $\theta$ is the dependent variable, but in general any pair of $p_1$, $V_1$ and $\theta$ may be chosen as independent variables, and the equation of state then defines the value of the remaining (dependent) variable.

2.1 Work.

If a thermodynamic system as a whole exerts a force on its surroundings, and a displacement takes place, then external work is said to be done. Internal work, namely the work done by one part of the system on another part plays no role in thermodynamics.

The displacements of the system will be supposed to be carried out in such a way that the state of the system moves along a quasi-static path in state space, i.e., so that the system is at all times infinitesimally near a state of thermal equilibrium.

Suppose, for example, that the container of a gas at pressure \( p \) increases its volume an infinitesimal amount \( \delta V \), then the work done during this change will be \( \delta W = p \delta V \), or taking \( V \) to be an independent variable, and therefore writing \( \delta V = dV \), (see \( \delta \) Equations) we have

\[
\delta W = pdV \quad (10)
\]

In a finite (and quasi-static) displacement from \( (p_0, v_0) \) to \( (p_1, v_1) \) the work done by the system will be

\[
W = \int_{(p_0, v_0)}^{(p_1, v_1)} p(v, \theta) \, dV, \quad (11)
\]

but this equation alone is insufficient to define \( W \) uniquely — we need to know the path in the \( p, v \) diagram. For example if \( \theta \) is given as a function of \( v \) (or \( p \)), then the equation of state permits the \( p, v \) relation to be found, and the integral in (11) to be evaluated. In other words \( W \) is not a function of state as it depends on more than just the terminal values of \( p \) and \( v \), and consequently it is not a differentiable function. For this reason we must be careful not to replace \( \delta W \) by \( dW \).

The work done by other thermodynamic systems usually follows from an equation similar to (11), and is a function of state only in
special cases. Notice that work is the product of an intensive coordinate \( p \) with an extensive coordinate \( \gamma \).

2.2 Mathematical Note

**Infinitesimals and Differentials** — It is necessary at this stage to ensure that the reader clearly understands the meaning of a differential. Few text books make the distinctions between derivatives, differentials and infinitesimals sufficiently clear (for an exception see Phillips "Analysis", C.U.P. 1932, chapters 4 and 9).

(a) **Infinitesimals** — A variable \( \alpha \) is said to be infinitesimal with respect to another variable \( \beta \) if the ratio \( \alpha /\beta \) tends to zero as \( \alpha \) tends to zero. An increment to a variable \( \alpha \), which is infinitesimal with respect to it, is often denoted by \( \delta \alpha \). Infinitesimals \( \beta, \gamma \) are described as being of the same order if a positive constant \( k \) exists such that \( |\beta| \leq k|\gamma| \). These definitions are expressed concisely by the notation

\[
\alpha = o(\beta) \quad \delta \alpha = o(\alpha) \quad \beta = O(\gamma). \quad (12)
\]

A particular infinitesimal \( \varepsilon \) can be selected for reference, and called the principal infinitesimal. Then if \( \beta = O(\varepsilon^n) \), \( \beta \) is said to be an infinitesimal of order \( n \).

Notice that the concept of functional dependence does not enter here.

(b) **Differentiability** — A function \( u = u(x,y,z) \) is differentiable at the point \( (x,y,z) \) if it has a determinant value in the neighbourhood of this point, and if for arbitrary increments \( \Delta x, \Delta y, \Delta z \) in \( x,y,z \) (not necessarily infinitesimals) the corresponding increment to \( u \) can be expressed in the form

\[
\Delta u = A\Delta x + B\Delta y + C\Delta z + \varepsilon \rho, \quad (13)
\]
where \( \rho = \sqrt{\Delta x^2 + \Delta y^2 + \Delta z^2} \). \( A, B, C \) are independent of \( \Delta x, \Delta y, \) and \( \Delta z, \) and \( \epsilon \) tends to zero as \( \rho \) tends to zero.

(c) Partial Derivatives — If the limit

\[
\lim_{\Delta x \to 0} \frac{u(x + \Delta x, y, z) - u(x, y, z)}{\Delta x} = \lim_{\Delta x \to 0} \frac{\Delta u}{\Delta x}
\]

exists uniquely, it is termed the partial derivative of \( u \) with respect to \( x \), and is written \( \frac{\partial u}{\partial x} \) or \( u_x \). Similar definitions hold for \( u_y, u_z \).

If \( \Delta y, \Delta z = 0 \) in (13) then \( \Delta u = A \Delta x + \epsilon |\Delta x| \), so

\[ u_x = \lim_{\Delta x \to 0} (A + \epsilon) = A, \]

as \( \epsilon = O(\Delta x) \) and \( A \) is independent of \( \Delta x \). Thus when the function

\( u = u(x, y, z) \) is differentiable the partial derivatives \( \frac{\partial u}{\partial x}, \frac{\partial u}{\partial y}, \frac{\partial u}{\partial z} \)

are the differential coefficients \( A, B, C \). Hence (13) can be written

\[
\Delta u = u_x \Delta x + u_y \Delta y + u_z \Delta z + \epsilon \rho.
\]

(d) Differentials — If \( \rho \) is infinitesimal with respect to \( x, y \) and \( z \), the last term of (15) is \( O(\rho^2) \), while the three terms preceding it are \( O(\rho) \). For this reason, these three terms are called the principal part of \( \Delta u \), and denoted by the symbol \( du \), thus

\[ du = u_x \Delta x + u_y \Delta y + u_z \Delta z, \]

and

\[ \Delta u = du + \epsilon \rho. \]

The number \( du \) is termed the differential of the dependent variable \( u \).

Suppose the function \( u(x, y, z) \) is simply \( u = x \), then \( d(x) = 1 \times \Delta x \), and similarly \( d(y) = \Delta y, \ d(z) = \Delta z \). We can therefore use the more general relation

\[ du = u_x \, dx + u_y \, dy + u_z \, dz \]

(17)
11.

for $du$. It is important to notice that we have placed no restriction on the size of the differentials $du, \, dx, \, dy$ and $dz$——and they need not be infinitesimals. Figure 3 shows the relation between $\Delta u, \, du, \, \Delta x$ and $dx$ when $dy$ and $dz$ are zero. In this particular case

$$\frac{du}{dx} = u_x$$

and $du, \, dx$ are finite non-zero numbers.

(e) Relation between Differentials and Infinitesimals. We now show that if $dx, \, dy, \, dz$ are infinitesimal, and if the derivatives $u_x, \, u_y, \, u_z$ are finite and non-zero at a point $(x, y, z)$, then $\Delta u$ and $du$ are equivalent infinitesimals.

To simplify the argument put $dy, \, dz = 0$, then (15) gives

$$\Delta u = u_x \Delta x + \epsilon |dx|, \text{ but } \Delta u = u_x \Delta x, \text{ so}$$

$$\frac{\Delta u}{du} = 1 + \frac{\epsilon}{u_x}, \text{ where } \epsilon \to 0 \text{ as } dx \to 0,$$

as by hypothesis $u_x$ does not vanish. Thus as $dx \to 0$

$$\frac{\Delta u}{du} \to 1,$$

and it follows that $\Delta u$ and $du$ are two infinitesimals which may be substituted for each other.

In thermodynamics the differentials are always infinitesimals, but not all infinitesimals are differentials, e.g. in equation (10) $\delta W$ is an infinitesimal which is not a differential, whereas $dV$ is an infinitesimal which is a differential.
2.3 The First Law of Thermodynamics.

This may be stated:
"If a system in an adiabatic enclosure is caused to change from an initial equilibrium state to a final equilibrium state by applying some form of external work, the work done is the same for all paths connecting the two states."

Let the state change from a fixed initial state \((P_0, V_0)\) to a final state \((P, V)\) then by (11) the adiabatic work done on the system by the external agency is *

\[
\int_L (P, V) \text{pdV},
\]

and as this work does not depend on the path from \((P_0, V_0)\) to \((P, V)\), it must be a function only of the final and initial states. Thus we can define a function of state \(E(P, V)\) by

\[
E(P, V) - E(P_0, V_0) = \int_L (P, V) \text{pdV}.
\]

This function which has the dimensions of energy is known as the internal-energy function. From (18) \(dE = -pdV\), or

\[
0 = dE + pdV,
\]

for adiabatic changes.

2.4 Heat

Now suppose the adiabatic walls enclosing the system are replaced by diathermic walls, then it will be found that in any non-adiabatic change from \((P_0, V_0)\) to \((P, V)\) the quantity

* \(\int_L \) denotes integration over the adiabatic path connecting \((P_0, V_0)\) and \((P, V)\).
E(p,V) - E(p_0,V_0) + \int_{(p_0,V_0)}^{(p,V)} p\,dV

cf. (18) is no longer zero. It will in fact have a value which depends on the path taken from \((p_0,V_0)\) to \((p,V)\). We can therefore define a quantity \(Q\), which is not a function of state by

\[ Q = E(p,V) - E(p_0,V_0) + \int_{(p_0,V_0)}^{(p,V)} p\,dV. \]

This quantity \(Q\) is termed the heat supplied from the surroundings of the system during the process. It clearly has the dimensions of energy — energy which must pass through the diathermic walls during the change of state. For this reason heat is often described as being energy in transit.

Let \(p-p_0, V-V_0\) be infinitesimals, then (11) and (12) give

\[ \delta Q = \delta E + p\delta V, \]

i.e. by (10) \(\delta Q = \delta E + p\,dV\). Now \(E\) is a function of state so we can write \(\delta E = \frac{\partial E}{\partial p} \delta p + \frac{\partial E}{\partial V} \delta V\). Thus finally

\[ \delta Q = \frac{\partial E}{\partial p} \delta p + \frac{\partial E}{\partial V} \delta V. \]

In the case of more general systems it is only necessary to replace the equation \(\delta W = p\,dV\) by an equation of the form \(\delta W = \sum \psi_i dx_i\), where \(\psi_i\) represents one of the intensive quantities or generalized forces, and \(x_i\) is the corresponding generalized displacement. For example in the case of a liquid and its surface, \(\delta W = p\,dV - S\,dA\), where \(S\) is the surface tension and \(A\) is the area of the surface. Then (21) becomes

\[ \delta Q = \delta E + p\,dV - S\,dA, \]

where \(E\) is now a function of three of \(p, V, \theta, S, A\).
It has been claimed (Green, 1954) that the first law suffers from an extravagance in its formulation, and that its present quantitative form can be deduced from a simpler qualitative form. Green's form of the first law is essentially that "if two states can be connected by one adiabatic path for which the net work is zero, then the net work is zero for all other adiabatic paths connecting these states." The usual form of the first law follows by considering two paths connecting the states which are identical up to some intermediate state, and which then separate into two branches. Green's formulation only formally reduces the quantitative content of the law, and there seems to be no real advantage in using it. The distinction between the two forms of the first law corresponds to that between the two methods of defining a conservative force, namely that either the work it does is independent of the path taken, or that it does zero work in any closed circuit, but of course "closed circuits" are best avoided in the thermodynamic case.

3.1 Statement of the Law.

There are two distinct but equivalent formulations of the second law of thermodynamics. The classical formulation has several forms, the best of which is probably the following:

"It is impossible to construct an engine that, operating in a cycle, will produce no effect other than the extraction of heat from a reservoir, and the performance of an equivalent amount of work."

The first thing to notice is that in contrast to the zeroth and first laws, which introduce the minimum of physical concepts (adiabatic and diathermic walls, and the possibility of moving these walls) the second law invokes several physical concepts borrowed from engineering. This is also true of the classical development of the second law, which deduces in turn (i) Carnot's theorem on the "efficiency" of a "Carnot Engine", (ii) Kelvin's absolute temperature scale (based on the efficiency of a Carnot Engine), (iii) Clausius's theorem on the contour integral of $\delta Q/T$, using a mesh of Carnot cycles, and (iv) finally the existence of an entropy function is established. Neither the indirectness of this approach, nor the extravagance with which physical concepts are introduced contribute anything that is essential to the understanding of the foundations of thermodynamics. Of course in the applications of thermodynamics to engineering (but not physics and chemistry) the concepts of "Carnot cycles", "ideal engines" and so on, will always be important but they ought to be eliminated from the foundations of the subject.

The position has been succinctly summarized by Bridgman (1941). He writes "It must be admitted, I think, that the laws of thermodynamics have a different feel from most of the other laws of the physicist. There is something more palpably verbal about them —— they smell more of their human origin. The guiding motif is strange to most of physics; namely a capitalizing of the universal failure of human beings to construct perpetual motion machines either of the first or
second kind. Why should we expect nature to be interested either positively or negatively in the purposes of human beings, particularly purposes of such an unblushingly economic tinge?"

If engineering notions are to be avoided it is clear that the classical version of the second law must be abandoned. A restatement of the law, sufficient for the derivation of the entropy and absolute temperature functions has been given by Carathéodory (1909). His principle can be stated thus:

"In the neighbourhood of any given state there exist states inaccessible from the given state by adiabatic processes."

This may be called the strong form of Carathéodory's principle for as stated it includes both real and reversible (imaginary) processes. The weak form of the principle is that:

"In any neighbourhood of a given state there exist states inaccessible from the given state by quasi-static adiabatic processes." This form is sufficient to establish the existence of the entropy and absolute temperature functions.

The strong form of the principle is a direct induction from experiment, for all the evidence indicates that any real adiabatic thermodynamic change is irreversible, that is the original state cannot be regained from the final state by simply reversing the change.

The weak form of the law, applying as it does to imaginary changes, can never be a direct induction from experiment, but the following experimental process does support it. It is an experimental fact that if points A and B lie on one isotherm of a given system, there is no real adiabatic process by which the system can be made to leave state A and arrive at state B, and this result is quite independent of the rate at which walls are moved, or external work is applied to the system. It is therefore reasonable to assume that in the unattainable limit as this rate tends to zero — which gives the quasi-static process
defined in § 1.2—the result still holds. Thus on this assumption \( A \) is inaccessible from \( B \) by a quasi-static adiabatic process.

3.2 Mathematical Expression of Carathéodory's Principle

The entropy and absolute temperature functions can be derived from Carathéodory's principle by considering quasi-static changes of a general thermodynamic system characterised by \( n \) independent coordinates (see Buchdahl 1949b, 1954), but it is sufficient (as is easily seen a posteriori), and certainly more expedient for the purpose of understanding the theory, to confine our attention to a system defined by three coordinates. The theory for this case given below can be easily generalized by some minor modifications to the general case.

Perhaps the most convenient system for our purpose is that used by Born (1949). Consider any two systems, each defined by two variables \( p \) and \( v \), adiabatically enclosed and separated by a diathermic wall. As these systems are in thermal contact, the state of the combined system can be specified by just three variables, say \( v_1 \), \( v_2 \) and \( \theta \), the empirical temperature. Let \( E_1 \) and \( E_2 \) be the internal energies of the two systems, then since energy is an additive function (being extensive in character) we can add

\[
\delta Q_1 = dE_1 + p_1 dV_1, \quad \delta Q_2 = dE_2 + p_2 dV_2.
\]

to get for the combined system

\[
\delta Q_1 + \delta Q_2 = dE_1 + dE_2 + p_1 dV_1 + p_2 dV_2 = 0.
\]

Hence, since \( v_1 \), \( v_2 \) and \( \theta \) are the independent variables, \( E_1 = E_1(v_1, \theta) \) and \( E_2 = E_2(v_2, \theta) \), it follows that
From Carathéodory's principle we have that if \((v_1, v_2, \theta)\) is a point in our state space, there exist neighbouring points which cannot be reached from \((v_1, v_2, \theta)\) by paths in this space satisfying (22).

Before we can proceed with the thermodynamic problem we need a theorem on expressions of the type \(Xdx + Ydy + Zdz\), where \(X, Y, Z\) are each functions of \(x, y, z\). Such an expression is termed a Pfaffian in three variables. The left hand side of (22) is such a Pfaffian, and the problem is "what restriction, if any, does Carathéodory's principle impose on this Pfaffian?" The answer is given in the next section.

3.7 The Theorem of Inaccessibility.

To simplify the algebra we shall consider here a Pfaffian of the form \(Xdx + Ydy + Zdz\), instead of that appearing in (22). The theorem of inaccessibility (see Born 1049) can be expressed as follows.

"If there exist points \(D(x, y, z)\) in the neighbourhood of a given point \(B(x^0, y^0, z^0)\) inaccessible from \(B\) by a continuous curve satisfying the equation

\[
Xdx + Ydy + Zdz = 0, \tag{27}
\]

then the Pfaffian \(Xdx + Ydy + Zdz\) has an integrating factor \(\frac{1}{\lambda}\) (which may be unity), and can therefore be written as \(\lambda d\phi\), where \(\phi\) is a function of \(x, y, z\)."

The converse of this theorem is obvious. If (27) can be written in the form \(\lambda d\phi = 0\), it defines a surface \(\phi = \text{constant}\), and since all curves satisfying (27) must lie in this surface completely or not at all, all points just off the surface will be "inaccessible" from points lying on the surface.
1st Proof of Theorem

Let the curve $AB$ shown in figure 5 be a solution curve satisfying $(2^2)$, and let $s$ be the distance measured along this curve from $A$. Equation $(2^2)$ can be rewritten in the vector form

$$R_i \frac{dx_i}{ds} = 0,$$

or

$$R_i \dot{x}_i = 0, \quad (i = 1, 2, 3) \quad (24)$$

where the dot indicates differentiation with respect to the distance $s$. $R_1 = x$, $R_2 = y$, $R_3 = z$, $x_1 = x$, $x_2 = y$, $x_3 = z$, and we have adopted the summation convention of the tensor notation.

Now consider a neighbouring solution curve $AD$ of the same length as $AB$. Let the vector joining points at the same value of $s$ on these curves be denoted by $\delta x_i$, then $\delta x_i$ will be a function of $s$ varying from zero to $A$ to some value $\delta x^0_i$, say, at $B$. The existence of points in the neighbourhood of $B$ inaccessible from $B$ by solution curves of $(2^4)$ clearly imposes restriction on the vector $\delta x^0_i$, for otherwise all points in the neighbourhood of $B$ could be reached by using paths each as $BAD$.

The increment in $R_i$ due to a small change $\delta x_i$ in $x_i$ is

$$\delta R_i = \frac{\partial R_i}{\partial x_j} \delta x_j.$$  Hence from $(24)$

$$\delta R_i \dot{x}_i = \frac{\partial R_i}{\partial x_j} \delta x_j \dot{x}_i + R_i \delta \dot{x}_i = 0.$$  \quad (25)

Similarly

$$\frac{d}{ds} (R_i \delta x_i) = \frac{\partial R_i}{\partial x_j} \dot{x}_j \delta x_i + R_i \delta \dot{x}_i = \frac{\partial R_i}{\partial x_j} (\dot{x}_j \delta x_i - \dot{x}_i \delta x_j).$$
by (25). If we introduce the Kronecker tensor, $\delta_{ij}$, here we can express this result as

$$
\frac{d}{ds} (R_i \delta x_i) = \frac{\partial R_i}{\partial x_j} (\delta_{mj} \delta_{ni} - \delta_{mi} \delta_{nj}) \delta x_m \delta x_n
$$

$$
= \frac{\partial R_i}{\partial x_j} \epsilon_{kmn} \epsilon_{kji} \delta x_m \delta x_n, \quad (26)
$$

$\epsilon_{kmn}$ being the alternate tensor.

Equation (24) shows that $R_i$ and $\dot{x}_i$ are orthogonal vectors, therefore $\dot{x}_m = (a \wedge R)_m = \epsilon_{mpq} a_p R_q$, where $a_p$ is a vector which can be determined as a function of $s$ on $AB$. Thus (26) can be written

$$
\frac{d}{ds} (R_i \delta x_i) = \epsilon_{kji} \frac{\partial R_i}{\partial x_j} \epsilon_{mnk} \epsilon_{mpq} a_p R_q \delta x_n
$$

$$
= \epsilon_{kji} \frac{\partial R_i}{\partial x_j} (\delta_{np} \delta_{kq} - \delta_{nq} \delta_{kp}) a_p R_q \delta x_n
$$

$$
= (R_k \epsilon_{kji} \frac{\partial R_i}{\partial x_j}) (\delta_{n} \delta x_n) - (a_k \epsilon_{kji} \frac{\partial R_i}{\partial x_j}) (R_n \delta x_n).
$$

Interchanging the subscripts $i$ and $n$ on the right hand side, and rearranging we get the following first order differential equation for $(R_i \delta x_i)$.

$$
\frac{d}{ds} (R_i \delta x_i) + (a_k \epsilon_{kji} \frac{\partial R_n}{\partial x_j}) (R_i \delta x_i) = (R_k \epsilon_{kji} \frac{\partial R_n}{\partial x_j} (a_i \delta x_i).
$$

Integrating this along $AB$ gives
\[ P_i \delta x_i^o = \exp \left( \int a_k \epsilon_{kjn} \frac{\partial R_n}{\partial x_j} \, ds \right) S^o \delta x_i^o = \exp \left( - \int a_k \epsilon_{kjn} \frac{\partial R_n}{\partial x_j} \, ds \right) \]

\[
(R_k \epsilon_{kjn} \frac{\partial R_n}{\partial x_j}) \delta x_i^o \, ds, \tag{27}
\]

where \( \circ \) indicates values at \( B \), and the fact that \( R_i \delta x_i^o = 0 \) at \( A \) (\( |\delta x_i^o| = 0 \)) has been used.

The functions \( a_i \) and \( R_i \) occurring in (27) are fixed by the path \( AB \), but as there are infinitely many solution curves \( AD \) neighbouring \( AB \) — the only restriction being that at any point the increment to the solution curve must lie in the plane to which \( R_i \) is the normal — there are infinitely many functions \( \delta x_i(s) \) that can be introduced under the integral sign in (27). This means in general that there can be no restriction on the attainable values of \( \delta x_i^o \).

However if \( R_k \epsilon_{kjn} \frac{\partial R_n}{\partial x_j} = \) \( (R \circ \nabla \wedge R) \) vanishes on \( AB \) then by (27) \( R_i \delta x_i^o \) must also vanish on \( AB \), and in particular \( \delta x_i^o \) must be subject to the restriction

\[ R_i^o \delta x_i^o = 0. \tag{28} \]

Conversely if we know that \( \delta x_i^o \) is subject to a restriction regardless of the path taken, then we must have

\[ R_k \epsilon_{kjn} \frac{\partial R_n}{\partial x_j} = 0, \tag{29} \]

on the vector \( R_k \). Equation (29), or equivalently

\[ R \circ \nabla \wedge R = 0. \tag{30} \]
is thus the necessary and sufficient condition for the existence of inaccessible points in the neighbourhood of any given point. It is well-known that (29) is also the necessary and sufficient condition that \( R_i \delta x_i \) has an integrating factor, and can be written in the form \( \lambda d \phi \). This completes our first proof of the theorem.

Second Proof of the Theorem

An alternative proof of the Theorem of Inaccessibility (due essentially to Mr. W. P. Smith-White of the Pure Mathematics Department of the University of Sydney), which is probably a little easier to follow than the first proof, is as follows.

We know that if \( R_i \, dx_i \) can be written in the form \( v \, dw \), say, where \( v \) and \( w \) are functions of \( x_1, x_2, x_3 \), then \( R_i \, dx_i = v \, dw = 0 \) defines a surface \( w = \text{constant} \), and that points just off this surface will be inaccessible from points lying in the surface. Suppose therefore we generalize a little and write \( R_i \, dx_i = du + v \, dw \), where \( u \) is a further function of \( x_1, x_2, x_3 \). Then \( R_i \, dx_i = (\frac{\partial u}{\partial x_i} + v \frac{\partial w}{\partial x_i}) \, dx_i \) and the forms will be equivalent provided

\[
R_i = \frac{\partial u}{\partial x_i} + v \frac{\partial w}{\partial x_i} \tag{31}
\]

The curl of this equation is

\[
\sum_{kji} \epsilon_{kji} \frac{\partial R_i}{\partial x_j} = \sum_{kji} \epsilon_{kji} \left( \frac{\partial^2 u}{\partial x_j \partial x_i} + \frac{\partial v}{\partial x_j} \left( \frac{\partial w}{\partial x_i} \right) \right) = \sum_{kji} \epsilon_{kji} \frac{\partial v}{\partial x_j} \frac{\partial w}{\partial x_i} = 0, \tag{32}
\]

from which it follows that each of \( v \) and \( w \) satisfy a first order partial differential equation of the type

\[
\left( \sum_{kji} \epsilon_{kji} \frac{\partial R_i}{\partial x_j} \right) \frac{\partial \psi}{\partial x_k} = 0. \tag{33}
\]

Combining (31) and (32)
Existence theorems for the solutions of linear differential equations of the type (77) and (75) ensure that $u$, $v$ and $w$ do exist, and therefore that, in general, $R_i$ can be written in the form (71).

First suppose that $\sim R \circ \nabla \wedge \sim R = 0$, i.e. by (74)

$$\epsilon_{kji} \frac{\partial R_i}{\partial x_j} = 0.$$  

This means that $\frac{\partial u}{\partial x_i}$ lies in the plane of $\frac{\partial v}{\partial x_i}$ and $\frac{\partial w}{\partial x_i}$, and so can be expressed as a linear combination of $\frac{\partial v}{\partial x_i}$ and $\frac{\partial w}{\partial x_i}$, i.e.

$$\frac{\partial u}{\partial x_i} = a \frac{\partial v}{\partial x_i} + b \frac{\partial w}{\partial x_i}.$$  

Hence a functional relation exists between $u$, $v$ and $w$, say $v = F(u, w)$. Then $R_i \, dx_i = du + F(u, w) \, dw$, the right hand side of which is now a Pfaffian in two variables, and it is well known that such Pfaffians can always be integrated, i.e. can always be written in the form $\lambda \, d\phi$ (see § 7.4).

Secondly suppose that $\sim R \circ \nabla \wedge \sim R \neq 0$, then $u$, $v$, $w$ are independent functions, and the transformation from $(x_1, x_2, x_3)$ space to $(u, v, w)$ space implicit in equation (71) is non-singular. We shall show that in this case any point $P(u, v, w)$ in the $(u, v, w)$-space is
accessible from the origin (and hence any other point in the space) by curves satisfying

\[ R_i \, dx_i = du + v dw = 0. \quad (36) \]

Let \( f(w) \) be any increasing monotonic function of \( w \), such that \( f(0) = 0 \), then the curve

\[ u = \int_0^w f(w) \, dw, \quad v = -f(w), \]

clearly satisfies (36), and also passes through the origin. Let the point \( P \) be at \( u_o, v_o, w_o \), and let \( \bar{w} \) be the value of \( w \) at which

\[ u = u_o = \int_0^{\bar{w}} f(w) \, dw, \]

(always possible as the integrand increases indefinitely with \( w \)). Now join the point \( (u_o, -f(\bar{w}), \bar{w}) \) to \((u_o, 0, w_o)\) by a straight line, which must also satisfy (36) as \( du \) and \( dw \) vanish on this line. Next join \((u_o, 0, w_o)\) to \((u_o, 0, w_o)\) by a straight line. For this line \( v = 0 \) and \( du = 0 \), so (36) is again satisfied. Finally draw another straight line from \((u_o, 0, w_o)\) to \( P \) at \((u_o, v_o, w_o)\); this also satisfies (36). Our construction thus shows that any point \( P \) is accessible from the origin.

More generally any point \( P_o \) is accessible by curves satisfying (36) from any other point \( P \).

As the \((u,v,w)\)-space is a non-singular transformation of the \((x_1,x_2,x_3)\)-space this result is also true in the \((x_1,x_2,x_3)\)-space. It therefore follows that the existence of inaccessible points requires that \( R \circ \nabla \wedge R = 0 \), i.e. that \( R \circ dx \) has an integrating factor and can be expressed in the form \( \lambda \, d\phi \).

7.4 The Case of Two Independent Variables

In Cartesian coordinates equation (29) reads

\[ X \left( \frac{\partial z}{\partial y} - \frac{\partial y}{\partial z} \right) + Y \left( \frac{\partial x}{\partial z} - \frac{\partial z}{\partial x} \right) + Z \left( \frac{\partial y}{\partial x} - \frac{\partial x}{\partial y} \right) = 0 \]
Suppose the Pfaffian has the special form

\[ X(x, y, z) \, dx + Y(x, y, z) \, dy = 0, \]  

(38)
i.e. \( z = 0 \), but \( x \) and \( Y \) are functions of all three variables \( x, y, z \).

Then (37) reduces to \( x \frac{\partial Y}{\partial z} = Y \frac{\partial x}{\partial z} \), or

\[ \frac{\partial}{\partial z} \ln X = \frac{\partial}{\partial z} \ln Y. \]  

(39)

This case occurs in the thermodynamic application of the theorem.

Now consider the case of two independent variables, when the Pfaffian in (38) can be written

\[ X(x, y) \, dx + Y(x, y) \, dy = 0. \]

Neither \( x \) nor \( Y \) are functions of \( z \) so (39) is always satisfied. Hence a Pfaffian in two variables always satisfies equation (30), and can therefore always be written in the form \( \lambda d\phi \). It is quite unnecessary to assert the existence of inaccessible points here for there is no other possibility.

The distinction between the cases of two and three (or more) independent variables is of vital importance, and is the reason for our choice of system in § 7.2. Any proof of the existence of the entropy and absolute temperature functions based on a system defined by only two variables is quite inadequate, as it depends on a degenerate case. This point is seldom, if ever, made clear in the textbooks, and it does not emerge in the classical treatment of the second law.
Returning now to equation (32) we have from Carathéodory’s principle and the theorem given in § 3.7 that the left hand side of the equation can be written in the form $\lambda d\phi$, where $\lambda$ and $\phi$ are functions of $v_1$, $v_2$, and $\theta$. Also for each system separately

$$ \delta q_1 = \lambda_1 d\phi_1, \quad \delta q_2 = \lambda_2 d\phi_2, \quad (40) $$

where $\phi_1$, $\phi_2$ are functions of $v_1$, $\theta$ and $v_2$, $\theta$ respectively. (Equations (40) follow without appeal to the theorem, since the state of each system separately is a function of only two variables (cf. § 3.4), but this is an incidental consequence of our particular choice of system, and has no importance.) Thus

$$ \delta q_1 + \delta q_2 = \lambda d\phi = \lambda_1 d\phi_1 + \lambda_2 d\phi_2. \quad (41) $$

For the combined system the independent variables $v_1$, $v_2$, $\theta$ can be replaced by $\phi_1$, $\phi_2$, $\theta$; then as the differential $d\theta$ is absent from (41) we have the special case considered in the first paragraph of § 3.4. Hence from (41) and (30) we conclude that

$$ \frac{\partial}{\partial \theta} (\ln \lambda_1) = \frac{\partial}{\partial \theta} (\ln \lambda_2) $$

This equation is possible only if each side depends on $\theta$ alone, as $\lambda_1$ and $\lambda_2$ depend on $\phi_1$, $\theta$ and $\phi_2$, $\theta$ respectively. Thus

$$ \frac{\partial}{\partial \theta} (\ln \lambda_1) = \frac{\partial}{\partial \theta} (\ln \lambda_2) = f(\theta), \quad (42) $$

where $f(\theta)$ is a universal function numerically equal for different fluids.

From (42) it follows that for each system

$$ \ln \lambda_i = \int f(\theta) \, d\theta + \ln \phi_i(\phi_i), \quad i = 1, 2. $$
where $\tilde{f}^1$ is an arbitrary function of $\phi_1$. Therefore

$$\lambda_1 = \tilde{f}^1 \exp(\int f(\Theta) \, d\Theta).$$  \hfill (47)

We now define $T(\Theta) = C \exp(\int f(\Theta) \, d\Theta)$,

$$V_1, V_2 \rightarrow T_1, T_2,$$

and

$$S_1(\phi_1) = \frac{1}{C} \int \tilde{f}_1(\phi_1) \, d\phi_1.$$  \hfill (45)

where $C$ is a scale factor, which must be assigned empirically — for example by prescribing the value of $T_1-T_2$ for two reproducible states $1$ and $2$ of some fluid. From (47) to (45) it follows that for each system

$$Tds = \lambda_1 d\phi_1 = \delta Q,$$

i.e.

$$\delta Q = Tds = dE + pdV.$$  \hfill (46)

From (44) and (45) it is clear that except for a scale factor, the function $T$, which is termed the absolute temperature, is defined uniquely, i.e. independent of particular systems, whereas $S$, the entropy function, is not.

The theory given above applies only to reversible processes. An adiabatic reversible change is one for which

$$Tds = \delta Q = 0,$$

i.e.

$$S = \text{constant}.$$  \hfill (47)

so that such changes are often described as being isentropic.

3.6 Irreversible Processes

The strong form of Carathéodory's principle yields an important result for real dynamical phenomena.
To obtain this consider a finite transition of the adiabatically enclosed system shown in figure 4. The transition from an initial state $\overline{V}_1, \overline{V}_2, \overline{S}$ (introducing $S$ instead of $\theta$ as an independent variable) to a final state $V_1, V_2, S$ is carried out in the following steps: first a quasi-static change is made from $\overline{V}_1, \overline{V}_2, \overline{S}$ to $V_1, V_2, \overline{S}$, and then $\overline{S}$ changed to $S$ by an adiabatic but irreversible process (e.g. by stirring). If by this method any neighbouring value $S$ of $\overline{S}$ could be reached, Carathéodory's principle would be violated, for there is clearly no restriction on the volume changes. Hence the value of $S$ attainable from $\overline{S}$ must be such that either $S \leq \overline{S}$, or $S \geq \overline{S}$, as continuity will permit no other type of restriction.

Now the same sign ($<$ or $>$) must hold for all processes of the type described, otherwise by combining processes having opposite signs any value of $S$ near $\overline{S}$ could be attained. Further since the entropy is an additive function (this follows directly from the additive nature of heat), the same sign must also hold for different substances. The actual sign depends on whether the factor $c$ in (47) is positive or negative. Taking this to be such to make $T$ positive, we find from a single experiment that the entropy of a closed system never decreases, i.e.

$$\Delta S \geq 0.$$  \hspace{1cm} (50)

7.7 The Special Case of a System of Two Variables

In the case of a system defined by two independent variables the existence of entropy and temperature functions can be deduced without appeal to the second law of thermodynamics.

For example consider the case of an ideal gas. For this gas the isotherms are given by Boyle's law, and further the internal energy is dependent only on the empirical temperature. That is

$$pV = F(\theta), \quad E = E(\theta).$$
Hence
\[ \delta Q = \left( \frac{dE}{d\theta} \right) d\theta + F(\theta) \frac{dV}{V} \]

\[ = F d\left\{ \int \left( \frac{dE}{d\theta} \right) \frac{d\theta}{F} + \ln V \right\} \]

Thus if we set \( \lambda = \frac{F(\theta)}{g'(\psi)} \),
\[ \psi = \ln V + \int \left( \frac{dE}{d\theta} \right) \frac{d\theta}{F} \]
and
\[ \phi = g(\psi), \]
where \( g \) denotes an arbitrary function, then
\[ \delta Q = \lambda d\phi. \quad (51) \]

Thus temperature and entropy functions can be defined, but they are not unique.

We now use Carathéodory's principle. From (A3), (44) and (45) it now follows that
\[ RT = F(\theta) = pV \]
and
\[ S = S_0 + R \ln V + R \int \left( \frac{dE}{d\theta} \right) \frac{d\theta}{F'}, \]
on writing \( C = 1/R \).

The essential point here is that a Pfaffian in two variables can always be expressed in the form \( \lambda d\phi \), but such an expression is not unique. In this case the second law, or Carathéodory's principle, is still necessary to the unique definition of the absolute temperature function. For the particular system considered here the principle also leads to a unique entropy function, but this is not generally the case. The principle is also still required to establish (50).
As mentioned above, this distinction between the cases of two and three (or more) independent variables is seldom made clear in the textbooks. It does not emerge in the classical treatment of the second law, and must be a source of confusion to students, who are given the lengthy and indirect classical proof of the existence of entropy and absolute temperature functions in the face of the three line argument giving (51).

1.3 Derivation of Carathéodory's Principle from the Classical Form of the Second Law.

Consider a given system in a state $A$, and select a quasi-static isothermal path starting at $A$, along which $\delta Q > 0$. Let $B$ be a second point on this path. If we can return adiabatically from $B$ to $A$, then as $\delta Q = 0$ on the return path we have for the complete cycle

$$0 < Q = \int \delta Q = \int (dE + pdV) = \delta dW = W.$$ 

Thus in this cycle we have absorbed heat $Q$ at a fixed temperature and converted it into an equal amount of mechanical work. The classical form of the second law states that such a cycle is impossible (the important concept is the cycle not the engine), and therefore we conclude that the point $A$ is not adiabatically accessible from $B$, and we have recovered Carathéodory's principle.
4. The Third Law of Thermodynamics.

Fowler and Guggenheim (1939) have elevated the Nernst Heat Theorem to the position of a fundamental law, and termed it the third law of thermodynamics. This law can be stated:

"It is impossible by any procedure, no matter how idealized, to reduce any system to the absolute zero of temperature in a finite number of operations."

The real understanding and fruitful applications of this law really lie in the realm of statistical mechanics, so we shall not dwell on it. But it is worth noting that this law can be considered as being a consequence of the second law, and therefore not fundamental at all. (Apply the classical form of the second law to an engine operating between some temperature $T$ and absolute zero.) For a discussion of this point of view and for further references the reader can consult Landsberg (1956), who incidentally provides an interesting, if somewhat complicated and abstract, account of the axiomatic treatment (i.e. the treatment adopted in these lectures) of thermodynamics.
Acknowledgment

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The first University Bulletin, issued in April, 1957 was "A Bibliographical Survey of Hydraulic Analogies", by R.A.A. Bryant of the School of Mechanical Engineering.