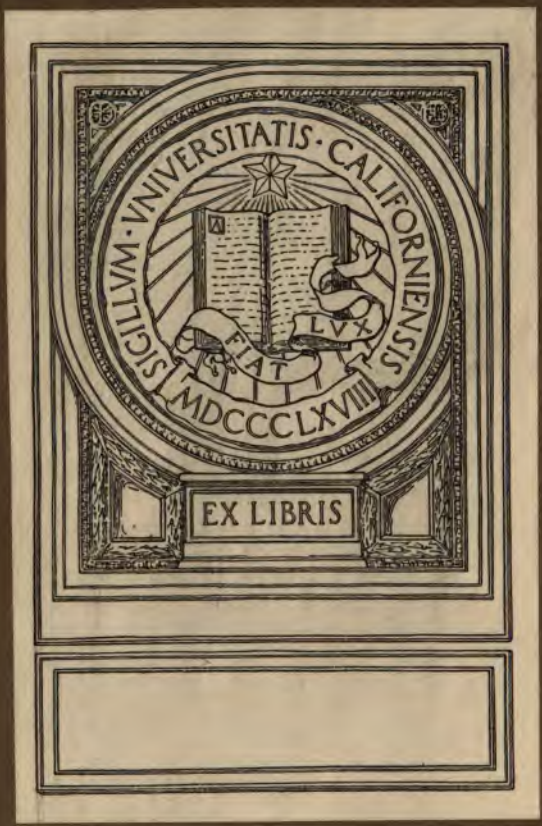

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AUF DEM GEBIETE DER
MATHEMATISCHEN WISSENSCHAFTEN
MIT EINSCHLUSZ IHRER ANWENDUNGEN.
BAND XXI.

THERMODYNAMICS

AN INTRODUCTORY TREATISE DEALING MAINLY WITH FIRST PRINCIPLES AND THEIR DIRECT APPLICATIONS

BY

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PREFACE.

When I accepted an invitation to write the article for the *Encyklopädie* on the General Foundations of Thermodynamics, it was understood that the article should deal, as far as possible, exclusively with the laws of thermodynamics and consequences immediately deducible from them, and that all properties of particular substances and states which depended partially on experimental knowledge or other hypotheses should be left for another article. I had long felt the want of a book in which thermodynamics was treated by purely deductive methods, and it has been my object in the following pages to develop the subject still more on this line than was possible in an article professing to be to some extent an exposition of the history and actual state of knowledge of the subject.

It cannot be denied that the perfection which the study of ordinary dynamics has attained is largely due to the number of books that have been written on *rational* dynamics in which the consequences of the laws of motion have been studied from a purely deductive stand-point. This method in no way obviates the necessity of having books on experimental mechanics, but it has enabled people to discriminate clearly between results of experiment and the consequences of mathematical reasoning. It is maintained by many people (rightly or wrongly) that in studying any branch of mathematical physics, theoretical and experimental methods should be studied simultaneously. It is however very important that the two different modes of treatment should be kept carefully apart and if possible *studied from different books,* and this is particularly important in a subject like thermodynamics.

In most text books the treatment of the first and second laws is based more or less on the historic order, according to which a considerable knowledge of the phenomena depending on heat and temperature preceded the identification of these phenomena with energy-transformations. For a logical order of treatment it is better to regard the laws of thermodynamics as affording definitions of heat and temperature, just as Newton's laws afford definitions (so far as definitions are possible) of force and mass. But in any case there is great danger of assuming some property of temperature without realising that an assumption has been made, and of this danger we have an excellent illustration in the assumption commonly made, but rarely if ever explicitly stated, that the temperature of a body at any point is the same in all directions.

To lessen such risks and at the same time to carry the deductive method further back it appeared to me desirable to adopt the principles of conservation and degradation of energy as the fundamental laws of

thermodynamics, and to deduce the ordinary forms of these laws from those principles. A paper was published by me on this subject in the Boltzmann *Festschrift,* and some criticisms on it sent to me by Mr. Burbury have led to a more extended examination of the foundations upon which thermodynamics rests. Degradation of energy in some form or other is a necessary consequence of *irreversibility* of energy phenomena. We therefore go still further back and assume the principle of irreversibility as our starting point. When an irreversible transformation takes place the number of subsequent possible transformations is thereby from the very nature of the case reduced and we thus have a *loss of availability* in its most general sense. When we want to identify the more and less available forms of energy with those forms of energy which we see around us, an appeal to experience is necessary. It is in fact possible to conceive a universe in which irreversible phenomena tend in a different direction to what they do in our own. A mere reversal of the whole of the phenomena of our universe would give us one example, and if we want another we should only have to imagine ourselves of molecular dimensions when we should find that the whole progress of irreversible phenomena (whether regarded statistically or otherwise) would assume an entirely different aspect to that to which we are accustomed. The laws of thermodynamics are thus restricted to phenomena of a *particular size* in the scale of nature, and the lower limit of size is about the same as the limit involved in the applications of the infinitesimal calculus to the physical properties of material bodies e. g. in hydrodynamics, elasticity and so forth. The term "differential element" is introduced in the present book to represent the smallest element which can be regarded, for the purpose of these applications, as being formed of a continuous distribution of matter, and the notion of temperature *at* a point is regarded as not more nor less justifiable than the corresponding conventions as to pressure and density at a point.

It is, however, in connection with entropy and with thermodynamic equilibria and stability, that the present method of treatment is found to be the most advantageous. A controversy on entropy between English mathematicians, physicists and electrical and other engineers took place in England in 1903 at the instigation of Mr. Swinburne, an electrical engineer, who defined entropy by means of what he called "incurred waste". In the present book it is shown that if entropy be defined in terms of increase of unavailable energy this definition will apply not only in the case of entropy imparted to a system by heat conduction but also in the case of entropy produced by the irreversible changes within a system, of which a number of simple illustrations are given.

Moreover the available energy method possesses considerable advantages in the treatment of thermodynamical equilibria. If we assume that in a state of equilibrium the available energy of a system is a minimum it follows immediately that the conditions of equilibrium can be deduced from the equations of reversible thermodynamics and that it is only when the stability of the equilibrium is discussed that recourse must be had to the inequalities of irreversible thermodynamics.

The old and defunct caloric theory has left us an inheritance in the terms "heat" and "quantity of heat" the vagueness of which does much to cause confusion in the study of thermodynamics. The quantity of heat which one body receives from or imparts to another is a perfectly definite conception, and throughout this book the symbols dQ and dq refer to this quantity of heat thus received from without by a whole body or system and a unit mass respectively. It was my original intention not to consider any other kind of quantity of heat. But there are many intrinsically irreversible phenomena of common experience such as the flow of viscous liquids, in which it is usual to regard work as being converted into heat in the interior of a system, moreover in many such cases it is possible to assign a perfectly definite meaning to the "quantity of heat" so generated. It appeared desirable for several reasons to discuss examples of such transformations at some length and in these examples the so-called quantity of heat generated internally by the irreversible transformation of work has been denoted by dH or dh, and the total quantity of heat gained, according to this stand-point viz. $dQ + dH$ for the entire system or $dq + dh$ for unit mass, has been denoted respectively by $d\mathfrak{Q}$ or $d\mathfrak{q}$. This convention sometimes enables the increase of entropy to be put into the form of $d\mathfrak{Q}/T$ or $d\mathfrak{q}/T$ when the expressions dQ/T and dq/T are inapplicable.

Into the difficulties connected with the extension of thermodynamic formulae to irreversible processes, some insight is afforded notably at the end of Chapter XI. Even the simple statement that we may put $dq = l_v\,dv + \gamma_v\,dT$ cannot be admitted without due reserve when irreversible changes are taken into account. The method of treatment given in the section referred to is not the only one that could be proposed and it may be said with considerable justification that the truth or otherwise of any proposed formula in irreversible thermodynamics depends largely on the particular interpretation which is assigned to the symbols in that formula. In the controversy of English engineers on entropy already referred to much importance was attached to the question whether dQ/T did or did not always represent the change of entropy, and from what we have said either party had considerable justification for believing himself to be right according to his own particular interpretation of dQ.

A few words must be said as to the order of treatment in this book, as this is a very important point. The deductive method here proposed is not started till Part II (Chapter IV). This chapter might well be taken as the starting point of a course of lectures given to a class of students who are already familiar with the elements of thermodynamics, and it was my original intention to place it at the beginning of the book. But it appeared that the necessarily somewhat philosophical discussion of Chapters IV—VIII hardly made a sufficiently easy starting point for a beginner, and moreover it is important in building up a theory that the main facts for which that theory has to account should be prominently borne in mind. Accordingly Chapters I, II contain a general sketch of the most important facts and definitions of thermodynamics as based on experience; Chapter I containing definitions of the

principal thermal magnitudes, such as specific heat and latent heat, and Chapter II containing a brief summary of the conventional or "classical" treatment of the first and second laws. In these chapters no attempt has been made to define heat and temperature, or to aim at anything like a complete or rigorous discussion. Chapter III contains the matter included in my *Encyklopädie* article under the heading "Change of the Independent Variable". It was difficult to find a suitable place for this subject matter in any sequence but its present position was chosen as the best. The formulae there discussed are immediate deductions from the principles of the differential calculus, which are in no way dependent on the dynamical theory of heat; they would be equally true on the old caloric hypothesis; and for this reason they would be out of place in Part II. It is important that such formulae should be kept apart from formulae which are properly described as thermodynamical. The formulae of Chapter III are not practically required before Chapter XI.

In Part III, which deals with particular systems, the discussions are confined as far as possible to direct consequences of the principles of Thermodynamics.

Mr. Ferguson, B. Sc. has kindly assisted in revising the manuscript and proofs.

July 1906.

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Note. The thermodynamical magnitudes connected with a homogeneous substance fall into two classes, those whose magnitude is proportional to the mass of the portion of the substance under consideration and those which are independent of the mass. The first category includes the volume, energy, entropy and thermodynamic potentials, while the second includes pressure and temperature. In representing quantities of the first category, we shall use capital letters when they refer to the whole body or portion of substance considered, and small letters when they refer to a unit mass of the substance. For example the volumes of the whole body and of unit mass of the body are denoted by V and v respectively, so that if M is the mass we have $V = Mv$.

In the case of the thermodynamic potentials it would be sufficient to make the distinction in the suffixes, $\mathfrak{F}_P$ referring to the whole body and $\mathfrak{F}_p$ to a unit mass. This was done in the "Encyklopädie" article but for greater definiteness we have used $\mathfrak{f}_p$ for unit mass in this book.

The following list gives the symbols used in the present book and the corresponding notation of many other writers. The formulae are only given for the purpose of greater definiteness in distinguishing the various symbols. In most cases therefore they refer only to simple systems and hold good only in the case of reversible transformations.

Generally speaking the symbols indicated in the third column by [1]) are most frequently used in Germany (*Clausius* and others), by [2]) in America (*Gibbs*), by [3]) in England (*Thomson, Tait*), by [4]) in France (*Duhem*). The numbers [5]), [6]) refer to *Helmholtz* and *Massieu* respectively.

Name	Symbol	Other Notations	Formulae
Volume	V v		
Density	ϱ		$\varrho = \frac{1}{v}$
Pressure	p		
Absolute Temperature	T [1])	θ, t [2])	
Heat communicated to a system from without	dQ [1]) dq	dH	

Name	Symbol	Other Notations	Formulae
Heat generated in the interior of a system by irreversible transformation of work into heat (where measurable)	dH, dh		See Chapter IX, § 117
Total heat added to body . . .	$d\mathfrak{Q}$, dq		$d\mathfrak{Q} = dQ + dH$ $dq = l_v\,dv + \gamma_v dT$
Entropy	S[1] s	η[2], φ[3]	$dS = dQ/T$ (reversible)
External work	dW dw		$dW = p\,dV$ (simple system)
Intrinsic Energy	U[1] u	ε[2], E[3]	$dU = dQ - dW$
Available Energy or Motivity. .	A		
Thermodynamic Potentials. . . .	$\mathfrak{F}_V$ $\mathfrak{f}_v$	ψ[2], F[4][5], $-H$[6]	$\mathfrak{F}_V = U - TS$
	$\mathfrak{F}_P$ $\mathfrak{f}_p$	ζ[2], Φ[4], $-H'$[6]	$\mathfrak{F}_P = U - TS + pV$
	$\mathfrak{F}_S$ $\mathfrak{f}_s$	χ[2]	$\mathfrak{F}_S = U + pV$
Generalised position-coordinates	$x_1, x_2, \ldots$		$dW = \Sigma X\,dx$
Corresponding force-components	$X_1, X_2, \ldots$		
Partial differential coefficient of y with respect to x with z constant	$\left(\frac{dy}{dx}\right)_z$	$\frac{d_z y}{dx}$	
Specific heat or heat capacity (generally)	C γ		
Specific heat at constant volume	γ_v	c[1], k, c_v	$\gamma_v = \left(\frac{dq}{dT}\right)_v$
Specific heat at constant pressure	γ_p	c'[1] N[3], K, c_p	$\gamma_p = \left(\frac{dq}{dT}\right)_p$
Ratio of the specific heats . . .	$\varkappa$	k[1], γ	$\varkappa = \frac{\gamma_p}{\gamma_v}$
Latent heat of expansion at constant temperature	l_v	M[3] c_θ	$l_v = \left(\frac{dq}{dv}\right)_T$
			$dq = \gamma_v dT + l_v\,dv$

Name	Symbol	Other Notations	Formulae
Latent heat of pressure variation at constant temperature	l_p	γ_θ	$l_p = \left(\frac{dq}{dp}\right)_T$ $dq = \gamma_p dT + l_p dv$
Coefficients of cubic expansion at constant pressure and constant entropy respectively	α_p, α_s		$\alpha_p = \frac{1}{v}\left(\frac{dv}{dT}\right)_p$ $\alpha_s = \frac{1}{v}\left(\frac{dv}{dT}\right)_s$
Moduli of elasticity at constant temperature and constant entropy respectively	ε_T, ε_s		$\varepsilon_T = -v\left(\frac{dp}{dv}\right)_T$ $\varepsilon_s = -v\left(\frac{dp}{dv}\right)_s$
Mechanical Equivalent of heat or specific heat of water in work units	J	$1/A$[1], E[4]	
The constant in the equation of a perfect gas	B	R	$pv = BT$
Masses of the different phases of a complex (small letters for unit mass of complex)	$M', M'', \ldots$ m', m'', m'''		
For a binary complex also denoted by	X and $M - X$ x and $1 - x$		
Specific Volumes of the two Phases of a complex	v', v''		$v = xv' + (1-x)v''$
Entropy, energy and potentials of the phases of a complex	Distinguished by accents in like manner		
Equation of curve of saturation	$G(p,T)=0$		$\mathfrak{f}_p' = \mathfrak{f}_p''$
Specific heats of the phases of a saturated complex	γ', γ''	c_1, c_2[1], h_1, h_2[1]	$\gamma' = \left(\frac{dq'}{dT}\right)_G$ $\gamma'' = \left(\frac{dq''}{dT}\right)_G$ where $G(p,T) = 0$

Name	Symbol	Other Notations	Formulae
Latent heat of transformation .	λ	r[1]	$\lambda = \left(\frac{dq}{dx}\right)_T$
Masses of the components of a mixture (small letters for unit mass of mixture)	$M_a, M_b, \ldots M_k$ $m_a, m_b, \ldots m_k$		
Partial potentials of the components	$\mu_a, \mu_b, \ldots \mu_k$[2]		$dU = TdS - pdV + \Sigma\mu\, dM$ $\mathfrak{F}_P = \Sigma\mu M$
In a galvanic cell the electromotive force	E		
Quantity of electricity passing through the circuit	e		$dV = TdS - Ede$
Entropy of unit charge at any point of a reversible thermoelectric network	χ		
Coefficient of Peltier Effect . . .	Π		$\Pi_{ab} = T(\chi_a - \chi_b)$
Specific heat of electricity . . .	σ		$\sigma = T\frac{d\chi}{dt}$

PART I

PHYSICAL ASPECT OF THERMODYNAMICS

CHAPTER I.

DEFINITIONS AND ELEMENTARY FACTS.

1. In this chapter, we shall give a brief outline of the more important facts, as based on actual experience, to account for which is the purpose of a dynamical theory of heat.

The phenomena known as heat phenomena involve the consideration among others, of the two following concepts:

(1) The *quality* of a body known as *temperature.*

(2) The *quantity* of heat passing to or from a body under given conditions.

As the definitions of these concepts are best based on dynamical considerations, we at present only assume their existence together with such of their properties as are revealed by simple experiments.

2. Measurement of temperature. — Gas-Temperature. Any number of bodies may be arranged in order of temperature by means of the following property, which may be regarded as a definition of equal and unequal temperatures.

When heat tends to flow from a body A to a body B, the body A is said to have a higher temperature than B. When no transference of heat tends to take place, even under conditions which render such a transference possible, A and B are said to have the same temperature.

The choice of a scale of temperature is, apart from thermodynamic considerations, perfectly arbitrary. The most convenient thermometers, or instruments for measuring temperatures within ordinary ranges, are those in which changes of temperature are indicated by the changes they produce in the volume of a definite quantity of matter, usually a liquid or a gas, subject to given external conditions as to pressure, etc.

In physical investigations the substances most commonly employed to define a scale of temperature are the so-called permanent gases such as air, hydrogen, etc.

The *constant-pressure gas-scale* of temperature is a scale in which temperature is taken to be numerically proportional to the correspond-

ing volume occupied by a constant mass of some permanent gas, maintained at a constant pressure.

The *unit or degree* of temperature is commonly defined as in Celsius' scale by the assumption that from the freezing to the boiling point of water represents an interval of 100°. With this assumption the gas-temperatures of the freezing and boiling points of water are about 273° and 373° respectively.

The advantage of a gas-scale of temperature is that it is found to be *approximately* the same whatever be the constant pressure or the nature of the gas employed, provided the gas is sufficiently far from the point at which liquefaction takes place.

As, however, gases may be liquefied under the action of extreme cold, the gas-scale does not, in itself, apart from thermodynamical considerations, afford warranty for the statement that "the absolute zero of temperature is -273° C".

3. Measurement of Quantity of Heat. In practical calorimetry quantities of heat are measured by the quantity of a certain assumed standard substance to which they would impart a certain definite assumed change of temperature. The *unit of heat* commonly adopted is known by the name *calorie*. The *small calorie* or *gram calorie*, often called *calorie*, is the quantity of heat required to raise the temperature of a gram of water through an interval of 1° C in a definite assumed part of the thermometric scale. The interval formerly assumed in the definition of the calorie was from 0° to 1° C, but in certain modern investigations, a calorie defined by the temperature-interval $14\frac{1}{2}^\circ$ to $15\frac{1}{2}^\circ$ has been adopted. The *great calorie* or *kilogram calorie* is the quantity of heat which raises 1 kg. of water through the same temperature-interval of 1° C, and is equal to 1000 small calories.

4. Heating a Body. In ordinary language when we speak of *heating a body*, either of two things may be meant, viz.,

(a) that the temperature of the body is being raised,

(b) that a certain quantity of heat is being imparted to the body.

This ambiguity does not usually cause confusion in every day life, because in the majority of cases, the two operations (a) and (b) occur simultaneously. But if a mass of gas is rapidly compressed its temperature may be increasing while it is at the same time giving heat to surrounding bodies; the gas would then be being heated according to definition (a) and cooled according to definition (b). In thermodynamics it is therefore desirable to avoid the use of terms such as heating or cooling a body, whenever any ambiguity can possibly arise.

On the contrary, when a body is spoken of as growing *hotter* or *colder* an increase of temperature is always implied, for the hotness and coldness of a body are qualitative terms which can only refer to temperature.

5. Isothermal and Adiabatic Transformations. A body is said to undergo an *isothermal* transformation when its state varies in such a way that the temperature remains constant. When the body neither gains nor loses heat the transformation is said to be *adiabatic.*

6. Simple systems. The simplest kinds of systems occurring in the study of heat are homogeneous fluids or solids subjected to no external stresses except a uniform hydrostatic pressure. The mechanical properties of such a substance are expressible in terms of two quantities, namely, its pressure and volume.

The changes occurring in such systems can be expressed in terms of one variable alone if the transformations contemplated are *either* isothermal *or* adiabatic, and in such cases the pressure would be a function of the volume. We might speak of the systems as having *one degree of mechanical freedom*, but we shall prefer to call them *simple systems.*

When the above restriction is removed these systems will be seen to have at least *two degrees of freedom.* If a fluid receives heat or has its temperature raised, its pressure can be varied keeping its volume constant, or its volume may be varied keeping its pressure constant, but no third independent variation is possible in which both the pressure and volume remain constant and the fluid remains homogeneous. The state of the system is therefore completely defined by *two* independent variables, and any third variable is connected with these two; thus between pressure (p), volume of unit mass (v) and temperature (t) there must exist for any particular kind of matter an equation of the form

$$f(p, v, t) = 0. \tag{1}$$

Another example is afforded by a stretched wire subject to the condition that only the longitudinal tension varies, the cylindrical surface of the wire being maintained at constant (usually atmospheric) pressure. Here the length of the wire and its tension will be dependent on each other in the case of an isothermal or an adiabatic transformation, but will be capable of independent variation under the influence of heating effects of a general character.

Where the number of independent variables is greater than two, the system will be called a *compound system.* If the system has n degrees of mechanical freedom for isothermal or adiabatic transformations, the total number of variables will be at least $n + 1$.

7. Use of capital and small letters. In dealing with the properties of homogeneous substances, there are certain quantities, such as the volume, which are proportional to the mass of the substance, and others which are independent of the mass. In designating the former class of quantities we shall use capital letters when they refer to the whole body, and small letters when they refer to the unit of mass. Thus taking the case of volumes, if m is the mass, the whole volume will be called V, and the volume of unit mass v, and the relation connecting all such pairs of quantities will be of the form $V = mv$.

8. Indicator diagrams. If the pressure p and volume v of a simple substance be taken as coordinates of a point in a plane, then any continuous variation of the state of the substance will be represented by a curve described by the point (v, p). The curves corresponding to isothermal and adiabatic transformations will be called isothermal and adiabatic curves. Any diagram drawn in this way will be called an *indicator diagram.*

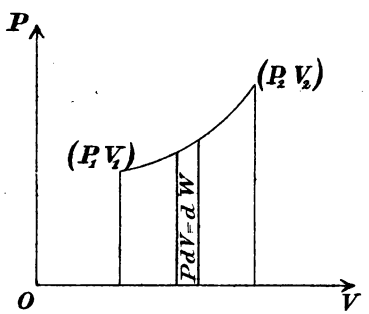

Fig. 1.

Taking the pressure p and *total* volume V as coordinates we observe that since the work done in any expansion is $\int p\,dV$ it is measured by the area contained by the arc of the curve in the (V, p) plane and the two bounding ordinates to the axis of V.

9. Cycle. When a system starts from a given state and returns to the same state by passing through a different series of intermediate states it is said to perform a *cycle* or undergo a *cyclic transformation.* For a cyclic transformation of a simple system the indicator diagram will be a closed curve in the (V, p) plane, and the total work done by the body, measured by the integral $\left(\int\right) p\,dV$ will be represented by the area of the closed curve described.

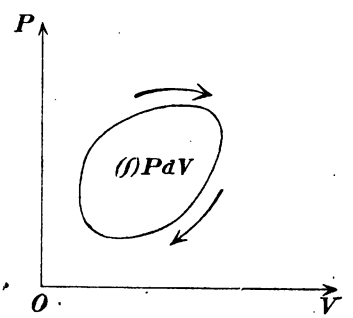

Fig. 2.

If the axis of p makes with the axis of V an angle 90^0 in the counter-clockwise direction this work is evidently positive when the curve is described in the clockwise direction.

The sign $\left(\int\right)$ is used to denote an integral taken round a cycle.

[For a system with two degrees of mechanical freedom, the state could be defined by the coordinates of a point in three dimensional space, and a cycle would be represented by a closed curve in space, but the work done would not admit of such a simple geometric representation. For a larger number of degrees of freedom even this geometrical representation would be impossible.]

10. The Boyle-Mariotte Law for Gases. The equation of the isothermals of gases was first investigated by *Boyle* in England and *Mariotte* in France. The relation obtained by them, which is now known to be *approximately* satisfied by the majority of gases except near the point of liquefaction is implied in the statement that

When the temperature of a gas is constant the volume varies inversely as the pressure.

This statement is known as Boyle's Law or the Boyle-Mariotte Law. According to this law the equation of the isothermals of a gas takes the form

$$pv = \text{constant}$$

and every isothermal curve is a rectangular hyperbola.

If t be the gas-temperature as defined in § 2 it follows that in general

$$pv = Rt \tag{2}$$

where R is constant.

According to Van der Waals a better approximation to the isothermals is given by

$$\left(p + \frac{a}{v^2}\right)\left(v - b\right) = \text{constant} \tag{3}$$

where a, b are small constants. To this order of approximation the relation between pressure, volume, and temperature cannot be conveniently expressed in terms of gas-temperature *as defined in § 2.* But if the right hand side of (3) is put equal to Rt', where R is a constant, the quantity t' will give a measure of temperature which is independent of the substance chosen to a higher order of approximation than the gas-temperature defined by § 2.

11. Thermal Coefficients. — Specific Heat. The coefficients defined below express the ratios of the small changes in the physical properties of simple systems on the assumption that no internal friction, viscosity, or resistances of a similar character exist in the system, and no chemical changes take place during the transformations considered.

The term *specific heat*, or as it might better be called, *specific heat-capacity* is used generally to denote the ratio of the quantity of heat given to a unit mass of any substance to the increase of temperature which it produces. As, however, this ratio may vary with the temperature, a precise definition of specific heat-capacity in any state is given by the differential coefficient

$$\gamma = \frac{dq}{dt} \quad \text{or} \quad \frac{1}{m}\frac{dQ}{dt}$$

where an infinitesimal increase of temperature dt requires the addition of a quantity of heat dq to a unit mass or dQ to a mass m of the substance.

The whole capacity of the body for heat will be represented by

$$\Gamma = \frac{dQ}{dt}.$$

Moreover, as changes of temperature produced by the addition of heat usually involve other changes in the physical state of a body, it is necessary to distinguish different kinds of specific heat. In the simplest case of a fluid or a solid subjected only to uniform external pressure, two kinds of specific heat are distinguished according to whether the pressure p or volume v is kept constant.

Taking for example a unit mass, the specific heat at constant volume v is defined by

$$\gamma_v = \frac{dq}{dt}$$

subject to the condition $v = \text{const.}$

The notation

$$\left(\frac{dy}{dx}\right)_z \quad \text{or} \quad \frac{d_z y}{dx}$$

is commonly used in thermodynamics to denote the differential coefficient of a variable y with respect to a second variable x when a third variable z is kept constant. With this notation *the specific heat at constant volume* is defined by

$$\gamma_v = \left(\frac{dq}{dt}\right)_v \quad \text{or} \quad \frac{d_v q}{dt}. \tag{4}$$

Similarly *the specific heat at constant pressure* is defined by

$$\gamma_p = \left(\frac{dq}{dt}\right)_p. \tag{5}$$

The *ratio of the specific heats* is a quantity frequently occurring in physics, and will be represented by $\varkappa$ so that

$$\varkappa = \frac{\gamma_p}{\gamma_v}. \tag{6}$$

12. Latent Heats of Expansion. The *latent heat of expansion* of a simple substance at constant temperature is the ratio of the heat communicated to a unit mass of the substance to the increase of volume if the temperature remain constant; in other words, it is given by

$$l_v = \left(\frac{dq}{dv}\right)_t. \tag{7}$$

Similarly *the latent heat of pressure-variation* at constant temperature is given by

$$l_p = \left(\frac{dq}{dp}\right)_t \tag{8}$$

and we notice that for a given small change, which must be isothermal, dq is the same in both expressions, and the relation between dp and dv is determined by the isothermal equation of the substance, so that

$$l_v = l_p\left(\frac{dp}{dv}\right)_t, \quad l_p = l_v\left(\frac{dv}{dp}\right)_t. \tag{9}$$

The latent heats here referred to must not be confused with the latent heat of transformation connected with the passage of a substance from the solid to the liquid or from the liquid to the gaseous phase.

13. The Coefficient of Cubic Expansion *at constant pressure* p is the ratio of the increase of volume, expressed as a fraction of the total original volume, to the increase of temperature; in other words it is given by

$$\alpha_p = \frac{1}{v}\left(\frac{dv}{dt}\right)_p = \frac{1}{V}\left(\frac{dV}{dt}\right)_p. \tag{10}$$

14. The Modulus of Elasticity *at constant temperature* is given in like manner by

$$\varepsilon_t = -v\left(\frac{dp}{dv}\right)_t = -V\left(\frac{dp}{dV}\right)_t. \tag{11}$$

The reciprocal of this is called the *compressibility*, and calling it β_t we have

$$\beta_t = -\frac{1}{V}\left(\frac{dV}{dp}\right)_t. \tag{11a}$$

There is also a coefficient of cubic expansion and a modulus of elasticity for adiabatic transformations, these being defined respectively by

$$\alpha_s = \frac{1}{V}\left(\frac{dV}{dt}\right)_s, \quad \varepsilon_s = -V\left(\frac{dp}{dV}\right)_s, \tag{12}$$

the suffix s denoting that in differentiation the variations must correspond be an adiabatic transformation. These coefficients are also often called the *isentropic coefficient of expansion* and *modulus of elasticity.*

15. Changes of phase. The passage of a substance such as water at ordinary atmospheric pressure from the solid to the liquid or from the liquid to the gaseous state affords an example of a general class of phenomena known as *changes of phase*. If the pressure be kept constant, such a change takes place at a certain temperature called the *temperature of transformation* or *temperature of equilibrium;* thus the boiling point of water is the temperature of transformation from the liquid to the gaseous state at normal atmospheric pressure.

If the temperature is given the change takes place at a certain pressure called the *equilibrium pressure;* in the case of transition from the liquid to the gaseous state this pressure is also known as the *vapour pressure* corresponding to the given temperature.

The different states are particular cases of what are known as different *phases* of the same substance, and the change from one phase to the other is discontinuous, the substance passing through no continuous series of intermediate states. The quantities of the substance existing in the given phases usually vary continuously during the process of transformation, and the two phases may be maintained in equilibrium with each other for an indefinite time at any temperature and pressure at which transformation takes place.

Thus, let water and steam be in equilibrium in a cylinder with a moveable piston kept at constant temperature. If the volume be increased, a portion of the water will be converted into vapour until the pressure is the same as before, and the phases will then be remain in equilibrium; if the volume be reduced, the reverse will take place.

A system in which two or more phases are in equilibrium is called a *saturated complex* of the phases. The name *mixture* is also commonly applied to such a system, but it is better to apply this name exclusively to *homogeneous* systems in which various substances or phases are really mixed, instead of the *heterogeneous* systems in which the phases are separate and distinct.

From the above explanation it follows that a saturated complex of two phases of a single substance can only exist when the pressure p and temperature t are connected by a certain definite relation, say

$$G(p, t) = 0. \tag{13}$$

The curve which represents this equation in terms of p, t as coordinates is called the *curve of saturation.*

In the passage of a substance from one phase to another a certain quantity of heat is given out or absorbed. The quantity of heat λ required to transform a unit of mass of the substance from one phase to the other is called the **Latent Heat of Transformation** or *specific heat of reaction* (called by *Zeuner* the "*Wärmeinhalt*" of the

process). If heat is absorbed the substance is said to pass from a *lower* to a *higher* phase and conversely.

The *specific volumes of the phases* are the volumes of a unit mass of the substance in these phases, and will be denoted by v' and v'' in the case where there are only two phases.

16. Relation between the latent heat of transformation and the latent heat of expansion of the complex. We shall now prove the very important relation

$$l_v = \frac{\lambda}{v' - v''} \tag{14}$$

connecting the latent heat of expansion of the complex at constant temperature with the latent heat of transformation.

Suppose a quantity dm of the substance to pass from the phase v'' to the phase v', the temperature being kept constant. The quantity of heat dQ absorbed is $\lambda\, dm$ while the total increase of volume is $dV = (v' - v'')\, dm$. Hence

$$\left(\frac{dQ}{dV}\right)_t = \frac{\lambda}{v' - v''}.$$

By taking the total mass of the complex to be unity it is easily seen that the left hand member is equal to $\left(\frac{dq}{dv}\right)_t$, which is the quantity defined as the latent heat of expansion of the complex, or l_v. (§ 12.)

17. The Specific Heats of the higher and lower phases *in the state of saturation* are the quantities γ', γ'' defined by

$$\gamma' = \frac{dq'}{dt}, \quad \gamma'' = \frac{dq''}{dt}$$

where dq', dq'' are the quantities of heat required to raise a unit mass of the substances in the two phases respectively through a temperature difference dt, when the pressure varies in such a way that the phases continue in equilibrium (i. e. when the changes of pressure and temperature take place in accordance with the equation $G(p, t) = 0$). We may thus write our definitions

$$\gamma' = \left(\frac{dq'}{dt}\right)_G, \quad \gamma'' = \left(\frac{dq''}{dt}\right)_G. \tag{15}$$

18. The Triple Point. When a substance is capable of existing in three different phases there exist generally a unique temperature and pressure at which all three phases can be in equilibrium with each other. This temperature and pressure define what is known as a *triple point.*

Thus for water the temperature of the triple point is 0.0074° C and the pressure is 0.00614 atmospheres. At this temperature and pressure ice, water, and vapour can coexist in equilibrium with each other.

19. Other examples of phase equilibrium. In sulphur we have an example of a substance of which two phases, both solid, (monoclinic and rhomboidal) can coexist in equilibrium with each other, if the temperature and pressure are connected by a certain relation.

As an example of phase equilibrium in which more than one substance is concerned, we may take a saturated solution of any salt in presence of undissolved salt, and vapour of the solvent. The solvent may or may not occur in all three phases, in the vapour, in the solution, and in the undissolved salt in the form of water of crystallisation, similarly the salt may or may not occur in all the three phases, since, if volatile, its vapour may be mixed with the vapour of the solvent.

20. The Critical Point. When a gas is condensed by increase of pressure at constant temperature it becomes changed into liquid at a certain pressure provided that the temperature does not exceed a certain limit. If the temperature is greater than this limit, no sudden change takes place. This property was first discovered by *Cagniard de la Tour* in 1822 and studied by *Andrews* for carbon dioxide (CO_2). The limiting temperature at which the distinction between the liquid and gaseous phases vanishes is called the *critical temperature*, and the corresponding limiting value of the pressure of liquefaction is the *critical pressure*.

If the existence of a critical point be assumed, it is always possible to transform a substance from one phase to the other by a *continuous* series of transformations by suitably heating it above the critical temperature during the process.

21. Point of Maximum Density. When water is cooled at constant atmospheric pressure its volume decreases till a temperature of about 4° C is reached, but any further diminution of temperature causes it to expand, a further expansion accompanying the process of freezing. The temperature at which contraction changes to expansion is called the *temperature of maximum density*.

The specific volume is then a minimum for variations in which the pressure remains constant so that

$$\left(\frac{dv}{dt}\right)_p = 0 \quad \text{and} \quad \left(\frac{d^2v}{dt^2}\right)_p > 0. \tag{16}$$

CHAPTER II.

CLASSICAL TREATMENT OF THE FIRST AND SECOND LAWS.

22. Equivalence of Heat and Work. Till the end of the 18th century it was commonly believed that heat was a substance, which was called caloric, igneous fluid, or Phlogiston, although there are to be found attempts at a kinetic theory, according to which heat is attributed to molecular motion, in the writings of *Hooke*, *Descartes*, *Locke* and others.

In 1798 *Count Rumford* described experiments at Munich on the heat produced by the boring of cannon; finding that the thermal capacity of the borings was the same as that of the metal of which the cannon were made, he inferred that the heat was not taken from the borings and therefore could not be a material substance, and he was thus led to believe that heat was nothing else than motion. About the same time *Davy* produced heat by rubbing two pieces of ice together and melting them, although the thermal capacity of water was greater than that of ice. The new view received so little support, however, that *Fourier* in his Théorie de la chaleur (1822) still held to the materialistic view regarding the nature of heat.

The first determinations of a numerical relation between quantity of work and quantity of heat were published by *Robert Mayer*, of Heilbronn in May 1842, and by *James Prescott Joule* of Manchester in August 1843.

Among the various experiments performed by these writers we may quote Joule's well known determinations of the heating effects produced by the friction of fluids. A quantity of water in a closed vessel was agitated by a rotating paddle set in motion by a falling weight, and Joule thus determined the work-quantity required to raise the temperature of the water by a given amount. Other experiments were made by *Mayer* and *Joule* on the heat produced by the compression of gases, and later experiments have been made on the heating effects produced by electric currents, as well as by various other methods.

The agreement between the results obtained by these different methods is as close as could be expected when errors of experiment are taken into account, and we are thus led to the so-called *Principle of Equivalence*, *First Law of Thermodynamics*, or *Mayer-Joule Principle* according to which:

When heat is transformed into work or conversely work is transformed into heat, the quantity of heat gained or lost is proportional to the quantity of work lost or gained.

23. The Absolute Unit of Heat. Just as Newton's Laws of motion afford an absolute quantitative measure of force, so the First Law of Thermodynamics gives us an absolute measure of quantity of heat. The *dynamical or absolute unit of heat* (introduced by Rankine) is that quantity of heat which is the equivalent of a unit of work. In the C. G. S. system of units the dynamical unit of heat is therefore the erg. This unit of heat will always be used in future in the present work unless the contrary is stated.

The so-called *mechanical equivalent* of a given unit of heat is the number of units of work that must be transformed into heat in order to produce that unit of heat or its equivalent effect. Its value depends on the units adopted for the measurement of work and heat respectively, and it is commonly denoted by the letter E or J. From the experiments of *Joule*, *Hirn*, and others it is found that if heat be measured in small calories and work in ergs, J is equal to about 4.18×10^7.

If heat be measured in dynamical units the mechanical equivalent becomes equal to unity, and the equations of thermodynamics assume a simpler and more symmetrical form.

It is to be observed that from this stand-point the measurements of the mechanical equivalent of a calorie assume a new meaning. For from the definition of a calorie it follows that its mechanical equivalent is the number of work units of heat required to heat the unit of mass (a gramme) of water through 1^0, and this number therefore now represents the *specific heat of water.*

24. Conservation or non-conservation of heat. While the principle of conservation of energy shows that the total energy gained by a body is equal to the energy supplied from without in the form of work or heat, (or any other form of energy which may exist), properly the fact that energy supplied in the form of work can be withdrawn in the form of heat, and that under certain limitations the reverse process is possible, illustrates the fact that no definite portion of the energy of a body can be called work and heat respectively, and we shall never in Thermodynamics speak of a body as containing a definite quantity of *heat.*

There are however a great many ordinary phenomena to which the old caloric hypothesis is perfectly applicable, and it is so common to think of a body as containing so much heat that we must examine why such ideas, though thermodynamically erroneous, lead in many cases to consistent results by simplified methods.

If energy only passes to and from bodies in the form of heat, the caloric hypothesis will of course give perfectly correct results, and there will be no error arising from speaking of the total energy of a body as the quantity of heat contained in it.

Now this is approximately true in dealing with ordinary solid or liquid bodies at atmospheric pressure, owing to their small coefficients of expansion and large specific heats.

For example, if one gram of water is heated from 0° C to 100° C at atmospheric pressure, its volume increases from 1 to 1.045 c. c. and the work done in expansion, if this pressure is 10,000 dynes per square centimetre, is 450 ergs, or only about 0.0000001 of the energy required to raise the temperature of the gram of water by 1° C (taking 4.18×10^7 as the value of the specific heat J). This exemplifies the fact that in bodies other than gases the work of expansion is usually negligible in comparison with the energy required to produce measurable changes of temperature.

Thus the somewhat vague term "quantity of heat contained in a body" in common use probably means in many cases the same as the more precise thermodynamical term *"intrinsic energy"*. But the word heat is used in such a vague way to denote temperature, quantity of heat, or indeed mere coefficients of thermal capacity such as latent heat and specific heat, that it has ceased to have any precise meaning.

25. The Second Law. While any quantity of work can be transformed into heat by friction or otherwise, it is generally impossible to transform the whole of the heat again into work, and the former transformation is for this reason said to be *irreversible*. As an instance of this property we have the common steam engine, in which part of the heat produced by the combustion of the coal is carried off by the escaping steam, or is absorbed by the condenser in a condensing engine, and this portion of heat is not transformed into work.

The exact law determining the maximum quantity of heat which can be converted into work by any machine depends on a principle which was first enunciated on the materialistic view of heat by *Sadi Carnot* in 1824, and was discussed from the same stand point by *Clapeyron* in 1834. Its correct form and significance for the dynamical theory of heat were made clear by *Clausius* in a paper of 1850 and by *Lord Kelvin* in a paper of 1851.

The principle thus discovered is known as the Principle of *Carnot-Clausius* or the *Second Law of Thermodynamics*, and it is virtually contained in the following axiom:

Heat cannot pass from a colder to a warmer body without some compensating transformation taking place.

26. Carnot's Cycle. If we have two bodies H and K maintained at constant unequal temperatures t_1 and t_2 ($t_1 > t_2$), an indefinite amount of work may be obtained from them by means of a third intermediate

body S, by causing this body to undergo a series of cyclic transformations of the kind known as *Carnot's cycle*. We shall call H the source, K the refrigerator, and S the working substance. This latter may be taken to be, e. g., a mass of gas contained in a cylinder furnished with a piston, and it must be capable of being brought into thermal contact with either H or K. The process consists of four parts.

(1) The system S starts at temperature t_2 and is brought, without gain or loss of heat, to temperature t_1 by suitable external mechanical actions (e. g. compression).

(2) The system S is placed in thermal contact with the source H and receives from it a certain quantity of heat Q_1 while its temperature remains constant and equal to t_1.

(3) The temperature of the body is allowed to fall to t_2 (by expansion) without its receiving or parting with heat.

(4) The system is brought into contact with the cooler K and its state is allowed to change until the initial state (i. e. the same volume as at the commencement) has been obtained. In this process a certain quantity of heat Q_2 is given to the cooler.

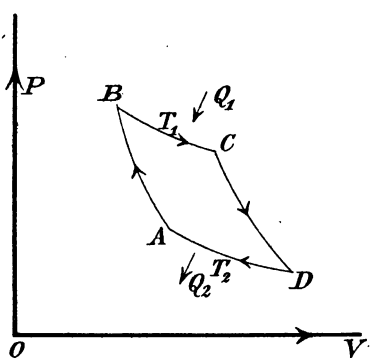

Fig. 3.

If S is a simple system, characterized by the variables p, V (§ 6) the cycle will be represented geometrically by a curvilinear quadrilateral $ABCD$. In the first process the characteristic point will describe an adiabatic line AB, in the second an isothermal line BC, in the third an adiabatic line CD, and in the fourth an isothermal line DA.

The work W done in the cycle is represented by the curvilinear area $ABCD$, and by the *Mayer-Joule* Principle it is equal to the lost heat $Q_1 - Q_2$ expressed in dynamical units.

Carnot's cycle is *perfectly reversible*. If we imagine the characteristic point to describe the same quadrilateral in the order $ADCBA$, we shall have a cyclic process in which the system (1) receives Q_2 at temperature t_2 from the cooler, (2) undergoes adiabatic changes till its temperature is t_1, (3) imparts Q_1 at temperature t_1 to the source, and (4) is brought back to its initial state by an adiabatic transformation which reduces its temperature to t_2.

In this case a quantity of work $Q_1 - Q_2$ is converted into heat, the area encircled by the representative point in describing the quadrilateral being negative.

Carnot's cycle is the only perfectly reversible process by which work can be derived indefinitely from a single source and refrigerator maintained at given constant temperatures. If, owing to imperfect thermal contact such as occurs in practice, a difference of temperature occurs between the working substance and the source and refrigerator respectively when heat passes between them, or if the intermediate transformations are not perfectly adiabatic owing to radiation, or, again, if the expansions and contractions of the intermediary system S are retarded by friction, viscosity, or such resistances, the resulting cycle is irreversible.

27. Efficiency of a heat engine. The *efficiency* of a heat engine or motor is defined to be the ratio of the quantity of work produced to the quantity of heat absorbed from the source, and hence if Q_1 and Q_2 are the quantities of heat absorbed from the source and given to the refrigerator, expressed in work units, the work done is $Q_1 - Q_2$ and the efficiency is $\frac{Q_1 - Q_2}{Q_1}$.

From the *Clausius* axiom we now deduce the following:

Of all heat motors working between given temperatures that which is perfectly reversible has the greatest efficiency.

Let M and N be two heat motors, and if possible let N be perfectly reversible, and let M be more efficient than N. Let the two motors have the same source and refrigerator, and let the motor M transform heat into work, while N, performing the reverse cycle, transforms this work back into heat. Then since M is more efficient than N, the quantity of heat absorbed from the source by M is less than the quantity which N would have to absorb to perform the same amount of work, and is therefore less than the quantity of heat N gives to the source when N performs the reverse transformation. Hence the source receives more heat than it loses, and since no work is performed on the whole, this heat must be taken from the refrigerator. Thus heat passes from a colder body (the refrigerator) to a hotter body (the source) without work being absorbed. But this is contrary to Clausius' axiom. Therefore M cannot be more efficient than N. By similar reasoning we may also show that *all reversible motors working between the same temperatures have the same efficiency.*

It follows that the efficiency $1 - \frac{Q_2}{Q_1}$ of every such reversible transformation between temperatures t_1 and t_2 is the same; this efficiency must therefore be a function of the temperatures only. Hence $\frac{Q_2}{Q_1}$ is a function of t_1 and t_2 only and therefore we may write

$$\frac{Q_1}{Q_2} = f(t_1, t_2). \tag{17}$$

Now suppose, instead of a single cycle, we take two working substances S_1 and S_2, one performing a cycle between the temperatures t_1 and t_2 and the other performing a cycle between t_2 and t_3, so that the heat Q_2 given out by S_1 at temperature t_2 is absorbed by S_2 at that temperature. This combinations of two cycles is represented graphically by a figure like Fig. 4, and since its only ultimate effect is to take a quantity of heat Q_1 from the source at temperature t_1 and give a quantity of heat Q_3 out to the refrigerator at t_3 its efficiency must be equivalent to that of a single cycle acting between t_1 and t_3.

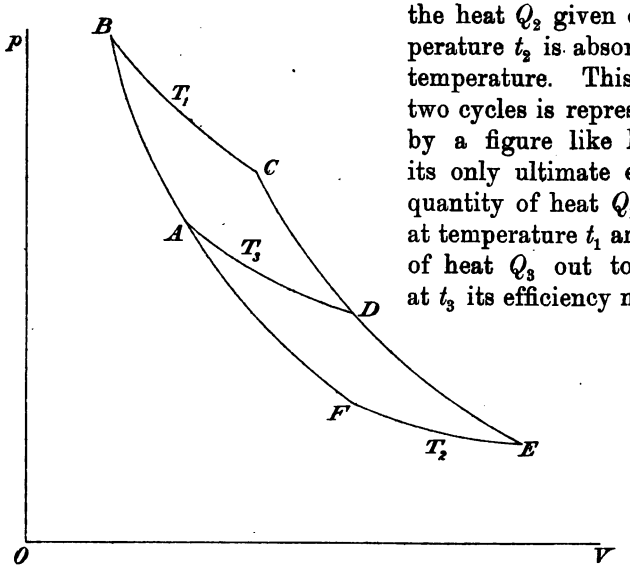

Fig. 4.

Thus

$$\frac{Q_1}{Q_2} = f(t_1, t_2),$$

$$\frac{Q_2}{Q_3} = f(t_2, t_3),$$

$$\frac{Q_1}{Q_3} = f(t_1, t_3)$$

and therefore for all values of t_1, t_2 and t_3

$$f(t_1, t_3) = f(t_1, t_2) \cdot f(t_2, t_3).$$

Hence

$$f(t_1, t_2) = \frac{f(t_1, t_3)}{f(t_2, t_3)}. \tag{18}$$

Now let t_3 be put equal to a constant C while t_1 and t_2 are left variable. Under these conditions the constant temperature t_3 may be omitted from the expressions $f(t_1, t_3)$ and $f(t_2, t_3)$, and these expressions may be written $\varphi(t_1)$ and $\varphi(t_2)$ respectively, that is

$$\frac{Q_1}{Q_2} \equiv f(t_1, t_2) = \frac{\varphi(t_1)}{\varphi(t_2)}. \tag{19}$$

28. Absolute Temperature. The form of the function $\varphi(t)$ will depend on the scale of measurement of temperature intervals. We may therefore chose this scale so that $\varphi(t)$ is proportional to the temperature T, or $\varphi(t) = kT$, where k is constant. If this assumption be made, T is said to be the *absolute temperature*, and the equation gives

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}, \quad \frac{Q_2}{Q_3} = \frac{T_2}{T_3}, \quad \frac{Q_1}{Q_3} = \frac{T_1}{T_3}. \tag{20}$$

Hence we have the following definition.

The absolute temperature is a quantity defined by the property that the absolute temperatures of two bodies are proportional to the

quantities of heat lost by one and gained by the other in a perfectly reversible cyclic transformation in which the bodies play the part of source and refrigerator.

The *unit absolute temperature* still remains undetermined, and for this the degree Celsius is usually taken, so that the difference of absolute temperature between the freezing point and boiling point of water becomes equal to 100 degrees. Under this assumption it is found from experiment that the absolute temperatures of the freezing and boiling points of water respectively are proportional to 273 and 373, hence these temperatures must be called 273 and 373 degrees approximately. In this sense it is commonly said in experimental treatises on heat that the temperature of the absolute zero is -273° C.

The gas-scale of temperature is very approximately but not actually identical with the absolute scale, as will be seen later.

29. Carnot's Function is a quantity μ such that the efficiency of a reversible engine between temperatures t and $t - \delta t$ when δt is infinitesimal is $\mu \delta t$. It therefore equals $\frac{\varphi'(t)}{\varphi(t)}$ of equation (19) or equals $\frac{1}{T}$ if T is in absolute units.

In the earlier writings of *Carnot*, *Clapeyron*, *Thomson*, *Tait*, and *Rankine*, a different method was employed. Consider the limiting case of Carnot's cycle when the area $ABCD$ becomes an infinitesimal parallelogram, the isothermals AD, CB corresponding to temperatures t, $t - \delta t$, and the heat taken from the source being δQ. Let l_v be the latent heat of expansion at temperature T, so that $l_v \delta V$ is the quantity of heat required to increase the volume of the working substance by δV at constant temperature t. Then

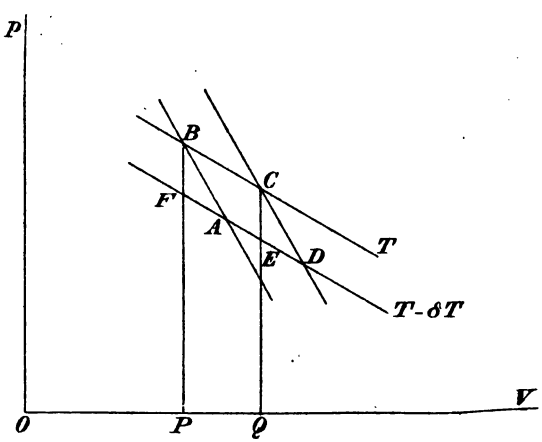

Fig. 5.

work done in complete cycle = area $ABCD$ = area $FBCE$ (Fig. 5)
$= BF \cdot PQ$.

Now $BF = \left(\frac{\partial p}{\partial t}\right)_v \delta t$ where v is kept constant in $\left(\frac{\partial p}{\partial t}\right)$, and $PQ = \frac{\delta Q}{l_v}$ whence

$$\text{work of the cycle} = \frac{\partial p}{\partial t} \delta T \frac{\delta Q}{l_v}.$$

But this by definition equals $\mu \delta T \delta Q$. Hence

$$\left(\frac{\partial p}{\partial t}\right)_v = \mu l_v. \tag{21}$$

By the Second Law μ is a function of t. If the temperature T be absolute, $\mu = \frac{1}{T}$ and (21) becomes

$$\frac{\partial p}{\partial T} = \frac{l_v}{T} \quad \text{or} \quad \frac{\partial p}{\partial \log T} = l_v. \tag{22}$$

This result will be obtained later by analytical methods.

30. Lord Kelvin's "First Scale" of Absolute Temperature. Before the present scale of absolute temperature had been introduced, Lord *Kelvin*, in 1848, suggested a scale based on the assumption that $\mu = 1$. If ϑ is the temperature on such a scale we obtain

$$d\vartheta = \mu\, dt \text{ (referred to any arbitrary scale)}$$
$$= \frac{dT}{T} \text{ (referred to the present absolute scale)}$$

whence (23) $\vartheta = \text{lognat } T + \text{const.}$

The temperature on the "first scale", ϑ is therefore equal to the logarithm of the absolute temperature plus an arbitrary constant. This scale will be found to possess the following peculiarities.

(1) The "absolute zero" of the ordinary scale is represented by $\vartheta = -\infty$.

(2) The indeterminateness of the unit of absolute temperature is represented on this "first scale" by an indeterminateness in the position of the zero, which indeterminateness is introduced above in the constant of integration. Obviously if we take this constant to be zero (as we naturally should) $\vartheta = 0$ when $T = 1$.

(3) The temperature T has been stated above (§ 28) to be approximately proportional to the volume v of a unit mass of gas at constant pressure. To this degree of approximation,

$$\vartheta = \log v + \text{const.},$$

whence

$$\frac{1}{v}\left(\frac{dv}{d\vartheta}\right)_p = 1. \tag{24}$$

The left hand side is defined (§ 13) to be the coefficient of cubical expansion of the gas. Hence on the "first scale" the coefficient of cubical expansion of any gas would be approximately equal to unity.

CHAPTER III.

TRANSFORMATION OF THERMAL COEFFICIENTS.

31. Formulae which are independent of thermodynamic hypotheses. The various coefficients defined in Chapter I are not all independent, but are subject to certain relations. Some of these

relations are independent of the First and Second Laws of thermodynamics, and it is therefore desirable to deduce them outside the portion of this work which deals with the principles of thermodynamics proper. They may be described in reference to this characteristic as *non-thermodynamical* formulae, by which it is to be understood that they would still be true even if the first and second laws did not exist, provided that the existence of the concepts heat and temperature were assumed. If the existence of temperature be regarded as a corollary of the Second Law of Thermodynamics, as it should be from the theoretical aspect, these formulae will be to that extent dependent on thermodynamics. They do not assume any hypothesis as to the equivalence of heat and work.

The conditions imposed in the definition of the thermal coefficients of a substance may be now more definitely expressed by the statement that *the small transformations under consideration are reversible*, that no changes occur in the chemical constitution of the system, and that the only changes which take place are those specified in the definitions or formulae.

32. Case of a simple system. Of the three variables p, v, t any two suffice to determine the state of a homogeneous fluid (taken as a type of a simple system); and for each such system there is an equation connecting these variables, of the form $f(p, v, t) = 0$ determinable by experiment. By differentiation

$$\frac{\partial f}{\partial p}dp + \frac{\partial f}{\partial v}dv + \frac{\partial f}{\partial t}dt = 0.$$

Hence

$$\left(\frac{dp}{dv}\right)_t = -\frac{\dfrac{\partial f}{\partial v}}{\dfrac{\partial f}{\partial p}} \text{ and two similar}$$

whence

$$\left(\frac{dp}{dv}\right)_t \left(\frac{dv}{dp}\right)_t = 1 \text{ and two similar} \tag{25}$$

and

$$\left(\frac{dp}{dv}\right)_t \left(\frac{dv}{dt}\right)_p \left(\frac{dt}{dp}\right)_v = -1. \tag{26}$$

Again the added heat dq can be put[1]) in the forms

$$dq = \gamma_v dt + l_v dv, \tag{27}$$

$$dq = \gamma_p dt + l_p dp \tag{28}$$

according to whether t and v or t and p are independent variables, γ_v, γ_p, l_v, l_p being the specific and latent heats defined in §§ 11, 12. Eliminating dt from these two equations we obtain

1) It is here assumed that no "irreversible conversion of work into heat" or other irreversible process is occurring in the interior of the substance.

$$dq = \frac{\gamma_p l_v dv - \gamma_v l_p dp}{\gamma_p - \gamma_v} \tag{29}$$

so that if p and v are taken as independent variables and if

$$dq = Mdv + Ndp \tag{30}$$

the coefficients M and N are not new quantities but are given in terms of the previous ones by the expressions

$$M = \frac{\gamma_p l_v}{\gamma_p - \gamma_v}, \quad N = \frac{\gamma_v l_p}{\gamma_v - \gamma_p}. \tag{31}$$

Again changing the independent variables from v, t to p, t in (27) we obtain

$$dq = \gamma_v dt + l_v \left\{ \frac{\partial v}{\partial t} dt + \frac{\partial v}{\partial p} dp \right\}$$

and comparing with (28)

$$\gamma_p = \gamma_v + l_v \frac{\partial v}{\partial t}, \quad l_p = l_v \frac{\partial v}{\partial p}. \tag{32}$$

The reverse transformation of (28) leads to

$$\gamma_v = \gamma_p + l_p \frac{\partial p}{\partial t}, \quad l_v = l_p \frac{\partial p}{\partial v}. \tag{33}$$

In virtue of (25, 26) the two last relations are immediately deducible from the previous two.

33. For an adiabatic transformation, $dq = 0$, giving

$$dv = -\frac{\gamma_v}{l_v} dt, \quad dp = -\frac{\gamma_p}{l_p} dt$$

whence denoting the corresponding differential coefficients by suffix s

$$\left(\frac{dp}{dv}\right)_S = \frac{\gamma_p l_v}{\gamma_v l_p} = \frac{\gamma_p}{\gamma_v} \left(\frac{dp}{dv}\right)_T \tag{34}$$

and therefore with the notation of § 14,

$$\frac{\varepsilon_S}{\varepsilon_T} = \frac{\gamma_p}{\gamma_v} = \varkappa \tag{35}$$

i. e. the moduli of elasticity for adiabatic and isothermal transformations are in the ratio of the specific heats at constant pressure and volume.

Again we have such formulae as

$$\left(\frac{dv}{dt}\right)_S = -\frac{\gamma_v}{l_v} = -\frac{\gamma_v}{\gamma_p - \gamma_v} \left(\frac{dv}{dt}\right)_p \tag{36a}$$

$$\left(\frac{dp}{dt}\right)_S = -\frac{\gamma_p}{l_p} = -\frac{\gamma_p}{\gamma_v - \gamma_p} \left(\frac{dp}{dt}\right)_v. \tag{36b}$$

34. Generalisation for any number of variables. The above results depend on the fact that if we have two independent variables the

relations between the small variations in any quantities dependent on them can be expressed in terms of the partial differential coefficients of these variables. Thus, taking v and t as the independent variables above, the relations between the differentials dQ, dp, dv, dt are all expressible in terms of the partial differential coefficients $\frac{\partial p}{\partial v}$, $\frac{\partial p}{\partial t}$, $\frac{\partial Q}{\partial v}$, $\frac{\partial Q}{\partial t}$, of which the two last are denoted by l_v and γ_v.

The general formulae of which these are particular consequences may be worked out as follows.

Let a system be defined by n independent variables, or coordinates $x_1, x_2, \ldots x_n$, the "state of the system" being known when definite values are assigned to these variables.

Let $dy_1, dy_2, \ldots dy_m$ be variations in certain other quantities associated with the system, these variations being completely determined when the values of $x_1, x_2, \ldots x_n$ and their variations $dx_1, dx_2, \ldots dx_n$ are known. The quantities $dy_1, dy_2, \ldots dy_m$ need not be the perfect differentials of actual functions $y_1, y_2, \ldots y_m$ of the coordinates (for instance dQ in thermodynamics is not the perfect differential of a function Q of the coordinates).

In defining any differential coefficient say $\frac{dy_1}{dx_1}$ it is necessary that $n-1$ variables shall be kept constant. The ordinary partial differential coefficients $\frac{\partial y_1}{\partial x_1}$ are defined by the condition that the remaining $n-1$ independent variables $x_2, x_3, \ldots x_n$ are constant, but it is also possible to calculate $\frac{dy}{dx}$ on the supposition that dy_2, $dy_3, \ldots dy_n$ vanish (if there are n or more y's), or again on the supposition that some of the dy and some of the dx differentials, $n-1$ altogether in number vanish.

If $r-1$ of the differentials $dy_2, \ldots dy_m$ are put equal to zero, then $n-r-1$ of the variables $x_1, x_2, \ldots x_n$ must be made constant and the general type of differential coefficient will be

$$\left(\frac{dy_1}{dx_1}\right)_{y_2, y_3, \ldots y_r, x_{r+1} \ldots x_n}.$$

We have the following equations

$$\begin{aligned}
dy_1 &= \frac{\partial y_1}{\partial x_1} dx_1 + \frac{\partial y_1}{\partial x_2} dx_2 + \cdots + \frac{\partial y_1}{\partial x_r} dx_r \\
0 &= \frac{\partial y_2}{\partial x_1} dx_1 + \frac{\partial y_2}{\partial x_2} dx_2 + \cdots + \frac{\partial y_2}{\partial x_r} dx_r \\
&\cdots\cdots\cdots\cdots\cdots\cdots \\
&\cdots\cdots\cdots\cdots\cdots\cdots \\
0 &= \frac{\partial y_r}{\partial x_1} dx_1 + \frac{\partial y_r}{\partial x_2} dx_2 + \cdots + \frac{\partial y_r}{\partial x_r} dx_r.
\end{aligned}$$

Employing the notation of functional determinants we obtain on elimination

$$dy_1 \frac{\partial(y_2, y_3, \dots y_r)}{\partial(x_2, x_3, \dots x_r)} = dx_1 \frac{\partial(y_1, y_2, y_3, \dots y_r)}{\partial(x_1, x_2, x_3, \dots x_r)}$$

or

$$\left(\frac{dy_1}{dx_1}\right)_{y_2, y_3, y_r \cdot x_{r+1} \dots x_n} = \frac{\dfrac{\partial(y_1, y_2, \dots y_r)}{\partial(x_1, x_2, \dots x_r)}}{\dfrac{\partial(y_2 \dots y_r)}{\partial(x_2 \dots x_r)}} \tag{37}$$

and the value of $\frac{dx_1}{dy_1}$ *subject to the same equations of condition* is evidently the reciprocal of this.

We may also have to find such differential coefficients as $\frac{dx_1}{dx_2}$ or $\frac{dy_1}{dy_2}$ subject to $n-1$ equations of condition.

Let $\frac{dx_1}{dx_2}$ be required on the hypothesis that $y_2, y_3, \dots y_r$ are constant and $x_{r+1}, \dots x_n$ constant, then we obtain

$$\left(\frac{dx_1}{dx_2}\right)_{y_2, y_3, \dots y_r, x_{r+1} \dots x_n} = -\frac{\dfrac{\partial(y_2, y_3, \dots y_r)}{\partial(x_2, x_3, \dots x_r)}}{\dfrac{\partial(y_2, y_3, \dots y_r)}{\partial(x_1, x_2, \dots x_r)}}. \tag{38}$$

Again if $\frac{dy_1}{dy_2}$ be required on the hypothesis that $y_3, y_4, \dots y_r$ are kept constant and $x_1, x_{r+1} \dots x_n$ constant we get

$$\left(\frac{dy_1}{dy_2}\right)_{x_1, y_3, y_4, \dots y_r, x_{r+1} \dots x_n} = \frac{\dfrac{\partial(y_1, y_3, y_4, \dots y_r)}{\partial(x_1, x_3, x_4, \dots x_r)}}{\dfrac{\partial(y_2, y_3, y_4, \dots y_r)}{\partial(x_2, x_3, x_4, \dots x_r)}}. \tag{39}$$

34a. Case of two independent variables. The case where there are only two independent variables ξ, η and several dependent variables $x, y, z \dots$ is of so frequent occurrence in the thermodynamics of simple systems, that we give below the necessary formulae of transformation for this particular case:

$$\left(\frac{dx}{d\xi}\right)_\eta = \frac{1}{\left(\frac{d\xi}{dx}\right)_\eta} = \frac{\partial x}{\partial \xi}. \tag{40a}$$

$$\left(\frac{dx}{dy}\right)_\xi = \frac{1}{\left(\frac{dy}{dx}\right)_\xi} = \frac{\dfrac{\partial x}{\partial \eta}}{\dfrac{\partial y}{\partial \eta}}. \tag{40b}$$

$$\left(\frac{d\xi}{d\eta}\right)_x = \frac{1}{\left(\frac{d\eta}{d\xi}\right)_x} = -\frac{\dfrac{\partial x}{\partial \eta}}{\dfrac{\partial x}{\partial \xi}}. \tag{40c}$$

$$(40\mathrm{d}) \qquad \left(\frac{dx}{d\xi}\right)_y = \frac{1}{\left(\frac{d\xi}{dx}\right)_y} = \frac{\frac{\partial(x,\,y)}{\partial(\xi,\,\eta)}}{\frac{\partial y}{\partial \eta}} = \frac{\frac{\partial x}{\partial \xi}\frac{\partial y}{\partial \eta} - \frac{\partial x}{\partial \eta}\frac{\partial y}{\partial \xi}}{\frac{\partial y}{\partial \eta}}.$$

$$(40\mathrm{e}) \qquad \left(\frac{dx}{dy}\right)_z = \frac{1}{\left(\frac{dy}{dx}\right)_z} = \frac{\frac{\partial(x,\,z)}{\partial(\xi,\,\eta)}}{\frac{\partial(y,\,z)}{\partial(\xi,\,\eta)}} = \frac{\frac{\partial x}{\partial \xi}\frac{\partial z}{\partial \eta} - \frac{\partial x}{\partial \eta}\frac{\partial z}{\partial \xi}}{\frac{\partial y}{\partial \xi}\frac{\partial z}{\partial \eta} - \frac{\partial y}{\partial \eta}\frac{\partial z}{\partial \xi}}.$$

Of these the first three are the ordinary formulae of the differential calculus, and the fifth can be obtained from the fourth by dividing $\left(\frac{dx}{d\xi}\right)_z$ by $\left(\frac{dy}{d\xi}\right)_z$. The fourth is proved geometrically in most books on thermodynamics as follows.

Let $\xi = f(x, y)$, $\eta = \varphi(x, y)$, and consider the curvilinear parallelogram $ABCD$ bounded by the curves

$$f(x, y) = \xi, \quad f(x, y) = \xi + d\xi, \quad \varphi(x, y) = \eta, \quad \varphi(x, y) = \eta + d\eta.$$

If the coordinates of A, B, C, D are $(x_1 y_1)(x_2 y_2)(x_3 y_3)(x_4 y_4)$ we have

$$x_2 = x_1 + \frac{\partial x}{\partial \eta} d\eta,$$

$$x_3 = x_1 + \frac{\partial x}{\partial \xi} d\xi + \frac{\partial x}{\partial y} dy,$$

$$x_4 = x_1 + \frac{\partial x}{\partial \xi} d\xi$$

and the area of the parallelogram $ABCD$ is twice the triangle ABD or

$$(x_4 - x_1)(y_2 - y_1) - (x_2 - x_1)(y_4 - y_1),$$

that is

$$\left(\frac{\partial x}{\partial \xi}\frac{\partial y}{\partial \eta} - \frac{\partial y}{\partial \xi}\frac{\partial x}{\partial \eta}\right) d\xi d\eta.$$

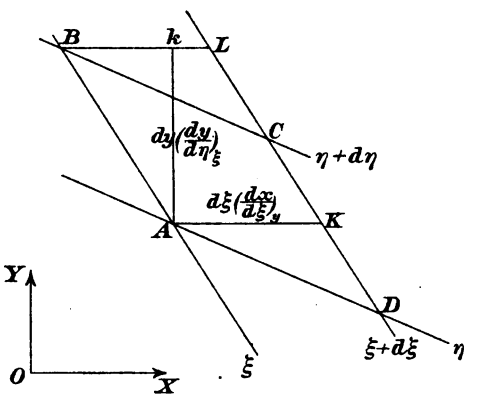

Fig. 6.

Again if we wish to express say $\left(\frac{dx}{d\xi}\right)_y$, we notice that $\left(\frac{dx}{d\xi}\right)_y d\xi$ is the length of the horizontal line AK intercepted between the curves $f(x, y) = \xi$ and $f(x, y) = \xi + d\xi$. Complete the parallelogram $AKLB$ and draw Ak perpendicular on BL.

Then

$$\square\, ABCD = \square\, AKLB = AK \cdot Ak = \left(\frac{dx}{d\xi}\right)_y d\xi \cdot \left(\frac{dy}{d\eta}\right)_\xi d\eta$$

and comparing the two expressions for the area, (40d) follows at once.

By applying similar methods to $\left(\frac{dx}{d\eta}\right)_y$, $\left(\frac{dy}{d\xi}\right)_x$, $\left(\frac{dy}{d\eta}\right)_x$ we obtain

$$(41)\quad \left(\frac{dx}{d\xi}\right)_y \cdot \frac{\partial y}{\partial \eta} = -\left(\frac{dx}{d\eta}\right)_y \cdot \frac{\partial y}{\partial \xi} = -\left(\frac{dy}{d\xi}\right)_x \cdot \frac{\partial x}{\partial \eta} = \left(\frac{dy}{d\eta}\right)_x \cdot \frac{\partial x}{\partial \xi} = \frac{\partial x}{\partial \xi}\frac{\partial y}{\partial \eta} - \frac{\partial x}{\partial \eta}\frac{\partial y}{\partial \xi}.$$

35. Other illustrations. As a further example of the mere use of the Calculus, let us discuss the effect of variation of pressure on the temperature of maximum density of water.

Take p and t as independent, v as dependent variable. Then at the point of maximum density

$$(16)\quad \frac{\partial v}{\partial t} = 0, \quad \frac{\partial^2 v}{\partial t^2} > 0.$$

Differentiating the first we have

$$\frac{\partial^2 v}{\partial t\, \partial p}\, dp + \frac{\partial^2 v}{\partial t^2}\, dt = 0$$

as the condition that the state $p + dp$, $t + dt$ shall also be a state of maximum density. This gives for the variations of the temperature and pressure of maximum density the relation

$$(42)\quad \left(\frac{dp}{dt}\right)_{\text{max. dens.}} = -\frac{\frac{\partial^2 v}{\partial t^2}}{\frac{\partial^2 v}{\partial t\, \partial p}}.$$

In virtue of (16), the denominator is equal to

$$(43)\quad v\frac{d}{dt}\left(\frac{1}{v}\frac{\partial v}{\partial p}\right)_t = -v\frac{\partial \beta_t}{\partial t}$$

where β_t is the compressibility at constant temperature (§ 14) and $\frac{dp}{dt}$ therefore has the same sign as $\frac{\partial \beta_t}{\partial t}$.

It follows that the temperature of maximum density decreases as the pressure increases if the compressibility β_t decreases as the temperature increases, which is the case for water. Moreover by observing $\frac{\partial \beta_t}{\partial t}$ and the relation between volume and temperature near the point of maximum density, the ratio $\frac{dp}{dt}$ can be found.

PART II

THE FOUNDATIONS OF A RATIONAL THERMODYNAMICS

CHAPTER IV.

RECAPITULATION OF CERTAIN PRINCIPLES OF RATIONAL MECHANICS.

36. Characteristics of a Rational Dynamical System. *Thermodynamics* is a branch of physics which treats of certain properties of the Universe which cannot be deduced from the principles of Rational Mechanics without some further assumption.

Before enunciating the fundamental axioms which may be regarded as the definitions of a thermodynamical system, it is necessary to recapitulate briefly the properties which characterise the systems usually considered in Rational Mechanics. (Holonomic systems.)

Whatever views be held as to the best axioms to take as the foundations of dynamics we may say, for the purposes of our enquiry that a *rational dynamical system* is defined by the Hamiltonian system of differential equations

$$\frac{dq_r}{dt} = \frac{\partial U}{\partial p_r}, \quad \frac{dp_r}{dt} = -\frac{\partial U}{\partial q_r} = P_r. \tag{44}$$

In these equations:

(1) The only independent variable is the time t.

(2) There are any number (say n) of dependent variables q_r called the position coordinates and an equal number of dependent variables p_r the generalised momenta or impulse coordinates of the system. The *state* of the system is said to be defined when the values of t and the $2n$ variables $q_r \ldots p_r \ldots$ are known.

(3) The expression U, which is called the energy of the system is a known function of the dependent variables $p_r \ldots q_r \ldots$.

This function is of the form $U \equiv L + V$ where L is a homogeneous quadratic function of the impulse coordinates p_r, and V is independent of these coordinates. L is the kinetic energy and V the potential energy of the system. Both the coefficients in L and V may in general involve the position-coordinates q_r in any form whatever, and the particular system under consideration is characterised by the particular forms of the functions L and V.

(4) The quantities P_r, called the generalised force coordinates are usually functions of the quantities by which the state of the system is defined, according to the nature of the problem. When the quantities $P_r \ldots$ vanish, the system is said to be isolated.

(5) The principle of action and reaction may be regarded as embodied in the statement that every non-isolated system is part of a larger isolated system.

The external forces P_r acting on any finite portion S of the universe being due to actions and reactions between this portion and neighbouring portions, must be derivable from the mutual energy of these portions and S, and by extending the system so as to include all those bodies which exert actions on S, the forces P_r will be eliminated just as the mutual actions and reactions of the particles of a rigid body are eliminated in forming the equations of motion by *D'Alembert's* Principle.

37. Dynamical and granular theories of the Universe. By a proper choice of coordinates many typical phenomena may easily be brought under the scheme of the last article. We may instance the electric and magnetic phenomena occurring in a system of bodies which are either perfect conductors or perfect insulators, and in which no magnetic hysteresis occurs.

If it be possible to bring all physical phenomena under this scheme, then we have a dynamical theory of the Universe.

A further simplification occurs if it be possible to reduce the system to a collection of isolated mass-points, devoid of rotatory inertia, moving in accordance with Newton's Laws, and attracting or repelling each other with forces which are continuous or discontinuous functions of the distance between them. A medium formed of such mass-points might be called a *Newtonian* or *granular* medium. The medium considered by Prof. Osborne Reynolds[1]) is of this character. It will be seen that for such a medium, taking x_r, y_r, z_r to be the coordinates of a grain and ξ_r, η_r, ζ_r the corresponding impulse coordinates, the expressions for the energy must assume the forms

$$L = \Sigma \frac{\xi_r^2 + \eta_r^2 + \zeta_r^2}{2m_r},$$

$$V = \Sigma\Sigma F_{rs}\left\{[(x_r - x_s)^2 + (y_r - y_s)^2 + (z_r - z_s)^2]^{\frac{1}{2}}\right\}$$

and if further the grains are to be alike in all respects m_r must be the same for all grains, and the function F_{rs} the same for all pairs of grains.

1) *Scientific Papers* vol. III.

38. The Principle of the Conservation of Energy. Now every system included within the scheme of § 36 obeys two fundamental laws, which are known as the *Principles of Conservation* of *Energy*, and *Reversibility*.

To obtain the former, consider an isolated system, satisfying the equations

$$\frac{dq_r}{dt} = \frac{\partial U}{\partial p_r}, \quad \frac{dp_r}{dt} = -\frac{\partial U}{\partial q_r}.$$

Multiplying the former by $\frac{dq_r}{dt}$, the latter by $-\frac{dp_r}{dt}$, and summing for the different variables we have

$$\Sigma\left(\frac{\partial U}{\partial p_r}\frac{dp_r}{dt} + \frac{\partial U}{\partial q_r}\frac{dq_r}{dt}\right) = 0, \quad \text{i. e. } \frac{dU}{dt} = 0$$

whence

$$U = \text{const.} \tag{45}$$

If the system is not isolated we have

$$\Sigma\left(\frac{\partial U}{\partial p_r}\frac{dp_r}{dt} + \frac{\partial U}{\partial q_r}\frac{dq_r}{dt}\right) + \Sigma P_r \frac{dq_r}{dt} = 0$$

which when integrated gives

$$U_2 - U_1 + \Sigma \int P_r dq_r = 0 \tag{46}$$

or the gain of energy $U_2 - U_1$ in any time interval is equal to the external work $-\Sigma \int P_r dq_r$ done on the system.

39. Localisation of Energy. The property, that the equations of motion of different parts of the universe (e. g. different bodies), which are not completely isolated, can be worked out independently of the rest by equations of the above form involving the introduction of the notion of "impressed forces", depends on the fact that the coordinates of an isolated system can often be divided into groups corresponding in general to different *bodies*, A, B, C of the system, but not excluding from the investigation different portions of the ether when such are taken into account, these groups being usually characterised by the following properties:

(1) The kinetic energy usually takes the form

$$T = T_A + T_B + T_C \tag{47}$$

where T_A is the kinetic energy of A or kinetic energy located in A, and depends on the position and velocity coordinates of A and not on those of the other parts B, C, ... This not necessarily true in dealing with electric phenomena, where we may have to take account

of mutual kinetic energy. In the case of the mutual induction of two circuits we have an instance in point and the equations of motion of the two circuits are interdependent and cannot be separated.

We shall assume such exceptional cases excluded where they would invalidate our arguments.

(2) The potential energy takes the form

$$V_A + V_{AB} + V_B + \cdots \tag{48}$$

where V_A is the potential energy located in A V_{AB} the mutual potential energy of A and B.

Taking $q_A, q_B, \ldots$ to be types of the coordinates of the parts $A, B, \ldots$, then in any change

$$\Sigma \frac{\partial V_A}{\partial q_A} dq_A = dV_A \tag{49}$$

is the increase in the potential energy of A, and is a complete differential, V_A being a function of the coordinates q_A.

$$\Sigma \frac{\partial V_{AB}}{\partial q_A} dq_A = dW_A \tag{50}$$

is the external work done by the body against the external forces which are given by the type

$$P_A = \frac{\partial V_{AB}}{\partial q_A}. \tag{51}$$

In the case of two bodies in contact the actions and reactions are equal and opposite, and in any motion the displacements of their points of application are equal. In such cases as this the works done on the bodies are equal and opposite so that

$$\Sigma \frac{\partial V_{AB}}{\partial q_A} dq_A + \Sigma \frac{\partial V_{AB}}{\partial q_B} dq_B = dW_A + dW_B = 0. \tag{52}$$

In other cases as where actions at a distance occur

$$\Sigma \frac{\partial V_{AB}}{\partial q_A} dq_A + \Sigma \frac{\partial V_{AB}}{\partial q_B} dq_B = dV_{AB} \tag{52a}$$

gives the increase of mutual potential energy of the two A, B bodies, and this is equal to the algebraic sum of the works done by the bodies.

This mutual potential energy may be regarded as located in the medium by which the forces are transmitted from one body to the other. With this assumption *all energy may be regarded as located either in separate bodies or in the ether.*

By the *intrinsic energy of the body* A is meant only the kinetic and potential energy *located in* A, that is U_A, where

$$U_A = T_A + V_A. \tag{53}$$

The principle of conservation of energy may now be written

$$dU_A + dW_A = 0 \tag{54}$$

or the decrease of intrinsic energy is equal to the work done by the body.

40. Reversibility. In the next place the motions of a dynamical system possess an important peculiarity which is expressed by saying that they are perfectly reversible.

We may illustrate the meaning of reversibility by considering the motion of a projectile under gravity alone. Let a body be projected from A with velocity U at an elevation α, and in any time T suppose it to describe the arc AB, arriving at B with velocity V making an angle β with the horizon. Then we know that if the body is projected from B with a equal velocity V in the opposite direction it will retrace its steps over the same parabola, and will after a further interval T return to A with a velocity U equal and opposite to the original velocity of projection. We may therefore say that the parabolic motion of a projectile is reversible, meaning that corresponding to any motion, which we may call a direct motion, a reversed motion is possible in which the projectile retraces its steps, describing the same path backwards, taking the same time over the same arc, and passing through the same points with equal and opposite velocity.

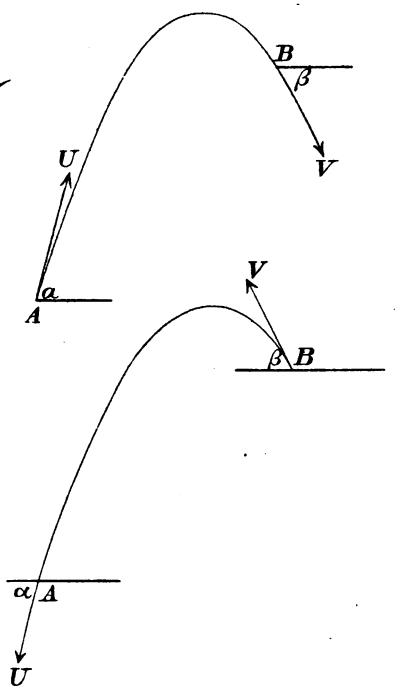

Fig. 7.

On the other hand the motion of a projectile in a resisting medium is irreversible. Thus if in the direct motion the medium exerts a retardation proportional to the square of the velocity, a reversed motion which is an exact counterpart of the direct motion could only be obtained by postulating an acceleration proportional to the square of the velocity, whereas in reality a retardation would again be exerted by the medium.

If the differential equations of motion of a system be expressed in terms of the position coordinates only as dependent variables, the motions which they determine will be perfectly reversible if the

equations of motion are unaltered by writing $-dt$ for dt, that is if they only involve even powers of dt in the differential coefficients. Thus motions uniquely determined by the differential equations in x

$$\frac{d^2x}{dt^2} + a\left(\frac{dx}{dt}\right)^2 + bx = 0 \tag{55}$$

are reversible, while those determined by

$$\frac{d^2x}{dt^2} + a\frac{dx}{dt} + bx = 0 \tag{56}$$

are irreversible.[1])

The equations of rational mechanics always represent reversible motions, provided that (1) the kinetic energy is a homogeneous quadratic function of the velocity or impulse coordinates and (2) that the external forces are functions of the position coordinates only. To prove this it is most convenient to take the equations in the Lagrangian form

$$\frac{d}{dt}\left(\frac{\partial L}{\partial q_r}\right) - \frac{\partial L}{\partial q_r} + \frac{\partial V}{\partial q_r} = P_r.$$

41. Physical unreality of reversible processes. In Nature all phenomena are irreversible in a greater or less degree. The motions of the celestial bodies afford the closest approximations to reversible motions, but motions which occur on this earth are largely retarded by friction, viscosity, electric and other resistances, and if the relative velocities of the moving bodies were reversed, these resistances would still retard the relative motions and would not accelerate them as they should do if the motions were perfectly reversible.

Irreversibility may be either *statistical* or *actual*. If the molecules of a body form a rational dynamical system satisfying the conditions of § 36, the changes which take place would be perfectly reversible, if in reversal, the velocity of every molecule of the system were reversed. As however it is impossible to control the motions of individual molecules, the phenomena which can be observed in such a system by means which we are able to command may take the form of irreversible effects. In such a case the system is *statistically irreversible*. On the other hand if the motions of the ultimate parts of the system (atoms or molecules) are themselves irreversible we

1) *When* $\frac{dx}{dt}$ *is positive* equation (55) represents the motion of a particle under a force to the origin varying as the distance, subject to a retardation varying as the square of the velocity. But *in a resisting medium* the motion is not *uniquely* defined by equation 55 for as soon as the velocity becomes negative the equation of motion is changed to

$$\frac{d^2x}{dt^2} - a\left(\frac{dx}{dt}\right)^2 + bx = 0. \tag{55 a}$$

have a case of *actual irreversibility*, and the changes in the system can no longer be represented by assuming the conditions of § 36.

The hypotheses that not only are the phenomena of nature only statistically irreversible but that the universe is a rational dynamical system with the properties of § 36 are confirmed by many results of the Kinetic Theory of Gases. But whether the reversibility is actual or statistical, a dynamical scheme which takes account of motions of individual molecules is far too elaborate and minute to be employed in all practical calculations relating to the phenomena observed in nature as irreversible. It therefore becomes necessary to formulate a new scheme, and the simplest way of doing this is by the introduction of additional variables not conforming to all the conditions of § 36.

42. Available Energy. If a system is statistically irreversible in the sense here considered, and its ultimate parts conform to the properties of § 36, the system will satisfy the Principle of Conservation of Energy, so that as long as no energy is supplied to the system from without the total energy will remain constant. But only a limited portion of this energy will be capable of being utilised for conversion into mechanical work. For in order to utilise the whole of the kinetic energy of the molecules, it would be necessary to reduce each molecule individually to rest. The impulses which would have to be applied to the molecules would be exactly half those necessary to reverse the motions of the system. The process is impossible in reality. Maxwell however gave the name *demon* to a hypothetical agent capable of controlling the motions of individual molecules, and with this nomenclature, statistical irreversibility consists in the property that "Maxwell's demons" exist only in imagination and not in reality.

We are thus led to the conclusion that under any given conditions only a limited portion of the energy of a system can be converted into mechanical work. This portion is called the *available energy* of the system subject to the given conditions. In order, however, to completely define the available energy of a system, it is necessary to specify not only the external conditions to which the system is subject, but also the means at our disposal for converting energy into useful work.

43. A parallel in mechanics. Owing to the Earth's rotation about its axis and its orbital motion about the Sun, the Earth possesses an enormous store of *unavailable* energy. The only mechanical energy which is available, is that depending on the relative displacements and motions of bodies on the Earth's surface. It is in general impossible to influence the Earth's motions as a whole, for this would necessitate producing equal and opposite reactions on some other body. Hence it is impossible to draw on the store of energy contained in

these motions. An exception occurs in the case of the tides which are produced by action and reaction between the Earth and the Moon and Sun, and which may to some extent be utilised for driving machinery in suitable places.

Generally (a) if one imagines an isolated system of bodies moving freely through space with a common uniform velocity, the mechanical energy which is available without going outside the system is zero, but if the parts of the system are in relative motion among themselves the available energy will be the amount of work that can be obtained by reducing the system to a state of uniform translation combined with rotation in a configuration of stable relative equilibrium[1]) without altering its linear and angular momenta.

On the other hand (b) if a system is in the presence of a very large uniformly moving body or base such as the earth, its available mechanical energy is the amount of work that can be produced in making its velocity the same as that of the large body.

Cases (a) and (b) have their parallels in thermodynamics in the cases of an isolated system of unequally heated bodies and of a system in the presence of a large body of uniform temperature, as we shall see later. But the problems are essentially distinct and in Thermodynamics, we shall not as a rule find it necessary to take account of the unavailable *mechanical* energy considered in this article.

44. Dependence of available energy on external conditions. In the dynamical illustration of the preceding paragraph it will be seen that the available energy of the system depends not only on the actual state of the system, but also on the external conditions to which the system is subjected. Thus if the system is moving with velocity V in the presence of a base moving with the *same* velocity, none of the kinetic energy of the system is available for conversion into work, and the only energy which is available is the potential energy. The total available energy is therefore a minimum. On the other hand a system *at rest* may become a source of available energy when brought into the presence of a moving base and the amount of this available energy (apart from any potential energy due to the mutual actions of the body and base) is easily seen to be $\frac{1}{2} m V^2$ where m is the mass of the system.

Lastly, if we have two bases moving with different velocities it is possible to generate work indefinitely by bringing a third body alternately under the influence of the two bases.

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1) If the configuration of stable relative equilibrium is not uniquely determined by the momenta, that configuration must be selected which has the least energy.

The thermodynamical analogues of these properties, which will be discussed more fully later, are that if a body is surrounded by a medium at temperature T the total available energy is a minimum when the temperature of the body is T; that a cold body may become a source of available energy in the presence of a hotter one, and that work may be generated indefinitely by bringing a body alternately into the presence of a hotter and colder medium, as in Carnot's cycle

45. Another illustration. A mass of gas can do work by expanding and it therefore possesses energy which in the process of expansion is converted into work. But if the gas is surrounded by a medium at constant pressure the only available energy is the work which would be done by the gas in expanding till its pressure is equal to that of the medium. Again, a vacuum or a region containing gas at a lower pressure would become a source of available energy in the presence of such a medium. Lastly for several gases surrounded by a closed envelope the available energy would be the work done in expanding till the pressure was uniform throughout the interior of the envelope. [We may suppose for the sake of simplicity that the pressures of the gases are functions of their volumes only and that the temperature is everywhere constant. This assumption enables us to omit temperature altogether from our equations and consider the phenomena in their purely dynamical aspect.]

46. Differential elements. In studying the dynamical properties of extended distributions of matter, the conception of a *differential element* is frequently introduced. Thus, in order to define the density of a substance, when variable, we take a volume-element $(dx\,dy\,dz)$ enclosing any point (x, y, z) of the substance, then if the mass of this element is $\rho dx\,dy\,dz$ and the dimensions of the element are suitably chosen, ρ will represent the density of the body at the point (x, y, z). Similarly in defining pressure of a fluid at a point, we take a plane surface-element dS containing the point and suppose the thrust on it is $p dS$, then if the dimensions of the element are snitably chosen, p will be the pressure at the point.

The difficulty in these definitions arises from the fact that mathematical theory requires the element in either case to be infinitely small while physical considerations require it to be infinitely great. It is only by taking the element infinitely small compared with the dimensions whose measurements we are considering that the methods of the differential and integral calculus become strictly applicable, and that the measures of density and pressure tend to approach limits which are independent of the size of the elements of volume and area. On the other hand if matter is made up of molecules, density and

pressure have no meaning as applied to elements of molecular dimensions, and it is only by taking the respective elements infinitely large compared with the corresponding spaces occupied by individual molecules that the measures of these quantities become independent of the effects of individual molecules.

The property that infinitesimal analysis can be applied to the solution of many problems in dynamics or other branches of mathematical physics, involving space distributions of matter, is explained by the extreme smallness of the space occupied by each individual molecule in comparison with bodies which are regard as "of finite size". This smallness is illustrated by the fact that in a cubic centimetre of gas there are about 5.4×10^{19} molecules. It is therefore possible to choose an element of length, area, or volume so small that it may regarded as infinitesimal for purposes of analysis and yet so large in comparison with molecular dimensions that its structure may be treated as homogeneous instead of molecular.

Such an element we shall define to be a "*differential element*" of volume, mass, area or length as the case may be.[1]) We notice that similar considerations also lead to the conception and definition of a differential element of *time*, which shall be small compared with the times (such as a second) during which finite motions of finite bodies take place, and large compared with the time intervals defined by the motions of individual molecules.

The difference between thermodynamics and the kinetic theory (statistical mechanics), is that the former branch of study seeks to investigate certain properties of matter in terms of their effects considered with respect to differential elements of time and space as a whole, while the latter seeks to investigate the progress of events within these individual elements themselves.

CHAPTER V.

GENERALISED CONCEPTIONS OF ENERGY. IRREVERSIBILITY.

47. The notion of energy in its most general aspect. From considerations such as those briefly indicated in the last chapter, it can be seen that the principles of rational mechanics (at any rate apart from statistical methods) can be only applied to explain phenomena that are both *conservative* and *reversible*.

1) The term *physically small* has also been suggested for such elements and is used by *Leathem*, "Volume and Surface Integrals used in Physics", p. 5.

In order to deal with irreversible phenomena and in particular with the class of phenomena falling under the head of thermodynamics, it is necessary in the first place to introduce a broader and more general conception of energy than suffices for the study of the particular class of phenomena included under Rational Dynamics.

The following statements may be regarded in the light partly of a definition of energy, and partly of an enunciation of its properties which are assumed as fundamental.

There is a certain entity called energy which is characterised by the following properties:

(1) *In an isolated system the total quantity of this entity always remains constant.*

(2) *The energy of a system cannot be changed without some real physical changes taking place in the state of the system.*

(3) *The kinetic and potential energies of dynamics are particular forms of this entity.*

The first statement is the *Principle of Conservation of Energy*, and it leads to the following conclusions.

If the energy of a finite non-isolated system or part of a system changes in amount, then changes of equal but opposite amount must occur somewhere outside the system or part considered, so as to make the total amount unaltered.

According to (2) if the physical state of a system is completely defined by certain variables, the energy is a function of those variables only, and does not depend on the past history of the system previous to attaining the state in question.

On the other hand, if the state of the system is defined so far as certain physical phenomena are concerned by certain variables, and we have evidence, from the existence of irreversible phenomena, or from any other cause, that energy changes have occurred in the system which are independent of the changes of these variables, we infer that the variables originally assumed are not sufficient to completely determine the physical state of the system, but that this state depends on some other variables as well.

48. Observations. In connection with the above statements we notice the following points:

(1) The *energy* of an isolated system is not the only quantity which remains constant. The components of momentum also remain constant, but the energy is the *only* quantity which possesses the property of being wholly or partially transformable into the forms of energy defined in Dynamics.

(2) As it is impossible to conceive or realise a state of *zero energy*, it is necessary to include an unknown constant in the expression

for the energy. But this constant, though unknown, is perfectly *definite* and unchanging in value, and thus the principle of conservation of energy is not made less definite by its presence.

(3) Under the general term *physical state* of a system, we include such data as the positions of its parts, its state of rest or motion, the chemical constitutions of the various parts of the system, its state of electrification and magnetisation, its state of stress or strain and other properties. We establish Thermodynamics on a footing independent of preconceived notions as to heat by assuming that the list of variables by which the state of the system was defined, in the first instance, excluded all reference to the phenomena of heat and temperature. Under such circumstances experience shows that phenomena occur indicating changes of energy which are independent of the variables originally postulated. We conclude that the original choice of variables was not sufficient to completely specify the physical state of the system. It then becomes the object of Thermodynamics to investigate the additional changes of physical state postulated by experience, and to discuss their representation by a suitable choice of variables and formulae.

49. Irreversibility. If a system passes from a state A to a state B the change is said to be *irreversible* when the system cannot pass *of itself* back from the state B to the state A, and can only be made to do so by the action of outside influences.

In connection with irreversible phenomena the following axioms have to be assumed.

(1) *If a system can undergo an irreversible change it will do so.*

(2) *A perfectly reversible change cannot take place of itself; such a change can only be regarded as the limiting form of an irreversible change.*

We shall call a transformation *positive*, when that transformation tends to take place of itself; the reverse transformation will then be *negative*, so that a negative transformation cannot take place of itself.

Since the total quantity of energy is by hypothesis constant, any change which occurs and which involves energy may be regarded as implying a *transformation of energy* from one form to another. If then a system undergoes an irreversible transformation from the state A to the state B this energy of the system is necessarily less capable of being transformed into other forms of energy in the final state than it was in the initial state.

For every state C of the system which can be reached by starting from the state B can also be reached by starting from the state A and passing through the state B. On the other hand, if in passing from A to B by any irreversible process, the system passes

through any intermediate state D, the state D can be reached by starting from A, but can *not* be reached by starting from the state B.

If then we use the term *availability* to designate the extent to which the energy of any given system in any given state is capable of being transformed into other forms of energy, we may regard it as a self evident truth that *in any irreversible transformation there is a loss of availability.*

50. Compensating transformations. When a transformation AB of a given system S is in itself irreversible and therefore positive, the reverse or negative transformation BA can nevertheless (*sometimes* at any rate) be made to take place by the introduction of a *compensating transformation.* The meaning of this will be made clearer by considering in the first instance the simple mechanical illustration of two weights connected by a pulley in such a way that when one rises the other falls. Each weight tends to fall to the ground but it can only do so by raising the other weight. The weight which preponderates will raise the other. If neither weight preponderates, there will be equilibrium, and a slight disturbance one way or the other will determine the direction in which the system moves.

Now let Σ be a second system capable of performing a positive transformation CD, and let the systems be combined together in such a way that the positive transformation CD can only take place simultaneously with the negative transformation BA and *vice versa.* Then if the two simultaneous transformations BA, CD taken as a whole constitute a positive transformation, this transformation will, if it can, take place of itself by axiom (1) above, and will be irreversible; if the combined transformation is negative the reverse transformation will, if it can, take place of itself, and the system Σ will undergo the negative transformation DC while S undergoes the positive transformation AB. In the limiting case when the opposite tendencies of the systems exactly balance each other, there will be no tendency for the combined system to undergo transformation in one direction more than the other, and a transformation in either direction will be perfectly reversible. In this case a positive transformation of one system is said to be *compensated* by a negative transformation of the other.

In reality this limiting case can never be actually realised because loss of availability must necessarily take place in the connections by which the two systems are bound together, or elsewhere. We may exemplify this point if we think of the mechanical illustration of two equal weights hanging by a string passing over a rough pulley. Although the weights theoretically balance one another a considerable effort must be made to overcome friction in order

to move the system in either direction. Again, in order that the system may move of itself, the descending weight must exceed the ascending one by an amount depending on the friction of the pulley. Still, if one irreversible physical phenomenon can be reversed by coupling it with a different irreversible phenomenon, we know that the irreversibility is comparable in the two phenomena, and that it is at least theoretically possible to adjust the magnitudes of the two changes in such a way as to make them compensate each other. In this case we may say that in both transformations the irreversibilities are *of the same kind* or *convertible.*

51. Availability measured in terms of energy. When a number of irreversible transformations are of the same kind, it is possible to make quantitative comparisons of their *irreversibility* or *loss of availability* by choosing as the compensating transformations, changes in which energy is transformed from one particular form to another less available form, the initial and final forms being the same in each case. The *quantity of energy* so transformed in the transformation required to compensate any given irreversible transformation will then afford a numerical measure of the irreversible changes connected with the given transformation. We may thus replace the words "loss of availability" by the more precise wording "quantity of available energy lost". In order to make this measure a definite one it is necessary to specify what is meant by *available energy*, i. e., when energy is available and when it is not, and this necessarily depends on the assumed conditions under which energy is transformable from one form to another.

There is of course no *a priori* reason for asserting that all the irreversible phenomena of the Universe are of the same kind, as it is possible to conceive transformations which bear no relation whatever to each other. If such exist, they must be discussed separately, and cannot be made the subject of quantitative mathematical investigations common to them. It must be regarded as the result of experience and not as a self-evident truth that a very large class of actual physical and chemical phenomena lend themselves to investigation by the methods described in this book.

52. Availability of known forms of energy a matter of experience. We now see that the Principle of Irreversibility as applied to energy phenomena, naturally leads to the conceptions of *availability*, and of *available energy*, provided that these conceptions are defined exclusively with reference to the power of transforming energy from one form to another. In order to build up a theory which will account for the irreversible phenomena of our universe, it is necessary to appeal

to experience when we attempt to identify the available energy thus defined with different forms of energy with which we are familiar. We are thus led to assume the following axiom which may be regarded as the simplest form of the Second Law of Thermodynamics:

Energy in the form of mechanical work is always wholly convertible into any other forms of energy to which the present theory is applicable, but the converse processes are not in general possible.

From this axiom, it may be seen that:

The available energy of a system subject to given external conditions is the maximum amount of mechanical work theoretically derivable from the system without violating the given conditions.

We may regard this statement coupled with the statement that:

In all irreversible transformations available energy is lost, never gained

as constituting a fundamental law of nature which we shall call the Principle of Degradation of Energy. Either of the two statements may be regarded as a definition of available energy, and the other statement will then be an axiom based on experience.

The necessity of the appeal to experience is manifest from the following considerations: If in our Universe events occur in a certain definite sequence, it is possible to conceive a universe in which events occur in the opposite sequence, by merely reversing the scale of *time*. In such a universe the transformations of energy would be exactly the opposite to those of which we have experience, and the forms of energy which are least capable of being converted into other forms in our Universe would become the most convertible. In stating this it is assumed that the individuals living in either universe possess the power of influencing the progress only of future events and possess a knowledge only of past events. This assumption is implicitly involved in all our ideas relating to irreversibility.

53. Theoretical and practical limitations to conversion of energy. In practice a system may often possess a considerable amount of energy which is easily recognisable as mechanical, potential or kinetic energy, although it would be very difficult to devise mechanisms for employing this energy to drive machinery. Thus when a ship goes through the water a large amount of energy is expended in setting up waves and vortices and is still recognisable as mechanical energy, although it is practically impossible to recover this energy or to apply it to a useful purpose. Energy of vibration or of sound waves may be taken as another instance. There is thus an apparent difficulty in drawing the line between energy which is, and energy which is not directly convertible into mechanical work. To overcome this difficulty it will probably be at least sufficient for our present purpose to

agree to classify under the title *mechanical energy* all those forms of energy which occur in the study of reversible rational mechanics. This would include the energy of wave motion and vortex motion referred to above; since these forms of energy occur in the reversible dynamics of a perfect fluid. They become associated with irreversibility when the fluid is assumed to be viscous, and then the effect of viscosity is to absorb, or rather convert them into less available forms in accordance with the principle of degradation of energy. Again if we introduce the conception of differential elements as introduced in § 46 the energies due to the motions of such elements as a whole, and to strains in the elements which in the limit may be regarded as homogeneous, will all be of the nature of mechanical energy.

In *most* problems in thermodynamics we are able to assume that such forms of energy as those of wave motion or vibration have been transformed, and that the mechanical energy of the systems is either due to simple homogeneous strains, or is, at any rate, a function of a small number of independent variables. In such cases it is easy to draw the line between the energy which is and that which is not wholly available.

54. Qualitative nature of irreversible thermodynamics. The principle of degradation of energy merely deals with the *direction* in which energy transformation tends to take place and makes no statement as to the *rate* at which the change proceeds. The study of the rates of change is necessarily based on experiment; no general laws can be enunciated, and each transformation has to be studied in detail as in the theories of friction, viscosity, conduction of heat, law of electric resistance, and other phenomena. Hence irreversible thermodynamics is in general a purely qualitative and not quantitative study, and its phenomena are represented by inequalities, not equations. When, however, we pass to the study of reversible processes by treating them as the limit of irreversible ones, the inequalities of irreversible thermodynamics become equalities and the results become quantitative. The same is the case, frequently, when we consider the ultimate distribution of energy in a system that has been left for such a long time that no further irreversible changes can occur.

CHAPTER VI.

THE CHARACTERISTICS OF A THERMODYNAMICAL SYSTEM. THE NOTION OF TEMPERATURE.

55. Characteristics of a thermodynamical system. We are now led to the consideration of conservative and irreversible systems in which degradation of energy takes place in such a way as to diminish the amount of energy utilisable in the form of mechanical work. Even this statement allows considerable latitude in regard to the general character of the phenomena occurring in such systems, and further assumptions are necessary in order that the system should reproduce the effects observed in the experimental study of heat.

At the outset we shall confine our attention to endeavouring to account for such irreversible processes as might be conveniently characterised as "thermo-mechanical" phenomena. By this *we exclude all chemical actions* for the present, and indeed *until Chapter XV*, where such actions are treated for the first time. Moreover, we limit ourselves *until Chapter X* to discussing energy changes *in a system of material bodies.* By this we do not exclude the possibility of energy passing by radiation from one body to the other, but we assume that the bodies are so near together that the passage may be regarded as instantaneous, and the quantity of energy in transit in the intervening ether may be neglected.

We commence by supposing the system divided into differential elements of mass dm occupying differential elements of volume $dx\,dy\,dz$ subject to the conventions contained in the definitions of § 46.

There are two methods in which degradation of available energy may take place in the system:

(a) by changes which take place entirely within the mass-elements (dm) without energy being transformed from one element to another;

(b) by changes in which energy passes from one mass-element to another, or more generally from any portion of the system to the other, where such changes cause a decrease of the total amount of *available* energy.

Now there are certain processes in Nature, such as the friction of fluids, in which available energy is absorbed according to method (a) within the volume elements themselves. Such processes are commonly spoken of in text books on Theoretical Mechanics as *non-conservative.* They can be equally well explained, as is indeed generally done in these books, by restricting the term "energy" to dynamical energy, kinetic and potential. In this case it is commonly stated that "energy is lost" in the system, meaning that "available energy

is lost", and the phenomena occurring in the system can often be adequately discussed without making enquiries as to what becomes of this lost energy.

If energy were unable to pass from one portion of a system to another otherwise than by the performance of mechanical work, only the available energy could be so transferred, and any energy rendered unavailable by irreversible changes in an element would remain permanently locked up in that element. If the unavailable energy thus accumulated were not to affect the physical properties of the element, this energy would be completely lost, and we should have no evidence of its existence or of the truth of the principle of conservation of energy. On the other hand if the accumulated unavailable energy were to affect the physical state of the element, we should have a state of affairs in which the properties of all bodies were continuously changing and no body could ever be brought back to its initial state by any external agency whatever. Such a condition of affairs is contrary to our experience.

We are thus led to postulate a system in which *energy can pass from one element to another otherwise than by the performance of mechanical work.*

56. Still confining ourselves to the consideration of purely hypothetical systems, it is again possible to postulate any one of the following assumptions with regard to this assumed transference of energy.

(1) The whole of the energy so transferred is, under all conditions, unavailable for transformation into mechanical work.

or (2) The transferred energy is partly available and partly unavailable, but the transference does not alter the quantity of available energy present in the system as a whole.

or (3) The transference of energy tends, in general, to decrease the total quantity of available energy present in the system.

If assumption (1) be made, the transferred energy can be disregarded in considering the progress of dynamical events in the system, and the dynamical phenomena will be identical with those of a non-conservative system such as is considered above.

If assumption (2) be made, the available and unavailable portions of the transferred energy may be considered separately. The transferences of the available portions may, by a proper choice of coordinates, be represented by the equations of rational dynamics, in which case the transferred energy assumes the form of work done by the variation of the coordinates so chosen, and if the unavailable energy be neglected, we are left with a system which is again equivalent to the same non-conservative system as before.

In thermodynamics we shall find an illustration of this very point. So long as only reversible transformations are considered we shall find that the equations of thermodynamics are identical in form with the equations of dynamics with the addition of an extra position coordinate (the entropy) and its corresponding generalised force coordinate (the temperature).

We are thus led to adopt assumption (3) as the simplest characteristic feature of a system which cannot be better represented by the equations of non-conservative dynamics.

57. We accordingly define a *thermodynamical system* as one possessing the following properties distinguishing it from the systems considered in rational mechanics.

(1) Its energy is not a function of the position coordinates and the corresponding generalised velocity components alone, but is capable of undergoing independent variations.

(2) These variations consist in transferences of energy between different parts of the system or between the system and other systems, in conformity with the principle of conservation of energy.

(3) These transferences of energy are distinguished from those considered in rational dynamics, in that they are in general accompanied by a loss of available energy, and are therefore in general, by the principle of degradation of energy, irreversible. In the systems of rational dynamics all energy is available and all transformations are reversible.

(4) As in § 39, the total energy may be expressed as a sum of terms representing respectively the parts of the energy which are located in different bodies and in the ether.

58. Quantity of Heat. Definition. When energy flows from one system or part of a system to another otherwise than by the performance of mechanical work, the energy so transferred in called *heat.*

If the energy of a body increases by dU while the body at the same time performs external mechanical work of amount dW, the body is said to receive a *quantity of heat* dQ, defined by the relation

$$dQ = dU + dW. \tag{57}$$

This relation thus affords a definition of the quantity of heat absorbed or emitted by a body. It is to be observed that we cannot speak of the quantity of heat *contained* in the body.

For if the body undergoes a cyclic transformation so that its initial and final states are identical it must have the same energy at the end as at the beginning. But it does not necessarily follow that the algebraic sums of quantities of heat absorbed and of work done

by the body are each separately zero. What we do learn by integration of (57) is that since the total energy is the same at the end as at the beginning [i. e. since $(\int) dU = 0$] therefore

$$(\int) dQ = (\int) dW \tag{58}$$

or the total quantity of heat absorbed is equal to the total quantity of work done in the cycle, the sign $(\int)$ indicating integration taken round a complete cycle. If we were to imagine the body at every instant to contain a definite quantity of heat, this quantity would be greater at the end than at the beginning of the cycle by an amount $(\int) dQ$, and either it would be implied that there was some difference between the initial and final states — such difference being contrary to the definition of a cycle, — or the statement would be meaning less. The other alternative, that of assuming that a cycle could only exist in which $(\int) dQ$ and $(\int) dW$ were both zero would imply an independence of heat energy and work energy, which is not only contrary to experience, but which would fail to account for degradation of the latter form of energy.

If, instead, we consider a change of the system from a state A to a state B, and let U_A and U_B denote the energy of the system in the two states, we have

$$U_B - U_A = \int_A^B dQ - \int_A^B dW. \tag{59}$$

From what has been said above it follows too that dQ and dW are not themselves perfect differentials but that their difference $dQ - dW$ is a perfect differential of the function U which is the energy of the system.

59. When two bodies act thermically on one another the quantities of heat gained by one and lost by the other are not necessarily equal.

In the case of bodies at a distance, heat may be taken from or given to the intervening medium.

The quantity of heat received by any portion of the ether may be defined in the same way as that received by a material body.

Another important exception occurs when sliding takes place between two rough bodies in contact. The algebraic sum of the works done is different from zero, because, although the action and reaction are equal and opposite the velocities of the parts of the bodies in contact are different. Moreover, the work lost in the process

does not increase the mutual potential energy of the system and there is no intervening medium between the bodies. Unless then the lost energy can be accounted for in other ways, (as when friction produces electrification), it follows from the principle of Conservation of Energy that the algebraic sum of the quantities of heat gained by the two bodies is equal to the quantity of work lost by friction. From the observed result of experience that friction tends to decrease the relative velocity of the moving parts we can easily prove that this total quantity of heat gained is positive. This result is in accordance with the principle of Degradation of Energy, although it is not a necessary consequence of that principle.[1])

60. Condition of internal heat equilibrium. It follows from the principle of degradation of energy, that any body or system subjected to given external conditions will tend to assume an equilibrium state in which the available energy is a minimum for all virtual variations of the distribution of energy in the system such as could be produced by heat passing from one mass-element of the system to another, without violating the given external conditions. When this is the case, the system may be said to be in *thermal equilibrium* or *thermically homogeneous.*

The state of such a system can then only be varied either (*a*) by imparting energy in the form of heat to the system as a whole, in which case the system will tend to assume a new equilibrium distribution, or (*b*) by variations in the generalised coordinates defining the dynamical state of the system.

It follows that if the state of a thermically homogeneous system is defined by n variables or generalised coordinates for changes which involve no transmission of heat to or from the system as a whole, then, when such transmissions of heat are taken into account, $n + 1$ variables will be required to define the state of the system. Since the passage of heat to or from the body involves gain or loss of energy, we may, in the first instance, choose these $n + 1$ variables to be the energy U and the generalised position-coordinates of the system.

A transformation in which no heat is gained or lost is called an *adiabatic transformation* (cf. § 5). If $x_1, x_2, \ldots x_n$ are the generalised position-coordinates, $X_1, X_2, \ldots X_n$ the corresponding gene-

1) Conceive a hot body placed in contact with a cold one and slipping on it. There is nothing contrary to the principles of thermodynamics in imagining that as heat passes from the hot body to the cold one, a certain proportion of heat might be absorbed at the common surface and employed in *increasing* the relative velocity of the sliding parts. Hence the appeal to experience cannot be dispensed with.

ralised force-coordinates, it follows that adiabatic transformations are given by the differential equation

$$dU = \Sigma X dx \tag{60}$$

connecting the $n + 1$ independent variables $U, x_1, x_2, \ldots x_n$.

In the case of a homogeneous fluid substance (taken as a type of a simple system) the state will be completely defined either by the total volume V and energy U or by the volume and energy of unit mass, which we shall call v, u. If p is the pressure, and we adopt the former alternative, then since

$$dU = dQ - pdV \tag{61}$$

$$p = -\left(\frac{dU}{dV}\right)_{dQ=0}. \tag{62}$$

Hence p is known when U, V are known, and conversely, the state of the system is in general known when p and U are known. For such a system the state may be completely defined by the variables p and V or p and v instead of U and V or u and v. By the new choice of variables, the transformations can be represented by an indicator diagram as is explained in § 8.

61. The Second Law of Thermodynamics. Let M and N be two independent thermically homogeneous systems. If the states of these systems are such that their total available energy is decreased by the passage of a small quantity of heat from M to N, it follows at once from the principle of degradation of energy:

(1) *that heat will, if it can, flow of itself from M to N,*

(2) *that heat cannot be made to pass from N to M without supplying available energy from without.*

If we define one system as being *hotter* or *colder* than another, according as the available energy of the two is decreased or increased by transporting a small quantity of heat from the first to the second, statement (*b*) is identical with the usual statement of the second law which asserts that heat cannot pass from a colder to a hotter body without some other change taking place.

In the limiting case of thermal equilibrium the available energy will to the first order of small quantities be unaffected by the transference of a small quantity of heat in either direction — a result closely analogous to the Principle of Virtual Work in Statics.

62. The thermal equilibrium between two bodies is independent of their relative positions. This important property, though frequently overlooked and tacitly assumed in thermodynamical treatises, requires somewhat careful consideration.

We may in the first place consider two bodies or systems M, N, which are not both in thermically homogeneous states. Some part of M may be hotter than some part of N, in which case if these parts are brought into contact or otherwise favourably placed heat will pass from M to N, while at the same time some part of M may be colder than some other part of N, so that by varying the relative positions of the systems heat may be made to flow from N to M. It is necessary to show that such cases cannot occur when the bodies are in thermically homogeneous states, provided that the displacement merely alters their *relative* positions and not the configuration of either body.

Suppose M hotter than N, and suppose if possible that by varying their relative positions heat could be made to flow from N to M, and that after any quantity Q had thus been transferred the bodies were brought back to their initial positions. Thus we should have transferred a quantity Q of heat from the colder body N to the hotter body M, and by making Q sufficiently small, M would still remain hotter than N after the transformation. From the last paragraph this result could only take place if available energy were supplied from without, and the only way in which such energy could be supplied would be by means of work done during the displacement of the bodies from the first to the second position and back again. This would imply not only that the bodies exerted attractive or other forces on each other during the displacements, but that these forces were different during the return displacement from what they were in the outward displacement. Hence the truth of the proposition to be proved depends on the following *axiom*:

The attractions between any two bodies depend only on the relative positions and configurations of the bodies and are unaltered by the transference of heat to or from either or both of the bodies.

That this axiom is in accordance with experience affords evidence that

(1) *if one thermically homogeneous body is hotter than another the same will remain the case when their relative positions are altered.*

Similarly (2) *if the two bodies are in thermal equilibrium, the same will be true when their relative positions are altered.*

These results no longer hold if the dimensions or configurations of the bodies are altered by the displacement, for example a mass of gas which is colder than a given body may be made hotter than it by compression.

63. Carnot's Cycle. To transport heat from a colder body N to a hotter body M (according to the above definition) available energy must be supplied from without. The simplest way of doing this is

by processes identical in character with those of *Carnot's* cycle reversed, in which an auxiliary body L is taken which first receives heat from N, and is then, by compression or otherwise, brought to a state capable of imparting heat to M.

To complete the cycle the body L must then be allowed to expand without gain or loss of heat until it is in a suitable state to receive a further supply of heat from N.

To supply the available energy absorbed in a cyclic transformation of the auxiliary body a balance of work-energy must be supplied to this body in each cycle, and by the principle of conservation an equivalent amount of heat-energy must be given to the body M, over and above that taken from N. We may thus suppose a quantity of heat dQ_N taken from N, a quantity dQ_M given to M, and a quantity of work $dA = dQ_M - dQ_N$ performed on the auxiliary body during the process.

The reverse process is identical in character with the direct *Carnot's* cycle of § 26 in which dQ'_M is received from M, dQ'_N is given to N, and work $dA' = dQ'_M - dQ'_N$ is done by the auxiliary body during the cycle.

Since a combination of the direct and reversed cycles can never result in a gain of available energy, the ratio of the work to the heat taken from or given to the hotter body M must be greater in the cycle in which work is absorbed than in the one in which work is generated (compare § 27). In other words, by the well known proof of combining the direct and reversed motions, the principle of limited availability gives that

$$\frac{dA'}{dQ'_M} \leqq \frac{dA}{dQ_M} \tag{63}$$

and therefore

$$\frac{dQ'_N}{dQ'_M} \geqq \frac{dQ_N}{dQ_M} \quad \text{or} \quad \frac{dQ'_M}{dQ'_N} \leqq \frac{dQ_M}{dQ_N} \tag{64}$$

and by considering the limiting case where the combination of the direct and reversed cycles is accompanied by no loss of availability and the processes are all therefore reversible, we get

$$\left(\frac{dQ_M}{dQ_N}\right)_{maximum} = \left(\frac{dQ'_M}{dQ'_N}\right)_{minimum}. \tag{65}$$

64. Let each of these limiting ratios be written equal to T_{MN} for the bodies M and N. Then the following properties are readily shown to be satisfied by the function T_{MN}.

(1) T_{MN} is constant for the same two thermically homogeneous systems in the same two states. It is independent of their relative

positions and therefore only a function of the variables by which the states of the bodies M and N are separately specified.

This may be proved exactly as in § 62, and the truth of the statement depends on the axiom there enunciated.

(2) The ratio T_{MN} for two systems M, N, is equal to the corresponding ratio $T_{M'N'}$ for any other two systems M', N', of which M' is in thermal equilibrium with M and N' is in thermal equilibrium with N.

For if $T_{MN} > T_{M'N'}$ combine a direct Carnot's cycle between M and N with a reversed cycle between M' and N' so that the work generated in the former cycle is absorbed in the latter. Then the heat received by M will be greater than that lost by M' and that lost by N will be greater than that gained by N'.[1])

Now the heat lost by M' may be taken from M and that gained by N' may be given to N without loss of available energy. There remains a balance of heat gained by the hotter body M and lost by the colder body N which is not compensated for by any loss of available energy in any other part of the system, which is contrary to the principle of degradation of Energy. Similarly T_{MN} cannot be less than $T_{M'N'}$.

(3) T_{MN} is independent of the size of the systems M and N provided that they are thermically homogeneous. In the case of homogeneous fluids, T_{MN} is therefore a function of their volumes and energies *per unit mass*, not of their total volumes and energies.

This result follows from the previous one by observing that the ratio in question is the same for any two parts of the same two thermically homogeneous systems.

(4) T_{MN} is equal to unity when heat-equilibrium exists between M and N, it is greater than unity when heat can flow of itself from M to N, and less than unity when heat can only flow of itself from N to M.

(5) We have the relation

$$T_{MN} \times T_{NM} = 1. \tag{66}$$

This is simply the property of the differential calculus according to which $\frac{dQ_M}{dQ_N} \times \frac{dQ_N}{dQ_M} = 1$.

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1) For by hypothesis $dQ_M - dQ_N = dA$, and $dQ_{M'} - dQ_{N'} = dA$ whence

$\frac{dQ_M}{dQ_N} - 1 = \frac{dA}{dQ_N}$ and $\frac{dQ_{M'}}{dQ_{N'}} - 1 = \frac{dA}{dQ_{N'}}$. But $\frac{dQ_M}{dQ_N} < \frac{dQ_{M'}}{dQ_{N'}} \cdots \frac{dA}{dQ_N} > \frac{dA}{dQ_{N'}}$

whence if dA is the same for both cycles $dQ_N > dQ'_N$ and $dQ_M > dQ'_M$.

(6) Taking a third system P, we have by comparing the cycle between M and N with a combination of two cycles between M and P and between P and N respectively

$$T_{MN} = T_{MP} \times T_{PN} = \frac{T_{MP}}{T_{NP}}. \tag{67}$$

This is proved exactly as in § 27.

65. Absolute Temperature. Now let the system P be taken to be a standard system whose state is kept constantly fixed, while other systems are compared with it.

The expression T_{MP} will then be a function only of the variables which define the state of the system M.

T_{MP} is said to be the *absolute temperature* of the body M referred to P as unit of absolute temperature.

If any other body Q be substituted for P, the unit of absolute temperature will be altered, but the numerical measures of the temperatures of all bodies will be altered in the same ratio. For by (67) above

$$T_{MQ} = T_{MP} \times T_{PQ}$$

in other words the absolute temperature of M relative to Q is equal to absolute temperature of M relative to P multiplied by the absolute temperature of P relative to Q. Hence all the new absolute temperatures are obtained by multiplying the old ones by the same constant factor T_{PQ}.

The properties proved in the last article are identical with the properties of temperature proved in treatises on experimental heat and mentioned in Chapter I. We thus have a deduction of these temperature properties from the Principle of Availability, which is independent of any preconceived ideas regarding temperature.

66. Temperature at a point. When a body is not in a thermically homogeneous state its *temperature at any point* can be defined by considering a differential element of mass containing that point, in the same way that we define density at a point or pressure at a point in hydrostatics. We might, for example, say that the temperature at any point P was equal to T, if when a mass element dM containing the point P is removed without changing its physical state and placed in contact with a body of uniform temperature T, no passage of heat takes place in either direction.

The property that *temperature is a scalar not a vector quantity* or that *the temperature of matter at a point is the same in all directions* follows from the considerations contained in § 62, and depends on the same axiom. As an instance of this point, if we suppose two

uniformly heated cubical blocks of material to be in thermal equilibrium with two of their faces in contact, they will remain in thermal equilibrium when any other two faces are brought into contact. An exception to this statement could only occur under the conditions discussed in § 62. It would require work to be done in turning the cubes over into their new positions, and the amount of this work to be altered if heat were to flow from one cube to the other. It is not to be inferred that when radiation takes place through the ether in a particular direction the temperature at a point of the ether is *necessarily* the same in all directions, or even that the *ether* has a temperature, for the above proof only applies to material bodies.

67. Temperature of moving body. When of two bodies M, N, one is at rest and the other is in motion, or both are moving with different velocities, their temperature ratio can still be defined by means of an auxiliary body L performing a Carnot's cycle between the two, but in this case the velocity of the body L will have to be changed in the course of the adiabatic transformations in such a way that when L is in contact with M it is moving with the same velocity as M, and when in contact with N it is moving with the same velocity as N.

This definition gives rise to no special difficulties in the cases ordinarily occurring in nature. The work done in changing the velocity of the auxiliary body being equal to the alteration of kinetic energy of the body as a whole, the sum of the works thus done in the two adiabatics of the cycle is zero. In order that the sum of the works should be different from zero it would appear necessary that the *inertia* of the auxiliary body should be altered by communicating heat-energy to it; if such a phenomenon were to exist the present arguments would break down.

We can also suppose heat equilibrium to be maintained by radiation between two bodies whose velocities are unequal and which are not actually in contact. We here assume that either the transmission of heat between the bodies is instantaneous, the heat-capacity of the intervening ether being neglected, or that an equilibrium state has been attained between the bodies and the ether. (See Chapter X.)

From considerations such as the above, it is evidently possible to define the *temperature at a point at any instant* in a system whose parts are in motion among themselves and are not in thermal equilibrium; at all events in the majority of conceivable cases.

A body which is in the course of undergoing shearing strain, for instance a fluid, appears to present the most favourable conditions for finding an exception, if such exist, to the property that the temperature at a point is the same in all directions.

CHAPTER VII.

UNAVAILABLE ENERGY AND ENTROPY.

68. Unavailable energy. The Principle of Conservation of Energy involves the result that *any loss of available energy implies the gain of an equal amount of unavailable energy.* But whereas the phenomena of Rational Mechanics involve changes in the location of the available energy of a system, they do not imply any transformations of unavailable energy. Hence in many cases it is simpler to study the properties of the *unavailable* part of the energy rather than those of the available portion, for the reversible transformations of energy in the form of work do not have to be taken into account.

In the last chapter we have seen that the ratio of the absolute temperatures of two bodies is defined by the relation

$$\frac{T_M}{T_N} = \frac{dQ_M}{dQ_N}$$

where dQ_M, dQ_N are the quantities of heat gained by one and lost by the other in a perfectly reversible Carnot's cycle working in either direction between the two bodies. In future we shall use the word "temperature" to denote absolute temperature unless otherwise stated.

As the transference of heat between bodies of finite size changes their temperature, dQ_M and dQ_N must in general be infinitesimal. If however the bodies are very large, or are by other means maintained at a constant temperature, this restriction may be removed and we may write

$$\frac{T_M}{T_N} = \frac{Q_M}{Q_N} \tag{68}$$

where Q_M, Q_N are the quantities of heat gained and lost either in one cycle or in a number of cycles.

The maximum amount of work obtainable from Q_M under these circumstances is

$$Q_M - Q_N \quad \text{or} \quad Q_M\left(1 - \frac{T_N}{T_M}\right).$$

The balance Q_N or $Q_M \times \frac{T_N}{T_M}$ represents energy given in the form of heat to the body at temperature T_N, from which no further work can be obtained if T_N is the lowest available temperature. Under this condition Q_N is to be regarded as *wholly unavailable energy.*

If we had another body capable of receiving heat continuously at a lower temperature T_0 we might obtain a further amount of work

$$Q_N\left(1 - \frac{T_0}{T_N}\right)$$

out of the heat Q_N, and then the balance of unavailable energy Q_0 communicated to the latter body would only be given by

$$Q_0 = Q_N \frac{T_0}{T_N} = Q_M \frac{T_0}{T_M}$$

and would be the same as if the cycle were performed directly between the temperatures T_M and T_0.

From these forms we deduce that *the unavailable energy associated with a given quantity of heat*

(1) *is directly proportional to the loiwest absolute temperature available for a refrigerator*

(2) *is inversely proportional to the temperature of the body which the heat is entering or leaving.*

69. The auxiliary medium. — Entropy. In the above statements we have estimated unavailable energy with reference to a medium of constant temperature which can be used as a refrigerator in connection with any necessary reversible cyclic transformations involving gain or loss of heat. Such a medium may be called an *auxiliary medium* and its temperature the *auxiliary temperature.*

If we take a steam engine as a practical illustration we should take as auxiliary temperature, the lowest temperature at which water could be obtained for the condenser of the engine. The lower the auxiliary temperature the less energy unavailable.

Taking now a quantity Q of heat entering or leaving a body at temperature T, we see that if the unavailable energy Q_0 associated with it be divided by the auxiliary temperature T_0 we have

$$\frac{Q_0}{T_0} = \frac{Q}{T}$$

or the quotient is independent of the auxiliary temperature.

Thus $\frac{Q}{T}$ may be regarded as a *measure of unavailability* or factor which only requires to be multiplied by any assumed auxiliary temperature T_0 in order to give the quantity of unavailable energy relative to that temperature.

This factor is called *entropy*, and may be defined more precisely in two ways.

70. First definition of Entropy. *If a system or part of a system at temperature T receives a quantity of heat dQ the quotient $\frac{dQ}{T}$ is called the increase of entropy of the system arising from this cause.*

If A and B denote two different states of a system which are capable of being connected together by a continuous series of reversible transformations, then the change of entropy of the system in passing from the state A to the state B is defined by the expression

$$\Sigma \int_A^B \frac{dQ}{T}$$

where the summation extends to all parts of the system and the integral is taken along the reversible series of transformations referred to.

This definition is the one most commonly known though it is frequently stated in a somewhat less precise form. In dealing with reversible phenomena it leads to consistent results and is sufficient. But there are many irreversible phenomena, for which this definition is either inapplicable or can only be made applicable by somewhat cumbersome extensions. It is in many ways unsatisfactory or at least inconvenient.

71. Second Definition of Entropy. *If from any cause whatever, the unavailable energy of a system with reference to an auxiliary medium of temperature T_0 undergoes any (positive or negative) increase and if this increase be divided by the temperature T_0 the quotient is called the increase of entropy of the system.*

As it is only possible to investigate changes of unavailable energy, and not its total amount, the expression for the entropy involves an unknown constant. This constant occurs in the form of a constant of integration in any expressions which are obtained for the entropy of particular systems such as perfect gases etc. In most cases the entropy takes the form of a logarithm.

The second definition makes no restrictions as to the nature of the transformations which take place; it holds if the unavailable energy is imported into the system in the form of heat received from without, as well as when irreversible changes occur in the system itself, producing an increase of unavailable at the expense of available energy.

The second definition of entropy may perhaps be stated more briefly by saying that *the entropy of any system is equal to, or differs by a constant from the unavailable energy of the system relative to an auxiliary medium of unit temperature.*

72. Clausius' Inequalities. It follows from the second definition that *the entropy of a finite system is a function of the physical state of the system only*, for no change can take place in the amount of energy unavailable with reference to a given auxiliary medium without some change occurring in the physical state of the system.

(1) *If no irreversible changes occur in the interior of the system*, unavailable energy is only imparted to the system from without in connection with heat received, and it follows from § 70, that the change of entropy of the system $S_B - S_A$ between states A and B is given by

$$S_B - S_A = \Sigma \int_A^B \frac{dQ}{T}. \tag{69}$$

(2) *If however irreversible changes have occurred in the interior* then since these changes involve an increase of unavailable energy the total increase of entropy is greater than that due to the heat gained from without, in other words

$$S_B - S_A > \Sigma \int_A^B \frac{dQ}{T} \tag{70}$$

and the difference represents increase of entropy due to the internal changes.

(3) *If the system undergoes a reversible cyclic transformation* then since the initial and final entropies are the same

$$\Sigma\left(\int\right)\frac{dQ}{T} = 0, \tag{71}$$

the integral being taken round the cycle.

(4) *If the cycle involves irreversible changes* in the interior of the system (70) gives

$$\Sigma\left(\int\right)\frac{dQ}{T} < 0. \tag{72}$$

In this case the quantity of entropy received from without during the cycle in connection with the heat imparted must be *negative* in order to balance the *increase* of entropy produced by the irreversible changes within the system.

The inequalities (70), (72) are known as the *inequalities of Clausius.*

(5) It is not usually possible, however, for a system to undergo a reversible transformation unless at any instant all the parts of the system are at the same temperature T, this temperature being a function of the time alone. For if any difference of temperature existed between the parts, heat would, in general, flow from the hotter

to the colder parts and this process would be irreversible. Under these circumstances we take dQ to denote the heat received by the whole system at the instant when its temperature is T and the equalities take the form

$$\int_A^B \frac{dQ}{T} = S_B - S_A.$$

$$\left(\int\right)\frac{dQ}{T} = 0.$$

73. A more detailed investigation. We may examine in greater detail the processes involved in the proof of Clausius' inequality for a closed cycle as follows.[1])

Let us suppose that we are dealing with any thermodynamical system M in the presence of an indefinitely extended medium M_0 of absolute temperature T_0, this being the lowest temperature continuously available for the refrigerator of a Carnot's cycle.

Under these circumstances a quantity of heat dQ at temperature T represents a quantity of available energy of amount

$$dA = dQ\left(1 - \frac{T_0}{T}\right)$$

that being the maximum work obtainable from dQ subject to the given conditions.

It follows, then, that if a quantity of heat dQ is imparted to the system *from without* at a point where the absolute temperature is T, the available energy of the system is increased by the above amount dA. Again, if the system performs external work dW, this work represents available energy taken *from* the system M and given to some outside system on which the work is done. So far as the system M is concerned we thus have a *loss* of available energy dW.

Hence the quantity of available energy absorbed by the system from without in any small transformation is

$$dA = \Sigma\left[dQ\left(1 - \frac{T_0}{T}\right) - dW\right]$$

the Σ referring to different parts of the system. Now by the First Law

1) Many articles in this chapter have been written and rewritten a large number of times, with the result that a certain amount of repetition occurs in some of the arguments, especially in connection with Clausius' Inequalities. Some of this repetition is necessitated by the two alternative definitions of entropy. In other cases it is hoped that the repetition will merely call the attention of the reader to the number of different ways of arriving at the same result.

$$\Sigma(dQ - dW) = dU$$

where U is the total energy of the system. Hence the total amount of available energy absorbed takes the form

$$dA = dU - \Sigma dQ \frac{T_0}{T}$$

and if the system changes from state A to state B we get the total available energy absorbed

$$= U_B - U_A - \Sigma \int_A^B dQ \frac{T_0}{T}.$$

If the system is made to undergo a cyclic transformation the energy U is the same at the beginning as at the end, and therefore if (A) is the available energy taken from without in the cycle

$$(A) = - T_0 \Sigma \left(\int \right) \frac{dQ}{T} \tag{73}$$

the integral being taken round the cycle. This expression is equal and opposite to the gain of unavailable energy, as it should be since the total gain of energy in the cycle is necessarily zero.

Now let us apply the principle of degradation of energy to the changes which take place in the *interior* of the system, between its different parts. In these changes, available energy is always lost, never gained; and it is only in the limiting case of reversible transformations that the loss vanishes. But, at the end of a cyclic transformation, the system M is exactly in the same condition as at the beginning, and therefore its available energy in the presence of the medium M_0 must be the same. Therefore *available energy must have been increased in the system in connection with heat received from without* to compensate for the loss within, and hence (A) in equation (73) must be positive.

Therefore (1) *in any cyclic non-reversible transformation*

$$\Sigma \left(\int \right) \frac{dQ}{T} < 0.$$

This relation is the **Inequality of Clausius.**

(2) The left hand member of this inequality is equal to $-\frac{A}{T_0}$, where A represents the amount of energy rendered unavailable subject to the condition that T_0 is the lowest outside temperature available for the purposes of a refrigerator.

(3) The loss of available energy in the cycle is proportional to T_0. If a colder medium were substituted for M_0 *we should obtain increased facilities for the conversion of energy into work*, and a

proportionately smaller amount of energy would be rendered unavailable under the new conditions though the cycle was identically the same.

The difficulty of understanding Clausius' Theorems lies, not so much in the proof, as in the interpretation of their meaning in the case of the different irreversible phenomena with which we have to deal in applications. Even the statement of the theorems admits of some ambiguity, for there exist a number of inequalities of the form

$$\Sigma\left(\int\right)\frac{dQ}{T} < 0$$

obtainable by assigning different meanings to dQ and T. For this reason we shall now illustrate the particular cases which occur by easy and gradual stages, starting with reversible cycles and then considering in detail the simpler classes of irreversible phenomena with which we have to deal in practice.

74. Particular cases. Simple systems. We start with a simple system, and first suppose it to be the working substance performing a Carnot's cycle between a source at temperature T_M and a refrigerator at temperature T_N. We transform the equation

$$\frac{dQ_M}{dQ_N} = \frac{T_M}{T_N}$$

firstly, by letting dQ_1, dQ_2 denote the heats received *by the system* from the source and refrigerator, so that $dQ_1 = dQ_M$, $dQ_2 = -dQ_N$, into the form

$$\frac{dQ_1}{T_M} + \frac{dQ_2}{T_N} = 0.$$

The conditions of reversibility require that when the working substance is in contact with either the source or the refrigerator the temperatures of the two shall be equal. Letting T_1, T_2 denote the temperatures of the *working substance*, so that $T_1 = T_M$, $T_2 = T_N$, the equation last written down transforms into

$$\frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} = 0$$

an equation now involving only quantities which refer to the working substance, and not to the source or refrigerator.

Next suppose the working substance to undergo a reversible cyclic transformation, its temperature being any function of the time. Let the indicator diagram of the cycle be the curve $APBQ$. Divide this curve into narrow strips by adiabatic lines crossing it and join the ends of these adiabatics by isothermals. The diagram is thus divided into a series of Carnot's cycles such as $PMQN$, and from what we have first shown the values of $\frac{dQ}{T}$ contributed by the

elements PM and QN must be equal and opposite so that their sum is zero. Passing to the limit when the elements $PMQN$ are indefinitely narrow, we shall now show that

$$\left(\int\right)\frac{dQ}{T}=0$$

the integral being taken round the circuit $APBQ$.

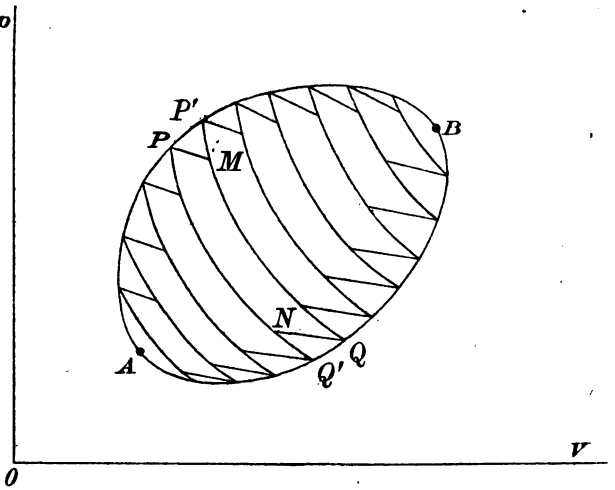

Fig. 8.

To prove this it is necessary to show that the value of dQ for the element of arc PP' is ultimately equal to the value for the corresponding isothermal element PM. Using suffixes to denote the quantities of heat absorbed in the corresponding elements we see from the principle of energy that $dQ_{PP'}+dQ_{P'M}+dQ_{MP}$ is equal to the work done in the elementary cycle $PP'MP$; this is represented by the area of the $\Delta PP'M$ and is therefore a small quantity of the second order, PP' and PM being of the first order. Also $dQ_{MP'}=0$, the transformation being adiabatic. Therefore $dQ_{PP'}+dQ_{MP}=0$ or $dQ_{PP'}=dQ_{PM}$ to first order. Hence the cyclic integral

$$\left(\int\right)\frac{dQ}{T}$$

for the circuit $APBQ$ is ultimately the same as the sum of the corresponding expressions for the elementary Carnot's cycles inscribed in it as above, and is therefore zero.

75. Extension to compound systems; reversible cycles. We now consider a compound system with any number of degrees of freedom, whose temperature at any instant is the same at every point, and is therefore a function of the time alone. In a reversible cycle, the position coordinates may be varied in different ways, and consequently the proof of the relation

$$\left(\int\right)\frac{dQ}{T}=0$$

given in the last article usually breaks down, or at least gives rise to difficulties, depending on the impossibility of drawing an indicator

diagram and the consequent difficulty of dividing the cycle into a network of Carnot's cycles. The following proof is convenient, and bears a considerable analogy to the more general proof of § 72.

Let the system M describe any reversible cycle K and let dQ be the heat received by M at any stage of the process when T is its temperature. Then without loss of generality we may suppose the quantity dQ taken from an auxiliary body, such as a mass of gas, performing a Carnot's cycle between the system M at temperature T and a large reservoir of heat M_0 at temperature T_0. In this case the auxiliary body will receive from the reservoir a quantity of heat dQ_0 determined by

$$\frac{dQ_0}{T_0} = \frac{dQ}{T}$$

or

$$dQ_0 = T_0 \frac{dQ}{T}.$$

If, now, we assume that every transformation of the system under consideration is connected with an auxiliary Carnot's cycle working in combination with the same reservoir M_0, the total amount of heat taken from the reservoir in the cycle will be

$$Q_0 = T_0 \left(\int\right) \frac{dQ}{T}.$$

If this quantity Q_0 were positive, a quantity of work Q_0 would have to be done somewhere or other, since all the bodies have returned to their initial state. We should thus have the conversion of Q_0 units of heat into work with no compensating transformation, and in this way all the energy taken from M_0 in the form of heat would be capable of being rendered available, even if M_0 were the coldest body of the system. It follows that Q_0 cannot be negative, and moreover if Q_0 is positive the series of processes is irreversible. Hence for a reversible series of processes we must have $Q_0 = 0$ and therefore

$$\left(\int\right) \frac{dQ}{T} = 0.$$

76. Entropy. — (Definition I.) The property that for a given thermically homogeneous system, simple or compound, the integral

$$\left(\int\right) \frac{dQ}{T}$$

vanishes round a reversible closed cycle leads immediately to the result that the integral

$$\int_A^B \frac{dQ}{T}$$

is the same for all reversible transformations of the system from a given initial state A to a given final state B. In illustration taking a simple system and supposing the integral to vanish round the circuit $APBQ$ (Fig. 9), it follows that the parts contributed by the paths APB and BQA are equal and opposite, and therefore the line integrals taken along APB and AQB from A to B are equal, the initial state $(p_1 V_1)$ and final state $(p_2 V_2)$ being the same for both.

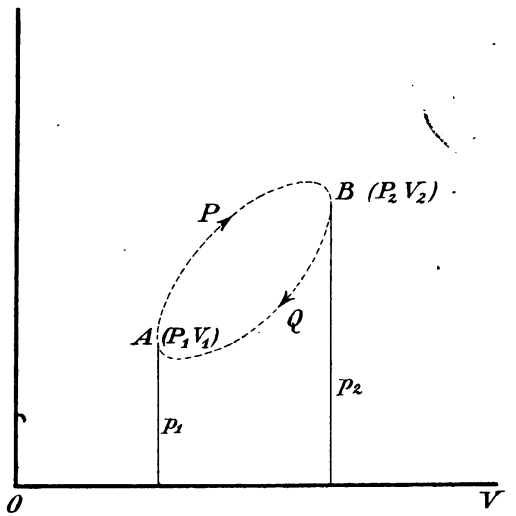

Fig. 9.

We may therefore write, for a simple system

$$(74) \qquad \int_A^B \frac{dQ}{T} = f(p_2, V_2) - f(p_1, V_1) = S_B - S_A$$

and for a compound system we have in like manner

$$\int_A^B \frac{dQ}{T} = S_B - S_A$$

where S denotes a certain quantity dependent on the actual state of the system, and S_A, S_B denote its values in the states A, B. We are thus led to associate irreversible transformations with a new quantity S whose value at any instant depends only on the state of the system at that instant. This quantity we call **entropy** and we are led to the first definition of § 70, which for the systems here considered may be stated as follows:

Let A and B be two different thermically homogeneous states of the same system, which are capable of being connected together by continuous reversible transformations. Then the integral

$$\int_A^B \frac{dQ}{T}$$

taken along any such transformation is called the entropy of the system in the state B relative to the state A, or the difference of the entropies in the states A and B.

The entropy in any state is thus determined, to within an arbitrary constant of integration, by the indefinite integral

$$\int \frac{dQ}{T} + C.$$

The constant of integration is to a certain extent arbitrary, but for the same substance in the same state (as to pressure, temperature etc.) the entropy of unit mass must always be taken to be the same.

We may also give the following definition: The *entropy* of a thermically homogeneous system is a quantity such that when in any reversible transformation the system receives a quantity dQ of heat at absolute temperature T the entropy increases by an amount $\frac{dQ}{T}$. This is merely a re-statement of the First Definition of Entropy, given above.

It is clear that to produce a given change in the physical state of a body of given material the quantity of heat communicated must be doubled if the mass of the body is doubled, so that the entropy of a body in a given physical state is proportional to its mass. The entropy of unit mass, which, in accordance with previous conventions we shall denote by s, depends only on the state of the substance, as defined e. g. by its pressure and temperature.

The progress of events within the working substance depends on the various temperatures of the substance at different stages and the quantities of heat received by it. It does not depend on whether the heat is received from a body of the same temperature or a body of different temperature provided that the transformation is the same. Hence the relation

$$\left(\int\right) \frac{dQ}{T} = 0$$

and the definition of entropy is extended to all cyclic transformations of the working substance, provided that the processes which take place in the substance itself are reversible.

77. Connection between entropy and available energy. — Second Definition of Entropy for thermically homogeneous systems undergoing reversible changes (Definition II). We now revert to the methods of § 73, but assume for the present, that the system M with which

we are dealing is at every instant at uniform temperature T throughout, and that the transformations which it undergoes are all reversible. As before, the facilities for conversion of energy into work are assumed to be limited by the presence of a surrounding medium M_0 of temperature T_0.

Under these circumstances the change of available energy in the system itself in any non-cyclic transformation from state A to state B has been shown (§ 73) to be

$$U_B - U_A - T_0 \int_A^B \frac{dQ}{T}.$$

The total change of energy is $U_B - U_A$.

Hence the quantity of non-available energy gained by the system in transformation is equal to

$$T_0 \int_A^B \frac{dQ}{T},$$

that is to T_0 times the increase of entropy (Definition I).

We thus obtain the second definition of entropy of § 71, according to which the increase of entropy is found by dividing by T_0 the increase of unavailable energy estimated with reference to an auxiliary medium of temperature T_0.

78. Entropy in non-reversible transformations. The extension of the first definition of entropy to irreversible transformations is a subject of considerable difficulty, which has led to many controversial discussions. There is not the same difficulty with the second definition, nevertheless it is only possible to arrive at a clear understanding of entropy by examining the various possible methods of treatment which present themselves, and by a minute consideration of the simpler irreversible phenomena.

We start by laying down the following

Fundamental Condition. *The entropy of a system shall be defined in such a way that its value at any instant depends only on the physical state of the system at that instant, and not on the previous history of the system.*

If this assumption were not made the theory of thermodynamics would involve the consideration of changes of entropy of a purely arbitrary character corresponding to no real physical phenomena.

If, for example, a given mass of gas undergoes any series of transformations, reversible or irreversible, and is finally brought back to its original volume and temperature, the condition we lay down

is that the entropy shall be the same as it was at the beginning. The initial and final states of the gas are by hypothesis indistinguishable from each other in every respect, and if we made the entropies different, this difference would be devoid of physical meaning.[1])

If irreversible phenomena have occurred in the gas, the return to the original state can only be made at the expense of compensating transformations elsewhere. It is not in the gas itself but in the external systems that a permanent change has occurred which may affect the value of their entropy.

Subject to this assumption, we may proceed in two ways, according as we start from the first or second definition above.

(1) Starting with the first definition, we may define the entropy of a thermically heterogeneous system (i. e. system at non-uniform temperature) as the sum of the entropies of its differential mass elements.

The change of entropy in an irreversible transformation can now be defined when it is possible to find a reversible transformation that would produce identically the same changes as actually take place in the system. The change of entropy in the irreversible transformation is then *defined* as being equal to the change which would take place in the corresponding reversible transformation between the same initial and final states.

[This convention must be made if entropy is to be considered as a definite physical entity obeying the above fundamental condition.]

This definition applies to all cases in which the initial and final states *can* be connected by a reversible transformation. If this is not possible, there is no *a priori* reason for asserting that a definite meaning can be assigned to entropy changes according to the first definition.

(2) We may start with the second definition which, we observe, always gives a definite meaning to the concept entropy in accordance with our assumed fundamental condition, and we may deduce from it expressions representing the entropy changes corresponding to different irreversible phenomena.

79. Entropy of a thermically heterogeneous system. If a system of bodies consists of different parts m_1, m_2 ... at uniform temperatures T_1, T_2 ... the *whole* entropy of the system is the sum of the entropies of the parts of the system[2]), and hence is given by

1) We do not deny that it is possible to build up a mathematical theory based on a definition according to which the entropy of a body depends on its past history, and even, by suitably interpreting this theory, to deduce results in accordance with facts. But such a theory would of necessity be an artificial one.

2) The use of the word "whole" as in whole volume, whole entropy or whole energy is convenient to distinguish these from the volume, entropy and energy of a unit mass. Compare also § 7.

$$S = m_1 s_1 + m_2 s_2 + \cdots + m_n s_n$$

where m_1, m_2 are the masses of the parts, s_1, s_2 their entropies per unit mass. We see also that the increment of entropy is given by

$$dS = \frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} + \cdots = \Sigma \frac{dQ}{T}$$

where dQ_1 is the whole heat received by the part m_1 at temperature T_1, whether this heat be received from outside or from other parts of the system. The only limitation to this statement is that no irreversible changes must occur within the separate portions m_1, m_2 ...

Where the temperature varies from point to point the system must be divided into "differential" elements of mass, as explained in § 46, these elements being so small that the temperature is uniform over a single element, but the element is large compared with the molecular structure of the substance. The summations of the last case must be replaced by integrals and we shall write the resulting equations

$$S = \int s\,dm$$

$$dS = \int \frac{dq'}{T}\,dm$$

where $dq'\,dm$ is the quantity of heat absorbed by the element dm when its temperature is T. In this notation dq' will stand for quantity of heat absorbed *per unit mass* in the neighbourhood of the point whose temperature is T, and the sign of integration will refer to the various "differential" mass elements of the body.

We notice that the second definition of entropy of § 71 is applicable without modification in the present case, since a quantity dQ_1 received by the part at temperature T_1 represents an increase of energy dQ_1 of which $dQ_1\left(1 - \frac{T_0}{T_1}\right)$ is available and $dQ_1 \frac{T_0}{T_1}$ is non-available relatively to the refrigerator T_0.

80. Changes of entropy due to conduction or radiation of heat. Let a quantity dQ_i of heat flow by radiation or conduction from a hotter part of the system whose temperature is T_1 to a colder part where the temperature is T_2. Then the entropy of the first part decreases by $\frac{dQ_i}{T_1}$ and that of the second increases by $\frac{dQ_i}{T_2}$ hence the total entropy increases by an amount

$$dQ_i\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

This increase is always positive since T_1 must be $> T_2$ for the flow to take place from T_1 to T_2. Hence

(1) *The effect of irreversible heat flow between the parts of a system is to increase the entropy of the system.*

(2) *There is no difficulty about representing the entropy changes due to this cause as a sum of differentials of the form* $\frac{dQ}{T}$ *where the differentials* dQ *refer to the actual transformation.*

We have here assumed the passage of heat from one part of the system to the other to be instantaneous. When a finite time is taken by radiation from one body to reach another, account must be taken of the heat gained and lost by the intervening ether, and this problem is discussed in Chapter X.

If the system undergoes a complete cycle, we may divide the heat dQ received by any element when at temperature T into two parts, one dQ_i due to conduction or radiation from neighbouring elements, and the other dQ_e being due to bodies outside the considered system.

Hence for the cycle, we have

$$\Sigma\left(\int\right)\frac{dQ}{T} = \Sigma\left(\int\right)\frac{dQ_i}{T} + \Sigma\left(\int\right)\frac{dQ_e}{T}$$

the sign of summation Σ referring to the different bodies or mass elements of the system.

Now the first integral vanishes, the total entropy being the same at the beginning and end of the transformation[1]), and from what has been just shown the second integral is positive; therefore

$$\Sigma\left(\int\right)\frac{dQ_e}{T} < 0.$$

This is a particular case of the inequality of Clausius proved in § 72. The entropy of the system is the same at the end as at the beginning of the cycle, but the irreversible flow of heat causes an increase of entropy inside the system. To compensate for this a negative quantity of entropy must be taken from without, and we may now enunciate Clausius' inequality as follows:

In any non-reversible cycle, the quantity of entropy gained by the system from without must be negative.

We may obtain a further modification of the last inequality, in which the temperature of the system itself is replaced by the temperature of the external body or medium from which the system is heated.

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1) Although irreversible changes take place *between* the elements or parts of the system, we are assuming in this paragraph that the processes within any element are reversible, so that for every individual element $\left(\int\right)\frac{dQ}{T}$ vanishes for the complete cycle.

If the quantity of heat dQ is taken from a body at temperature T_e, and given to a part of the working substance at temperature T_i, the entropy of the latter is by definition increased by

$$\frac{dQ}{T_i}$$

but that of the source of heat is decreased by $\frac{dQ}{T_e}$.

If heat is absorbed from the source so that dQ is positive $T_e > T_i$ and hence

$$\frac{dQ}{T_i} - \frac{dQ}{T_e} > 0$$

while if heat is given out the same result still holds because $T_e < T_i$ and dQ is negative. The *total entropy* consisting of the sum of the entropies of the working substance and the surrounding media is therefore increased. Moreover

$$\Sigma\left(\int\right)\frac{dQ}{T_e} < \Sigma\left(\int\right)\frac{dQ}{T_i}$$

and therefore *a fortiori* from (1)

$$\Sigma\left(\int\right)\frac{dQ}{T_e} < 0.$$

A particular illustration of the difference of the two forms of inequality is afforded by a system performing what is called a *conditionally irreversible* cycle. By this we mean "a cycle which under existing external conditions is irreversible but which may be made reversible by the substitution of other external conditions". As an example we may take a simple system performing the series of operations of Carnot's cycle, but suppose that when it receives heat from the source it is at a slightly *lower* temperature than the source, and that when it gives heat to the refrigerator it is at a slightly *higher* temperature than the refrigerator — a condition of things which always exists in actual cycles. In this case the cycle would be made reversible by an suitable alteration in the temperatures of the source and refrigerator. For such cycles we have

$$\Sigma\left(\int\right)\frac{dQ}{T_i} = 0 \quad \text{but} \quad \Sigma\left(\int\right)\frac{dQ}{T_e} < 0.$$

81. Irreversible conversion of Work into Heat. There are a large number of cases in which irreversible changes take place, often within the ultimate elements of the system, in such a way that it is very difficult to analyse the exact process of events during the change. We may take the following as illustrations of one such class of phenomena.

(1) Friction between two rough bodies.
(2) Impact of two imperfectly elastic bodies.
(3) Gas rushing into vacuum.
(4) Stretched wire which is suddenly cut.
(5) Retardation of fluid motions due to viscosity.
(6) Flow of electricity in imperfectly conducting bodies.

All these phenomena may take place in the interior of a closed vessel, impervious to heat, and then no entropy or energy (available or otherwise) is imported into the systems from without. In the present cases the visible effects produced include an apparent absorption of mechanical work in the interior of the system. By the principle of conservation of energy, this lost work must reappear in the system in the form of some other kind of energy. We may define this energy as *heat generated internally* in the system, the *quantity of heat* so generated being measured by the quantity of work lost.[1]) We shall speak of the phenomenon as an irreversible *conversion of work into heat* in the interior of the system. Experience shows that a rise of temperature or some other equivalent effect invariably accompanies the transformation and is exactly the same in amount as if the heat said to be generated in the system had been supplied from without.

What we can safely assert is that the ultimate effect of the irreversible changes on the system is the same as could be produced by reversible means if energy in the form of work was taken from the system, and energy in the form of heat imparted to the system. To make things clearer, we consider the separate cases.

(1) *Friction between imperfectly rough bodies.* If we were to replace the rough surfaces by smooth ones, or introduce balls or other anti-friction bearings, it would be necessary in order to make the other effects the same, to apply equal and opposite external resistances to the sliding parts, equal to the forces of friction which previously existed. To make up for the energy thus taken from the system, and to reproduce the temperature changes actually observable in the bodies, heat energy would have to be supplied to the opposing surfaces. If dH is a quantity of work lost by friction, then in the reversible alternative system, the work dH is taken from the system, and heat dH is given to it. If T is the temperature of the point at which this "generated heat" is applied to the system, the gain of entropy in the reversible process is $\frac{dH}{T}$, and hence by definition the same is true in the irreversible process. It therefore follows that in defining entropy by the first method "quantities of heat generated

1) We are here using the term "quantity of heat" generated internally to denote something different from the "quantity of heat" received by one body from another, as defined in § 58.

in the body" must be taken into account, a procedure open to some objection.

But the removal of dH units of work reduces the available energy of the system by dH, and the substitution of dH units of heat at temperature T, increases its available energy by $dH\left(1-\frac{T_o}{T}\right)$ relative to a refrigerator T_o. It follows that the gain of unavailable energy in the system is $dH\frac{T_o}{T}$ and is equal to T_o times the corresponding gain of entropy. *Therefore the second definition of entropy becomes applicable in this case.*

(2) *Impact of imperfectly elastic bodies.* Here no energy passes to or from the bodies from without, and their total energy is therefore constant. The changes in the translational and rotational energy produced by impact could be effected by external forces, but the bodies would then do external work. Hence to reproduce the same results including the observed changes of temperature, by reversible means energy equal to this external work must be supplied from without in the form of heat. The change of entropy in the reversible transformation will be the resulting value of $\left(\int\right)\frac{dH}{T}$ dependent on this supplied heat, and this *by definition* will represent the change of entropy in the actual transformation. As before it is easy to see that $T_o\left(\int\right)\frac{dH}{T}$ represents the non-available energy gained by the system relative to a refrigerator T_o, so that Definition II is still valid.

(3) *Gas rushing into a vacuum.* The gas appears to do work in expanding, but no work is done on the containing vessel, so that the energy all remains in the gas. If the gas expanded against a piston external work would be done, and heat would have to be supplied to maintain its energy constant. Otherwise it would be found that the temperature of the gas was lower than when it expanded freely. This heat would increase the entropy but Definition II would still hold.

(4) *For a stretched wire that is suddenly cut* the arguments are precisely similar to the last case.

(5) *Fluid motion brought to rest by viscosity.* Instead of reproducing the same change by artificial means, it is here easier to bring back the system to its original state by imparting kinetic energy to the fluid and withdrawing heat energy from it. The entropy taken from the fluid in the latter change must be equal to that which it gains in the former.

(6) *Flow of electricity along a wire.* If the electricity were transported by convection from the higher to the lower potential,

outside work would be done, and a corresponding quantity of heat would have to be supplied to the wire, reproducing the observed temperature changes caused by the current, and producing an increase of entropy. Both in this and the last case, Definition II still holds.

In the class of systems here considered, if we suppose for greater generality that work is being irreversibly converted into heat in the interior, and at the same time heat is being received from without, and is also passing between the parts of the system, the change of entropy takes the form

$$S_B - S_A = \Sigma \int_A^B \frac{dQ_e}{T_i} + \Sigma \int_A^B \frac{dQ_i}{T_i} + \Sigma \int_A^B \frac{dH}{T_i} \tag{76}$$

where dQ_e is the heat received from without the system at the part whose temperature is T_i, dQ_i is the heat received from other parts of the system, and dH the heat internally generated in the part itself.

Thus the change of entropy can only be expressed as a sum of differentials of the form $\frac{dQ}{T}$ *by assigning a second meaning to the term "quantity of heat".*

In equation (76) we notice that dH is from the nature of the case essentially positive, since heat cannot be converted into work without some compensating transformation. Also the second term $\Sigma \int \frac{dQ_i}{T_i}$ is positive as in the last article. Hence it follows that

$$\Sigma \int_A^B \frac{dQ_e}{T_i} < S_B - S_A \tag{77}$$

and for a closed cycle we have

$$\Sigma \left(\int \right) \frac{dQ_e}{T_i} < 0. \tag{78}$$

If we replace T_i by T_e the external temperature at the point from which the heat dQ_e was obtained we have, *a fortiori*

$$\Sigma \int_A^B \frac{dQ_e}{T_e} < S_B - S_A. \tag{79}$$

$$\Sigma \left(\int \right) \frac{dQ_e}{T_e} < 0. \tag{80}$$

Inequalities (77—80) all constitute forms or modifications of Clausius' Inequalities as applied to closed and unclosed transformations.

82. Cases where the previous method fails. The following irreversible phenomena may here be cited as examples:

(7) Diffusion of gases.

(8) Combustion and other chemical changes.

(7) *Diffusion of gases* will be treated more fully in chapter XII. If the diffusion takes place at constant pressure, volume, and temperature, and without gain or loss of heat, no expression of the form $\frac{dQ}{T}$ can be associated with the change, and the First Definition of entropy is calculated to give the incorrect impression that the entropy is necessarily unaltered by diffusion. The Second Definition is free from this objection and rightly suggests that the matter can only be decided by studying the conditions under which the mixed gases can be separated or work obtained by mixing the gases in some different way.

(8) *Combustion and other chemical changes.* Here we may have to deal with cases in which heat is suddenly generated, producing a discontinuous change of temperature. It is evident that differentials of the form $\frac{dQ}{T}$ can only be integrated when the temperature varies continuously. If however the energy, available and unavailable, is at any instant definite, the entropy of the system will be definite according to Definition II, even when Definition I fails.

Thus in the last two cases, the change of entropy cannot be expressed as a sum of differentials of the form $\frac{dQ}{T}$.

We thus conclude that *while the second definition of entropy is applicable to irreversible as well as reversible changes, the first definition cannot be extended to irreversible changes except in a limited number of cases.*

[This of course does not refer to definitions of entropy based on the substitution of a reversible change for an irreversible one and the wording of the First Definition adopted in § 70 seems free from objection.]

83. Dependence of non-available energy on temperature of auxiliary medium. In connection with Definition II, we have seen that the non-available energy gained by a system relative to an auxiliary medium of temperature T_o is proportional to T_o. It is important to observe that *this property does not imply any physical peculiarity of th esystem itself* **which changes** when a different medium is substituted as refrigerator.

When we speak of a system as containing a quantity Q_o of energy non-available relative to a refrigerator T_o, we imply that when as much energy as possible has been converted into work by Carnots' cycles working with this refrigerator the quantity Q_o will be absorbed

by the refrigerator. If however another refrigerator T_w be substituted the quantity Q_o must be further transformed by a Carnots' cycle from T_o to T_w, and the quantity of non-available energy Q_w now absorbed will be given by

$$\frac{Q_w}{T_w} = \frac{Q_o}{T_o}$$

and will be to the former quantity as T_w is to T_o without any difference occurring in the system itself.

84. Clausius' Statements. According to Clausius the First and Second Laws are summed up in the following statements.

I. The Energy of the Universe is Constant.

II. The Entropy of the Universe tends to a maximum.

According to Definition II, the latter statement immediately follows from the fact that the available energy tends to decrease, and therefore the non-available energy necessarily tends to increase.

Further, Clausius' Inequalities for non-cyclic transformations follow at once from this definition. For the increase of non-available energy in the system in a transformation from A to B is by the Second Definition of Entropy equal to $T_o(S_B - S_A)$. The quantity of non-available energy imported from without amounts respectively to

$$T_o \int \frac{dQ_e}{T_e} \quad \text{and} \quad T_o \int \frac{dQ_e}{T_i}$$

according as this energy is measured when it leaves the external systems or when it reaches the system itself. Now the changes occurring within the system tend to decrease the available energy without altering the total energy, and therefore they must increase the non-available energy. Hence

$$T_o(S_B - S_A) > T_o \int_A^B \frac{dQ_e}{T_i} > T_o \int_A^B \frac{dQ_e}{T_e}$$

whence

$$\int_A^B \frac{dQ_e}{T_e} < \int_A^B \frac{dQ_e}{T_i} < S_B - S_A$$

and moreover, the loss of available energy due to changes occurring in the interior of the system itself is measured by

$$T_o \left[S_B - S_A - \int_A^B \frac{dQ_e}{T_i} \right]$$

while the loss of available energy in transit to and from the system is measured by

$$T_o \left[\int_A^B \frac{dQ_e}{T_i} - \int_A^B \frac{dQ_e}{T_e} \right].$$

85. Examples of Entropy. *Heat Conduction.* We may apply *Fourier's* method of analysis to determine the rate at which entropy is being generated in a solid through which heat is passing.

Taking k to be the thermal conductivity, γ the specific heat and ρ the density, consider a portion of the solid bounded by a surface S, the direction cosines of the outward drawn normal at any point of which are l, m, n.

The rate at which entropy is increasing in the portion is

$$\iiint \frac{\gamma \rho}{T} \frac{dT}{dt} dx\,dy\,dz.$$

The rate at which entropy is flowing in from outside

$$= \iint \frac{k}{T} \left(l \frac{dT}{dx} + m \frac{dT}{dy} + n \frac{dT}{dz} \right) dS$$

$$= \iiint \frac{1}{T} \left\{ \frac{d}{dx}\left(k \frac{dT}{dx}\right) + \frac{d}{dy}\left(k \frac{dT}{dy}\right) + \frac{d}{dz}\left(k \frac{dT}{dz}\right) \right\} dx\,dy\,dz$$

$$- \iiint \frac{k}{T^2} \left\{ \left(\frac{dT}{dx}\right)^2 + \left(\frac{dT}{dy}\right)^2 + \left(\frac{dT}{dz}\right)^2 \right\} dx\,dy\,dz.$$

The difference of these two expressions gives the rate at which entropy is being generated in the solid. By the equations of conduction this reduces to the last term, namely

$$\iiint \frac{k}{T^2} \left\{ \left(\frac{dT}{dx}\right)^2 + \left(\frac{dT}{dy}\right)^2 + \left(\frac{dT}{dz}\right)^2 \right\} dx\,dy\,dz$$

an expression which is essentially positive.

This expression can also be written

$$\iiint F \frac{d}{ds}\left(\frac{1}{T}\right) dx\,dy\,dz$$

where F is the resultant flux of heat, ds an element of length in the direction of this flux at the point (x, y, z). The interpretation of the last expression is obvious.

Numerical examples. The quantity of entropy absorbed by 1 gram of water when its temperature is increased from 0° C to 1° C is found by dividing the work measure of the heat $4{\cdot}18 \times 10^7$ ergs by the mean absolute temperature $273{\cdot}5^\circ$ C and is therefore $1{\cdot}529 \times 10^5$ units.

If a mass of 1 kilogram moving with a velocity of 1 metre per second is brought to rest by friction at a temperature of 15° C or 288° absolute, the work energy rendered unavailable is $\frac{1}{2} 10^3 \cdot 100^2$ or $\cdot 5 \times 10^6$ ergs and the gain of entropy $1{\cdot}736 \times 10^4$ units.

86. The Laws of Conservation, Localisation and Transmission of Entropy. We may now enunciate the following principles:

(1) The entropy of an isolated system of bodies can be divided into a sum of terms representing respectively the portions of entropy located in the several bodies and in the medium.

(2) The entropy of a body is always the same whenever the body is in the same physical state. It may have undergone any number of reversible or irreversible changes but if it is brought back to its former condition it will contain the same quantity of entropy as before.

(3) The expression for the entropy, like that for the energy involves an unknown integration constant. It is possible that the entropy of a body at absolute zero may be $-\infty$. The constant introduces no difficulties as we are only concerned with changes of entropy.

(4) Entropy can be generated but never destroyed.

(5) Entropy is always generated when irreversible processes take place, and the quantity of entropy so generated affords a measure of the irreversibility.

(6) From (2) and (5) we see that although phenomena may repeat themselves in certain limited parts of the Universe, irreversible changes will leave an indelible imprint on the progress of events somewhere or other, and the increase of entropy will represent a real change in the physical condition of the Universe as a whole.

(7) When irreversible changes take place in the interior of a system, the gain of entropy is greater than the quantity of entropy imported into the system from without, the difference representing the quantity of entropy generated by the irreversible changes. If the system undergoes an irreversible cycle a positive quantity of entropy will have to be exported from the body equal to the quantity generated internally.

(8) When heat flows from a hot to a cold body entropy is generated. If the flow take place by radiation, this entropy may be said (provisionally) to be generated in the intervening medium or at the surfaces of the two bodies. At the same time, it must be remembered that we have not yet discussed the thermodynamics of the ether, which will be dealt with in Chapter X.

(9) The reversible phenomena of *thermo-electricity* show that the localisation of entropy may be altered by electric currents, leading to the inference that the entropy of a system depends on its electric state. For a detailed discussion of these phenomena, and a comparison of the two definitions of entropy as applied to them, the reader is referred to Chapter XVI.

87. Temperature-entropy diagrams. In the practical applications of thermodynamics to steam-engines and other heat-motors much use is made of the *temperature-entropy* diagram, i. e. the diagram of a cyclic or other process formed by taking as coordinates temperature and entropy. As ϑ and φ instead of T and S are the usual symbols for temperature and entropy in English books, such a diagram is known in England as a "thetaphi diagram".

The following are some of the most important properties of such a diagram when the working substance is a simple system:

(1) For a Carnot's Cycle the diagram is a rectangle bounded by two lines $T =$ constant and two lines $S =$ constant.

(2) For a reversible cycle, integrating the equation

$$dU = TdS - pdV,$$

we obtain

$$\left(\int\right) TdS = \left(\int\right) pdV$$

or *the areas of the* (T, S), *and* (p, V) *diagrams are equal.*

(3) For a working substance performing an intrinsically irreversible cycle, the temperature entropy diagram is a closed curve. If the cycle be replaced by a reversible one having the same temperature-entropy diagram the amount of work obtained will be greater than before. It readily follows that the area of the (p, V) diagram is less than that of the (T, S) diagram, and that the ratio of these areas gives the ratio of the efficiency of the cycle to that of a perfectly reversible one, i. e. the efficiency of the cycle taking that of a perfectly reversible cycle as unity.

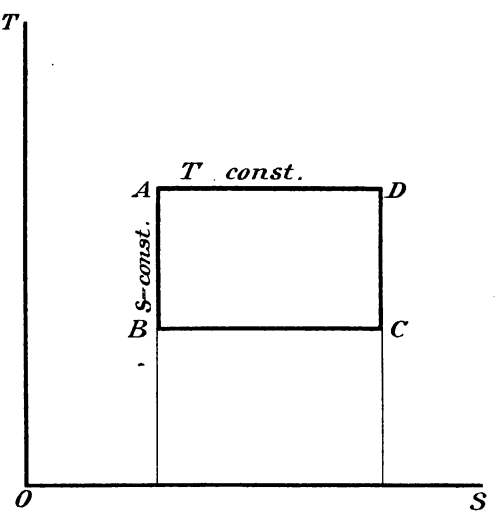

Fig. 10.

(4) If however we seek to represent in a diagram the temperature-entropy changes occurring in the *source and refrigerator*, we do not necessarily obtain a closed curve. In this case if T_1 and T_2 are the temperatures of the source and refrigerator, S the entropy *taken from the source* in one cycle, the work which *would* be obtainable from the same quantity of heat in a perfectly reversible cycle is represented

by a rectangular area of height S and base $T_1 - T_2$ and the ratio of the indicator or (p, V) diagram to *this* diagram is the proper measure of the efficiency ratio. The reason for this choice is that in practice we want to economise the heat taken from the source as far as possible, and we do not mind so much what happens at the refrigerator provided we get the greatest possible amount of work out of this heat.

The complete study of these diagrams belongs to treatises on technical thermodynamics.

CHAPTER VIII.

EXPRESSIONS FOR THE AVAILABLE ENERGY UNDER PARTICULAR CONDITIONS. — CONDITIONS OF STABILITY.

88. The energy test of stability. The discussions of the preceding chapters lead to the general conclusions expressed by the formula

$$dU = dQ - dW \tag{81}$$

and for reversible transformations at temperature T

$$dS = \frac{dQ}{T} \tag{82}$$

whence also

$$dU = T\,dS - dW \tag{83}$$

where dU and dS are the perfect differentials of two functions whose values are determined by the state of the system, these two functions being called energy and entropy of the system.

We now proceed to discuss the conditions of equilibrium and stability of certain systems subject to given external conditions, assuming the First Definition of Entropy. We provisionally exclude chemical and other changes for which the First Definition fails, and in particular we exclude radiation phenomena except in cases where the energy capacity of the ether is negligible (§ 66).

From the energy test of stability in Rational Mechanics, combined with the principle of degradation of energy, it follows that a thermodynamic system subject to given conditions will be in stable equilibrium if its available energy is a minimum for all small variations consistent with the given conditions.

If $x, y, z, \ldots$ be any variables specifying the state of the system subject to given conditions, and $A = f(x, y, z)$ represents the available energy, the usual theory of maxima and minima requires that if

$f(x+h, y+k, z+l \ldots) - f(x, y, z)$ be a function capable of expansion in powers of h, k, l then (a) the terms of the first degree must vanish, and (b) those of the second must be essentially positive. Also we infer by analogy with the corresponding problem in Rational Mechanics that the first condition (a) is required for equilibrium, and condition (b) for stability; in other words we shall in general assume that

For equilibrium, the variation of the available energy must vanish to the first order.

For stability the variation of the available energy must be positive to the second order.

The first of these conditions may be stated in the following form: *In the neighbourhood of any equilibrium state any small change may be regarded as perfectly reversible to the first order of small quantities.*

This property is of fundamental importance as it shows that problems of thermodynamic equilibrium can in general be correctly solved by means of the methods of reversible thermodynamics alone. Most applications of thermodynamics depend on this fact.

89. Exceptional Cases. In applying the energy test of equilibrium and stability exceptional cases may occur, of which the following simple illustrations from elementary mechanics sufficiently indicate the nature. These exceptions must be borne in mind in any general treatment:

(a) *State of Stable Equilibrium not unique.* A heavy particle may be in stable equilibrium on the curve of Fig. 11 either at A, B, or C, although its potential energy is greater at B than at A, and greater at A than at C. Thus the condition of stability does not require the energy to have the least possible value but only to be less than in neighbouring positions.

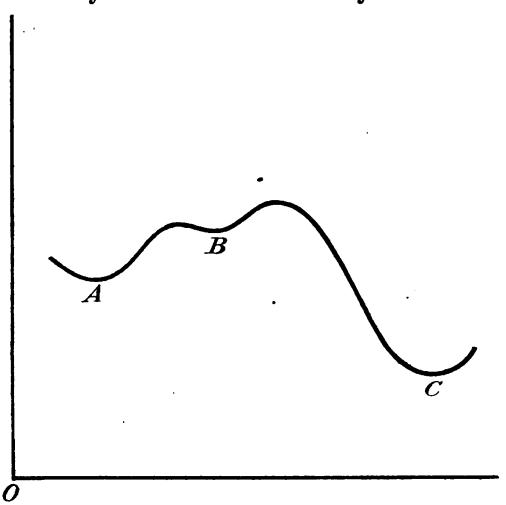

Fig. 11.

(b) *The variation of energy does not vanish to the first order.* When a weight rests with its base AB on a table a small angular displacement about A or B will produce a change of the same order in the potential energy. We might speak of the system as having

unilateral freedom, the constraint due to the table allowing the base to be raised but not lowered. For a system to rest in such a state it is necessary for the energy variation to be positive for any possible displacement consistent with the constraint, but when a displacement in the opposite sense is excluded, this energy variation is not necessarily a quantity of the second order.

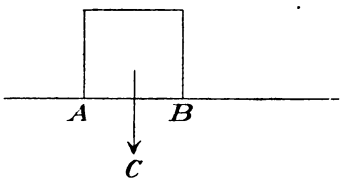

Fig. 12.

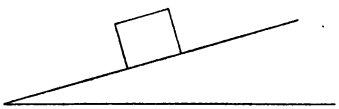

Fig. 13.

(c) *Equilibrium maintained by friction.* A body placed on a plane inclined at an angle less than the angle of friction will remain at rest, although if friction were removed it would slide down.

Thermodynamical analogues of these cases exist in chemical phenomena; according to *Duhem* case (c) has its analogue in certain phenomena called "false equilibria".

With these prefatory statements, we shall now show how the principle of degradation of available energy can be used to obtain the conditions of equilibrium and stability of a thermodynamical system in certain particular cases. To do this it is only necessary to construct expressions for the available energy of the system subject to the given external conditions.

Some of the results obtained — as for instance that for equilibrium the temperature and pressure of a system (under no forces except pressure) must be the same throughout — are so obvious that it is of course superfluous to prove them by this means, but the investigation is necessary in order to deal with the question of stability, and to extend the conditions of thermodynamic equilibrium to more general systems.

90. System at rest surrounded by an indefinite medium of uniform temperature T_0 and pressure p_0. We do not suppose the system to have attained its equilibrium state, so that its pressure and temperature are not necessarily the same as those of the medium. Suppose for the sake of simplicity that the system consists of r simple systems characterised by the suffixes $1, 2, \ldots r$ and that the state of the rth part is fully specified by the variables p_r, V_r, T_r, S_r, U_r, representing pressure, whole volume, temperature, whole entropy and energy, of which only two are independent.

Then if a quantity dQ_r of heat be withdrawn from the rth part, it follows from above that a quantity of *at least* $dQ_r \times \frac{T_0}{T_r}$ will have to be given to the medium, and hence that the maximum amount of mechanical work derivable from dQ_r is

$$dQ_r\left(1 - \frac{T_0}{T_r}\right).$$

Moreover, when the volume expands by an amount dV_r against the external pressure, the amount of work done is $(p_r - p_0)dV_r$. Hence the total differential of the available energy of the system is measured by

$$dA = \sum dQ_r\left(1 - \frac{T_0}{T_r}\right) + \sum (p_r - p_0)dV_r.$$

For equilibrium dA must vanish, giving the conditions $T_r = T_0$, $p_r = p_0$, hence the available energy can only be a minimum when the temperature is everywhere T_0 and pressure p_0, as is otherwise obvious.

We may take the available energy in this state to be zero since no work can be obtained from the system by the transformations, subject to the conditions *under consideration*. This does not mean that the system cannot undergo other transformations such as chemical changes, or that further energy cannot be rendered available by a change of external conditions, but merely that our estimate refers to the amount of energy which is available for conversion into work when such extraneous changes are excluded.

Moreover $dQ_r = -T_r dS_r$ (dQ_r represents heat withdrawn whence the minus sign). Hence the integral representing the available energy of the whole system becomes

$$A = -\sum \int (T_r - T_0)dS_r + \sum \int (p_r - p_0)dV_r.$$

But by the equations of reversible thermodynamics

$$dU_r = T_r dS_r - p_r dV_r.$$

Hence the total available energy is

$$A = -\sum \int (dU_r - T_0 dS_r + p_0 dV_r)$$

taken from the initial state to the state (T_0, p_0)

$$= \sum (U_r - T_0 S_r + p_0 V_r) - \sum (U^0_r - T_0 S^0_r + p_0 V^0_r)$$

where U_r^0, S_r^0, V_r^0 refer to the rth body in the final state (T_0, p_0). This expression gives on summation

(84) $$A = (U - U_0) - T_0(S - S_0) + p_0(V - V_0).$$

It follows from this expression that if

$$U - T_0 S + p_0 V > U_0 - T_0 S_0 + p_0 V_0 \tag{85}$$

the system can pass from the state (U, S, V) to the state (U_0, S_0, V_0) but cannot pass in the reverse direction unless available energy be supplied from without. This condition is therefore the condition that the state (U_0, S_0, V_0) should be one of stable equilibrium.

91. System surrounded by an envelope of invariable volume V_0 kept at constant temperature T_0. In this case the differential of the available energy is given by

$$dA = -\sum (T_r - T_0) dS_r + \sum p_r dV_r$$

and the condition of constancy of volume gives

$$\sum dV_r = 0.$$

The state of minimum available energy is thus defined by

$$0 = dA = -\sum (T_r - T_0) dS_r + \sum p_r dV_r$$

for all variations consistent with $\sum dV_r = 0$.

It follows that for this state of equilibrium

$$T_r = T_0, \; p_1 = p_2 \cdots = p_r$$

(results which are otherwise obvious).

And since

$$dU_r = T_r dS_r - p_r dV_r,$$

we have

$$dA = -\sum dU_r + T_0 \sum dS_r,$$

whence

$$\begin{aligned} A &= \sum (U_r - T_0 S_r) - \sum (U_r^0 - T_0 S_r^0) \\ &= U - U_0 - T_0 (S - S_0) \end{aligned} \tag{86}$$

leading to the result that for stable equilibrium in the state U_0, S_0 we must have for all possible neighbouring states U, S,

$$U - T_0 S > U_0 - T_0 S_0. \tag{87}$$

92. Stability of homogeneous fluids. Although a homogeneous fluid has been taken as the type of a simple system, and may be so taken as long as it remains homogeneous, it is necessary in order that the fluid may be in stable equilibrium that its available energy shall be a minimum for all displacements and not merely for displacements in which the fluid remains homogeneous. The same

consideration applies to thermodynamic systems of a more general character, and shows that in discussing the stability of a system with n degrees of mechanical freedom it is necessary to contemplate variations other than changes in the values of the $n+1$ variables which are sufficient to specify the state of the system as long as it remains homogeneous. For the present we confine ourselves to a detailed discussion of the case of a homogeneous fluid, which will sufficiently indicate the general character of the analytical results obtained when any case of thermodynamic stability is worked out by the methods of the differential calculus as a problem in maxima and minima.

We have to consider the possibility of displacements in which the fluid instead of remaining homogeneous divides itself into two or more parts differing in their physical properties, as illustrated, for example, by a liquid in contact with its vapour, or a substance partly in the solid and partly in the liquid state. If by such a change the available energy could be decreased the homogeneous state would be unstable, and examples of such unstable states are not uncommon in actual experience.

If we consider an element of the fluid whose mass is a very small fraction of the total mass, any change in the state of this element will produce a correspondingly very small change in the pressure and temperature of the remainder. By dividing the fluid up into differential elements of mass (§ 46) the condition of stability of each element is seen to be correctly obtainable by making the assumption that the fluid surrounding that element is kept at constant pressure and temperature. Taking T, p to be this temperature and pressure, u, v, s the energy, volume, and entropy of a *unit mass* of the fluid at any point in the equilibrium state, u', v', s' their values at any neighbouring state, we must have *at every point*

$$u' - Ts' + pv' > u - Ts + pv. \tag{88}$$

Now let the energy u be expressed as a function of the entropy s and volume v. Putting $s' - s = h$, $v' - v = k$ and expanding u in powers of h, k by *Taylor*'s Theorem we find to the second order in h, k

$$\begin{aligned}(u' - Ts' + pv') - (u - Ts + pv) \\ = h\left(\frac{\partial u}{\partial s} - T\right) + k\left(\frac{\partial u}{\partial v} + p\right) + \tfrac{1}{2}h^2\frac{\partial^2 u}{\partial s^2} + hk\frac{\partial^2 u}{\partial s\,\partial v} + k^2\frac{\partial^2 u}{\partial v^2}.\end{aligned}$$

For equilibrium the terms of the first order vanish; for stability those of the second order are positive. Therefore for equilibrium

$$\frac{\partial u}{\partial s} = T, \quad \frac{\partial u}{\partial v} = -p \tag{89}$$

and for stability

$$\frac{\partial^2 u}{\partial s^2} > 0, \quad \frac{\partial^2 u}{\partial v^2} > 0, \quad \frac{d^2 u}{\partial s^2}\frac{\partial^2 u}{\partial v^2} - \left(\frac{\partial^2 u}{\partial s\,\partial v}\right)^2 > 0. \tag{90}$$

Equations (89) lead to

$$du = Tds - pdv$$

in accordance with the Principle of Conservation of Energy and the property that a small transformation is reversible to the first order.

Of the inequalities (90) the first two now give

$$\left(\frac{\partial T}{\partial s}\right)_v > 0, \quad \left(\frac{\partial p}{\partial v}\right)_s < 0. \tag{91}$$

The third may be written

$$\frac{\partial T}{\partial s}\frac{\partial p}{\partial v} - \frac{\partial T}{\partial v}\frac{\partial p}{\partial s} < 0 \tag{92}$$

taking s and v as independent variables. Now

$$dT = \frac{\partial T}{\partial s}ds + \frac{\partial T}{\partial v}dv$$

$$dp = \frac{\partial p}{\partial s}ds + \frac{\partial p}{\partial v}dv.$$

It follows as in § 34 that

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

and therefore (91), (92) are equivalent to the four statements

$$\left(\frac{\partial T}{\partial s}\right)_v > 0, \quad \left(\frac{\partial T}{\partial s}\right)_p > 0, \quad \left(\frac{\partial p}{\partial v}\right)_T < 0, \quad \left(\frac{\partial p}{\partial v}\right)_s < 0.$$

These signify that

The addition of heat at constant pressure or at constant volume raises the temperature; that is the specific heats at constant volume and pressure are positive (§ 11).

The increase of pressure at constant temperature or entropy decreases the volume, that is the moduli of elasticity at constant temperature or entropy are positive (§ 14).

These conditions are obvious from general considerations.

93. When the pressures are everywhere in equilibrium the expressions for the variation of the available energy in the presence of a medium of temperature T_0 take the form

$$dA = \sum dQ_r\left(1 - \frac{T_0}{T_r}\right).$$

If we have a mass m of a homogeneous substance whose specific heat is γ, and temperature T_1, the available energy obtainable in

reducing it to a uniform temperature T_0 by reversible means is therefore given by

$$A = \int_{T_0}^{T_1} m\gamma\left(1 - \frac{T_0}{T}\right) dT.$$

Here γ must be taken to be the specific heat at constant pressure or constant volume according as the external conditions are those of § 90 or § 91.

This is all the available energy obtainable from the system (unless the final state is unstable or the stable state is not unique, § 89 (a) or other variations may take place). We may say that the available energy in the final state is zero. If *subject to the assumed conditions* a medium of temperature different to T_0 were procured, the conditions would be altered and further energy would be rendered available.

If the body is colder than the surrounding medium ($T_1 < T_0$) the expression for the available energy obtainable in bringing it to temperature T_0 may be thrown into the form

$$A = \int_{T_1}^{T_0} m\gamma\left(\frac{T_0}{T} - 1\right) dT$$

and since $T_0 > T$ throughout the integration A is again positive. Thus available energy is obtainable from a cold body such as a glacier; conversely to cool a body below the temperature of the surrounding air, as in the manufacture of artificial ice, available energy must be supplied from without, by means of a steam engine or otherwise.

94. System enclosed in a rigid envelope impervious to heat. — Gibbs' First Condition of Stability. The work done by the expansions of the different parts of the system is equal to

$$\sum p_r dV_r,$$

subject to the condition $\sum dV_r = 0$.

To estimate the available energy which can be converted into work by expansion and transference of heat between different parts of the system, assume an auxiliary body at temperature T_0, and in the first place suppose heat is transferred between the various bodies of the system and the auxiliary body by means of Carnot's cycles.

If dQ_r is the quantity of heat, dS_r the quantity of entropy taken from the rth body then a quantity of heat $dQ_r \times \frac{T_0}{T_r}$ is given to the auxiliary body and the amount of work done is

$$dQ_r\left(1-\frac{T_0}{T_r}\right)$$

and

$$dA=\sum dQ_r\left(1-\frac{T_0}{T_r}\right)+\sum pdV_r. \tag{93}$$

If the total quantity of heat received in any time-interval by the auxiliary body is made equal to zero, the auxiliary body may be removed, and if the volume be kept constant the conditions will be those of a system completely closed from outside influence. Equating to zero the heat received by the auxiliary body we have

$$0=\sum dQ_r\frac{T_0}{T_r}=T_0\sum dS_r=T_0dS$$

whence

$$S=\text{constant}$$

also

$$dA=\sum dQ_r+\sum pdV_r. \tag{94}$$

For equilibrium $dA=0$ subject to

$$\sum\frac{dQ_r}{T_r}=0 \quad \text{and} \quad \sum dV_r=0. \tag{95}$$

This requires the obvious conditions

$$T_1=T_2=\cdots=T_r \quad \text{and} \quad p_1=p_2=\cdots=p_r$$

and the maximum work obtainable under these conditions is

$$A=\sum\int(dQ_r+p_rdV_r).$$

Since dQ_r here represents heat taken from the rth body instead of heat given to that body, dQ_r is equal and of opposite sign to the ordinary dQ of thermodynamics, and therefore $dQ_r+p_rdV_r=-dU_r$, and the expression for the available energy becomes

$$A=-\sum\int dU_r=-\int dU=U-U_0 \quad \text{(say)} \tag{96}$$

the integration being made along an isentropic path from the given state to the state in which the energy U_0 is a minimum subject to the condition of constant entropy.

The condition for stable equilibrium requires that the available energy shall be a minimum, and therefore that the total energy U shall be a minimum for variations which keep the entropy S constant. This is one of the two alternative conditions of stability of an isolated system given by *Gibbs* in the following statement: —

For the equilibrium of any isolated system it is necessary and sufficient that

(1) *for all variations of the system which do not alter its energy, the variation of its entropy shall be either zero or negative*

(2) *for all variations of the system which do not alter its entropy the variation of its energy shall be either zero or positive.*

In other words

$$(\delta S)_U \leqq 0 \quad \text{or} \quad (\delta U)_S \geqq 0. \tag{97}$$

95. Gibbs' Second Condition of Stability. Let any system be isolated from all external influences for any given interval of time. If the parts of the system are not in equilibrium amongst themselves, irreversible changes will occur in the internal state of the system, and the principle of degradation of energy states that these changes will be of such a character as to decrease and never to increase the available energy which the system would have when subjected to given external conditions.

Now we have obtained for the available energy of a system of constant volume in the presence of an indefinitely extended medium at temperature T_0 the form

$$A = (U - T_0 S) - (U_0 - T_0 S_0)$$

according to whether the pressure of the medium or the volume of the system is kept constant.

For changes which take place in the interior of the system alone, the total energy U remains constant. The only quantity which can vary is the entropy S, and we see that the changes of entropy and available energy are connected by the relation

$$\delta A = - T_0 \delta S.$$

Since A tends to decrease S tends to increase, and hence in the position of stable equilibrium in which A is a minimum for constant U, S is a maximum as stated by Gibbs.

The expression $T_0(S_0 - S)$ subject to $U = U_0$ represents the amount of work which may be made available subject to the conditions that no energy either in the form of heat or of work is to leave the system as a whole.

In the previous article it was assumed that no heat was gained or lost by the *auxiliary body*. The present expression, on the other hand, assumes that no heat is gained or lost by the *system*. The energy which is made available in the form of work is really taken from the *auxiliary body* by transformations compensating the transformations of heat from the hotter to the colder parts of the *system*.

It will thus be seen that the available energy of an isolated system, though it appears at first sight to be simpler, is really more difficult to evaluate than that of a system in the presence of a thermically homogeneous medium. Under either hypothesis it is doubtful how far the system can be correctly described as *isolated*,

for, strictly speaking, this term implies that it can exert no outside influences whatever. At the same time irreversible changes may occur in the interior of the system; what we do know is that if communication be established with the outside in any given way, the energy thus rendered available will be greater before than after the changes.

Again, the energy which is available in a system which is more or less isolated is necessarily not greater than its available energy in the presence of a medium T_0. For we may always in the latter case assume the system to undergo the same transformation as if the medium were absent, and if the final temperature which it reaches under that condition is different from T_0 there will still be available energy between the system and the medium.

96. Lord Kelvin's Expressions. The expressions of § 94 for the available energy of an isolated system have been thrown into a simpler form by *Lord Kelvin* in the particular case in which the pressures are in equilibrium amongst themselves (so that the work of expansion is zero), and the heat capacities of the various portions remain constant throughout the range of temperatures concerned. Taking the equations (94), (95) which now become

$$0 = \sum \frac{dQ_r}{T_r} \quad \text{and} \quad dA = \sum dQ_r$$

and supposing Γ_r to be the total capacity for heat of the rth body and T the final temperature, we obtain

$$0 = \sum \int_{T}^{T_r} \Gamma_r \frac{dT}{T}, \quad A = \sum \int_{T}^{T_r} \Gamma_r dT$$

or since Γ_r is constant

$$\log T = \frac{\Sigma \Gamma_r \log T_r}{\Sigma \Gamma_r}, \quad A = \sum \Gamma_r T_r - T \sum \Gamma_r.$$

In the case of two bodies of equal thermal capacity

$$\Gamma_1 = \Gamma_2 = \frac{\Gamma}{2}$$

where Γ is the thermal capacity of the whole. Lord Kelvin finds

$$T = \sqrt{(T_1 T_2)}, \quad A = \frac{\Gamma}{2} (\sqrt{T_1} - \sqrt{T_2})^2.$$

In the general case an equally simple result can be obtained by dividing the system into a number of parts or elements whose capacities for heat are equal. If n is the number of parts and Γ the total capacity for heat of the system, we write

$$\Gamma_1 = \Gamma_2 = \cdots = \Gamma_n = \frac{\Gamma}{n}$$

in the above equations and obtain

$$T = (T_1, T_2, \ldots T_n)^{\frac{1}{n}} = \text{geom } T,$$

$$A = \Gamma \frac{T_1 + T_2 + \cdots + T_n}{n} - \Gamma T = \Gamma(\text{arm } T - \text{geom } T)$$

where arm T and geom T denote the arithmetic and geometric means of the initial temperatures.

The precise meaning of this result is as follows:

When the system is brought to a common temperature by reversible processes, that final temperature is the geometric mean of the initial temperatures. If it is allowed to come to a common temperature by heat conduction between the several parts thereby losing all its available energy, that common temperature will be the arithmetic mean of those of the parts. The available energy is equal to the quantity of heat required to raise the temperature of the system from the final value it would obtain by reversible processes to the value it would obtain by irreversible conduction.

CHAPTER IX.

THERMODYNAMIC POTENTIALS.

97. Thermodynamic Potentials of a Simple System. In this chapter we shall consider the statics of an ideal thermodynamic system, and shall show that the properties of such a system when in equilibrium are completely determined by a single function of the independent variables required to define the state of the system. We start with equation (83) of the preceding chapter,

$$dU = TdS - dW,$$

and we observe that this relation holds (a) for reversible transformations in which the system remains thermically homogeneous, and (b) in general for small displacements from a state of equilibrium, the uniformity of temperature being a necessary condition of equilibrium (§§ 88, 94).

Taking now a homogeneous fluid as the type of a simple system, we write $dW = pdV$, and therefore $dU = TdS - pdV$ whence

$$\left(\frac{\partial U}{\partial S}\right)_V = T, \quad \left(\frac{\partial U}{\partial V}\right)_S = -p. \tag{98}$$

It follows that if the volume V and entropy S are chosen as the two independent variables specifying the state of the system and if $U = \mathfrak{F}_{SV}$ where $\mathfrak{F}_{SV}$ is a known function of S and V, the temperature and pressure are given by the two partial differential coefficients of this function (the second with its sign changed).

For this choice of independent variables the energy, therefore, plays the part of a potential function and may be regarded as the *thermodynamic potential* of the system.

We can compare these results with the analogous relations in statics; S and V will represent the generalised position coordinates of a system, $-T$ and p with the corresponding force-coordinates. Or again in the kinetic analogue S and V will represent generalised velocities, T and $-p$ the corresponding momenta or impulse-coordinates.

In practice it is usually more convenient to take the temperature instead of the entropy as an independent variable, and sometimes the pressure instead of the volume, and in such cases we use a "modified function" in place of the function U.

Let V and T be the independent variables and put

$$\mathfrak{F}_{TV} = U - ST \tag{99}$$

then

$$\begin{aligned} d\mathfrak{F}_{TV} &= dU - TdS - SdT \\ &= -SdT - pdV \end{aligned}$$

leading to

$$\frac{\partial \mathfrak{F}_{TV}}{\partial T} = -S, \quad \frac{\partial \mathfrak{F}_{TV}}{\partial V} = -p. \tag{100}$$

Again taking p and T as independent variables put

$$\mathfrak{F}_{TP} = U - ST + pV \tag{101}$$

then

$$d\mathfrak{F}_{TP} = -SdT + Vdp$$

leading to

$$\frac{\partial \mathfrak{F}_{TP}}{\partial T} = -S, \quad \frac{\partial \mathfrak{F}_{TP}}{\partial p} = +V. \tag{102}$$

Finally if S and p are independent variables and if

$$\mathfrak{F}_{SP} = U + pV \tag{103}$$

we get

$$d\mathfrak{F}_{SP} = TdS + Vdp,$$

$$\frac{\partial \mathfrak{F}_{SP}}{\partial S} = T, \quad \frac{\partial \mathfrak{F}_{SP}}{\partial p} = V. \tag{104}$$

The four functions $\mathfrak{F}_{SV}$, $\mathfrak{F}_{TV}$, $\mathfrak{F}_{TP}$, $\mathfrak{F}_{SP}$ are thermodynamic potentials of the system for the corresponding pairs of independent variables. As however the second and third are the most commonly used, they will be denoted for shortness by $\mathfrak{F}_V$ and $\mathfrak{F}_P$, and called the *thermodynamical potentials for given volume* and *pressure* respectively, the other variable being taken to be the temperature unless the entropy is actually specified.

When instead of the whole body we wish to refer to a unit mass of the working substance we use small letters to denote the volume, energy and entropy, and these are got by dividing the

$\mathfrak{F}_{SV} \equiv U(V,S)$ – Energy,
$\mathfrak{F}_{TV} \equiv \psi(V,T)$ – Work function,

corresponding quantities for the whole body by the mass. We shall denote the corresponding thermodynamic potentials per unit mass by

$$\mathfrak{f}_{sv} \text{ or } u, \quad \mathfrak{F}_v \text{ or } \mathfrak{f}_v, \quad \mathfrak{F}_p \text{ or } \mathfrak{f}_p \text{ and } \mathfrak{F}_s \text{ or } \mathfrak{f}_s$$

As the small suffixes are sufficient to distinguish the potentials of unit mass from the potentials of the whole body, it is immaterial whether a capital $\mathfrak{F}$ or small $\mathfrak{f}$ is used.

The fundamental property common to each of the thermodynamic potentials viz: that *all the coefficients which determine the physical and mechanical properties of a body are known when a certain function of the independent variables which define the state of the body is known,* was enunciated by *F. Massieu* in 1869—1876, who gave the name *characteristic function* to such functions.

98. Systems with any number of degrees of Freedom. Let us now consider a thermically homogeneous system with n degrees of mechanical freedom. The state of such a system is completely specified by its n generalised coordinates, $x_1, x_2, x_3, \ldots x_n$ and either its absolute temperature T or its entropy S. If $X_1, X_2, \ldots X_n$ are the generalised force components corresponding to $x_1, x_2, \ldots x_n$ the external work done in any displacement is

$$dW = X_1 dx_1 + X_2 dx_2 + \cdots + X_n dx_n.$$

From (83)

$$dU = T dS - X_1 dx_1 - X_2 dx_2 - \cdots - X_n dx_n \tag{105}$$

giving for independent variables $S, x_1, x_2, \ldots$ if $\mathfrak{F}_{Sx} = U$,

$$\frac{\partial \mathfrak{F}_{Sx}}{\partial S} = T, \quad \frac{\partial \mathfrak{F}_{Sx}}{\partial x_r} = - X_r.$$

Taking in like manner

$$\mathfrak{F}_{Tx} = U - TS,$$
$$\mathfrak{F}_{TX} = U - TS + \sum Xx,$$
$$\mathfrak{F}_{SX} = U + \sum Xx$$

we have for the corresponding choices of variables

$$\frac{\partial \mathfrak{F}_{Tx}}{\partial T} = - S, \quad \frac{\partial \mathfrak{F}_{Tx}}{\partial x_r} = - X_r,$$
$$\frac{\partial \mathfrak{F}_{TX}}{\partial T} = - S, \quad \frac{\partial \mathfrak{F}_{TX}}{\partial X_r} = + x_r,$$
$$\frac{\partial \mathfrak{F}_{SX}}{\partial S} = + T, \quad \frac{\partial \mathfrak{F}_{SX}}{\partial X_r} = + x_r.$$

We may also construct other modified forms of thermodynamic potential for cases in which it is convenient to take some of the independent variables to be coordinates and some to be force components.

$\mathfrak{F}_{TP} = \phi(p,T)$ – Free energy.
$\mathfrak{F}_{\ldots} = H(p,\ldots)$ – Heat content

99. Number of Arbitrary Constants in the Potentials. The energy and entropy of a system each involve an unknown arbitrary constant dependent on the fact that we are only able to take cognisance of changes of their values and that we cannot form a definite conception of a state of zero energy or entropy.

Consequently the thermodynamic potentials in which the temperature is an independent variable contain two arbitrary constants entering in the form $a + bT$.

If we agree to choose an arbitrary zero of energy and entropy, i. e. to make the entropy and energy zero in a state which is capable of experimental realisation, the constants disappear.

Whether a state at absolute zero of temperature can be taken as that of zero entropy depends on whether the heat capacity tends to a finite limit or to zero as the temperature approaches zero. If the former the entropy at absolute zero will be minus infinity.

100. Connection with available energy; Helmholtz's "Free Energy". If we compare the expressions for $\mathfrak{F}_V$ and $\mathfrak{F}_P$ with the expressions of §§ 90, 91 we see that by a proper choice of the arbitrary constants mentioned above $\mathfrak{F}_V$ becomes the available energy of the system *in the presence of a medium of the same temperature as itself,* and $\mathfrak{F}_P$ becomes its available energy *in the presence of a medium of the same temperature and pressure as itself.* The difference is that in §§ 90, 91 we do not necessarily suppose the temperature and pressure of the system to be the same as those of the medium, so that our expressions there obtained are of a more general character. When the system has come into a state of equilibrium with the surrounding medium its available energy will be equal to $\mathfrak{F}_V$ or $\mathfrak{F}_P$ as the case may be[1]), or will differ from these functions by the arbitrary constants $a + bT$.

In the case of a compound system, a method of proof identical with those of §§ 90, 91 shows that the available energy relative to a medium T_0 is of the form

$$U - U_0 - T_0(S - S_0)$$

or

$$U - U_0 - T_0(S - S_0) + \sum X_0(x - x_0)$$

1) This statement leads to little difficulty in connection with §§ 90, 91 in which we have assumed the zero of available energy to be obtained when the temperature (and pressure) of the system are the same as those of the medium. The fact is that many writers have deduced the conditions of thermodynamic equilibrium from the consideration of *isothermal displacements alone*, and for such displacements the thermodynamic potentials sufficiently determine the variations of available energy (or "free energy" in the sense adopted by Helmholtz).

according as the coordinates or the external forces $X_0 \ldots$ are maintained constant. It is easy to see that a similar connection here exists between the functions $\mathfrak{F}_{Tx}$ and $\mathfrak{F}_{TX}$ and the corresponding available energies of the system subject to the limitation that equilibrium exists between the system and medium.

The potential $\mathfrak{F}_{TV}$ or $\mathfrak{F}_{Tx}$ is the function used by *Helmholtz* under the name of *"free energy"*. This potential is known as the *inner thermodynamic potential* by *Duhem* while the other potential $\mathfrak{F}_{TP}$ or $\mathfrak{F}_{TX}$ is called the *total thermodynamical potential.*

101. Thermodynamic Surfaces. A function of one or more variables is not necessarily expressible in terms of those variables by any symbolic formula, however complicated, hence we are not justified in assuming *a priori* that a thermodynamic potential is so expressible in terms of the variables which are chosen to define the state of the system. In a simple system, where we have only two independent variables, and one dependent variable, namely the corresponding thermodynamic potential, we may take these as represented by the three rectangular coordinates of a point, and the locus of this point will be a geometric surface which is called a *thermodynamic surface.*

Taking a unit mass of a working substance, the surface obtained by taking (v, s, u) as coordinates is known as *Gibbs' thermodynamic model* of the substance, and has been constructed for various actual substances from experimental considerations. Taking x, y, z as the axes of v, s, u respectively, the polar reciprocal with respect to $y^2 = 2z$ keeping x constant gives the corresponding $(v, T, \mathfrak{F}_v)$ surface and the reciprocal with respect to $x^2 + y^2 = 2z$ gives the $(p, T, \mathfrak{F}_p)$ surface as will be shown later.

The condition of stability of § 92 also receives a simple geometric interpretation in connection with the (v, s, u) surface. It represents the condition that the surface in the neighbourhood of any point shall be below the tangent at that point, i. e. shall be concave upwards if the axis of u is drawn upwards.

102. Thermodynamical potentials of an Elastic Solid. In the theory of elasticity, the state of strain of a body at any point is determined by six components $(\varepsilon_x, \varepsilon_y, \varepsilon_z, \gamma_x, \gamma_y, \gamma_z)$, connected with the three displacements (ξ, η, ζ) of the point (x, y, z) by six relations of the forms

$$\varepsilon_x = \frac{\partial \xi}{\partial x}, \ldots, \quad \gamma_x = \frac{1}{2}\left(\frac{\partial \eta}{\partial z} + \frac{\partial \zeta}{\partial y}\right), \ldots$$

On the other hand the state of stress is defined by six components $(\sigma_x, \sigma_y, \sigma_z, \tau_x, \tau_y, \tau_z)$ so chosen that in any small displacement the work done referred to unit volume of the undeformed body at the point (x, y, z) is $\sigma_x d\varepsilon_x + \sigma_y d\varepsilon_y + \sigma_z d\varepsilon_z + \tau_x d\gamma_x + \tau_y d\gamma_y + \tau_z d\gamma_z$.

To refer this to unit mass instead of to unit volume we have to divide by ρ the density of the body in its original undeformed state, and taking u as the energy per unit mass, we have

$$du = Tds + \frac{1}{\rho}\left(\sum \sigma d\varepsilon + \sum \tau d\gamma\right).$$

Here ρu is the elastic potential of unit volume at constant entropy, giving for adiabatic changes

$$\rho\left(\frac{\partial u}{\partial \varepsilon_x}\right)_s = \sigma_x, \ldots, \quad \rho\left(\frac{\partial u}{\partial \gamma_x}\right)_s = \tau_x, \ldots,$$

the differentiations being made on the supposition that the entropy is constant. This condition holds in the case of rapid vibrations in which no heat passes between the parts of the body.

Introducing the thermodynamic potential $\mathfrak{F}_\varepsilon$, namely

$$\mathfrak{F}_\varepsilon = u - Ts,$$

we have

$$d\mathfrak{F}_\varepsilon = -sdT + \frac{1}{\rho}\left(\sum \sigma d\varepsilon + \sum \tau d\gamma\right)$$

leading to

$$\rho\left(\frac{\partial \mathfrak{F}_\varepsilon}{\partial \varepsilon_x}\right)_T = \sigma_x, \ldots, \quad \rho\left(\frac{\partial \mathfrak{F}_\varepsilon}{\partial \gamma_x}\right)_T = \tau_x, \ldots,$$

the condition $T =$ constant during partial differentiation showing that $\mathfrak{F}_\varepsilon$ is the proper elastic potential to use for slow displacements where the temperature remains constant.

If the stress components are given the potential functions to be used are obtained by subtracting from u and $\mathfrak{F}_\varepsilon$ the expression

$$\frac{1}{\rho}(\sigma_x\varepsilon_x + \sigma_y\varepsilon_y + \sigma_z\varepsilon_z + \tau_x\gamma_x + \tau_y\gamma_y + \tau_z\gamma_z)$$

and the corresponding potentials may be denoted by $\mathfrak{F}_{S\sigma}$ and $\mathfrak{F}_{T\sigma}$ respectively, or for brevity $\mathfrak{F}_S$ and $\mathfrak{F}_T$. We shall have

$$\text{for adiabatic changes } \varepsilon_x = -\frac{1}{\rho}\frac{\partial \mathfrak{F}_{S\sigma}}{\partial \sigma_x}, \quad \gamma_x = -\frac{1}{\rho}\frac{\partial \mathfrak{F}_{S\sigma}}{\partial \tau_x},$$

$$\text{for isothermal changes } \varepsilon_x = -\frac{1}{\rho}\frac{\partial \mathfrak{F}_{T\sigma}}{\partial \sigma_x}, \quad \gamma_x = -\frac{1}{\rho}\frac{\partial \mathfrak{F}_{T\sigma}}{\partial \tau_x}.$$

In the case of simple traction parallel to the axis of x, we have $\sigma_y, \sigma_z, \tau_x, \tau_y, \tau_z$ each equal to zero, and the corresponding value of τ_x/ε_x derived from the potential $\mathfrak{F}_{\tau\sigma}$ represents the ordinary modulus of elasticity (Young's modulus). It is also to be observed that in the ordinary theory of elasticity where small displacements are only taken into account, so that the stresses are assumed for the purposes of calculation to be linear functions of the strains and conversely, the potential functions are quadratic functions of the strains or stresses according to the choice of coordinates, and the entropy of unit mass must therefore be also a homogeneous quadratic function of the same variables, plus a constant.

PART III

THERMODYNAMICS OF PARTICULAR SYSTEMS

CHAPTER X.

APPLICATION OF THERMODYNAMICS TO RADIATION.

103. Black body radiations. The principle of degradation of energy is essentially based on our knowledge of phenomena associated with matter. The motions of the celestial bodies, and the propagation of light waves which reach the Earth from distant stars afford evidence that in the ether no such degradation of energy takes place, or, if degradation exist, it is immeasurably smaller than what occurs in the phenomena of material bodies.

While radiation may follow a body in a particular direction, the radiation emitted by a body is equally distributed in all directions. It follows that when the ether is traversed by radiation which is unequally distributed as regards direction no state of heat equilibrium can exist between the ether and a material body, and the notion of temperature at a point which is the same in all directions becomes inapplicable to the ether. Even if the heat absorbed and emitted by a body are equal in amount, they are different in direction, so that this condition, so far from representing an equilibrium state, corresponds to a steady irreversible transformation.

For heat equilibrium to exist between a body and the ether it is necessary that the radiation should be equally distributed in all directions, and that the intensity of the total radiation falling on the body should be equal to that of the radiation emitted by the body. If we imagine a body of uniform temperature containing a cavity unoccupied by matter this state of equilibrium will soon be attained and the intensity of the radiation inside the cavity will be the intensity of radiation of a "black body" of equal temperature. In this way a black body is capable of experimental realisation, and its radiation has been studied by Lummer, Wien, Pringsheim and others.

In many of the previous discussions it has been tacitly assumed that when heat passes from a hot to a cold body the transfer takes place instantaneously, and this is virtually equivalent to assuming that the heat capacity of the ether may be neglected. There is no *a priori* reason for asserting that heat could not be made to pass

from a cold to a hot body, and perpetual availability thus obtained, if it were possible to produce a suitable series of changes during the small time-intervals occupied by radiation in travelling from one body to the other. If such a possibility existed, it would be difficult if not impossible to put in practical working, and would in no way vitiate the validity of the principles of thermodynamics as applied to a large and important class of phenomena in which they would still hold good.

The only way of dealing with this point is to ask in the first instance the question: If the principle of degradation of energy still holds good what consequences are logically deducible from it? When this question has been answered the next step in the enquiry is to ascertain whether these consequences are in agreement with experiment.

104. Existence of radiation pressure. Now the first result arising out of this mode of reasoning is the existence of pressure due to radiation.

For let S be a perfectly reflecting tube, near the ends of which are placed perfectly reflecting partitions C, D, the space between which is devoid of radiation. Let a colder body B and warmer body A be placed in the two ends, and let the partition D be opened. Then radiation from B will pass into the tube until an equilibrium state is attained. If D be closed and B opened this radiation will certainly pass towards the warmer body A, but A will send radiation of greater intensity into the cavity so that heat will not as yet pass from the colder to the warmer body.

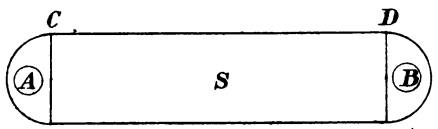

Fig. 14.

But if the plug D be moved up to the end C, the heat from B *will* be transferred to A.

If we assume that this case does not afford an exception to the principle of degradation of energy, available energy must be supplied from without, and the only form which this energy can assume is that of work done in moving the plug from D to C. The radiation must therefore exert a pressure on the plug.

Now the existence of such a radiation-pressure is verified by experiment as well as by theoretical considerations which are independent of the laws of thermodynamics, in connection with the electromagnetic theory of light. We may regard this result as a first step towards proving that it is impossible to restore lost availability by means of the ether.

105. Boltzmann's Investigation. We may now following the methods of *Boltzmann* construct a Carnot's cycle for the ether or "ether engine" as follows:

Let KC be a perfectly reflecting tube containing a perfectly reflecting piston C, and devoid of matter, A a hotter and B a colder radiating body.

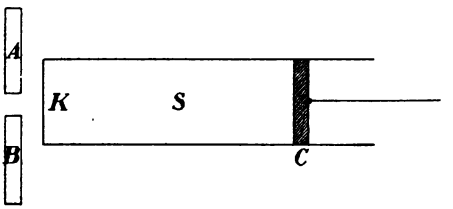

Fig. 15.

(1) The piston being at the end K, let it be placed in contact with A, and let the piston move outwards slowly, the space behind absorbing radiation from A and work being done by the radiation pressure.

(2) Let the body A be removed and the end K closed to further radiation. Let the piston move outwards until the intensity of radiation has diminished till it is exactly in equilibrium with that emitted by B.

(3) Let the body B be placed at the end K and the plug C pushed in until it is in contact with B, the whole radiation inside the tube being absorbed by B.

(4) Let the body A be substituted for B.

By applying the laws of thermodynamics to this cycle Boltzmann obtained an important relation connecting the energy of radiation per unit volume, the radiation pressure, and the temperature of the radiating body.

Suppose when the temperature of the radiating body is T, that the energy of radiation per unit volume in the ether, when equilibrium has been established is ψ, and the radiation pressure is f.

Let T_1, T_2 be the temperatures of the source and refrigerator, v_1, v_2 the volumes of the space enclosed by C at the beginning and end of the second process which is an adiabatic transformation.

The energy received by the medium in the first step is $\psi_1 v_1$ and the work done in expansion is $f_1 v_1$. Hence the total heat received from A is $(f_1 + \psi_1)v_1$.

In the second step the work of expansion is equal to $\int_{v_1}^{v_2} f dv$ and is equal to the loss of radiant energy $\psi_1 v_1 - \psi_2 v_2$.

In the third stage the work of compression is $f_2 v_2$ and the total heat received by B is $(f_2 + \psi_2)v_2$.

The principle of conservation of energy applied to the second process thus gives

$$\psi_1 v_1 - \psi_2 v_2 = \int_{v_1}^{v_2} f dv. \tag{106}$$

While the analytical expression for the second law (the cycle being reversible) namely

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

gives

$$\frac{v_1(f_1+\psi_1)}{T_1} = \frac{v_2(f_2+\psi_2)}{T_2}. \tag{107}$$

Equations (106), (107) involve the volume v and are only true for adiabatic processes. By eliminating v we get a relation which is not subject to this restriction, f and ψ being only functions of T. Making $T_1 - T_2$ an infinitesimal of the first order in (106), (107) we have

$$f dv = -v d\psi - \psi dv,$$

$$T[(f+\psi)dv + v d(f+\psi)] - v(f+\psi)dT = 0.$$

Eliminating $\frac{dv}{v}$ from these equations we have

$$Tdf - (f+\psi)dT = 0 \tag{108}$$

which is Boltzmann's Equation.

106. Stefan's Law. If we assume with *Maxwell* that the radiation pressure is equal to one-third the energy per unit volume, that is $f = \frac{1}{3}\psi$ we get $Td\psi = 4\psi dT$ or

$$\psi \propto T^4 \tag{109}$$

or the energy per unit volume in the ether in the presence of a "black body" varies as the fourth power of the temperature.

This is known as *Stefan's Law* and has been verified experimentally. Conversely if Stefan's Law and the formula for the radiation pressure be assumed as the result of experiment, we have a confirmation of our assumption that the laws of thermodynamics are applicable to the ether.

According to Stefan's law, the heat capacity of the ether per unit volume $\propto T^3$. Under these conditions we may state that the temperature of the ether is T, this being the temperature of a "black body" in thermal equilibrium with the ether, and the radiation being assumed to be equally distributed in all directions.

Stefan's law is not a pure deduction from thermodynamical principles, for if we had assumed $f = \psi$ instead of $\frac{1}{3}\psi$ we should have found $\psi \propto T^2$ instead of T^4. But if Stefan's Law be assumed it affords a measure of absolute temperature which is independent of any material body.

107. Entropy of black body radiation. If, following the old practice, we define entropy for reversible processes by the relation $dS = \frac{dQ}{T}$, the entropy, per unit volume, of black body radiation may be obtained by considering a black cavity the temperature of whose walls is gradually raised from the absolute zero to temperature T. Assuming Stefan's Law $\psi = kT^4$ this gives

$$S' = \int_0^T \frac{d\psi}{T} = \frac{4}{3} kT^3 = \frac{4}{3} \frac{\psi}{T} \tag{110}$$

where S' represents entropy per unit volume.

Referred to auxiliary temperature T, this represents a quantity of unavailable energy $\frac{4}{3}\psi$. Of this quantity ψ represents the actual energy of the cavity, and the remainder $\frac{1}{3}\psi$ is equal to f and represents unavailable energy arising out of the radiation pressure. It is obvious that if we wish to transfer the energy of the cavity to a body at temperature T, work ψ must be done by the radiation pressure, so that the total energy transferred which is unavailable at temperature T is equal to $\psi + f$.

If however we start with the second definition of entropy, it follows conversely that the entropy of the black cavity radiation is in every instance equal to $\frac{(\psi + f)}{T}$, and this conclusion is independent of Stefan's Law.

108. Impossibility of increasing availability by optical methods. If it were possible to cause heat to pass from a colder body to a hotter one by means of burning glasses, concave mirrors or indeed any optical combination, we should have an exception to the principle of degradation of energy, and should find it easy to obtain energy in the form of work from a thermically homogeneous system. That this is impossible was shown originally by *Clausius* in the case in which the extreme media were the same; and it was also shown that if the conclusion applies equally when the extreme media are different, then the intensity of emission of a body in any medium must be proportional to the square of the refractive index for that medium.[1])

When a ray falls on a surface separating two media, part is reflected and part refracted. It is obvious that the existence of the reflected portion reduces the efficiency of a burning glass for the

1) Pogg. Ann. CXXI (1864) 1. As an example of the property, it would be impossible to heat a body to a higher temperature than the Sun by concentrating the Sun's rays with a burning glass, even if atmospheric absorption did not exist.

purpose of concentrating heat, and it is to be noticed, further, that the splitting of the incident ray into two parts is in general *irreversible*; for, taking light of a certain definite wave length, a definite relation exists between the amplitudes, phases and polarisation of the reflected and refracted components, and unless this relation were preserved when the paths of the rays were reversed, they would not recombine to form a single ray. If such recombination were possible in the case of radiations emitted by different bodies we might have a means of restoring lost availability. We shall therefore assume, to shorten the discussion, that the loss of availability can in no case be less than it would be in the case of purely hypothetical media which refracted the whole of the incident light. Such a medium we might call a "perfect refractor", a "perfect reflector" being similarly defined with reference to reflection.

Let ds and ds' be elements of area of two radiating surfaces, and suppose that the rays from a point on ds which reach the element ds' lie within a cone of solid angle $d\omega'$ whose axis makes an angle ε with the normal to ds. Then if I be the intensity of normal radiation from ds, the total quantity of radiation falling on ds' is

$$dQ = I \cos \varepsilon \cdot d\omega\, ds. \tag{111}$$

With corresponding notation for the element ds', if dQ' denote the quantity of radiation received from ds on ds',

$$dQ' = I' \cos \varepsilon' \cdot d\omega' ds'.$$

The condition that $dQ = dQ'$ requires that

$$I \cos \varepsilon\, d\omega ds = I' \cos \varepsilon' d\omega' ds'.$$

If the extreme media are the same, I, I' are, for perfectly radiating bodies, functions of the temperature alone, and in order that heat equilibrium may represent equality of temperature we have to prove the relation

$$\cos \varepsilon d\omega ds = \cos \varepsilon' d\omega' ds'. \tag{112}$$

In the case of direct radiation through a homogeneous medium if r be the distance between the elements

$$d\omega = \frac{ds' \cos \varepsilon'}{r^2}, \quad d\omega' = \frac{ds \cos \varepsilon}{r^2},$$

$$\cos \varepsilon d\omega ds = \cos \varepsilon' d\omega' ds'.$$

It follows from this that the ratio

$$\frac{\cos \varepsilon' d\omega' ds'}{\cos \varepsilon d\omega ds}$$

is equal to unity for all pairs of points in the case of rectilinear propagation of light in a homogeneous medium. We may say that the product of the cross section $ds' \cos \varepsilon'$ into the solid angle $d\omega'$ of a pencil is invariant at all points of its course in the same medium.

109. Case of a perfect refractor. It now remains to show how this ratio is altered at a reflecting or refracting surface.

Let $d\sigma$ be any element of the refractive surface, μ, μ' the indices of refraction, φ, φ' the angles of incidence and refraction, ψ the azimuthal angle measured about the normal.

Then the solid angles $d\omega$, $d\omega'$ of a small pencil before incidence and refraction may be taken to be

$$d\omega = \sin \varphi d\varphi d\psi, \quad d\omega' = \sin \varphi' d\varphi' d\psi'.$$

But

$$\mu \sin \varphi = \mu' \sin \varphi',$$

$$\therefore \mu \cos \varphi d\varphi = \mu' \cos \varphi' d\varphi',$$

$$\therefore \mu^2 \cos \varphi d\omega d\sigma = \mu'^2 \cos \varphi' d\omega d\sigma$$

so that the ratio of the differentials

$$\frac{\cos \varphi' d\omega' d\sigma'}{\cos \varphi d\omega d\sigma} = \frac{\mu^2}{\mu'^2}$$

and when $dQ = dQ'$ we must have

$$\frac{I}{\mu^2} = \frac{I'}{\mu'^2}. \tag{113}$$

By extending this result to any number of reflections and refractions, we see that the ratio

$$\frac{\mu'^2 \cos \varepsilon' d\omega' ds'}{\mu^2 \cos \varepsilon d\omega ds}$$

at any two points traversed by the rays is equal to unity, or the product of the cross section into the solid angle of a pencil at any point is inversely proportional to the square of the refractive index (Fig. 16).

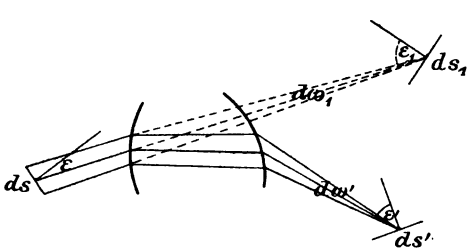

Fig. 16.

It should be noticed that *Helmholtz's* formula for the magnification of an optical combination is contained in this result.

110. Entropy of directed radiation. From the last article it follows that if radiation of intensity I is emitted in a medium of index μ, the quantity $\frac{I}{\mu^2}$ is an invariant in the sense that it represents

a quality of the radiation which is unaltered by perfect reflection or refraction or direct propagation. So long as this is the case the transmission of the rays does not necessarily involve passage from a hotter to a colder body.

If we imagine a perfectly black body of finite size emitting radiation, then at any distant point the directions of the rays will be confined to the solid angle which the body subtends at that point. By means of a suitable combination of perfect reflectors or refractors or both we may regard it as theoretically possible to make any portion of the rays converge into a smaller area in such a way that this solid angle is increased to 2π. When this is the case there will be equilibrium of radiation at the surface of convergence if the temperature of a body placed there is equal to that of the source.

On the other hand, if the source begins to send out radiation into empty space, radiation pressure will be set up where it did not previously exist, representing an increase of unavailable energy and, therefore, of entropy.

The entropy per unit volume at any point of the ether is a measurable quantity in the case of a radiating sphere surrounded by a perfectly reflecting concentric spherical surface. This case differs from the previous one in that we have everywhere to deal with emitted and reflected radiation of equal intensity confined within the same limits of direction.

If the radius of the reflecting sphere is decreased from r to $r - dr$, the radiation between these distances will be absorbed by the source, and work will be done against the radiation pressure. It follows that the entropy per unit volume again takes the form of § 107, viz $S = \frac{(\psi + f)}{T}$ where ψ is the total intensity of radiation, f the radiation pressure, and T the temperature of a perfectly black body emitting radiation of the intensity in question.

111. Summary of irreversible radiation phenomena. The irreversible processes connected with radiation may generally be summed up in *Planck's* statement that *emission without simultaneous absorption is possible but irreversible, absorption without simultaneous emission is impossible.*

Although the generation of entropy due to outward radiation considered in the last article may be naturally regarded as taking place in the ether, it will be seen that the change is really a direct consequence of this assumption. If it were possible to conceive a body at temperature T capable of absorbing without emitting the radiation due to that temperature, any portion of the ether could be cleared of radiation without doing work against radiation-pressure, and

without involving passage of heat from a hotter to a colder body, so that the gain of entropy in question would then cease to exist.

Another case of irreversibility occurs when a body absorbs radiation in certain directions and emits radiation in all outward directions without gaining or losing heat on the whole. Here the invariant of the radiation is changed, and the scattering of light by small particles affords a familiar instance.

A third case, not yet considered, arises in connection with imperfectly radiating or absorbing bodies. A discussion of such bodies will be found in elementary treatises on light and need not be given here. For our purpose the phenomena are sufficiently represented by considering that the invariant of the emitted radiation is the same as that of a perfectly black body of *lower* temperature while the invariant of the absorbed radiation is the same as that of a perfectly black body of higher temperature. The irreversible changes are thus measurable in terms of heat taken from a higher to a lower temperature, and therefore they define increases of entropy.

All these cases are covered by Planck's general statement quoted above. Whether all the irreversible phenomena of the universe can be deduced from this statement by the consideration of intermolecular radiations is a difficult question to answer, especially in connection with such phenomena as diffusion of gases.

Note. In this chapter no attempt has been made to give a complete account of the thermodynamics of radiation. The proof of Maxwell's expression for the radiation, and all considerations relating to the distribution of light-waves of different frequency in black cavity radiations have been omitted. For a full discussion of these and other questions, and further considerations relating to the entropy of radiation especially as treated from a statistical stand-point the reader is referred to Dr. Planck's recent treatise.[1])

CHAPTER XI.

THERMODYNAMIC FORMULAE OF A SIMPLE SYSTEM.

[CHAPTER III SHOULD BE REVISED BEFORE PROCEEDING FURTHER.]

112. Deductions from the First Law. In Chapter III we showed that the various thermal differential coefficients of a body are not all independent but are connected by the formulae of the Differential Calculus for change of the independent variable. The laws of thermo-

1) Vorlesungen über die Theorie der Wärmestrahlungen. Leipzig, Barth, 1906.

dynamics introduce two new quantities, namely, intrinsic energy and entropy, and differential coefficients involving these quantities fall under the general formulae there discussed.

We now have, however, the further properties that in reversible changes $dQ - dW$ and $\frac{dQ}{T}$ are perfect differentials of these two quantities, and we may apply the well known analytical theorem, that if $Mdx + Ndy$ is a perfect differential then $\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$.

Applying this property to $dQ - dW$ and assuming x and y to be independent variables by which the state of the body is defined, Clausius gives the formula

$$\frac{\partial}{\partial x}\frac{\partial Q}{\partial y} - \frac{\partial}{\partial y}\frac{\partial Q}{\partial x} = \frac{\partial}{\partial x}\frac{\partial W}{\partial y} - \frac{\partial}{\partial y}\frac{\partial W}{\partial x}. \tag{114}$$

Taking a *unit mass* of fluid as a simple system we may put $dW = pdv$, and for the added heat which we now call dq, if we write as in Chap. III

$$dq = l_v dv + \gamma_v dT, \tag{27}$$

$$dq = l_p dp + \gamma_p dT, \tag{28}$$

$$dq = Mdv + Ndp, \tag{30}$$

we obtain the particular forms

$$\frac{\partial(l_v - p)}{\partial T} = \frac{\partial \gamma_v}{\partial v}, \tag{115}$$

$$\frac{\partial(l_p + v)}{\partial T} = \frac{\partial \gamma_p}{\partial p}, \tag{116}$$

$$\frac{\partial M}{\partial p} - \frac{\partial N}{\partial v} = 1, \tag{117}$$

and since each of these expresses the condition that the same expression should be a perfect differential, each is analytically deducible from the others as can be readily verified.

113. Deductions from the Second Law. Again making $\frac{dQ}{T}$ a perfect differential, we obtain in the first place Clausius' formula

$$\frac{\partial}{\partial x}\frac{\partial Q}{\partial y} - \frac{\partial}{\partial y}\frac{\partial Q}{\partial x} = \frac{1}{T}\left(\frac{\partial Q}{\partial x}\frac{\partial T}{\partial y} - \frac{\partial Q}{\partial y}\frac{\partial T}{\partial x}\right) \tag{118}$$

and in the second place the particular forms

$$\frac{\partial l_v}{\partial T} - \frac{l_v}{T} = \frac{\partial \gamma_v}{\partial v}, \tag{119}$$

$$\frac{\partial l_p}{\partial T} - \frac{l_p}{T} = \frac{\partial \gamma_p}{\partial p}, \tag{120}$$

$$\frac{\partial N}{\partial v} - \frac{\partial M}{\partial p} = \frac{N}{T}\frac{\partial T}{\partial v} - \frac{M}{T}\frac{\partial T}{\partial p}. \tag{121}$$

Combining these with the previous set of equations we obtain

$$T\left(\frac{\partial}{\partial x}\frac{\partial W}{\partial y}-\frac{\partial}{\partial y}\frac{\partial W}{\partial x}\right)=\frac{\partial Q}{\partial x}\frac{\partial T}{\partial y}-\frac{\partial Q}{\partial y}\frac{\partial T}{\partial x}, \tag{122}$$

$$\left(\frac{dp}{dT}\right)_v=\frac{l_v}{T}, \tag{123}$$

$$\left(\frac{dv}{dT}\right)_p=-\frac{l_p}{T}, \tag{124}$$

$$M\frac{\partial T}{\partial p}-N\frac{\partial T}{\partial v}=T. \tag{125}$$

From (115), (123) and (116), (124) we deduce further, the relations

$$\left(\frac{d\gamma_v}{dv}\right)_T=T\left(\frac{d^2p}{dT^2}\right)_v, \tag{126}$$

$$\left(\frac{d\gamma_p}{dp}\right)_T=-T\left(\frac{d^2v}{dT^2}\right)_p \tag{127}$$

which are of use in experimental determinations of γ_p and γ_v.

114. Maxwell's Four Thermodynamic Relations. The last two articles, combined with the results of Chapter III, will show how easy it is to write down an almost endless number of thermodynamic formula. In order to evolve order out of the chaos which would very soon arise, it is best to introduce the thermodynamic potentials, which for unit mass we denote by

$$u \text{ or } \mathfrak{f}_{sv},\ \mathfrak{f}_v,\ \mathfrak{f}_p \text{ and } \mathfrak{f}_s \text{ or } \mathfrak{F}_{sp}.$$

Applying the conditions for a perfect differential to the differentials of these functions, as given by § 112 and writing $\frac{dq}{T}$ for ds

$$\left(\frac{dT}{dv}\right)_S=-T\left(\frac{dp}{dq}\right)_v, \tag{128}$$

$$\left(\frac{dq}{dv}\right)_T=+T\left(\frac{dp}{dT}\right)_v, \tag{129}$$

$$\left(\frac{dq}{dp}\right)_T=-T\left(\frac{dv}{dT}\right)_p, \tag{130}$$

$$\left(\frac{dT}{dp}\right)_S=+T\left(\frac{dv}{dq}\right)_p \tag{131}$$

of which (129) is identical with (123) and (130) with (124). Equation (123) is moreover the equation (22) given in Chapter II § 29 and known as Clapeyron's Equation.

These four relations are mutually dependent for if (128) is satisfied $Tds-pdv$ is a complete differential, therefore (*e.g.*) $Tds-pdv-d(Ts)$ is a perfect differential giving (129).

These relations are known as "*Maxwell's* four thermodynamical relations", and they may be readily interpreted in words.

Attending only to the signs of the differential coefficients, we draw the following conclusions.

(a) *If the substance expands adiabatically, the temperature will increase or decrease as the volume increases, according as addition of heat decreases or increases the pressure at constant volume.*

(b) *If the substance is compressed adiabatically, the temperature will increase or decrease with the pressure, according as addition of heat increases or decreases the volume at constant pressure.*

(c) *If the substance expands at constant temperature, it will absorb or give out heat as the volume increases, according as the pressure at constant volume increases or decreases with the temperature.*

(d) *If the substance is compressed at constant temperature, it will absorb or give out heat according as the pressure increases as the volume at constant pressure decreases or increases with the temperature.*

As an example we may take the case of water below the temperature of maximum density. Here when the pressure is kept constant the volume decreases as the *temperature* increases and "conversely". Hence $\left(\frac{dv}{dT}\right)_p$ and $\left(\frac{dv}{ds}\right)_p$ are both negative, and the second and fourth relations give $\left(\frac{dT}{dp}\right)_s$ negative and $\left(\frac{dq}{dp}\right)_T$ positive. We conclude that in such a substance *an increase of pressure causes cooling.*

The equations moreover give an exact numerical relation between the phenomena correlated by them. For example (124) may be stated quantitatively thus: "*The latent heat of expansion at constant temperature is equal to the product of the temperature into the rate of increase of pressure per unit increase of temperature at constant volume.*"

For a system defined by $n + 1$ variables viz: T or S, and either the n generalised coordinates $x_1, x_2, \ldots x_n$, or the corresponding generalised forces, $X_1, X_2, \ldots X_n$, we get $\frac{1}{2}(n+1)n$ independent relations from the condition of integrability of the differential of any thermodynamic potential.

We thus obtain the four sets

$$(132)\quad \begin{cases} \left(\frac{dT}{dx_1}\right)_{S,x_2} = -\left(\frac{dX_1}{dS}\right)_x, & \left(\frac{dX_1}{dx_2}\right)_{S,x_1} = \left(\frac{dX_2}{dx_1}\right)_{S,x_2}, \\ \left(\frac{dS}{dx_1}\right)_{T,x_2} = \left(\frac{dX_1}{dT}\right)_x, & \left(\frac{dX_1}{dx_2}\right)_{T,x_1} = \left(\frac{dX_2}{dx_1}\right)_{T,x_2}, \\ \left(\frac{dS}{dX_1}\right)_{T,X_2} = -\left(\frac{dx_1}{dT}\right)_X, & \left(\frac{dx_1}{dX_2}\right)_{T,X_1} = \left(\frac{dx_2}{dX_1}\right)_{T,X_2}, \\ \left(\frac{dT}{dX_1}\right)_{S,X_2} = \left(\frac{dx_1}{dS}\right)_X, & \left(\frac{dx_1}{dX_2}\right)_{S,X_1} = \left(\frac{dx_2}{dX_1}\right)_{S,X_2}. \end{cases}$$

As a further example, we may consider the case of an elastic wire subject to longitudinal tension only, here we obtain the following relations (see § 102 for notation)

$$\frac{1}{\varrho}\left(\frac{d\varepsilon_x}{ds}\right)_{\sigma_x} = -\left(\frac{dT}{d\sigma_x}\right)_S,$$

$$\frac{1}{\varrho}\left(\frac{d\varepsilon_x}{dT}\right)_{\sigma_x} = +\left(\frac{ds}{d\sigma_x}\right)_T.$$

These equations, like Maxwell's ordinary relations can be tested experimentally. For example the last equation but one asserts that a sudden (adiabatic) increase of tension will increase or lower the temperature of a wire according as the addition of heat produces contraction or elongation under constant tension. The former is the case in caoutchouc.

115. Geometrical proof. Maxwell's four relations may also be deduced from the property that the areas of the pressure-volume and temperature-entropy diagrams corresponding to a Carnot's cycle are equal and therefore, substituting these variables in equations (41) each member becomes numerically equal to unity. The question of sign is easily settled.

116. Expression in terms of thermodynamic potentials. A further simplification and coordination of formula is effected by expressing all the thermodynamic magnitudes in terms of one of the thermodynamic potentials and its derivatives with respect to the corresponding independent variables. There being four potentials for a simple system, every expression can thus be expressed in four different ways, and there will be a close analogy between the expressions for (e. g.) the specific heat at constant pressure referred to independent variables p, T and potential $\mathfrak{f}_{pT}$ and the specific heat at constant volume referred to independent variables v, T and potential $\mathfrak{f}_{vT}$. For the sake of brevity we only consider here expressions in terms of the two more important potential functions $\mathfrak{f}_v$ and $\mathfrak{f}_p$ (referred to unit mass) in which the temperature is the other independent variable, and these we write side by side in order to being out more clearly the kind of principle of duality between them.

$\mathfrak{f}_v$-Formulae.	$\mathfrak{f}_p$-Formulae.
Specific heat at constant volume	Specific heat at constant pressure
$\gamma_v = \left(\frac{dq}{dT}\right)_v = T\left(\frac{ds}{dT}\right)_v = -T\frac{\partial^2 \mathfrak{f}_v}{\partial T^2}.$	$\gamma_p = \left(\frac{dq}{dT}\right)_p = T\left(\frac{ds}{dT}\right)_p = T\frac{\partial^2 \mathfrak{f}_p}{\partial T^2}.$
Specific heat at constant pressure	Specific heat at constant volume

$$\gamma_p = T\left(\frac{ds}{dT}\right)_p$$
$$= T\frac{\frac{\partial s}{\partial T}\frac{\partial p}{\partial v} - \frac{\partial s}{\partial v}\frac{\partial p}{\partial T}}{\frac{\partial p}{\partial v}}$$

(by Chapter III Formula 40d)

$$\gamma_p = -T\frac{\frac{\partial^2 f_v}{\partial T^2}\frac{\partial^2 f_v}{\partial v^2} - \left(\frac{\partial^2 f_v}{\partial T \partial v}\right)^2}{\frac{\partial^2 f_v}{\partial v^2}}$$

moreover

$$\gamma_p - \gamma_v = T\frac{\left(\frac{\partial^2 f_v}{\partial T \partial v}\right)^2}{\frac{\partial^2 f_v}{\partial v^2}} = -T\frac{\left(\frac{\partial p}{\partial T}\right)^2}{\frac{\partial p}{\partial v}}.$$

Latent heat of expansion, at constant temperature

$$l_v = T\frac{\partial s}{\partial v} = -T\frac{\partial^2 f_v}{\partial T \partial v},$$

$$l_p = \frac{l_v}{\left(\frac{dp}{dv}\right)_T} = +T\frac{\frac{\partial^2 f_v}{\partial T \partial v}}{\frac{\partial^2 f_v}{\partial v^2}}.$$

Coefficient of Expansion under constant pressure

$$\alpha = \frac{1}{v}\left(\frac{dv}{dT}\right)_p.$$

For constant p we have found

$$0 = \frac{\partial^2 f_v}{\partial v \partial T} + \frac{\partial^2 f_v}{\partial v^2}\left(\frac{dv}{dT}\right)_p$$

whence

$$\alpha = -\frac{\frac{\partial^2 f_v}{\partial v \partial T}}{v\frac{\partial^2 f_v}{\partial v^2}}$$

on the other hand α' as just defined opposite is given by

$$\alpha' = \frac{1}{p}\left(\frac{dp}{dT}\right)_v = \frac{\frac{\partial^2 f_v}{\partial v \partial T}}{\frac{\partial f_v}{\partial v}}.$$

$$\gamma_v = T\left(\frac{ds}{dT}\right)_v$$
$$= T\frac{\frac{\partial s}{\partial T}\frac{\partial v}{\partial p} - \frac{\partial s}{\partial p}\frac{\partial v}{\partial T}}{\frac{\partial v}{\partial p}}$$

(by Chapter III Formula 40d)

$$\gamma_v = -T\frac{\frac{\partial^2 f_p}{\partial T^2}\frac{\partial^2 f_p}{\partial p^2} - \left(\frac{\partial^2 f_p}{\partial T \partial p}\right)^2}{\frac{\partial^2 f_p}{\partial p^2}}$$

moreover

$$\gamma_v - \gamma_p = T\frac{\left(\frac{\partial^2 f_p}{\partial T \partial p}\right)^2}{\frac{\partial^2 f_p}{\partial p^2}} = +T\frac{\left(\frac{\partial v}{\partial T}\right)^2}{\frac{\partial v}{\partial p}}$$

Latent heat of pressure-variation at constant temperature

$$l_p = T\frac{\partial s}{\partial p} = -T\frac{\partial^2 f_p}{\partial T \partial p},$$

$$l_v = \frac{l_p}{\left(\frac{dv}{dp}\right)_T} = -T\frac{\frac{\partial^2 f_p}{\partial T \partial p}}{\frac{\partial^2 f_v}{\partial p^2}}.$$

Temperature Coefficient of pressure at constant volume (similarly defined to α)

$$\alpha' = \frac{1}{p}\left(\frac{dp}{dT}\right)_v.$$

For constant v

$$0 = \frac{\partial^2 f_p}{\partial p \partial T} + \frac{\partial^2 f_p}{\partial p^2}\left(\frac{dp}{dT}\right)_v$$

whence

$$\alpha' = -\frac{\frac{\partial^2 f_p}{\partial p \partial T}}{p\frac{\partial^2 f_p}{\partial p^2}}$$

on the other hand the coefficient of expansion is given by

$$\alpha = \frac{1}{v}\left(\frac{dv}{dT}\right)_p = \frac{\frac{\partial^2 f_p}{\partial p \partial T}}{\frac{\partial f_p}{\partial p}}.$$

At constant temperature

$$\frac{\partial p}{\partial v} = -\frac{\partial^2 \mathsf{f}_v}{\partial v^2}.$$

The modulus of elasticity is therefore

$$e_T = v\left(\frac{dp}{dv}\right)_T = -v\frac{\partial^2 \mathsf{f}}{\partial v^2}.$$

The modulus of elasticity at constant entropy is $v\left(\frac{dp}{dv}\right)_s$ whence by Chap. III Formula (40d)

$$\left(\frac{dp}{dv}\right)_s = \frac{\frac{\partial p}{\partial v}\frac{\partial s}{\partial T} - \frac{\partial p}{\partial T}\frac{\partial s}{\partial v}}{\frac{\partial s}{\partial T}} = -\frac{\frac{\partial^2 \mathsf{f}_v}{\partial T^2}\frac{\partial^2 \mathsf{f}_v}{\partial v^2} - \left(\frac{\partial^2 \mathsf{f}_v}{\partial v \partial T}\right)^2}{\frac{\partial^2 \mathsf{f}_v}{\partial T^2}}.$$

To transform any other partial differential coefficient we refer to T and v as variables by the formulae of § 34 and finally substitute

$$s = -\frac{\partial \mathsf{f}_v}{\partial T}, \quad p = -\frac{\partial \mathsf{f}_v}{\partial v}.$$

At constant temperature

$$\frac{\partial v}{\partial p} = +\frac{\partial^2 \mathsf{f}_p}{\partial p^2}.$$

The modulus of elasticity is therefore

$$e_T = v\left(\frac{dv}{dp}\right)_T = \frac{\frac{\partial \mathsf{f}}{\partial p}}{\frac{\partial^2 \mathsf{f}}{\partial p^2}}.$$

The modulus of elasticity at constant entropy is $v\left(\frac{dp}{dv}\right)_s$, or $\frac{\frac{\partial \mathsf{f}}{\partial p}}{\left(\frac{dv}{dp}\right)_s}$ where

$$\left(\frac{dv}{dp}\right)_s = \frac{\frac{\partial v}{\partial p}\frac{\partial s}{\partial T} - \frac{\partial v}{\partial T}\frac{\partial s}{\partial p}}{\frac{\partial s}{\partial T}} = +\frac{\frac{\partial^2 \mathsf{f}_p}{\partial T^2}\frac{\partial^2 \mathsf{f}_p}{\partial p^2} - \left(\frac{\partial^2 \mathsf{f}_p}{\partial p \partial T}\right)^2}{\frac{\partial^2 \mathsf{f}_p}{\partial T^2}}.$$

To transform any other partial differential coefficient we refer to T and p as variables by the formulae of § 34 and finally substitute

$$s = -\frac{\partial \mathsf{f}_p}{\partial T}, \quad v = +\frac{\partial \mathsf{f}_p}{\partial p}.$$

117. Modifications in certain irreversible processes. The expressions for dq in § 112 are assumed on the hypothesis that the small change (dp, dv, dT) is reversible and that dq represents heat communicated to the system from without. The six coefficients $\gamma_v, l_v, \ldots$ are definite functions of any two of the variables (p, v, T) by which the state of the system is defined.

In the case of intrinsically irreversible processes by which heat is converted into work in the interior of the system, by friction, viscosity, or other causes, (as explained in § 81) our formulae require to be reconsidered and modified.

As a general rule a system does not remain homogeneous under such circumstances, and moreover its parts are usually in motion

among themselves. We may however apply the usual methods of analysis by supposing the system divided into differential mass elements. The kinetic energy of dm due to the motion will be a quantity kdm in which k is calculable by the methods of hydrodynamics. Moreover the intrinsic volume v of unit mass has a definite value for every differential element, and we shall assume the same is true of temperature T, and that the temperature at a point is the same in all directions. The following investigation will then refer to the progress of events in a differential mass-element of the system.

If the substance when at rest obeys the equation

$$f(p, v, t) = 0$$

this equation can be used to define the pressure at any point at any instant; in the case of a viscous fluid this will be the mean pressure considered in the theory of viscosity, and will be different from the actual stresses at that point.

If instead of dq we write $d\mathfrak{q}$ in equations (27, 28, 30), for example

$$d\mathfrak{q} = l_v dv + \gamma_v dT \tag{133}$$

$d\mathfrak{q}$ represents the quantity of heat which would be required to produce the transformation (dv, dT) by perfectly reversible processes.

We use dq as usual to denote the quantity of heat received from without, and we may put

$$d\mathfrak{q} = dq + dh. \tag{134}$$

The quantity dh, in accordance with § 81 will be defined as the quantity of heat generated in the interior of the system, and we notice that it is given by

$$dh = l_v dv + \gamma_v dT - dq. \tag{135}$$

Let dw be the external work done by the substance, k the kinetic energy due to the motion of its parts among themselves. Then if we put

$$d\varepsilon = dq - dw \tag{136}$$

$d\varepsilon$ represents the quantity of energy communicated to the substance from without.

Again if we put

$$du = d\mathfrak{q} - pdv = (l_v - p)dv + \gamma_v dT \tag{137}$$

du represents the increase in the intrinsic energy of the substance, i. e., in the energy depending on its volume and temperature. Because the coefficients l_v and γ_v are functions of v and T defined by the equations of reversible thermodynamics, du is the perfect differential of a function u, which is the same function of v and T as in reversible thermodynamics.

Now the energy communicated to the system from without is partly converted into kinetic energy of agitation, and partly into intrinsic energy, therefore by the Principle of Conservation of Energy

$$d\varepsilon = dk + du. \tag{138}$$

Hence

$$dq - dw = dk + d\mathfrak{q} - pdv, \tag{139}$$

whence

$$pdv - dw = dk + dh. \tag{140}$$

If the initial and final kinetic energy is zero we have

$$\int pdv - \int dw = \int dh. \tag{141}$$

The left hand side of this equation represents the quantity of work energy lost in the interior of the system, and the right hand the quantity of "internal heat" generated irreversibly in the system, and we notice that these are equal, as they should be.

The difference between $\int pdv$ and $\int dw$ may represent work done in agitating or stirring the system as in *Joule*'s experiment, or it may represent work energy lost by the substance in flowing from a place of higher to one of lower pressure, as in the case of a gas rushing suddenly into a vacuum or passing through a porous plug.

It will thus be seen that the equations which we have obtained so far are consistent with (a) the principle of Conservation of Energy, and also with (b) the axiom that the intrinsic energy of a simple system (excluding kinetic energy of agitation) is a function of its volume and temperature alone.

We shall now show how equally consistent results can be obtained in connection with the entropy-properties of the particular system under consideration. If we put

$$ds = \frac{l_v dv + \gamma_v dT}{T} \tag{142}$$

ds will represent the change of entropy per unit mass if the transformation dv, dT is reversible. On the hypothesis that the entropy of the system at any instant depends on the actual state of the system at that instant and not on its previous heating, we must assume the above expression to represent the change of entropy whatever be the means by which the change is effected, so that we now have with the above definition of $d\mathfrak{q}$

$$ds = \frac{d\mathfrak{q}}{T}. \tag{143}$$

The entropy per unit mass imported into the system from without is equal to $d\sigma$ where

(144) $$d\sigma = \frac{dq}{T}.$$

The difference represents the entropy per unit mass generated in the system and is by (134, 140) given by

(145) $$ds - d\sigma = \frac{dh}{T} = \frac{pdv - dw - dk}{T}$$

or

(146) $$ds = \frac{pdv - dw - dk + dq}{T}.$$

Now let T be taken as the standard temperature of a refrigerator used in defining available energy.

Then $pdv - dw$ denotes the quantity of potential energy lost in the interior of the system, and this energy is all available energy. Also $-dk$ represents the loss of kinetic energy which by previous conventions is to be regarded also as available energy, hence $pdv - dw - dk$ represents the total quantity of energy rendered unavailable within the system. Also dq represents energy imported into the system which is unavailable at temperature T. Hence $pdv - dw - dk + dq$ represents the total increase of energy which is unavailable at temperature T, and therefore

(147) $$ds = \frac{\textit{increase of energy unavailable at temperature } T}{T}.$$

Hence the entropy defined by (142) satisfies Definition 2 of Chapter VII, and conversely if Definition 2 be assumed the entropy will satisfy equation (142) and will be a function only of the coordinates (v, T) of the system, and its change in any small transformation (dv, dT) will be independent of whether that transformation is a reversible one or an irreversible one of the particular kind here considered.

CHAPTER XII.

PERFECT GASES.

118. Definitions of a perfect gas. The earliest experiments with gases led to the inference that the majority of gases obey the following laws, provided that their states as regards pressure and temperature differ considerably from that at which they liquefy.

1. *Boyle's Law* or *Mariotte's Law.* When the temperature is constant the volume varies inversely as the pressure. Hence $pv =$ constant when $T =$ constant, whence generally

(A) $$pv = f(T), \text{ a function of } T.$$

2. *Joule's Law.* All the work done in compressing a gas at constant temperature is converted into heat, and conversely when the gas expands at constant temperature the quantity of heat absorbed is equal to the quantity of work done.

3. *Clausius' Law.* The specific heat of a gas at constant volume is independent of the temperature.

More exact experiments show these laws to be only approximate (Chapter I § 10) but the properties of gases are greatly elucidated by studying what would happen in an ideal substance which obeyed them exactly.

A *perfect gas* is an ideal substance which can be defined in two ways. According to one definition, a perfect gas is considered to be a substance which conforms accurately to the first and second of these laws, according to the other definition, adopted by Clausius, a perfect gas is considered to be a substance which obeys all three laws.

119. Expansion of a perfect gas. We shall now deduce the principal properties of a perfect gas assuming in the first instance that it obeys Boyle's and Joule's Law only. When a unit mass of the gas expands slowly at constant temperature we have by putting $dT = 0$ in equation (27)

$$dq = l_v dv.$$

But from Joule's Law in this case

$$dq = p dv$$

therefore

$$l_v = p. \tag{148}$$

From Clapeyron's Equation (22) however

$$\left(\frac{dp}{dT}\right)_v = \frac{l_v}{T} = \frac{p}{T}. \tag{149}$$

By integration it follows that when v is constant p is proportional to T. Next, supposing v may vary, and combining this result with Boyle's Law, we have pv proportional to T or

$$pv = BT. \tag{150}$$

It follows that the absolute temperature of a perfect gas is proportional to the volume when the pressure is constant, and to the pressure when the volume is constant. The coefficient of cubical expansion of a gas at constant pressure is given by

$$\alpha_p \equiv \frac{1}{v}\left(\frac{dv}{dT}\right)_p = \frac{1}{T} \tag{151}$$

and therefore *at the same temperature, this coefficient of cubical expansion is the same for all perfect gases.* This result is known as *Charles'* or *Gay Lussac's* Law.

A perfect gas contained in a vessel in which it could expand or contract at constant pressure, would therefore constitute a thermometer for the measurement of absolute temperature, the volume of the gas being proportional to the absolute temperature. A second method would be to keep the volume constant, and take the pressure as a measure of the absolute temperature.

When an actual thermometer is thus constructed with any real gas, we obtain a *constant-pressure* or *constant-volume gas thermometer*; a convenient plan is to employ ordinary air, giving an *air-thermometer* (cf. Chap. I § 2). From the considerations discussed above such a thermometer only gives an *approximate* absolute scale of temperature, the degree of approximation of this scale depending on the degree of approximation with which Boyle's and Joule's Laws are satisfied.

120. The Universal Gas Constant. In the first place it is obvious that the constant B for any gas is inversely proportional to the density of that gas at given temperature and pressure.

In the second place it is readily proved from the dynamical theory of gases that in a medium consisting of a large number n of molecules moving about in all directions, the average kinetic energy of a molecule being L

$$pV = nL$$

and further for mixtures of different molecules L is the same for each kind, so that L may be put proportional to the temperature. If then M is the molecular weight of the gas, i. e. the ratio of the mass of a *molecule* of the gas to an *atom* of hydrogen it follows that (1) at given temperature and pressure, the number of molecules n occurring in a unit volume is constant, (2) the mass of unit volume is proportional to M, and (3) the volume of unit mass is therefore proportional to $\frac{1}{M}$. Hence if $B = \frac{R}{M}$ R will be a universal constant which has the same value for all gases. If moreover we write $v' = Mv$, then v' is the so-called *molecular volume* of the chemist, and with this notation we may write (150) in the form

$$pv' = RT. \tag{152}$$

121. Specific Heats. In the first place we notice that

$$l_p = l_v \left(\frac{dv}{dp}\right)_T = p \cdot \left(-\frac{v}{p}\right) = -v. \tag{153}$$

Again substituting $l_v = p$ in the equation for the energy

$$du = dq - pdv = \gamma_v dT + (l_v - p)dv$$

we have

$$du = \gamma_v dT; \tag{154}$$

$$\left(\frac{du}{dv}\right)_T = 0. \tag{155}$$

Therefore u and also γ_v are functions of T only. That is: *The specific heat at constant volume and the internal energy are functions of the temperature alone.*

Again from (32)

$$\gamma_p - \gamma_v = l_r \left(\frac{dv}{dT}\right)_p = p\frac{B}{p} = B. \tag{156}$$

That is *the difference of the specific heats is for the same perfect gas a constant.* For different gases the differences of the specific heats are inversely proportional to the molecular weights.

If, moreover the gas satisfies *Clausius'* Law (this has not so far been assumed), *the two specific heats are both constant*, and moreover the intrinsic energy of unit mass of the gas is given by

$$u = \gamma_v T + u_0. \tag{157}$$

We should *naturally* take the constant u_0 to be zero, i. e. assume that at the zero of absolute temperature the energy would vanish. It must not however be forgotten that a gas might possess forms of energy other than those considered in Thermodynamics, which did not vanish at the absolute zero of temperature. So long as we are dealing with a purely hypothetical substance we may assume any such property we like, but this is not justifiable if a perfect gas is intended as an approximation to an actual gas.

The equation of the adiabatics referred to p, v as coordinates is most easily obtained from the property that the ratio of the elasticities is equal to the ratio of the specific heats, i. e.

$$\left(\frac{dp}{dv}\right)_S = \varkappa \left(\frac{dp}{dv}\right)_T = -\varkappa \frac{p}{v}.$$

By integration we obtain *Poisson's* equation

$$pv^{\varkappa} = \text{constant}. \tag{158}$$

The same property enables the specific heat ratio $\varkappa$ to be found for any gas (not necessarily a perfect gas). This can be done in many ways, one of the simplest in principle being by determining the velocity of sound waves (a) in the gas, which, by the theory of sound, is given by $a^2 = -v^2\left(\frac{dp}{dv}\right)_S$. If the value of $\left(\frac{dp}{dv}\right)_T$ is found by experiments on the compression of the gas (Boyle's Law not being necessarily assumed) $\varkappa$ is at once obtained. For most ordinary gases such as air or hydrogen $\varkappa = 1{\cdot}40$ approximately, a result partly justified by the Kinetic Theory.

122. Thermodynamic Potentials. To find the entropy, energy and thermodynamic potentials per unit mass of a perfect gas satisfying *Clausius'* Law we have

$$ds = \frac{dq}{T} = \gamma_v \frac{dT}{T} + p\frac{dv}{T}$$

$$= \gamma_v \frac{dT}{T} + B\frac{dv}{v},$$

$$\therefore\ s = \gamma_v \log T + B \log v + s_0 \tag{159}$$

where s_0 is the arbitrary constant of integration.

Again

$$u = \gamma_v T + u_0,$$

$$\therefore\ \mathfrak{f}_v = u - Ts$$

$$= \gamma_v T + u_0 - T(\gamma_v \log T + B \log v + s_0)$$

$$= \gamma_v T(1 - \log T) - BT \log v + u_0 - Ts_0 \tag{160}$$

similarly

$$\mathfrak{f}_p = \mathfrak{f}_v + pv,$$

which when expressed in terms of T and p only becomes

$$\mathfrak{f}_p = \gamma_p T(1 - \log T) + BT \log p + u_0 - T\sigma_0 \tag{161}$$

where the constant σ_0 is equal to $s_0 + B \log B$.

It is to be noticed that the expressions for the entropy in terms of pressure and temperature or pressure and volume are

$$s = \gamma_p \log T - B \log p + \sigma_0, \tag{162}$$

$$s = \gamma_v \log p + \gamma_p \log v + \xi_0, \tag{163}$$

where

$$\xi_0 = s_0 - \gamma_v \log B = \sigma_0 - \gamma_p \log v.$$

Finally the thermodynamic potential $\mathfrak{f}_{sv}$, which is the energy expressed in terms of the volume and entropy, is given (for unit mass) by

$$\mathfrak{f}_{sv} = u = \gamma_v \left(\frac{e^{s-s_0}}{v^B}\right)^{\frac{1}{\gamma}} + u_0 \tag{164}$$

123. Case of a gas rushing into a vacuum. Joule's Law, as stated in § 111 was originally proved by the following experiment, due to Joule: Two vessels V' and V'' were taken, one V' containing air and the other V'' exhausted. They were connected by a stopcock and immersed in a reservoir of water. On opening the stopcock gas rushed from V' into V'' till the pressure was equal in the two vessels, and it was found (though later experiments showed the result to be only approximate) that no change of temperature occurred in the water. Hence (a) the temperature of the gas was unaltered, and (b) no heat was absorbed or emitted by the gas, so that no energy either in the form of work or heat passed in or out of the whole

space $V' + V''$. The whole energy of the gas when at volume V' was therefore equal to its whole energy at volume $V' + V''$ at the same temperature, and hence the energy of a given mass of gas at given temperature was independent of the volume. Taking the expression

$$du = (l_v - p)dv + \gamma_v dT$$

this gives $l_v = p$ as in § 112.

The relation between the increase of entropy due to the irreversible expansion and the quantity of energy rendered unavailable is readily verified. Taking a unit mass of gas and putting v_1 for V', v_2 for $V' + V''$, the work of expansion at temperature T

$$= \int_{v_1}^{v_2} p\,dv = \int_{v_1}^{v_2} \frac{BT}{v}\,dv = BT(\log v_2 - \log v_1).$$

This energy is all converted into a form which is unavailable at temperature T, and is equal (as it should be) to T times the increase of entropy, the latter increase being, by (159)

$$B(\log v_2 - \log v_1).$$

124. Gas mixtures. The definitions of a perfect gas in § 118 define only the properties of a *single* gas. Consistently with these definitions and in view of the fact that a perfect gas is a purely hypothetical substance, we *might* assume the mixing of two or more gases to obey any laws we chose to assume, but the investigation would be uninteresting unless (a) the laws were of the simplest possible kind, and (b) they were verified at any rate approximately in the case of actual gases.

In order that two gases may be mixed gradually, and without any accompanying mechanical or thermal effects, they must be first brought to the same temperature and pressure, and on communication being made between the vessels the mixture will take place slowly by diffusion. Experience with common gases then shows that, approximately, the temperature and pressure are unaltered by the process of diffusion, and therefore we assume the following as one *definition of a mixture of perfect gases:*

When two or more gases mix slowly by diffusion at a given temperature and pressure, their volume remains constant and no heat is absorbed or given out.

A corollary of this assumption is known as *Dalton*'s law and states that: *The pressure of a mixture of gases at volume V and temperature T is the sum of the partial pressures which the various constituent parts would separately produce if enclosed in a volume V at temperature T.*

For if V' and V'' are the total volumes of the two parts before mixing at temperature T and pressure p, the pressures which the parts would have at the same temperature and at volume V equal to $V' + V''$ would by the Boyle Mariotte Law be

$$\frac{pV'}{V' + V''} \quad \text{and} \quad \frac{pV''}{V' + V''},$$

and the sum of these is equal to p.

Let $m', m'', \ldots$ be the masses of the different components entering into a unit mass of the mixture. In the case of a mixture of two gases only we may write $m' = x$, $m'' = 1 - x$. Let accented letters such as v' and v'' denote the volumes per unit mass, and other thermodynamic quantities of the gases before mixing, and let unaccented letters refer to a unit mass of the mixture. Then if the mixing takes place at temperature T and pressure p

$$pv' = B'T, \quad pv'' = B''T$$

and

$$v = m'v' + m''v'' = xv' + (1 - x)v''.$$

Hence

$$pv = xpv' + (1 - x)pv''$$

$$= xB'T + (1 - x)B''T. \tag{165}$$

Hence the constant B for the mixture is given by

$$B = xB' + (1 - x)B''. \tag{166}$$

We now assume that the total energy of the gases is unaltered by mixing, i. e. that

$$u = xu' + (1 - x)u''.$$

Employing the expression $u = \gamma_v T + u_0$ (157), and remembering that the last result is true for all values of T, we have

$$u_0 = xu_0' + (1 - x)u_0'', \tag{167}$$

$$\gamma_v = x\gamma_v' + (1 - x)\gamma_v'' \tag{168}$$

and in virtue of (156)

$$\gamma_p = x\gamma_p' + (1 - x)\gamma_p'' \tag{169}$$

whence *the whole heat capacity of the mixture either at constant pressure or at constant volume is the sum of the whole heat capacities of the parts before mixing.*

Substituting in the expression for the entropy in terms of pressure and temperature, we have

$$s = \{x\gamma_p' + (1 - x)\gamma_p''\} \log T - \{xB' + (1 - x)B''\} \log p + \sigma_0, \tag{170}$$

that is the *whole entropy of the mixture can only differ by a constant from the sum of the whole entropies of the parts before mixing.* The constant difference C is given by

$$C = \sigma_0 - \{x\sigma_0' + (1 - x)\sigma_0''\}. \tag{171}$$

From the laws of thermodynamics, this difference cannot be negative. As two gases at equal pressure and temperature in general tend to mix by diffusion, not to separate, the process of diffusion is irreversible, and we cannot ascertain at the present stage whether the change of entropy C vanishes or is positive. In order that any definite conclusions may be found it is necessary that the gases should be capable of being separated as well as mixed by reversible methods. In the case of actual gases the separation may be effected by liquefying one of the components or by placing the mixture in the presence of a liquid which readily absorbs one component but not the other. What we have shown is that *if an increase of entropy takes place on mixing, this change is independent of the temperature and pressure at which mixing takes place.*

This conclusion is justified by the following general reasoning: It comes to the same thing whether we allow the gases to mix at temperature T_1 and pressure p_1, or first alter their temperature and pressure to T_2, p_2, then let them mix and finally bring the mixture back to T_1, p_1.

It is further to be observed that as the thermodynamic phenomena presented by a given system are unaffected by the values of the integration constants in its energy and entropy, the value of the constant C does not affect any transformations which are unaccompanied by mixing or separation of the gases.

125. Substituting in the formula for the thermodynamic potential $\mathfrak{f}_p$, this is given in terms of the corresponding potentials of the separate components at the same temperature and pressure by

$$\mathfrak{f}_p = x\mathfrak{f}_p' + (1-x)\mathfrak{f}_p'' - CT$$

subject to the condition $p = p' = p''$.

If we require the entropy as a function of v and T or the thermodynamical potential $\mathfrak{f}_v$ the best way is to express s_0 for the mixture in terms of σ_0 in equations (159, 160) which become

$$s = \gamma_v \log T + B \log\left(\frac{v}{B}\right) + \sigma_0, \tag{172}$$

$$\mathfrak{f}_v = \gamma_v T(1 - \log T) - BT \log\left(\frac{v}{B}\right) + u_0 - T\sigma_0. \tag{173}$$

The corresponding expressions for the components are of course of the same form with accented letters. The condition of equal pressure for the mixture and components is given by

$$\frac{v}{B} = \frac{v'}{B'} = \frac{v''}{B''}. \tag{174}$$

If this condition is satisfied we have undoubtedly

$$\mathfrak{f}_v = x\mathfrak{f}_v' + (1-x)\mathfrak{f}_v'' - CT \tag{175}$$

a relation connecting the thermodynamic potentials $\mathfrak{f}_v$ of the mixture with those of its components at the same pressure.

126. Physical evidence as to the value of the constant C. (a) *From liquefaction of one of the components.* We assume the following law as based on experiment:

When a liquid or solid is in contact with its vapour at any given temperature, and the vapour is mixed with other gases, the partial pressure of the vapour is the same as if the other gases were absent.

Thus if a vessel contains air and water at a given temperature, the partial pressure of the water vapour mixed with the air is the same as the pressure of the vapour in contact with the water would be if the air were exhausted. The actual pressure in the mixture is the sum of the partial pressures of the air and the vapour. The density of the vapour is the same in both cases.

Now let there be a mixture of two gases G_1, G_2, of which G_1 is more readily liquefied than G_2, and let the original whole volume of the mixture be V.

Let the mixture be cooled till the components separate out in the liquid form, one liquefying before the other and the two being kept separated. Let the components be then evaporated in separate vessels. Then in the course of evaporation the partial pressures p_1 and p_2 of the component gases at any temperature T are the same functions of T in the separated gases as in the mixture.

Assume further that the volumes of the liquids are negligible by comparison with those of their vapours.

Then the work done in compressing the mixture at any temperature will be equal to the works of expansion of the parts at the same temperature, if the volume of each part is equal to the previous volume of the mixture, as is evident from the relation $(p_1+p_2)dV = p_1dV + p_2dV$. Again, *assuming the constancy of the specific heats,* the heat given out in cooling the mixture by an amount dT is equal to the heat absorbed in raising the components through the same temperature interval.

Assume further that the latent heat of evaporation of either component is unaffected by the presence or absence of the other.

Then, if the separate constituents be finally each brought to volume V, the entropy changes in the processes of expansion will exactly balance those in the processes of condensation, and the whole process will be perfectly reversible and we conclude that:

The whole entropy of a mixture of gases at temperature T and volume V is equal to the sum of the whole entropies of the separate components at the same *temperature* and *whole volume V*.

Remembering that when the gases were allowed to mix by diffusion, the pressures of the components were equal to that of the mixture, and the whole volumes V', V'' were together equal to the volume of the mixture we see that:

When two gases at equal temperature and pressure mix by diffusion, the loss of available energy and consequent gain of entropy is the same as would occur if each component were to expand by rushing into a vacuum till it occupied the same volume as the mixture.

(b) *From diffusion through a membrane.* There are certain substances which allow some gases to pass through them more easily than others, and these lead to the conception of an ideal substance which is pervious to one gas and perfectly impervious to another.

In this case we make use of the result of experiment, according to which:

When a gas is in equilibrium on the two sides of a membrane through which it can pass freely, the partial pressures of the gas are the same on both sides, even if the gas is mixed with other gases on one side only, so that the total pressures on the two sides are different.

By means of two ideal membranes, one of which is pervious only to one component and the other pervious to the other component we could separate or recombine the two gases reversibly without expenditure or absorption of work, the volumes of the separated gases would then be equal to that of the mixture and the pressures of the separated gases would be equal respectively to their partial pressures in the mixture We conclude that under these circumstances the whole entropy of the mixture would be equal to the sum of those of the separated gases.

127. Corrected Relations between the Potentials. Value of *C*. We now see that the relations between the potentials per unit mass of the mixture and its constituents are connected by the relations

$$\text{(176)} \qquad \mathfrak{f}_v = x\mathfrak{f}_v' + (1-x)\mathfrak{f}_v''$$

$$\text{(177)} \qquad \mathfrak{f}_p = x\mathfrak{f}_p' + (1-x)\mathfrak{f}_p''$$

provided that the *whole volumes of the mixture and the two components are equal.* The volumes and pressures per unit mass are then connected by the relations

$$v = xv' = (1-x)v'',$$

$$\frac{p}{B} = \frac{p'}{xB'} = \frac{p''}{(1-x)B''},$$

the last necessarily involving the relation,

$$p = p' + p'', \quad \text{since} \quad B = xB' + (1-x)B''.$$

It is easily seen that the constant C in the previous equations is equal to

$$(178) \quad B \log B - xB' \log xB' - (1-x)B'' \log \{(1-x)B''\}.$$

This may be written

$$(179) \quad C = xB' \log \frac{xB' + (1-x)B''}{xB'} + (1-x)B'' \log \frac{xB' + (1-x)B''}{(1-x)B''}$$

and is obviously positive, the arguments of the logarithms both being greater than unity.

As a matter of fact these formulae are cumbersome to remember, and it is much more convenient to remember the statement that

The whole thermodynamic potential of a gas mixture at given volume or pressure is the sum of the corresponding potentials of the components at the same temperature and whole volume.

The same is also true of the whole energy of the gas mixture. The energy of a perfect gas depending only on its temperature, it makes no difference so far as energy is concerned whether the gases are mixed as in § 124 or as in § 126.

128. **Note.** The *qualitative* property that diffusion through a membrane may give rise to mechanical effects in the form of differences of pressure is of course easily verified. Since these differences can be utilised for the production of external work, although everything is at the same temperature, it follows that the separate gases possess available energy which is lost when the gases are mixed by diffusion *without* a membrane by the method of § 124. In regard to the difficulty of making *quantitative* experiments, experience does warrant the belief that a gas never passes through a membrane from a lower to a higher partial pressure even when the pressure of another gas would tend to force it through. In evidence of this property, *Planck* quotes his remarkable experiments made at Munich in 1883, in which a platinum tube originally containing hydrogen at atmospheric pressure was heated till the platinum became permeable to hydrogen, and it was found that almost the whole of the contents diffused out leaving a high vacuum.

It is obvious too that the ideal "semi-permeable partition" (so called) postulated above would afford the maximum efficiency either in separating mixed gases or in obtaining mechanical work from them while mixing. Moreover an actual partition or membrane will be the less efficient the more its properties differ from the ideal membrane. But this difference must be regarded as a peculiarity of the membrane and not of the gases, and the entropy changes caused by an imperfectly efficient membrane must be regarded as distinct from those necessarily associated with the gases themselves.

CHAPTER XIII.

DETERMINATION OF THERMODYNAMICAL MAGNITUDES.

129. Determination of absolute Temperature. Hitherto we have regarded absolute temperature, entropy, energy and thermodynamical potentials from a purely theoretical stand-point. We now proceed to show that these quantities can be determined experimentally for any particular substance.

The definition of absolute temperature in thermodynamics being a purely theoretical one, it remains to be shown that absolute temperatures are capable of being determined experimentally. The actual details of the experiments belong to the experimental study of heat rather than to theoretical thermodynamics; what we have to show is that the determinations can be effected by methods that are experimentally practicable.

Most of these methods depend on Clapeyron's equation or its analogue, which may be written

$$(180) \qquad \left(\frac{dp}{d \log T}\right)_v = l_v, \quad \left(\frac{dv}{d \log T}\right)_p = -l_p$$

in which it must not be forgotten that the latent heat l_v and coefficient l_p are referred to the work unit of heat and are obtained from the corresponding coefficients referred to the calorie by multiplying by the "mechanical equivalent" of the calorie, the determination of which was discussed in Chap. II.

The form of equations (180) indicates the presence of an arbitrary constant of integration in the value of $\log T$, giving an arbitrary factor in the value of T; corresponding to the fact (§ 28) that the thermodynamic definition does not determine the unit or degree of absolute temperature but merely the ratio of the absolute temperatures of two different states of a substance.

We have seen in the last chapter that a perfect gas would afford a measure of absolute temperature when used either as a constant pressure or a constant volume gas thermometer. If therefore an actual gas is used in either of these forms the small corrections which will have to be supplied to reduce its readings to the absolute scale will depend on

(a) the deviation of the (p, v) equation of its isothermals from the Boyle Mariotte Law,

(b) the deviations from Joule's Law.

Now the determination of the isothermal equation so far as is postulated above does not presuppose a knowledge of the absolute

scale, for constancy of temperature can be shown by any thermometer whatever. If t is the measure of temperature indicated by such a thermometer, it is obviously experimentally possible to determine for the gas an equation of the form

$$f(p, v, t) = 0 \tag{181}$$

in which t is a definite but for the present unknown function of the absolute temperature T. As an example of the result of such a determination we might cite *Van der Waals'* empirical formula in the form

$$\left(p + \frac{a}{v^2}\right)(v - b) = \varphi(T) \tag{182}$$

the form of $\varphi(T)$ being as yet undetermined.

To determine the deviations from Joule's Law one of the most usual methods is that adopted in the classical experiments of *Joule* and *Kelvin* of which we now proceed to give such details of principle as are necessary to understand the theory.

130. The porous plug experiments. A gas is allowed to flow steadily through a tube containing a series of holes or a porous plug in traversing which it undergoes a fall of pressure, and a certain quantity of mechanical work is done against the friction of the plug, the viscosity of the gas etc., the exact nature of such internal resistances being immaterial. We thus have a case of irreversible conversion of work into heat, and instead of the equations of reversible thermodynamics, the modifications of § 112 are applicable. The effects observed consist generally speaking in a cooling of the gas which can be determined quantitatively in two ways:

(a) The gas may be kept at its original temperature by enclosing the apparatus in a calorimeter, and the quantity of heat absorbed for every unit mass of gas that flows through the plug may be measured by the calorimeter and finally reduced to work units.

(b) The pipe and plugs may be enclosed in a non-conducting envelope, the gas receiving no heat from without, and the difference of temperature on the two sides of the plug may be measured by an ordinary thermometer.

The kinetic energy of the in- and outflowing gas is usually small enough to be neglected though, if desired, a correction for this could be easily applied.

(a) Taking the first method, let p_1, v_1 and p_2, v_2 be the pressure and volume of unit mass of the gas before and after passing the plug, q the heat which it absorbs from the calorimeter. To form an estimate of the external work done in forcing the gas through the plug, it may be assumed that moveable pistons are placed in the

tube before and behind the plug, by which the pressures on both sides are kept constant and the total mass of gas also kept constant. When a unit mass of gas flows through the plug work $p_1 v_1$ is done in pushing in the back piston, and work $p_2 v_2$ is done by the issuing gas in pushing the back piston out, hence energy $p_1 v_1 - p_2 v_2$ is supplied from without in this way. Moreover, energy q is supplied from the calorimeter. Hence the total quantity of energy supplied from without is $p_1 v_1 - p_2 v_2 + q$. At the end of the process the only visible result is that there is a unit mass less of gas at the back and a unit mass more gas at the front of the plug. Moreover the flow being steady, the energy of every unit mass at the back of the plug always remains the same, and the energy of every unit mass in front of the plug always remains the same. The principle of conservation of energy now leads to the inevitable conclusion[1]) that the intrinsic energies of the unit mass in front and the unit mass behind the plug must differ by an amount given by

$$u_2 - u_1 = p_1 v_1 - p_2 v_2 + q. \tag{183}$$

Again, the intrinsic energy of a gas depends only on its actual state, and the initial and final temperatures are equal. Hence the change of energy $u_2 - u_1$ must be the same as in an isothermal reversible transformation between the same two states. By the formula

$$\begin{aligned} du &= \gamma_v dT + (l_v - p)dv \\ &= \gamma_p dT + l_p dp - p dv \end{aligned}$$

we get therefore

$$u_2 - u_1 = \left(\int_{v_1}^{v_2} (l_v - p)\, dv \right)_T = \left(\int_{p_1}^{p_2} l_p dp - \int_{v_1}^{v_2} p dv \right)_T. \tag{184}$$

Substituting in (183) we obtain the two forms

$$q = (p_2 v_2 - p_1 v_1) + \int_{v_1}^{v_2} (l_v - p)\, dv, \tag{185}$$

$$q = \int_{p_1}^{p_2} (l_p + v)\, dp = - \int_{p_2}^{p_1} (l_p + v)\, dp. \tag{186}$$

For a perfect gas $p_2 v_2 = p_1 v_1$, $l_v = p$, $l_p = -v$, whence

$$q = 0, \tag{187}$$

1) This conclusion could easily be verified by assuming any simple law of frictional resistance in passing through the tube, remembering to add in a quantity of heat equal to the work lost in overcoming friction.

hence for ordinary gases q is small. Taking (186) we have on differentiation (remembering $p_1 > p_2$)

$$\frac{dq}{dp} = -(l_p + v) \tag{188}$$

where $\frac{dq}{dp}$ measures the "cooling effect" expressed as the ratio of the absorbed heat to the fall of pressure when the latter is small. Calling this quantity χ we have by (124)

$$\left(\frac{dv}{d \log T}\right)_p = v + \chi \tag{189}$$

or

$$\left\{d \log T = \frac{dv}{v + \chi}\right\}_{p \text{ const.}} \tag{190}$$

If for any given pressure p, the coefficient χ has been determined as a function of v, the above equation when integrated between suitable limits will give the ratio of the absolute temperatures corresponding to any two volumes of the gas contained in *a constant pressure gas thermometer*. As χ is small compared with v, various approximate methods can be adopted according to the particular case considered. Thus if between certain limits χ may be taken to be constant, the integral of the equation between these limits is of the form

$$T \propto v + \chi. \tag{191}$$

But if t is the temperature in a constant pressure gas thermometer

$$t \propto v$$

and if we suppose $t = \mu v$, equation (191) shows that the absolute zero is below the zero of gas temperature by an amount $\mu\chi$ or $\frac{t\chi}{v}$.

In like manner taking equation (185) we have

$$\frac{dq}{dv} = \frac{d(pv)}{dv} + l_v - p \tag{192}$$

or

$$\frac{dq}{dv} - \frac{d(pv)}{dv} = + \left(\frac{dp}{d \log T}\right)_v - p. \tag{193}$$

This equation might be used to find the corrections to the readings of a *constant volume gas thermometer*, but it will be seen that the correction depends on two terms, one $\frac{dq}{dv}$, representing the "cooling effect", and the other $\frac{d(pv)}{dv}$, representing the deviations from Boyle's Law, and both these terms may be equally important.

If the gas neither gains nor loses heat we have

$$u_2 - u_1 = p_1 v_1 - p_2 v_2 \tag{194}$$

whence the transformation satisfies the condition $u + pv =$ constant or $\mathfrak{H} =$ constant.

But

$$du = \gamma_p dT + l_p dp - p dv$$

hence substituting we have

$$\int \{\gamma_p dT + (l_p + v) dp\} = 0 \tag{195}$$

or for a small change of state

$$\gamma_p dT = -(l_p + v) dp. \tag{196}$$

To avoid introducing absolute temperature the left hand side may be put equal to $c_p dt$, where dt is the observed change of temperature on the scale of the thermometer used in the experiment, and c_p the specific heat at constant pressure referred to the same scale. Moreover if $c_p dt$ is now put equal to dq, dq will represent the heat which would have to be taken from a calorimeter to bring the gas back to its original temperature, and hence if $\frac{dq}{dp}$ be put equal to χ, this is the same measure of the cooling effect as in the previous case. In other words, cooling effect takes the form of a fall of temperature in the gas itself instead of an absorption of heat from the calorimeter, and the method is practically the same. A difference would of course exist between the two cases if the change of temperature were considerable.

131. Comparison with the case of a gas rushing into a vacuum. It is to be observed that while the porous plug experiment gives the correction for the *constant pressure* gas thermometer, *Joule*'s original experiment of a gas rushing into vacuum gives the correction for the *constant volume thermometer*. In that experiment the energy remains constant hence

$$\gamma_v dT + (l_v - p) dv = 0. \tag{197}$$

Writing

$$\chi' = -\frac{\gamma_v dT}{dv} = -\frac{c_v dt}{dv} \tag{198}$$

χ' affords a measure of the cooling effect and the equation becomes

$$\left\{\frac{dp}{d \log T}\right\}_v = p + \chi'. \tag{199}$$

With this method the correction for the *constant pressure* thermometer would contain terms depending on the deviations from Boyle's Law, which could not be neglected.

132. Inversion of the porous plug effect. It will be noticed that the cooling effect χ vanishes if

$$\left(\frac{dv}{d \log T}\right)_p = v \quad \text{or} \quad \left(\frac{dv}{dT}\right)_p = \frac{v}{T}.$$

If we assume as our known data, the (p, v, T) equation of a gas, and take any two of these variables as coordinates of a point in a plane, the present equation determines a curve in that plane which may be called the *curve of inversion*. This curve separates those states in which the cooling effect is positive from those in which it is negative. If we take v and T as our independent variables, the curve of inversion is obviously the locus of the points of contact of tangents drawn from the origin to the family of curves $p = \text{constant}$.

Secondly if the curve of inversion be determined experimentally the data may be utilised in determining the (p, v, T) equation of the gas.

Thirdly if the (p, v, t) equation of the gas referred to any arbitrary scale of temperature and its curve of inversion are known, we have sufficient data for comparing the assumed scale of temperature with the absolute scale. This method would really constitute a "null method" of determining absolute temperature since it depends on the vanishing of the cooling effect and not on determinations of its amount.

133. Determination of Entropy, Energy and Thermodynamical Potentials. The scale of absolute temperature having now been fixed, it follows that temperatures may be measured on any thermometer and reduced to absolute measure. It now remains to show how the entropy, energy, and thermodynamic potentials of a substance (which we take to be a simple system such as a gas or liquid) can be expressed in terms of quantities which can be experimentally determined.

Substituting from (123, 124) the values of l_p and l_v in the differentials of the entropy and energy we obtain on integration from state (p_0, v_0, T_0) to state (p_1, v_1, T_1):

With v and T as variables

$$s_1 - s_0 = \int_{v_0, T_0}^{v_1, T_1} \left\{ \frac{\gamma_v}{T} dT + \left(\frac{dp}{dT}\right)_v dv \right\}$$

$$u_1 - u_0 = \int_{v_0, T_0}^{v_1, T_1} \left\{ \gamma_v dT + \left(T \frac{\partial p}{\partial T} - p\right) dv \right\}.$$

With p, T as variables

$$s_1 - s_0 = \int_{p_0, T_0}^{p_1, T_1} \left\{ \frac{\gamma_p}{T} dT - \left(\frac{dv}{dT}\right)_p dp \right\}$$

$$(u_1 + p_1 v_1) - (u_0 + p_0 v_0) = \int_{p_0, T_0}^{p_1, T_1} \left\{ \gamma_p dT + \left(p - T \frac{\partial v}{\partial T}\right) dp \right\}.$$

Now the changes of entropy and energy depend only on the initial and final states, hence we may perform the integration along any path representing a continuous series of transformations from the initial to the final states. Thus

(1) Taking v and T as variables we may integrate keeping $v = v_0$ from $T = T_0$ to $T = T_1$ and then integrate keeping $T = T_1$ from $v = v_0$ to $v = v_1$. We thus obtain

$$(200) \qquad s_1 - s_0 = \left(\int_{T_0}^{T_1} \frac{\gamma_v}{T} dT\right)_{v=v_0} + \left(\int_{v_0}^{v_1} \left(\frac{\partial p}{\partial T}\right) dv\right)_{T=T_1},$$

$$(201) \qquad u_1 - u_0 = \left(\int_{T_0}^{T_1} \gamma_v dT\right)_{v=v_0} + \left(\int_{v_0}^{v_1} \left(T\frac{\partial p}{\partial T} - p\right) dv\right)_{T=T_1},$$

$$(202) \quad \mathfrak{f}_{v_1} - \mathfrak{f}_{v_0} = \left(\int_{T_0}^{T_1} \gamma_v \left(1 - \frac{T_1}{T}\right) dT\right)_{v=v_0} - (T_1 - T_0)s_0 - \left(\int_{v_0}^{v_1} p dv\right)_{T=T_1}.$$

(2) Similarly with p and T as variables keeping first p and then T constant, we have

$$(203) \qquad s - s_0 = \left(\int_{T_0}^{T_1} \frac{\gamma_p}{T} dT\right)_{p=p_0} + \left(\int_{p_0}^{p_1} \left(\frac{\partial v}{\partial T}\right) dp\right)_{T=T_1},$$

$$(204) \qquad (u_1 + p_1 v_1) - (u_0 + p_0 v_0) = \left(\int_{T_0}^{T_1} \gamma_p dT\right)_{p=p_0} + \left(\int_{p_0}^{p_1} \left(v - T\frac{\partial v}{\partial T}\right) dp\right)_{T=T_1}$$

and an expression for $\mathfrak{f}_{p_1} - \mathfrak{f}_{p_0}$ closely analogous to (202).

Now we may choose the state $p_0 v_0 T_0$ to be a standard state of the system with which other states are compared. The corresponding values of $s_0 u_0$ will be undetermined and will represent the unknown constants of integration which necessarily occur in the expressions for the entropy and energy of a system, and the above equations will then give the entropy and energy in any other state represented by the suffix 1.

On examination of the integrals we see that

In order that the entropy, energy, and thermodynamic potentials of a simple system may be determined for every possible state of that system, it is sufficient to know

(1) *The p, v, T equation of the system,*

and either

(2a) *The relation connecting the specific heat γ_v with the absolute temperature T when the specific volume remains constant and equal to v_0,*

or

(2b) *The relation connecting the specific heat γ_p with the absolute temperature T when the pressure remains constant and equal to p_0.*

We notice, moreover, that *the entropy, energy, and thermodynamic potentials of a simple system can each be expressed as the sum of two terms, one a function of v and T, or p and T determined completely by the form of the (p, v, T) equation, and the other a function of T alone, depending on the expression for the specific heat.*

134. Geometrical Interpretations. Taking for example v and T as variables and representing them as the coordinates of a point in a plane, the first of these conditions may be stated as follows:

In order that the thermodynamic properties of a simple system may be completely defined within any assigned limits of volume and temperature, it is necessary and sufficient that

(1) The pressure should be known at all points of the (v, T) *plane* within the assigned limits.

(2) The specific heat γ_v should be known at all points lying along a *straight line* $v =$ constant $(= v_0$, say) lying within the assigned limits.

The values of γ_v along any *other* line $v = v_1$ are completely determined by the assumed data. They are most easily deduced from the equation

$$\left(\frac{d\gamma_v}{dv}\right)_T = T\left(\frac{d^2p}{dT^2}\right)_v$$

which gives on integration along a line of constant temperature $T = T_1$

$$\gamma_v(v_1 T_1) - \gamma_v(v_0 T_1) = T_1\left(\int_{v_0}^{v_1}\left(\frac{d^2p}{dT^2}\right)_v dv\right)_{T=T_1} \tag{205}$$

and conversely, if we know γ_v at all points of the region considered we should know $\frac{\partial^2 p}{\partial T^2}$ and thus obtain a check on the correctness of our assumed expression for p in terms of v and T.

Exactly analogous results hold good if p and T are chosen as independent variables and as coordinates. The latter choice possesses an obvious advantage in the convenience of determining specific heats at a constant standard atmospheric pressure.

135. Advantages of a choice of method. It will thus be seen that the data which are necessary and sufficient to determine the thermodynamic properties of a substance fall considerably short of those which are capable of being determined experimentally with greater or less accuracy. A complete discussion of the advantages and disadvantages of different methods belongs to the study of experimental heat and would be out of place here. It will be sufficient to point out that the possibilities thus opened up have two important advantages

(1) by enabling those methods to be adopted which are best adapted for accurate experimental observations,

(2) by enabling the same results to be obtained by different methods, thus affording a check on the accuracy of the various observations.

As an instance, of how to put the above results into practical form, we should notice in the expressions for the energy-differences that $\int \gamma_v dT$ and $\int \gamma_p dT$ represent the total quantities of heat required to raise the temperature from T_0 to T_1 at volume v_0 and pressure p_0. Moreover the entropy difference $s_1 - s_0$ could be obtained by starting with the substance in the state (p_1, v_1, T_1) allowing it to expand reversibly and adiabatically till its temperature was T_0 and then cooling at constant temperature T_0 till its volume and pressure were v_0 and p_0. The quantity of heat given out in the last transformation when divided by T_0 would give the required entropy difference.

136. Illustrative Example. Consider a gas which obeys van der Waals' Equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = BT$$

where a, b, B are constants. We obtain

$$\frac{\partial p}{\partial T} = \frac{B}{v-b}, \quad \frac{\partial^2 p}{\partial T^2} = 0, \quad T\frac{\partial p}{\partial T} - p = \frac{a}{v^2}.$$

It follows that

$$\frac{\partial \gamma_v}{\partial v} = 0,$$

γ_v = function of T only and

$$(206) \quad s = \int \gamma_v \frac{dT}{T} + B \log (v - b) + \text{constant } C_1,$$

$$(207) \quad u = \int \gamma_v dT - \frac{a}{v} + \text{constant } C_2,$$

$$(208) \quad \mathfrak{f}_v = \int \gamma_v dT - T\int \frac{\gamma_v}{T} dT - \frac{a}{v} BT \log (v - b) + C_2 - C_1 T$$

but owing to the fact that the (p, v, T) equation is a cubic in v, the expression for $\mathfrak{f}_p$ *in terms of* p *and* T could not be given in a simple form.

CHAPTER XIV.

CHANGES OF STATE OF AGGREGATION.

137. Phenomena deducible from the van der Waals' Equation. We shall now show how, by assigning suitable forms to the (p, v, T) equation of a working substance, the phenomena of liquefaction of gases and of the critical point can be represented analytically.

We start by supposing the substance to obey van der Waals' empirical equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = BT$$

a relation satisfied to a considerable degree of approximation by most gases. We suppose the family of isothermal curves $T =$ constant represented taking p and v as rectangular coordinates.

Writing this as a cubic equation in v

$$v^3 - \left(b + \frac{BT}{p}\right)v^2 + \frac{a}{p}v - \frac{ab}{p} = 0 \tag{209}$$

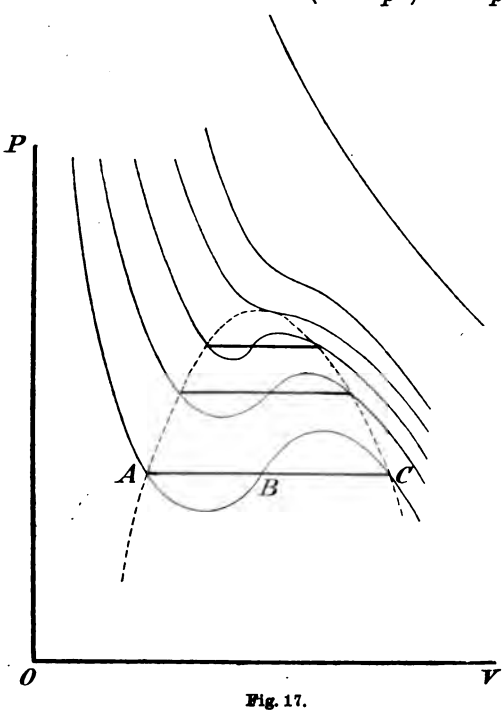

Fig. 17.

we see that the horizontal line $p =$ constant will cut the isothermal $T =$ constant in 3 or 1 real points according as the cubic has 3 or 1 real roots. In the former case, there would theoretically be three possible states at the given pressure and temperature corresponding to the points A, B, C (Fig. 17). But at B where the curve is ascending we have $\left(\frac{dp}{dv}\right)_T$ positive, hence (§ 92) the state B would be unstable, the effect of any slight deviation from uniform density being to cause the substance to flow from the points of lesser to those of greater density, and thus to separate into two stable phases represented by points on the descending parts of the curve.

It follows that if the isothermal line cuts *any* horizontal line in 3 real points, the substance, instead of following the curve in an

isothermal transformation, must undergo a discontinuous change of state, from the branch AD to the branch EC, while if the curve continually descends towards the axis $p = 0$ as v increases no such discontinuous change is possible. In the former case the sudden change reproduces the phenomena of liquefaction, in the latter case we have a perfectly continuous transformation similar to that observed when a gas is compressed at a temperature above its critical temperature (Chap. I § 20).

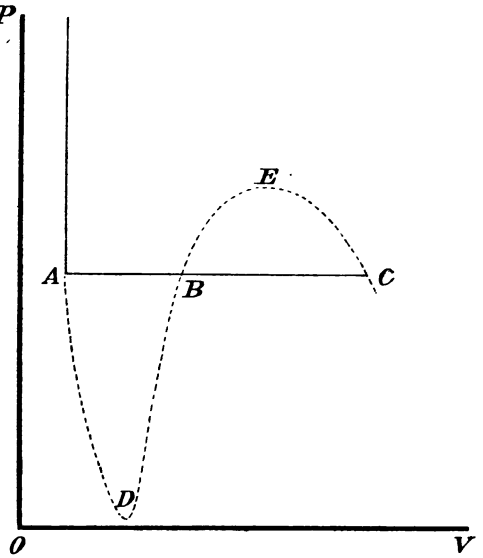

Fig. 18 (after Clausius).

The discontinuous transformation just vanishes when the isothermal line has a point of inflexion with a horizontal tangent. This point of inflexion is the critical point, and its coordinates determine the critical pressure, volume, and temperature which we denote by $p_c v_c T_c$.

At this point the cubic (209) has three equal roots each equal to v_c, hence

$$3v_c = b + \frac{BT_c}{p_c}, \quad 3v_c^2 = \frac{a}{p_c}, \quad v_c^3 = \frac{ab}{p_c}$$

giving

$$v_c = 3b, \quad p_c = \frac{a}{27b^2}, \quad T_c = \frac{8a}{27Bb} \tag{210}$$

conversely

$$b = \frac{v_c}{3}, \quad a = 3p_c v_c^2, \quad B = \frac{8}{3}\frac{p_c v_c}{T_c} \tag{211}$$

whence a, b, R can be determined if the critical pressure, volume, and temperature are known.

138. Properties peculiar to van der Waals' Equation. It will be observed in the first place that if *different* gases obey van der Waals' formula, their critical points must all satisfy the common relation

$$B = \frac{8}{3}\frac{p_c v_c}{T_c}.$$

Let π, ν, ϑ be the ratios of the pressure, volume, and temperature of the gas in any state to their critical values; these, which are called

the "reduced" pressure, volume, and temperature, will be the measures of these quantities taking their critical values for the particular gas considered to be the units. Then van der Waals' equation assumes the form

$$\left(\pi + \frac{3}{v^2}\right)\left(v - \frac{1}{3}\right) = \frac{8}{3}\vartheta \tag{212}$$

or

$$3\pi v^3 - (\pi + 8\vartheta)v^2 + 9v - 3 = 0. \tag{213}$$

This equation is independent of the gas considered and it follows that according to van der Waals' Law the isothermal curves of different gases are the same family of curves and differ only in the horizontal and vertical scales representing the pressure and volume.

139. Critical phenomena for other (p, v, T) equations. The general arguments of the last article but one as to the existence of discontinuous changes of state and critical points are not peculiar to van der Waals' Equation but lead to the following general conclusions:

(1) If for certain values of p, T, say p_1, T_1, the (p, v, T) equation of a substance when solved for v has three real roots, then when the substance is compressed or allowed to expand at temperature T_1 a discontinuous change of state must occur somewhere.

(2) If for some other value of T_1, say T_2, two of the roots remain imaginary for all values of p, the initial and final states corresponding to the discontinuous change can be connected by a continuous series of transformations by suitable changes of temperature.

(3) In this case a critical point will exist and will be determined by making *three* roots of the (pvT) transformation all equal.

(4) If the critical volume, pressure and temperature are known, we have three equations to determine the constants in the p, v, T equation of the gas.

For convenient reference we subjoin the following list of empirical equations that have been proposed by different physicists as representing approximately the (pvT) equations of imperfect gases. But of these it will be seen that the first three fail to account for liquefaction or critical phenomena; they have now been superseded, and are chiefly of historic interest

$$pv = BT - \frac{c}{vT} \quad (\textit{Rankine}^1) \tag{214}$$

$$\frac{pv}{T} = B - \frac{Kap}{3T^3} \quad (\textit{Joule \& Thomson}^2) \tag{215}$$

$$pv = BT\left(1 - \frac{B_T}{v}\right) \quad (\textit{Regnault}) \tag{216}$$

1) Phil. Trans. 1854. 2) Phil. Trans. 1862.

where B_T is a function of T, found to vary directly as the absolute temperature, and inversely as the pressure of saturated vapour at that temperature.

(217) $$\left\{p + \frac{C}{T(v+B)^2}\right\}(v-\alpha) = BT \quad (Clausius^1),$$

(218) $$pv = B\left\{1 + \frac{e}{v+\alpha}\right\}T + \frac{C}{v+\gamma} - \frac{A}{v+\alpha} \quad (Tait^2)$$

(219) $$p + \frac{v - \left[a + m(v-b) + \frac{c}{v-b}\right]T}{kv^2 - \alpha + n\sqrt{(v-B)^2+d^2}} = \frac{BT}{v} \quad (Amagat^3).$$

Finally *Dr. Kamerlingh Onnes*[4]) has abandoned the attempt to express the p, v, ϑ equation of a gas in a finite form, and has adopted infinite series involving negative powers of v.

If Clausius' Equation be assumed, the critical point is given by

(220) $$v_c = 3\alpha + 2B, \quad T_c^2 = \frac{8c}{27(\alpha+B)B}, \quad p_c^2 = \frac{cB}{216(\alpha+B)^2}$$

giving conversely

(221) $$\alpha = v_c - \frac{BT_c}{4p_c}, \quad B = \frac{3BT_c}{8p_c} - v_c, \quad C = \frac{27B^2T_c^2}{64p_c}.$$

With the virial equation of Tait the critical point is given by

(222) $$p_c = \frac{A - BeT_c}{(v_c+\alpha)^2} + \frac{C}{(v_c+\gamma)^2}, \quad 0 = \frac{A-BeT_c}{(v_c+\alpha)^3} - \frac{C}{(v_c+\gamma)^3}$$

whence

(223) $$A - BeT_c = \frac{p_c(v_c+\alpha)^3}{\alpha-\gamma}, \quad C = \frac{p_c(v_c+\gamma)^3}{\alpha-\gamma}$$

and it is also found that

(224) $$3v_c + \alpha + \gamma = \frac{BT_c}{p_c}$$

while by substitution the (p, v, T) equation becomes

(225) $$p = p_c\left\{1 - \frac{(v-v_c)^3}{v(v+\alpha)(v+\gamma)}\right\} + B\left\{1 + \frac{e}{v+\alpha}\right\}\frac{T-T_c}{v}$$

involving seven constants p_c, v_c, T_c, α, γ, e, B, connected by the single relation (225).

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1) Wied. Ann. 1880. Phil. Mag. 1880.
2) Foundations of the Kinetic Theory of Gases, Trans. R.S.E.
3) *Journal de Physique*, July 1899.
4) Leiden, Communications, 71.

140. Conditions of phase equilibrium. When two different phases of the same substance are in equilibrium with each other their pressures and temperatures are obviously equal, and we shall now show that the thermodynamic potentials $\mathfrak{f}_p$ of a unit mass in the two phases are also equal.

Let v', s', u', $\mathfrak{f}_p'$ be the volume, entropy, energy, and potential at given pressure per unit mass in one phase, say the higher phase (Chap. I, § 15), v'', s'', u'', $\mathfrak{f}_p''$ the corresponding quantities for the other phase. Then if a mass m passes from the first to the second phase by a *reversible* transformation at temperature T and pressure p the quantity of heat absorbed is $mT(s''-s')$, the work done by expansion is $mp(v''-v')$ and the increase of energy is $m(u''-u')$. Hence by conservation of energy

$$u''-u'=T(s''-s')-p(v''-v') \tag{226}$$

i. e.

$$u''-Ts''+pv''=u'-Ts'+pv' \tag{227}$$

or

$$\mathfrak{f}_p''=\mathfrak{f}_p'. \tag{228}$$

The same conclusion can be put into a more general form by considering the expression for the available energy of the complex when subjected to the condition of constant pressure and temperature. If m' and m'' are the masses of the substance in the two phases this available energy is by § 90 given by

$$A=m'\mathfrak{f}_p'+m''\mathfrak{f}_p''. \tag{229}$$

If $\mathfrak{f}_p'>\mathfrak{f}_p''$ A may be decreased by the transformation of part of the complex from the higher to the lower phase, and therefore this transformation will tend to take place and will be irreversible. Similarly if $\mathfrak{f}_p'<\mathfrak{f}_p''$ a transformation from the lower to the higher phase will tend to take place and will be irreversible.

The former case represents an instance of what is called a *supersaturated* complex, the latter of an *unsaturated* complex. For equilibrium we must have $\mathfrak{f}_p'=\mathfrak{f}_p''$ and the complex is then *saturated* (§ 15).

At the same time in an ordinary supersaturated or unsaturated complex, such as occurs with water and steam, when condensation or evaporation is taking place, the temperature is not necessarily uniform, nor is the pressure quite uniform when the parts are in rapid motion as when water is being boiled briskly. In no case does equilibrium exist except when p, T, $\mathfrak{f}_p$ are the same throughout the complex.

The thermodynamic potential $\mathfrak{f}_p$ involves two integration constants, one multiplied by T. But if the two phases can be connected by a

continuous series of transformations by passing above the critical temperature, these constants will be eliminated when we take the difference $\mathfrak{f}_p'' - \mathfrak{f}_p'$ at the *same* temperature and will not affect the form of the equilibrium equation $\mathfrak{f}_p'' = \mathfrak{f}_p'$.

This equation will therefore be a determinate equation in p and T, and if p and T be the coordinates of a point in a plane, the locus of the equation will be a curve in the (p, T) plane which is called the *curve of saturation*. By means of the (p, v, T) equation of the substance the corresponding curve of saturation can be transferred to the coordinates v, T or p, v.

141. Application to van der Waals' Equation. If the substance obeys van der Waals' Equation we have by § 116

$$\mathfrak{f}_p = \mathfrak{f}_v + pv = \int \gamma_v dT - T\int \frac{\gamma_v}{T} dT - \frac{a}{v} - BT\log(v-b) + C_1 - C_2 T + pv. \tag{230}$$

Here γ_v is a function of T alone. It is not impossible to conceive a substance where γ_v is a *different* function of T in the liquid and gaseous phases provided that is the same function of T for all values of v above the critical temperature. The following arguments would fail in such a case, we assume that γ_v is the same function of T in both. The equation $\mathfrak{f}_p' = \mathfrak{f}_p''$ then gives

$$p(v' - v'') = \frac{a}{v'} - \frac{a}{v''} + BT\log\frac{v'-b}{v''-b}. \tag{231}$$

This equation involves the two volumes v', v'' which are the greatest and least roots of the cubic (209), hence the elimination leads to a very cumbersome equation in (p, v) for the border curve. But writing the (p, v, T) equation in the form

$$p = \frac{BT}{v-b} - \frac{a}{v^2} \tag{232}$$

and assuming it to hold good for all values of p, v, T whether corresponding to possible states of the substance or not, the area of the curve $T =$ constant from $v = v'$ to $v = v''$ in the plane of (p, v) is equal to the right hand side, whereas the left hand side represents the corresponding area cut off by the line $p =$ constant between the same ordinates. We have thus the following rule: *Draw the isothermal curve for T, in the (p, v) plane and draw a horizontal line crossing it in such a position that the areas of the segments thus intercepted on the isothermal above and below this line are equal (Fig. 18).*

Then the points of intersection of this horizontal line with the isothermal will give the volumes and pressure at which change of phase occurs at temperature T.

The transformation will thus be represented by the horizontal line ABC instead of the curved line $ADBEC$ but the area swept out by the ordinate will be the same for both.

142. Extension of the Rule of Equal Areas. The same rule has been employed to fix the position of the horizontal lines in the (p, v) diagram of the isothermals in other cases than that afforded by van der Waals' Equation. Its generalisation is open to the objection that since the ascending parts of the isothermals represent unstable and therefore physically impossible states of the substance, no experimental data are available for tracing them, and it is clear that if these parts are merely filled in by drawing, the areas which they intercept on a horizontal line are perfectly arbitrary. We may get over the difficulty by stating the rule in the following form.

Let p and γ_v be two functions of v and T connected by the differential equation

$$\frac{\partial \gamma_v}{\partial v} = T\frac{\partial^2 p}{\partial T^2} \tag{233}$$

which are equal to the pressure and specific heat at constant volume of the substance over regions representing physically possible states, and which remain finite, single valued and continuous over the intermediate (or "unstable") region. Let the values of p for constant T be plotted in the (p, v) plane thus joining up the corresponding isothermals.

Then the horizontal line which intercepts segments of equal area on one of these curves will determine the points at which change of phase takes place.

Proof. From the above differential equation

$$\gamma_v dT + \left(T\frac{\partial p}{\partial T} - p\right)dv \quad \text{and} \quad \frac{\gamma_v}{T}dT + \frac{\partial p}{\partial T}dv$$

are perfect differentials throughout the whole region, therefore their integrals are the same taken along every curve joining the same two points in the (v, T) plane.

If the initial and final points represent physically possible states of the substance, the integrals must therefore represent the corresponding differences of energy and entropy respectively, whether the intermediate path passes through physically possible states only or not. We may therefore integrate across the unstable region along the path $T =$ constant and get

$$(234) \qquad u' - u'' = \left(\int_{v''}^{v'} \left(T \frac{\partial p}{\partial T} - p \right) dv \right)_T, \quad s' - s'' = \left(\int_{v''}^{v'} \frac{\partial p}{\partial T} dv \right)_T,$$

$$(235) \qquad \therefore \ \mathfrak{f}_v' - \mathfrak{f}_v'' = \left(- \int_{v''}^{v'} p dv \right)_T = - A$$

where A is the area of the isothermal between v'' and v'.

The condition of phase equilibrium is

$$(236) \qquad 0 = \mathfrak{f}_p' - \mathfrak{f}_p'' = (\mathfrak{f}_v' + pv') - (\mathfrak{f}_v'' + pv'')$$

or

$$(237) \qquad 0 = - A + p(v' - v'')$$

which is the rule of equal areas.

Example. Thus if Clausius' equation (217) be assumed equation (233) gives on integration

$$\gamma_v = \frac{2c}{T^2(v+B)} + f(T)$$

and if $f(T)$ is the same function of T in the liquid and gaseous states Clausius' equation may be assumed to hold across the gap separating the two states, and the rule becomes applicable and gives

$$(238) \qquad p = \frac{BT}{v' - v''} \log \frac{v' - \alpha}{v'' - \alpha} - \frac{c}{T(v'+B)(v''+B)}$$

where v' and v'' are the greatest and least roots of Clausius' equation when written as a cubic in v.

143. Metastable and essentially stable states. It is to be observed that the *descending* portions of the isothermal curves beyond the horizontal line may represent states of the substance which are physically possible if it exists only in one phase. Thus if $\mathfrak{f}_p' > \mathfrak{f}_p''$ the substance may exist in equilibrium in the higher phase if the lower phase is completely absent, but the presence of any quantity, however small, of the lower phase will destroy the equilibrium, and any disturbance may cause the substance to pass more or less suddenly into the lower phase. Such cases have been realised experimentally. This result does not of course apply to the *ascending* parts of the isothermal.

We may speak of the states in which $\mathfrak{f}_p$ is least as being *essentially stable*, to distinguish them from states which are only stable for continuous variations and whose equilibrium may be broken by a discontinuous change of phase. The latter are called *metastable*.

144. The Triple Point. The conditions of phase equilibrium when applied to a substance capable of existing in three different phases (as exemplified by the solid, liquid and gaseous states of matter), determine the phenomenon of the *triple point* (Chap. I § 18).

For if $\mathfrak{f}_p'$, $\mathfrak{f}_p''$, $\mathfrak{f}_p'''$ represent the potentials of the three phases expressed as functions of p and T, the condition of simultaneous equilibrium of the phases gives

$$\mathfrak{f}_p' = \mathfrak{f}_p'' = \mathfrak{f}_p''' . \tag{239}$$

We have thus two simultaneous equations which when solved give one or more values of p and T. This value or values are therefore finite in number.

A triple *line* could not in general exist, even if, owing to the peculiar forms of the potentials the two equations derived from (239) were not independent. For at points on either side of this line in the p, T plane, equilibrium would only be essentially stable in the phase for which $\mathfrak{f}_p$ was *least* (§ 140) and there could be only one phase on either side of the line satisfying this condition. An exception might occur if the potentials of two phases were equal over a finite area on one side of the line but the phases would then be thermodynamically identical.

If $\mathfrak{f}_p'$, $\mathfrak{f}_p''$, $\mathfrak{f}_p'''$ are the potentials of water in the gaseous, liquid and solid states, the p, T curves

$$\mathfrak{f}_p' = \mathfrak{f}_p'', \quad \mathfrak{f}_p'' = \mathfrak{f}_p''' \quad \text{and} \quad \mathfrak{f}_p''' = \mathfrak{f}_p' \tag{240}$$

are the so-called *steam line*, *ice line*, and *hoar-frost line*.

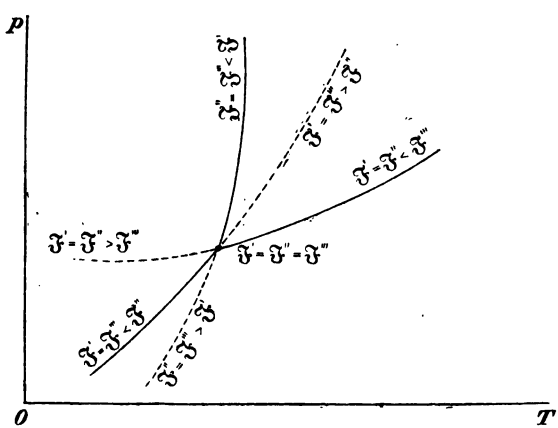

Fig. 19.

The three curves all pass through the triple point, but if they be produced through that point the produced parts do not in general represent essentially stable states of phase-equilibrium.

For if the line $\mathfrak{f}_p' = \mathfrak{f}_p''$ be produced through the triple point $\mathfrak{f}_p' - \mathfrak{f}_p'''$ vanishes and in general changes sign in passing that point. On the side on which $\mathfrak{f}_p'$ and $\mathfrak{f}_p'' < \mathfrak{f}_p'''$ equilibrium will be essentially stable between the first and second phases, but on the other side $\mathfrak{f}_p'$ and $\mathfrak{f}_p''$ will be

$> \mathfrak{f}_p'''$ and the substance will tend to pass into the *third* phase as the essentially stable condition.

Thus the three curves determine three regions about the triple point, and in the interior of each region only one phase can exist, namely, that with the lowest potential.

145. The Phase Rule for a single substance. When a substance can occur in *four* different phases a *quadruple point* does *not* in general exist. For equilibrium between four phases would require that the equations

$$\mathfrak{f}_p' = \mathfrak{f}_p'' = \mathfrak{f}_p''' = \mathfrak{f}_p''''$$

should be satisfied by the same values of p and T, and as we have three equations and only two variables this is in general impossible. If the forms of the potentials should happen to be such as to render the three equations consistent, a quadruple point would undoubtedly be formed, but it would be more correct to regard such a point as formed by the coincidence of *two*, and consequently of *four* triple points. Thus in general not more than three different phases of the same substance can coexist at the same pressure and temperature.

We thus arrive at the conclusions that so long as we are dealing with a single substance (1) *three* different phases can only coexist at one or more points in the plane of (p, T), (2) *two* phases may coexist along one or more *lines* in the (p, T) plane, (3) *one* phase can only exist at points lying within a certain *area* in the (p, T) plane.

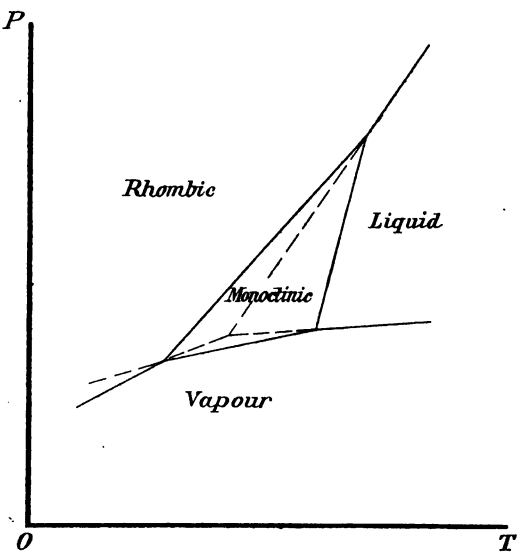

Fig. 20.

In the first case the system is called *avariant*, since neither the pressure nor the temperature can be varied without reducing the number of phases. In the second the system is called *univariant*, since *either* p or T may be varied if the other of these two variables is varied so that the point (p, T) moves along the proper line, in the third case the system is called *bivariant*, since either p or T can be varied independently provided that the point p, T does not pass

out of the region in which the phase considered exists in stable equilibrium.

Sulphur is a case in point. The substance can exist in four phases, two solid (monoclinic and rhombic), the liquid phase, and the gaseous phase. If the curves of equilibrium between the different phases in the (p, T) plane be drawn, as in Fig. 20, it is seen that the curves divide the plane of the diagram into 4 regions in which the systems are bivariant, bounded by six curves which correspond to univariant systems, the six curves intersecting in four triple points, at each of which the system is avariant.

The generalisations of these conclusions for the case where instead of a single substance, we have a number of different substances constitute the *Phase Rule* of Gibbs which is given in the next chapter.

146. Moutier's Rule. The distribution of the curves in the p, T plane in the neighbourhood of a triple point may be found by finding where they or their produced directions cut an isothermal line corresponding to a temperature differing from the triple temperature by a small amount ΔT. If Δp_{23} be the corresponding difference of pressure along the curve of separation $\mathfrak{f}_p'' - \mathfrak{f}_p''' = 0$ and Δp_{31}, Δp_{12} refer to the other curves, we have

$$(241) \qquad \left(\frac{d\mathfrak{f}''}{dp} - \frac{d\mathfrak{f}'''}{dp}\right)\Delta p_{23} + \left(\frac{d\mathfrak{f}''}{dT} - \frac{d\mathfrak{f}'''}{dT}\right)\Delta T = 0$$

and two similar equations. Now $\frac{d\mathfrak{f}'}{dp} = v'$ the volume of unit mass in the state $\mathfrak{f}_p'$, whence on substituting and adding we obtain

$$(242) \qquad (v'' - v''')\Delta p_{23} + (v''' - v')\Delta p_{31} + (v' - v'')\Delta p_{12} = 0$$

an equation equivalent to Moutier's three equations of the form

$$(243) \qquad (\Delta p_{31} - \Delta p_{23})(v''' - v') = (\Delta p_{12} - \Delta p_{23})(v'' - v').$$

If v', v'', v''' are in descending order of magnitude it follows that Δp_{31} is between Δp_{12} and Δp_{23}. Hence Moutier's rule, according to which *if a horizontal line* (T = constant) *be drawn cutting the three curves of transformation or their produced directions near the triple point the middle of the three points of section corresponds to the transformation involving the greatest change of volume.*

In like manner if a vertical line (p = constant) be drawn cutting the same curves or their produced directions near the triple point the middle of the points of section corresponds to the transformation involving the greatest change of entropy.

147. Properties of a saturated complex of two phases. We shall now show how the thermodynamical properties of a complex of two phases of the same substance considered as a whole can be expressed in terms of those of the substance in the separate phases.

Let M be the total mass of the complex, X and $M - X$ the masses of the portions in the two phases respectively, and let these phases be called by way of distinction the first and second phase. If we put $\frac{X}{M} = x$, then x and $1 - x$ will be *defined* to be the masses of the two phases in a unit mass of the complex, although this is of course a mere convention unless the whole mass of the complex is unity, because the complex is not homogeneous like a mixture of gases but the two phases are quite distinct and separate.

In the same way if V, U, S are the whole volume, energy and entropy, we may *define* $\frac{V}{M}, \frac{U}{M}, \frac{S}{M}$ as the volume, energy, and entropy of unit mass of the complex, these we denote by v, u, s, while we use accented letters $(v', u', s')(v'', u'', s'')$ to denote the volume, energy, and entropy per unit mass in the first and second phases respectively. It will be convenient in understanding what follows to suppose that the mass of the complex is actually equal to unity, though this is not necessary.

In the first place we notice that the complex like a simple system admits of two independent variations.

(1) The temperature may be varied without altering the masses x, $1 - x$ of the components. In this case the corresponding variation of pressure is determined by the condition of saturation

$$f_p' = f_p''$$

which we shall denote for convenience by the equation

$$G(p, T) = 0. \tag{244}$$

(2) The composition of the complex may be altered by the transformation of a quantity dx or Δx of matter from the second to the first phase — or *vice versa*, — the temperature, and consequently the pressure remaining constant. The volume, energy and entropy will in general be altered, and heat will be absorbed or given out. If $\lambda \Delta x$ is the quantity of heat absorbed in the transformation of Δx, whether this quantity be small or finite, λ will be the latent heat of transformation *from* the second *to* the first phase (Chap. I § 15).

The state of the complex is thus defined by the two independent variables T and x, and the difference from an ordinary simple system is that the equation $G(p, T) = 0$ takes the place of a relation between the *three* quantities p, v, T.

Since the *whole* volume, energy, and entropy of the complex are respectively equal to the sums of the corresponding *whole* volumes, energies, and entropies of the components we have

$$v = xv' + (1 - x)v'', \tag{245}$$

$$u = xu' + (1 - x)u'', \tag{246}$$

$$s = xs' + (1 - x)s''. \tag{247}$$

Consider now the effect of the transformation Δx at constant temperature T. We have from (245) and (247)

$$\Delta v = (v' - v'')\Delta x, \quad \Delta s = (s' - s'')\Delta x \tag{248}$$

and from above

$$\Delta q = \lambda \Delta x \tag{249}$$

where Δq is the absorbed heat. But

$$\frac{\Delta q}{\Delta v} = l_v, \quad \frac{\Delta q}{T} = \Delta s \tag{250}$$

where l_v is the latent heat of expansion of the complex.

Hence as in Chap. I § 16

$$l_v = \frac{\lambda}{v' - v''} \tag{251}$$

and further

$$s' - s'' = \frac{\lambda}{T}. \tag{252}$$

Clapeyron's Equation

$$\left(\frac{dp}{dT}\right)_v = \frac{l_v}{T},$$

when taken in conjunction with (251) gives

$$\frac{dp}{dT} = \frac{\lambda}{(v' - v'')T} \tag{253}$$

where the condition $v =$ constant is no longer required in the expression for $\frac{dp}{dT}$, because since the complex is saturated p is a function of T alone, and the differential coefficient in question is the same as would be obtained from $G(p, T) = 0$.

In the above work we have used the symbol Δ to denote variations which may be finite. In the more general case where the temperature also varies we are restricted however to infinitesimal changes. We now put for the added heat dq

$$dq = \lambda dx + x\gamma' dT + (1 - x)\gamma'' dT \tag{254}$$

where γ', γ'' are the specific heats of the two components in a state of saturation.

Thus we should have γ', γ'' connected with the specific heats γ_p', γ_p'' at constant pressure and latent heat coefficients l_p', l_p'' by the formulae

$$\gamma' = \gamma_p' + l_p' \left(\frac{dp}{dT}\right), \quad \gamma'' = \gamma_p'' + l_p'' \left(\frac{dp}{dT}\right).$$

Since $\frac{dq}{T}$ is a perfect differential we have

$$\frac{\partial}{\partial T}\left(\frac{\lambda}{T}\right) = \frac{\partial}{\partial x}\left\{\frac{x\gamma' + (1-x)\gamma''}{T}\right\} \tag{255}$$

whence

$$\frac{\partial \lambda}{\partial T} - \frac{\lambda}{T} = \gamma' - \gamma'' \tag{256}$$

a formula due to Clausius.

148. Applications. From (253) we see that increase of pressure will raise or lower the temperature of transformation according as latent heat is absorbed in passing from the state of lesser to that of greater specific volume or the reverse. The former is the case with water and steam, the latter with ice and water.

Let us next consider the effects of a sudden adiabatic compression. Putting $dq = 0$ in (254) we have

$$dx = -\frac{x\gamma' + (1-x)\gamma''}{\lambda} dT$$

$$= -\frac{x\gamma' + (1-x)\gamma''}{\lambda} \frac{v' - v''}{\lambda} T dp \tag{257}$$

and the sign of the coefficient of dp on the right hand side determines whether the effect of an increase of pressure will transform part of the complex from the second to the first phase or conversely.

If γ' and γ'' are both positive it is clear that dx and dp will be of opposite signs if $v' > v''$ and conversely. This means that increase of pressure transforms part of the complex from the phase of greater to that of less volume. For example, in a saturated complex of ice and water compression causes liquefaction.

If γ' is negative (as is the case for steam) and γ'' positive the same conclusion holds good if $x\gamma' + (1-x)\gamma''$ is positive, but the effect is reversed if this expression is negative. It appears that the effect will depend on the proportion of the two components, a slight adiabatic compression causing transformation to the phase of greater or less volume or no change according as

$$x < \frac{\gamma''}{\gamma' - \gamma''} \quad \text{or} \quad x > \frac{\gamma''}{\gamma' - \gamma''} \quad \text{or} \quad x = \frac{\gamma''}{\gamma' - \gamma''}.$$

The effect of a small change of temperature at constant volume may be discussed by means of the equation $v = xv' + (1-x)v''$, which gives on differentiation with v constant

$$dx(v' - v'') = dT\left(x\frac{\partial v'}{\partial T} + (1-x)\frac{\partial v''}{\partial T}\right) \tag{258}$$

a relation leading to conclusions closely similar in their general character to those just found.

Finally the relation between latent heat and temperature is given by

$$\frac{\partial \lambda}{\partial T} = \frac{\lambda}{T} + \gamma' - \gamma''. \tag{259}$$

If $\gamma' > \gamma''$ (as is the case with water and ice) the latent heat necessarily increases with the temperature. As another example if $\frac{\partial \lambda}{\partial T}$ is negative and $\frac{\lambda}{T} > \gamma''$, then γ' must be negative. This result is verified in the case of steam.

149. Properties at the Triple Point. If we have three phases of a substance in equilibrium at the triple point, p and T will both be constant. If the total mass is unity, the masses of the phases being x, y, $1 - x - y$, we have equations of the form

$$v = xv' + yv'' + (1-x-y)v''',$$
$$u = xu' + yu'' + (1-x-y)u''',$$
$$s = xs' + ys'' + (1-x-y)s'''.$$

The temperature being constant the specific heats do not enter into the question, but we get

$$dq = \lambda_{31}dx + \lambda_{32}dy \tag{260}$$

where λ_{31}, λ_{32} are the latent heats absorbed in passing from the third to the first and second states respectively. With this notation we should evidently write $\lambda_{31} = -\lambda_{13}$ and

$$\lambda_{23} + \lambda_{31} + \lambda_{12} = 0. \tag{261}$$

The complex involves two independent variables x and y. These are determined if v and s are known. Hence the composition of the complex can be varied by altering the volume or by adding or withdrawing heat so as to alter the entropy, and these variations may be made independent of one another. The variations dx, dy produced by these changes are in fact given by the equations

$$(v' - v''')dx + (v'' - v''')dy = dv \tag{262}$$

and

$$\lambda_{31}dx + \lambda_{32}dy = dq = Tds \tag{263}$$

or

$$(264) \qquad (s' - s''')dx + (s'' - s''')dy = ds$$

of which the last two are equivalent in virtue of the equations

$$(265) \qquad s' - s''' = \frac{\lambda_{31}}{T}, \quad s'' - s''' = \frac{\lambda_{32}}{T}.$$

The latent heat of expansion $\frac{\partial q}{\partial v}$ depends on the ratio of dx to dy and is indefinite. This is in agreement with Clapeyron's equation in which $\frac{\partial p}{\partial T}$ takes the form $\frac{0}{0}$.

CHAPTER XV.

PHASE EQUILIBRIUM WITH MORE THAN ONE SUBSTANCE.

150. Partial potentials of the constituents of a mixture. In this chapter we shall show how the methods of Thermodynamics can be applied to a mixture or compound of various substances when account is taken of variations in the composition of the mixture. This is the investigation first published by Gibbs under the title "Equilibrium of Heterogeneous Systems".

Suppose that a homogeneous mixture which we shall call our *system* is formed of masses $M_a, M_b, M_c, \ldots M_k$ of k different substances which we may call $A, B, C, \ldots K$ and that this mixture is at uniform pressure p and temperature T, the whole volume being V. Then so long as the mixture remains homogeneous (as is here assumed) the only independent variations of which it is capable of undergoing are

(a) variations in the masses $M_a, M_b, \ldots M_k$ of the constituents,

(b) variations of the whole volume V,

(c) variations produced by adding or withdrawing a quantity of heat dQ, i. e. variations of entropy.

It follows that the state of the system when homogeneous can be completely specified by the masses $M_a, M_b, \ldots M_k$, the whole volume V and the whole entropy S.

By the extended principle of Conservation of Energy (Chapter V) we regard it as an axiom that an entity exists called the whole energy of the system and that this energy U is a function of the variables above mentioned, i. e., that an equation exists for the system, of the form

$$(266) \qquad U = f(S, V, M_a, M_b, \ldots M_k)$$

by which its whole energy U is defined.

The variation of U is thus given by

$$dU = \frac{\partial U}{\partial S} dS + \frac{\partial U}{\partial V} dV + \sum \frac{\partial U}{\partial M_k} dM_k. \tag{267}$$

When the masses $M_a, M_b, \ldots M_k$ are kept constant the system behaves as a simple system for which

$$dU = TdS - pdV, \quad \therefore \frac{\partial U}{\partial S} = T, \quad \frac{\partial U}{\partial V} = -p. \tag{268}$$

If we write

$$\frac{\partial U}{\partial M_k} = \mu_k,$$

the differential of the energy assumes the form

$$dU = TdS - pdV + \sum \mu_k dM_k. \tag{269}$$

The coefficient μ_k is called the *partial potential* of the substance K in the mixture, or, according to Gibbs, simply its *potential*. From this we obtain the following definition in words.

Let the mass of the substance K in the mixture be increased by the differential quantity dM_k without altering the total volume or entropy of the mixture, and let the corresponding increase of total energy be $\mu_k dM_k$. Then μ_k is said to be the partial potential of the substance K in the mixture in question.

To increase the mass of one of the constituents without altering the whole entropy of the system we may conceive the mass dM_k added at temperature T equal to that of the system and a quantity of heat withdrawn equal to T times the gain of entropy caused by the addition in question.

151. Expression for the whole thermodynamical potential $\mathfrak{F}_P$ in terms of the partial potentials of the constituents. In the next place we notice that the assumption that the system is a *homogeneous mixture* imposes a certain limitation on the form of the function f by which the energy is expressed.

For the condition of being homogeneous involves the property that if different quantities of the same mixture be taken, the whole volume, entropy, and energy and the masses of the constituents are proportional to the quantities, that is, more exactly, to the whole masses of the mixture in question.

Hence, if the masses $M_a, M_b, \ldots M_k$, the whole volume V and the whole entropy S are each increased by a small fraction $d\varepsilon$ of their original values, the whole energy will be increased by the same fraction of its original value. Equation (267) must therefore be satisfied by

$dU = Ud\varepsilon,\quad dV = Vd\varepsilon,\quad dS = Sd\varepsilon,\quad dM_a = M_a d\varepsilon, \ldots, dM_k = M_k d\varepsilon$

whence we have by substitution

$$U = TS - pV + \sum M_k \mu_k \tag{270}$$

and therefore

$$\mathfrak{F}_P = U - TS + pV = \sum M_k \mu_k. \tag{271}$$

In other words the potential $\mathfrak{F}_P$ of the mixture is equal to the sum of the masses of the constituents multiplied by their corresponding partial potentials.

In the special case of a single substance, the partial potential μ becomes, therefore, identical with the thermodynamic potential $\mathfrak{f}_p$ of unit mass at given temperature and pressure.

The above result also follows from the fact that U is a homogeneous function of the first degree in $S, V, M_a, \ldots M_k$ (not in general a *linear* function) whence by Euler's Theorem of homogeneous functions

$$U = S\frac{\partial U}{\partial S} + V\frac{\partial U}{\partial V} + \sum M_k \frac{\partial U}{\partial M_k} = ST - pV + \sum M_k \mu_k. \tag{272}$$

In general the potentials μ depend on the *percentage composition* but are independent of the total quantity of mixture taken, so that if $m_a, m_b, \ldots m_k$ are the masses of the constituents, v, s the volume and entropy, $\mu_a, \mu_b, \ldots \mu_k$ are expressible as functions of $v, s, m_a, \ldots m_k$, or if preferred they can be expressed as functions of the pressure p, temperature T, and percentage composition as defined by the quantities $m_a, m_b, \ldots m_k$ subject to $\sum m_k = 1$. In other words $\mu_a, \mu_b, \ldots \mu_k$ are homogeneous functions of zero degree in $S, V, M_a, \ldots M_k$.

152. Transformation of the Fundamental Equation. The equation

$$U = f(S, V, M_a, \ldots M_k) \tag{266}$$

is called a fundamental equation, and as has been stated above, the existence of such an equation is an axiomatic consequence of the fundamental principles of thermodynamics, and for a homogeneous mixture f must be a homogeneous function of the first degree. We shall now show how to deduce other equivalent forms of fundamental equation suited to cases when the system is specified by different choices of variables.

We observe that equation (266) and the subsidiary equations

$$\frac{\partial U}{\partial S} = T,\quad \frac{\partial U}{\partial V} = -p,\quad \frac{\partial U}{\partial M_k} = \mu_k \tag{273}$$

form a system of $k + 3$ equations connecting the following $2k + 5$ variables, namely

$$(274) \qquad \begin{matrix} U, S, V, M_a, M_b, \ldots M_k, \\ T, p, \mu_a, \mu_b, \ldots \mu_k \end{matrix}$$

so that the variables are completely determined if the values of any $k+2$ of them are given. As in the ordinary case of a simple system the above system of equations is easily seen to be equivalent to the following:

$$(275) \qquad \mathfrak{F}_v \equiv U - TS = \text{a known function of } (T, V, M_a, \ldots M_k),$$

$$(276) \qquad \frac{\partial \mathfrak{F}_v}{\partial T} = -S, \quad \frac{\partial \mathfrak{F}_v}{\partial V} = -p, \quad \frac{\partial \mathfrak{F}_v}{\partial M_a} = \mu_a, \ldots \frac{\partial \mathfrak{F}_v}{\partial M_k} = \mu_k$$

or, again, to the following

$$(277) \qquad \mathfrak{F}_P \equiv U - TS + pV = \text{a known function of } (T, p, M_a, \ldots M_k),$$

$$(278) \qquad \frac{\partial \mathfrak{F}_P}{\partial T} = -S, \quad \frac{\partial \mathfrak{F}_P}{\partial p} = +V, \quad \frac{\partial \mathfrak{F}_p}{\partial M_a} = \mu_a, \ldots \frac{\partial \mathfrak{F}_p}{\partial M_k} = \mu_k$$

in which (275) and (277) are the *fundamental* equations respectively.

If, following an analogous method, we attempt to form a fundamental equation with $p, T, \mu_a, \mu_b, \ldots \mu_k$ as independent variables the potential function we should logically use would be

$$U - TS + pV - \sum \mu_k M_k$$

but this for a homogeneous mixture vanishes by (270). We conclude that the fundamental equation in this case takes the form of a relation between the variables $p, T, \mu_a, \mu_b, \ldots \mu_k$ alone so that these variables are not independent. This case may be best treated as follows.

(a) If we start with the system of equations (273), (266) we find that $p, T, \mu_a, \mu_b, \ldots \mu_k$ depend not on the whole mass of mixture taken, but only on its percentage composition so that if small letters refer to a unit mass, these $k+2$ variables are functions only of the $k+2$ quantities

$$v, s, m_a, m_b, \ldots m_k$$

which are subject to the relation

$$\sum m = 1.$$

By means of this additional relation we obtain on elimination an equation involving $p, T, \mu_a, \mu_b, \ldots \mu_k$ only and this relation we shall write in the form

$$(279) \qquad p = \varphi(T, \mu_a, \mu_b, \ldots \mu_k).$$

(b) Conversely, the last equation will now be shown to be equivalent to a fundamental equation of the form (266). For the elimination of dU from the equations

$$dU = TdS - pdV + \sum \mu_k dM_k, \tag{269}$$

$$U = TS - pV + \sum \mu_k M_k \tag{270}$$

gives

$$0 = SdT - Vdp + \sum M_k d\mu_k, \tag{280}$$

or

$$dp = \frac{S}{V} dT + \sum \frac{M_k}{V} d\mu_k. \tag{281}$$

Taking $T, \mu_a, \mu_b, \ldots \mu_k$ as independent variables we have

$$\frac{S}{V} = \frac{\partial p}{\partial T}, \quad \frac{M_a}{V} = \frac{\partial p}{\partial \mu_a}, \ldots \frac{M_k}{V} = \frac{\partial p}{\partial \mu_k} \tag{282}$$

so that an equation of the form

$$p = \varphi(T, \mu_a, \mu_b, \ldots \mu_k)$$

is sufficient to determine

$$\frac{S}{V}, \frac{M_a}{V}, \ldots \frac{M_k}{V}.$$

If the whole mass of the mixture $\sum M_k$ is also given, to be equal to M, we have for V the equation

$$V \sum \frac{\partial p}{\partial \mu_k} = M \tag{283}$$

whence V is found and the other variables $S, M_a, M_b, \ldots M_k$ are known. Finally the energy U is given by (270) whence

$$U = V\left\{T\left(\frac{dp}{dT}\right)_\mu - \varrho + \sum \mu_k \frac{\partial p}{\partial \mu_k}\right\}. \tag{284}$$

Equations (279), (282), (283), (284) are $k + 4$ in number and they involve $2k + 6$ variables namely the variables listed in (274) and the total mass M. It follows that any $k + 3$ of the variables may be eliminated and the result will be a single equation between the remaining $k + 3$ variables which we may take to be an equation between $U, S, V, M_a, \ldots M_k$.

If instead of the whole mass, the whole volume V is given equations (282) are necessary and sufficient to determine the pressure, whole entropy, and masses of the constituents, the total number of variables being now $2k + 5$ omitting the whole mass M. With this omission equation (283) becomes omitted and the general conclusions are the same as before.

We may also state our conclusions as follows: If the potentials of the constituents are given and also the temperature, then the pressure, percentage composition and generally the *state* of the mixture as apart from its total *quantity* are known.

153. Phase Equilibrium. While the preceding discussion refers only to a single phase of a chemical system we now proceed to find the condition for the equilibrium of a complex of different coexisting phases $\varphi', \varphi'', \ldots \varphi^{(n)}$ each of which consists of all or of a certain number of the k substances $A, B, \ldots K$. As illustrated by the complexes formed of different phases of the same substance discussed in the previous chapter, a complex consists of several portions of matter which remain in equilibrium without tending to mix or combine into a single homogeneous mixture or compound which would be described as a single phase. These different parts are called the *phases* of the complex. The difference between the phases considered in this chapter and those in the last chapter is that here we may have a difference in the percentage composition of two phases. As an example we may take the case where calcium carbonate, calcium oxide and carbonic anhydride (or carbon dioxide) ($CaCO_3$, CaO, CO_2) are in equilibrium, here we have *three phases* formed out of the *two constituents*, CaO and CO_2. In the case of ice, water and steam, as considered in the last chapter all three phases had the identical chemical composition (H_2O).

In *Gibbs'* treatment it is assumed that the effects of gravity, of capillary tensions and of electrical and similar forces are neglected.

If gravity be not neglected the energy per unit mass of a homogeneous mixture will not be the same throughout as has been assumed.

If capillary and electric actions between different phases be not neglected these phases will have mutual potential energy and the whole energy of the complex will no longer be equal to the sum of the whole energies of the parts in the separate phases, as we shall assume.

In the last chapter we found that in the case of a single substance, the conditions for equilibrium of two phases require that the pressure, temperature, and thermodynamic potential of unit mass $\mathfrak{f}_p$ shall be equal in both phases. For several substances we should expect that the third condition would be generalised by the substitution of the partial potentials μ of the different substances for the potential $\mathfrak{f}_p$, in other words, that in addition to the temperature and pressure being the same in all the phases, the partial potential of any substance would be the same in all the phases in which that substance occurred in order that these phases should be in equilibrium.

Consider variations in which the total volume of the complex remains constant and no heat enters or leaves it as a whole. From Chapter VIII § 94 the equilibrium condition of minimum available energy requires that for small variations of the first order in which the whole entropy of the complex remains constant the variation of

the whole energy shall vanish to the first order. Now let μ' and μ'' be the partial potentials of any substance in two phases. Then a variation in which a mass dM of the substance in question passes from the second to the first phase without altering the volume or entropy of either phase has been shown to be a physically conceiveable change (§ 150), and it is consistent with the condition of constancy of the whole entropy of the complex. By the definition of the partial potentials this change would increase the whole energy of the first phase by $\mu' dM$ and decrease the energy of the second by $\mu'' dM$. And since the two phases are assumed (as explained above) to have no mutual potential energy, the quantity

$$(\mu' - \mu'')dM$$

represents the increase of the whole energy of the complex. This increase vanishes, therefore

(285) $$\mu' = \mu''.$$

We may, if preferred, give the proof in the following analytical form. If quantities referring to the different phases φ', φ'' are denoted by corresponding accents, and unaccented letters refer to the whole complex, we have, since mutual potential energy of the phases is neglected

$$U = U' + U'' + \cdots + U^{(n)}$$

$$\therefore \delta U = \delta U' + \delta U'' + \cdots + \delta U^{(n)}$$

$$= T'\delta S' - p'\delta V' + \sum \mu_k' \delta M_k'$$

$$+ T''\delta S'' - p''\delta V'' + \sum \mu_k'' \delta M_k''$$

$$+ \cdots\cdots\cdots\cdots\cdots$$

$$+ T^{(n)}\delta S^{(n)} - p^{(n)} S V^{(n)} + \sum \mu_k^{(n)} \delta M_k^{(n)}.$$

Since the conditions of equilibrium hold for variations which do not alter the total volume of the complex or the total mass of any substance K and in which no heat passes to or from the complex, we have generally

$$\delta U = 0,$$

for all variations subject to

$$\delta S' + \delta S'' + \cdots + \delta S^{(n)} = 0,$$

$$\delta V' + \delta V'' + \cdots + \delta V^{(n)} = 0,$$

$$\delta M_a' + \delta M_a'' + \cdots + \delta M_a^{(n)} = 0,$$

$$\cdots\cdots\cdots\cdots\cdots$$

$$\delta M_k' + \delta M_k'' + \cdots + \delta M_k^{(n)} = 0.$$

This requires that

$$T' = T'' = \cdots = T^{(n)}, \quad p' = p'' = \cdots = p^{(n)},$$
$$\mu_a' = \mu_a'' = \cdots = \mu_a^{(n)}, \quad \mu_k' = \mu_k'' = \cdots = \mu_k^{(n)}.$$

By this method the conditions of equality of temperature and pressure as well as of the potentials are established.

We might if we preferred deduce the conditions of equilibrium by supposing the complex to be surrounded by a medium of temperature T_0 and pressure p_0, and forming the available energy according to § 90, in this case we should obtain the further condition that the temperature and pressure of each phase were equal to T_0 and p_0 respectively.

154. Case of absent constituents. If any component is entirely absent from any particular phase, it is necessary and sufficient that its partial potential where it occurs should be less than the potentials which it would have if it were present in infinitesimally small quantities in the phases from which it is absent.

Thus let μ' be the potential of a substance in the phase in which it is present, $\mu^{(0)}$ the potential it would have if present in infinitesimal quantities in a second phase. Then if a mass dm of the substance were to pass from the first to the second phase without altering the whole volume or entropy of either phase the increase of energy would be $(\mu^{(0)} - \mu')dm$.

This must be positive or zero, hence $\mu' < \mu^{(0)}$. But a change in the opposite direction is impossible, hence the energy does not necessarily satisfy the usual analytical conditions for a minimum, that is, its variation of the first order does not necessarily vanish, and μ' is not necessarily *equal* to $\mu^{(0)}$. We have in fact a case in which only "unilateral" variation is possible as considered in § 89b.

155. The Phase Rule. Now let us investigate the *maximum* number of different phases which can exist together in a single complex formed out of the k different substances $A, B, \ldots K$.

Since the temperature and pressure are the same throughout, and the partial potential of each substance is the same in all the phases in which that substance occurs, we have only $k + 2$ variables at our disposal, namely the common pressure and temperature and the *values*, common to each phase, of the partial potentials of the k substances. We may therefore denote these values by p, T, $\mu_a, \ldots \mu_k$ without using accents to distinguish the different phases.

Moreover we have shown that the existence of any phases φ involves a fundamental equation of condition, which may be written in the form

$$p = \varphi(T, \mu_a, \mu_b, \ldots \mu_k).$$

In general the number of equations of condition cannot exceed the number of variables at our disposal and we thus conclude that

(1) There cannot in general be more than $k+2$ phases in equilibrium formed of k substances.

(2) If these $k+2$ phases all coexist, the variables are all completely determined, and this case can only occur when the pressure, temperature and partial potentials have one or more definite discrete values. Such a complex is called *invariant* or *avariant* because no change of a physical character can take place without disturbing the equilibrium of one or more phases. The relative *quantities* of the different phases may however be varied, but their percentage compositions and the volumes and entropies *per unit mass* of each will remain constant. The state in question is called a *multiple point* of order $k+2$. The triple point of the last chapter is the special case for $k=1$.

(3) If only $k+1$ phases are coexistent, the complex possesses one degree of freedom and is called *univariant*. If the pressure or temperature is given, or more generally any single additional arbitrary condition is imposed, such as a relation between pressure, temperature, and potentials, the $k+2$ variables will be completely determined.

(4) If k phases coexist the complex has two degrees of freedom and is called *bivariant*. It can now be made to satisfy two additional arbitrary conditions, for example, both pressure and temperature may be given and may be independently varied.

(5) If generally i phases coexist the complex is called *multivariant*, its *variance* being of order $k+2-i$ and denoting the number of its degrees of freedom.

These conclusions constitute the *Phase Rule* of Gibbs. It will be noticed that the variations above considered have no reference to the *quantities* of the different phases present in a given complex. Moreover the conclusions are equally valid when the components are not present in all the phases. In the case of absent components the potentials of these components will not enter into the fundamental equations of the corresponding phases, but the number of equations and the number of variables will be the same as before.

A few examples will make this latter point clearer.

Ex. 1. Suppose A, B to be two substances which can never mix. If A is at the triple point, the temperature and pressure are known. These will not in general satisfy the condition for equilibrium between two phases of B, and hence B only can occur in one phase, giving four phases altogether, in accordance with the rule.

If however only two phases of A occur, we have a single relation between the temperature and pressure and we can make them satisfy a second relation necessary for the coexistence of two phases of B, giving, as before, four phases.

Ex. 2. Consider a saturated solution of salt in the presence of undissolved salt. We have two phases with two components. If the temperature and pressure are given the strength of the solution will be completely determined.

Ex. 3. If the solution of the last example is also in equilibrium with vapour of the solvent, then if the temperature alone is given, the vapour pressure will be known and the state of each of the three phases completely determined.

156. Application to the thermodynamic potentials of gas-mixtures. We may now give a more satisfactory discussion of the question treated in § 122.

We assume that if a liquid is in equilibrium with its vapour alone at temperature T and pressure p', it will also be in equilibrium at temperature T with its vapour mixed with other gases, if the partial pressure of the vapour be p'.

Now in the first case the potential $\mathfrak{f}_p$ of the liquid is equal to that of the vapour, and in the second case it is equal to the partial potential of the vapour in the mixture and a comparison of the equations of § 127

$$\mathfrak{f}_p = x\mathfrak{f}_p' + (1-x)\mathfrak{f}_p''$$

with the equations of § 151

$$\mathfrak{f}_p = \mu' m' + \mu'' m'' \qquad (m' = x, \quad m'' = 1 - x)$$

shows that this partial potential μ' is the same as the $\mathfrak{f}_p'$ of Chapter XII.

If the potential of the liquid were the same in both cases, we should have the potential of the vapour exactly equal to its partial potential in the mixture at the same temperature T and *partial* pressure p'.

This is not strictly the case, for if p'' be the partial pressure of the remaining gases, the surface of the liquid is in the one case subjected to the pressure p' and in the other case to the total pressure $p' + p''$, and the expression for $\mathfrak{f}_p$, viz.

$$\mathfrak{f}_p = u - Ts + pv$$

shows that even if the liquid has the same specific energy and entropy in the two cases, its potentials will differ by the amount $p''v$. But to obtain some idea of the percentage error commonly introduced by neglecting this term we may take, as an example, water and its vapour at 100° C. Here the volume of the vapour is 1650 times that of the liquid so that the percentage error is comparable with what would be introduced by an error of observation of 0.06 per cent in the estimation of the partial pressures or temperature.

In deciding as to the most suitable assumption to make in the hypothetical case of a perfect gas, the most natural plan is to regard the equation $pv = BT$ as a limiting case of van der Waals' equation or some analogous form. But when van der Waals' equation is written in the form of a cubic in v and the constants a, b in it are subsequently made equal to zero, two of the roots of the cubic vanish. We conclude that in order to bring the properties of perfect gases into harmony with those of ordinary gases we must take the limiting form of the result of the preceding investigation when the ratio of the volumes of the liquid and gaseous phases is made infinitely small.

We thus have the result that the partial potential of a perfect gas at given pressure and temperature is independent of the other gases with which it is mixed.

The loss of available energy and gain of entropy by the diffusion of two such gases then follows the laws discussed in Chapter XII.

[If we adopted any other hypothesis, as, for example, that no available energy was lost by the diffusion of perfect gases, the study of the properties deduced from such an assumption would be devoid of physical interest and the "perfect gases" so defined would possess no resemblance whatever to actual gases in regard to these properties.]

157. To find the fundamental equation of the mixture in the form of a relation between p, T and the potentials, we first transform the equation (Chapter XII § 122) for the potential of a single gas so as to give p explicitly thus

$$p = e^{\frac{\mathfrak{f}_p - u_0}{BT}} T^{\frac{\gamma_p}{B}} e^{\frac{\sigma_0 - \gamma_p}{B}}.$$

We now notice that when the gas occurs in a mixture the partial potential μ takes the place of $\mathfrak{f}_p$ and the partial pressure of the gas is determined by the same equation. And since the total pressure of the mixture is equal to the sum of the partial pressures of its components we get for the fundamental equation of the mixture

$$p = \Sigma\left(e^{\frac{\mu' - u'_0}{B'T}} T^{\frac{\gamma'_p}{B'}} e^{\frac{\sigma'_0 - \gamma'_p}{B'}}\right) \tag{286}$$

where the accented letters denote quantities which are different for the different gases[1]), and the sign of summation refers to these several gases.

1) This is reducible to the form given by *Gibbs* on substituting $\gamma_v + B$ for γ_p and $v_0 + \beta \log B$ for σ_0.

CHAPTER XVI.

REVERSIBLE THERMOELECTRIC PHENOMENA.

158. Definition of a Reversible Galvanic Element. The flow of electricity through conductors is associated with several heat phenomena, some of which are reversible and others irreversible.

When a current I flows through a wire of finite resistance R, and of uniform temperature throughout, available electrical energy of amount I^2R per unit time is absorbed, and either a quantity of heat equal to this is given to the surrounding media or a rise of temperature occurs in the wire equal to that which would be produced by imparting this quantity of heat to it. If the direction of the current be reversed the same transformation will take place. We have therefore a simple case of irreversible conversion of work into heat in the substance of the wire itself as explained in § 81, and entropy is generated in the wire at a rate per unit time represented by $\frac{I^2R}{T}$.

As however the laws of irreversible thermodynamics are represented by *inequalities* instead of equations, we must in order to study reversible phenomena, leave this heating effect out of account, and for this purpose it is necessary either to assume perfect conductivity ($R = 0$) or to suppose the flow of electricity to take place infinitely slowly. If e is the quantity of electricity flowing through the wire in time t and we consider the simple case of a uniform current, we have $e = It$, so that the quantity of energy transformed is equal to $\frac{e^2R}{t}$, and keeping e constant this quantity may be decreased indefinitely by increasing t, as well as by decreasing R. In either case the differences of potential in the conductors due to the currents vanish. In dealing therefore with a galvanic cell of finite electromotive force E we must therefore suppose a motor or a condenser (e. g. an air-condenser with parallel plates) included in the circuit giving rise to an equal and opposite electromotive force, and when a quantity of electricity de flows from the positive to the negative pole of the cell through the motor or in the same direction relative to the cell in connection with the condenser, a quantity of external work Ede will be done by the motor or by the attraction of the plates of the condenser. On reversing the process an equal quantity of available energy must be supplied from without, in the form of mechanical work. In this statement it is assumed, consistently with the principles of electrostatics or electromagnetism that the electrical energy passing to or from the condenser or motor is wholly of the nature of

available energy. This is true consistently with what is proved later on if the electrodes (i. e. the points at which the current enters or leaves the region included in the cell) are of the same material and at the same temperature. *This is assumed.*

A perfectly reversible element may therefore be defined as one in which no available energy is lost by the passage of electricity between the poles or by any of the other transformations contemplated in reversible thermodynamics. If then a quantity e of electricity passes between the poles in one direction and an equal quantity then passes in the opposite direction, no other change taking place (the transformation being adiabatic) the element will return to its original physical and chemical state.

159. Application of Thermodynamic Equations. When in addition to the last mentioned changes heat may pass to or from the element, other changes being excluded, the element behaves as a simple system, and its state at any instant can be specified by two coordinates, namely the whole quantity of electricity that has passed between the poles, denoted by e, and the entropy, *or* the temperature. That e can be regarded as a coordinate is most readily seen when the circuit is completed by a condenser.

Since $E\,de$ is the external work done corresponding to the variation de, we have by the laws of thermodynamics

$$dU = T\,dS - E\,de. \tag{287}$$

If then

$$\mathfrak{F}_e = U - TS,$$

$\mathfrak{F}_e$ will be the thermodynamic potential corresponding to $\mathfrak{F}_v$ for a simple substance, and we shall have

$$d\mathfrak{F}_e = -S\,dT - E\,de \tag{288}$$

whence

$$E = -\left(\frac{d\mathfrak{F}_e}{de}\right)_T \tag{288a}$$

a relation first obtained by *Gibbs*.

Since $d\mathfrak{F}_e$ is a perfect differential

$$\left(\frac{dE}{dT}\right)_e = \left(\frac{dS}{de}\right)_T = \frac{1}{T}\left\{\left(\frac{dU}{de}\right)_T + E\right\}. \tag{289}$$

Putting

$$\lambda = -\left(\frac{dU}{de}\right)_T$$

we obtain

$$\lambda = E - T\left(\frac{dE}{dT}\right)_e. \tag{290}$$

The interest in this equation, which is known as *Helmholtz'* equation lies in the physical meaning of λ. In fact λ is the loss of internal energy per unit quantity of electricity generated in the circuit at constant temperature T. The constancy of temperature and the exclusion of other variations shows that this energy has its origin in the chemical combinations formed in the element during the change. Now the quantities of the different substances combined in connection with the passage of a unit electricity are called the *electrochemical equivalents* of these substances. Moreover the quantities of energy evolved by them are called their *heats of formation* (expressed in work units) because in the simplest experiments on chemical combination the evolved energy takes the form of heat. Hence λ is said to be equal to the algebraic sum of the heats of formation of one electrochemical equivalent of each of the active substances contained in the cell.

160. Separation of the Thermoelectric Effects in the circuit. From the last section we see that E is not equal to λ unless E and therefore λ is independent of T. In other cases we have

$$E - \lambda = T\left(\frac{dE}{dT}\right)_e = T\left(\frac{dS}{de}\right)_T.$$

Here Ede is the total electric energy associated with the change de, λde the energy arising from chemical reaction and we see that the remainder is TdS, and represents the energy supplied from without in the form of heat. The coefficient which is equal to $\frac{dE}{dT}$ represents therefore the part of the electromotive force due to direct thermo-electric actions in the element.

When no chemical changes occur, so that $\lambda = 0$, equation (290) gives on integration

$$E = CT \tag{291}$$

where C is a constant. Hence the thermo-electromotive force in an ideal element consisting of metals or other substances in contact, between which no chemical action takes place is proportional to the absolute temperature.

In the more general case where λ is not zero, E and λ will be functions of T alone, so long as the battery is continuously working. In this case equation (290) gives on integration

$$E = T\left\{C - \int \frac{\lambda}{T^2} dT\right\}. \tag{292}$$

161. Gibbs' Formula. *If it is possible to assume* λ *to be independent of* T this gives

$$E = T\left(C + \frac{\lambda}{T}\right) \tag{293}$$

or putting $C = -\frac{\lambda}{T_0}$ (C may be positive or negative) this gives

$$E = \lambda \frac{T_0 - T}{T_0}. \tag{294}$$

This result was given by Gibbs, who deduced it by the application of a cyclic transformation to the element. It does not however appear to be deducible from purely thermodynamic reasoning without *some* assumption. It necessarily involves the converse property that λ (but not E unless $T_0 = 0$) is independent of T and further that the total thermo-electromotive force $E - \lambda$ is proportional to the absolute temperature T, as in the case where no chemical action takes place.

A very simple assumption which leads to Gibbs' formula is that *the thermal capacity of the cell is unaffected by any chemical changes which take place in it.* Thus supposing we are dealing with zinc and sulphuric acid we assume that the heat required to raise the temperature 1^0 is the same for the zinc sulphate as for the separate constituents. If we start from this assumption we have, taking T and e as variables,

$$\left(\frac{dS}{dT}\right)_e = \text{function of } T \text{ only},$$

$$\therefore \frac{d^2S}{dTde} = 0,$$

$$\therefore \left(\frac{dS}{de}\right)_T \text{ is independent of } T,$$

$$\therefore \frac{E-\lambda}{T} \text{ is independent of } T.$$

Also the assumption that the battery is in continuous action makes E and λ independent of e. Therefore

$$\frac{E-\lambda}{T} = \text{constant } C$$

as in (293). The converse is also true as may easily be seen.

162. Temperature of Transformation. The constant T_0 in the equation of the last article has an important physical meaning. For if the temperature $T = T_0$, E vanishes and as T increases past the value T_0, E changes sign.

At the temperature T_0 a current can flow through the circuit freely in either direction, and there being no electromotive force, no energy is absorbed or given out to the current. The chemical changes occurring in the cell will depend on the magnitude and direction of the current but the energy involved in them will be wholly transformed in the form of heating.

When the temperature exceeds T_0 the current tends to flow in the opposite direction, its flow being accompanied by dissociation of the compounds formed in the previous case. The process of combination can then only be continued by inserting an external electromotive force in the direction hitherto regarded as positive and thus supplying external electrical energy.

These conclusions which are verified by experiment, are not dependent on the particular form of equation (294).

Taking the perfectly general thermodynamic formula (290) we may write it in the form

$$E = T\int_{T}^{T_0} \frac{\lambda}{T^2}\, dT. \tag{295}$$

Here T_0 will be the temperature of transformation, and will possess all the properties above stated.

163. Effect of changes of volume or pressure. In such cases as that of a gas battery where expansion takes place under external pressure, an additional variable must be taken into account namely the volume V or the pressure p. The equations give

$$dU = T\,dS - E\,de - p\,dV$$

and taking the thermodynamic potentials

$$\mathfrak{F}_V = U - TS, \quad \mathfrak{F}_p = U - TS + pV$$

we obtain in the usual way

$$d\mathfrak{F}_V = -S\,dT - E\,de - p\,dV,$$
$$d\mathfrak{F}_p = -S\,dT - E\,de = V\,dp.$$

The conditions for a perfect differential now give rise to six reciprocal relations between the differential relations; of these the only ones which have not been already discussed in §§ 112—114, are

$$\left(\frac{dE}{dV}\right)_{e,T} = \left(\frac{dp}{de}\right)_{V,T}, \quad \left(\frac{dE}{dp}\right)_{e,T} = -\left(\frac{dV}{de}\right)_{p,T}. \tag{296}$$

The last relation shows that the electromotive force increases or decreases with the pressure according as the volume decreases or increases when a current flows through the battery.

In a constant pressure battery in continuous action at constant temperature the change of volume depends on the chemical transformations taking place in the battery, and is proportional to the quantities of the chemical constituents involved in the change, or again to the quantity of electricity that has passed through the battery, giving

$$\left(\frac{dV}{de}\right)_{pT} = \text{constant},$$

in accordance with *Faraday*'s Law. Thus for example if we take the case of hydrogen and oxygen, the value of $\left(\frac{dV}{de}\right)_{pT}$ will represent the difference between the volumes of one electrochemical equivalent of oxygen and hydrogen and that of water at the temperature and pressure of the cell. We may therefore write

$$\frac{\partial V}{\partial e} = \frac{V_0 - V}{e} = \text{function of } p, T \text{ only.}$$

Hence

$$\left(\frac{dE}{dp}\right)_T = \frac{V_0 - V}{e}. \tag{297}$$

This equation may be integrated *keeping T constant* in order to compare the electromotive forces of the same battery at two different pressures *at the same temperature* provided the (p, V, T) equations of the substances involved are known.

Example. Suppose the substances to consist partly of solids and liquids whose volume may be approximately assumed to be independent of the pressure, partly of gases which obey Boyle's Law. Then at constant temperature T

$$\frac{V_0 - V}{e} = A + \frac{BT}{p} \tag{298}$$

where A is the change of volume of one electro-chemical equivalent of the solids and liquids, $\frac{BT}{p}$ that of the gases. Then the integral becomes

$$E(p_1 T) - E(p_0 T) = A(p_1 - p_0) + BT \log \frac{p_1}{p_0}. \tag{299}$$

The experimental aspect of such equations has been studied by *Gilbault*.

164. The Peltier and Kelvin Effects. Hitherto we have considered thermo-electric phenomena that are associated with chemical action. We now proceed to discuss more fully those phenomena which occur in systems of conductors in which no chemical action takes place. Such conductors are called *conductors of the first class*, those previously considered being classed as *conductors of the second class*.

The thermo-electric phenomena occurring at the surface of separation of two conductors of the first class are known as the *Peltier Effect.* There is in general a difference of potential (Π) at the two sides of the surface, and when a quantity of electricity flows across the surface, the energy corresponding to the change takes the form of heat absorbed or given out at the surface, in just the same way that when friction occurs between two bodies each appears to receive heat from the common surface of separation.

From § 160 it appears that in an element in which the only electromotive forces are those due to contact, the sum of these, representing the total electromotive force, must be of the form CT, i. e. proportional to the absolute temperature.

This result may be generalised by taking a (non-resisting) circuit formed of any number of metals. Let Π_1, Π_2, Π_3 be the electromotive forces of contact at the various junctions taken in order round the circuit T_1, T_2, T_3 the absolute temperatures.

Let e units of electricity flow round the circuit in the positive direction. Then the quantities of energy gained at the junctions are $e\Pi_1, e\Pi_2, e\Pi_3$, and these represent the quantities of heat absorbed. Since the process is reversible, the sum of the corresponding changes of entropy is zero. That is

$$\frac{\Pi_1}{T_1} + \frac{\Pi_2}{T_2} + \frac{\Pi_3}{T_3} + \cdots = 0. \tag{300}$$

Now let all the temperatures of the junctions but one, T_r be kept constant. Then it follows immediately that

$$\frac{\Pi_r}{T_r} = \text{constant},$$

and calling this constant C we have

$$\Pi_r = C_r T_r \quad \text{and} \quad \Sigma C = 0. \tag{301}$$

Thus *in a reversible circuit in which no other electromotive forces occur the Peltier effect at any junction must be proportional to the absolute temperature of that junction and further the sum of the coefficients C_r must be algebraically zero.*

In particular the electromotive force in a circuit of two metals will be proportional to the difference of temperature of the junctions.

Now in practice it is found that when the temperature of one junction is kept constant and that of the other is raised, the current instead of always increasing may vanish and change sign. From this it follows that conformably with the laws of thermodynamics, other electromotive forces must exist in the circuit. From arguments of this character Lord Kelvin was led to the discovery of the *Thomson* or *Kelvin* effect according to which:

When differences of temperature exist at different points of the same substance, they are in general accompanied by a difference of potential.

These differences of potential which are here discussed in connection with an ideal reversible circuit are of course entirely independent of those due to resistance in irreversible circuits.

The energy absorbed when electricity passes from a place of lower to one of higher potential is necessarily supplied in the form of heat, and hence the phenomena give rise to reversible heating effects which are independent of the irreversible effects due to conduction of heat in the cases which occur in practice. To these heating effects the name "electric convection of heat" has been given. In order to eliminate the effects of irreversible heat conduction, it is necessary to assume that the thermal conductivity of the connections forming the circuit is negligible.

The laws of reversible thermodynamics show that under the assumed conditions, when a unit of electricity flows round the circuit, the sum of the energies given out in the form of heat at the junctions and in the conductors is equal to the whole electromotive force tending to produce a current in this direction in the circuit, and the sum of the entropies given out is zero.

The last statement shows that the total quantity of entropy absorbed when a unit of electricity is made to pass from one point O to another point P of a thermo-electric network is independent of the path by which the charge travels from O to P. If we denote this quantity by χ, we notice that since the present result is unaffected by the addition or substitution of hypothetical connections of the most general character between O and P, the quantity χ can only depend on the temperatures and nature of the substances at O and P. And by taking O to refer to a standard substance at a standard temperature we shall have χ a function of the temperature and the nature of the substances at P which we shall write $\chi(a, T)$ for substance a at temperature T. This function will determine all the thermo-electric phenomena occurring in the system.

Thus if Π_{ab} is the electromotive force at temperature T of the Peltier Effect between two substances a and b,

$$\Pi_{ab} = T\{\chi(a, T) - \chi(b, T)\}. \tag{302}$$

Again let $\sigma_a dT$ represent the electromotive force of the Kelvin effect corresponding to the temperature difference dT for substance a then since

$\sigma_a dT =$ increase of energy of unit charge corresponding to dT

$= T \times$ increase of entropy $= T d\chi(a, T)$,

$$\therefore \sigma_a = T \frac{d\chi(a, T)}{dT}. \tag{303}$$

The coefficient σ_a has been called by Lord Kelvin the specific heat of electricity for substance a at temperature T, because $\sigma_a dT$ represents the heat absorbed by unit charge for a change of temperature dT obtained by moving along the wire. It will be noticed that σ and Π are connected by the relation

$$\frac{d}{dT}\left(\frac{\Pi_{ab}}{T}\right) - \frac{\sigma_a - \sigma_b}{T} = 0 \tag{304}$$

which is identical with the relation between the specific heats and latent heat of transformation in a complex of two phases of the same substance. This identity is a necessary consequence of the physical interpretation of the two equations, which represent the fact that the sum of the entropy changes is zero in a circuit of two metals and a cycle between the two phases respectively for a temperature-difference dT in the neighbourhood of T.

165. Determination of the Total Electromotive Force. If two points are taken in the *same homogeneous conductor* at temperatures T_1, T_2 the electromotive force between them is given by

$$E = \int_{T_1}^{T_2} \sigma_a dT = \int_{T_1}^{T_2} T d\chi(aT) = \Phi(T_2) - \Phi(T_1) \tag{305}$$

where $\Phi(T)$ is a function of T alone. This follows since $\chi(aT)$ is a function of T alone so long as a is the same. Hence so long as the substance is the same, the thermo-electromotive force is derivable from a potential $\Phi(T)$ satisfying the relation

$$d\Phi = T d\chi. \tag{306}$$

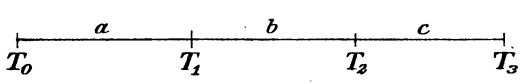

Fig. 21.

Next consider a number of conductors $a, b, c, \ldots k$ in series with their junctions at temperatures $T_1, T_2, \ldots T_{k-1}$. Then the expression for the whole electromotive force between (a, T_0) and (k, T_k) can be written in the following various forms

$$\begin{aligned} E = {} & \Phi(a, T_1) - \Phi(a, T_0) + \Pi_{ab}(T_1) \\ & + \Phi(b, T_2) - \Phi(b, T_0) + \Pi_{bc}(T_2) + \text{\&c.}, \end{aligned} \tag{307}$$

$$\begin{aligned} E = {} & \int_{T_0}^{T_1} T d\chi(aT) + T_1\{\chi(bT_1) - \chi(aT_1)\} \\ & + \int_{T_1}^{T_2} T d\chi(b, T) + T_2\{\chi(c, T_2) - \chi(b, T_2)\} + \text{\&c.}, \end{aligned} \tag{308}$$

or, again, by partial integration the last form gives

$$(309) \quad E = T_k\chi(k, T_k) - T_0\chi(aT_0) - \int_{T_0}^{T_1} \chi(aT)\,dT - \int_{T_1}^{T_2} \chi(b, T)\,dT - \text{\&c.}$$

which may be written

$$(310) \quad = T_k\chi(k, T_k) - T_0\chi(a, T_0) - \int_{a, T_0}^{k, T_k} \chi\,dT$$

whence for a complete circuit

$$(311) \quad E = -\left(\int\right)\chi\,dT.$$

We notice the following conclusions, which are in accordance with the results of general reasoning:

(1) *If the circuit is all formed of one metal* $E = 0$.

(2) *If the junctions are all at the same temperature* $E = 0$, *for as in any conductor* χ *is a function of* T *only, therefore if the two ends are at the same temperature, the portion of the integral contributed by that conductor vanishes.*

We further notice that the electromotive force *in the complete circuit* is the same as would be obtained by assuming an electromotive force $\chi\,dT$ to act between points of the same substance whose temperature difference is dT and no electromotive forces would then have to act at the junctions. In other words the whole electromotive force can be accounted for by a suitably formed expression for the Kelvin effect without any Peltier effects. But such an expression would not give rise to the same heating effects, nor would it bring these heating effects into accordance with the Second Law of Thermodynamics.

166. Converse Problem. — Specification of a Thermo-electric System. Next suppose that we have a circuit formed of two metals a, b and that we have determined its electromotive force for different values of the temperatures T_1, T_2 of the two junctions, so that

$$E = f(T_1, T_2)$$

a known function of T_1 and T_2.

Then we may write the relation (308) in the form

$$(312) \quad \int_{T_1}^{T_2} \{\chi(aT) - \chi(b, T)\}\,dT = f(T_1, T_2)$$

therefore

$$\chi(a, T_2) - \chi(b, T_2) = \frac{\partial f(T_1, T_2)}{\partial T_2}, \tag{313}$$

$$\chi(a, T_1) - \chi(b, T_1) = -\frac{\partial f(T_1, T_2)}{\partial T_1} \tag{314}$$

and by varying one or other of the temperature limits it follows that $\chi(a, T) - \chi(b, T)$ is determinable from these data for all values of T.

This information is sufficient to completely determine the Peltier effect at either junction, but it is not sufficient to determine the Thomson effects in the two separate conductors. All we know from the assumed data is the difference $\chi(a, T) - \chi(b, T)$. If the values of one of the expressions $\chi(a, T)$ be determined by observations of the heating produced by the Thomson effect in one of the metals the corresponding values of $\chi(b, T)$ are completely determined. Without this additional information the expression for χ in any substance must be regarded as containing *an unknown term in the form of an unknown function of T alone which is the same for all substances.*

It also readily follows that the thermo-electric properties of a number of different substances can be completely determined from the following data, each of which may be regarded as the *complete specification of an ideal thermo-electric system:*

(1) If the specific heat of electricity of each of the substances is known as a function of the temperature for all temperatures, and the Peltier electromotive forces are known at one particular temperature between one substance and each of the others.

(2) If the specific heat of electricity of *one* of the substances is known as a function of the temperature, and the Peltier electromotive force between that substance and each of the others is known as a function of the temperature for all temperatures.

In either case the remaining unknown data may be determined from the relation

$$\frac{d}{dT}\left(\frac{\Pi_{ab}}{T}\right) - \frac{\sigma_a - \sigma_b}{T} = 0 \tag{315}$$

or the expressions for χ may be obtained directly from (313) or (314).

Any further experimental data in excess of the minimum must be interpreted as tests either of the accuracy of the observations or of the validity of the laws of Thermodynamics.

Example. Let us assume for E the expression proposed by Tait namely

$$E = k_{ab}(T_1 - T_2)\left[T_{ab} - \tfrac{1}{2}(T_1 + T_2)\right] \tag{316}$$

where T_{ab}, k_{ab} are constants. Then

(317) $$\chi(a, T) - \chi(b, T) = k_{ab}(T_{ab} - T)$$

whence

(318) $$\Pi_{ab} = k_{ab}(T_{ab} - T)\,T$$

so that T_{ab} is the temperature at which the two metals are neutral to each other ($\Pi_{ab} = 0$), also

(319) $$\sigma_a - \sigma_b = -k_{ab}T.$$

This is as far as we can go by purely thermodynamic reasoning. The only *plausible* hypothesis is that σ_a and σ_b are both proportional to T. If for one substance σ is assumed as the result of experiment to be proportional to T within certain temperature limits, the same result is now established for other substances within the same limits, subject of course to (319) being true within these limits.

In the case of lead (say l) it is known from experiment that σ_l is sensibly zero over a considerable range of temperature; on this hypothesis

(320) $$\sigma_a = -k_{al}T, \quad \sigma_b = -k_{bl}T, \quad k_{ab} = k_{al} - k_{bl}$$

and if the above result for lead should be shown to be only approximately true, the first hypothesis would still give

(321) $$\sigma_a = -k_aT, \quad \sigma_b = -k_bT, \quad k_{ab} = k_a - k_b.$$

k_a, k_b in this case being referred to an ideal substance (l) for which $\sigma = 0$. We further have by cyclic addition of (319)

(322) $$(k_b - k_c)\,T_{bc} + (k_c - k_a)\,T_{ca} + (k_a - k_b)\,T_{ab} = 0$$

whence we may write

(323) $$\chi(a, T) = k_a(T_a - T),$$

(324) $$\chi(b, T) = k_b(T_b - T),$$

supposing T_a, T_b to be the neutral temperatures of a, b with respect to lead or the ideal substance (l) referred to. The integration constant which occurs in the value of χ (depending on the initial state assumed in the definition of χ) is here made to vanish by taking the initial state in the substance l.

167. Effects of the Currents on Localisation of Energy and Entropy. The phenomena discussed in the preceding articles afford evidence that *thermo-electric currents may alter the localisation both of energy and entropy.*

Suppose any number of conductors, maintained at a distribution of temperature which is independent of the time, to be placed in a thermo-electric circuit, and after a quantity of electricity e has

passed through the circuit suppose the conductors to be isolated. Then energy and entropy have been absorbed at the conductors during the passage of the current, yet at the end there is no change in the state of the conductors themselves. It is therefore clearly absurd to suppose that this energy and entropy have been stored in the conductors, and we have no alternative but to suppose them to be localised in the electric charge itself.

So far as energy is concerned, this view forms the basis of the most elementary theories and no better evidence can be adduced than the important applications of electric transmission of power, by which for example, energy is made to change its localisation from a waterfall to a tramcar.

Consistently with the theories of the previous articles we have now to assume that the entropy which for charge e at temperature T in substance a is denoted by $e\chi(a, T)$ *is localised in the charge itself*, and that during all peregrinations of the charge, a certain amount of entropy follows it about. When owing to the changes in a or T, the function χ increases, entropy is picked up by the charge, when it decreases, entropy is left behind.

In the case of a charged conductor whose temperature is being raised, we may first suppose the charge brought to the conductor from a fixed base, and after the conductor has been heated we may suppose the charge returned to the same base. The principle of conservation of entropy for reversible cycles requires that entropy shall be supplied during the process of heating, represented by the increase in the value of χ. *If no other phenomena exist* which can account for the change, we infer that heat must be supplied to the conductor, over and above the amount required if the conductor were uncharged, and that the "specific heat of electricity" is the proper thermal coefficient in this case as it is in connection with "electric convection of heat".

CHAPTER XVII.

GEOMETRICAL AND DYNAMICAL REPRESENTATIONS.

168. Thermodynamic Models of a Simple System. The method of representing the thermodynamic properties of a simple system, such as a homogeneous fluid by means of a geometrical surface in three dimensional space is due to J. Willard Gibbs. For convenience we shall suppose the quantities involved to refer to unit mass, though the methods will be closely analogous if the whole mass of the substance is considered.

Taking x, y, z to denote coordinates generally if we put

$$x = v, \quad y = s, \quad z = u$$

where v, s, u are the volume, entropy and energy of unit mass at the substance, we see that since for any given substance, u is a definite function of v, s, say

$$u = f(v, s),$$

the point (v, s, u) lies on a certain surface which may be regarded as a *thermodynamic model* of the substance.

We may construct other surfaces representing the thermodynamic properties of the substance by taking

$$x = v, \quad y = T, \quad z = \mathfrak{f}_v$$

or again

$$x = p, \quad y = T, \quad z = \mathfrak{f}_p$$

or lastly

$$x = p, \quad y = s, \quad z = \mathfrak{f}_s$$

where $\mathfrak{f}_v$, $\mathfrak{f}_p$, $\mathfrak{f}_s$ are the thermodynamic potentials,

$$\mathfrak{f}_v = u - Ts, \quad \mathfrak{f}_p = u - Ts + pv, \quad \mathfrak{f}_s = u + pv.$$

Of the four surfaces thus defined any one is sufficient to determine the thermodynamic properties of the substance. The most convenient however as a general rule are the (v, s, u) surface and the $(p, T, \mathfrak{f}_p)$ surface. The first is usually spoken of as the volume-entropy energy diagram, or thermodynamic model; the second is often called Gibbs' Zeta surface, the Greek letter ζ being used by Gibbs to denote the potential which we have denoted by $\mathfrak{f}_p$.

169. Reciprocal properties of the volume-entropy-energy and pressure-temperature-potential surfaces. We may conveniently study the properties of these two surfaces side by side, and it will be observed that they are connected by the principle of duality.

The (v, s, u) surface.

The equation of the tangent plane at any point of the surface is

$$z - u = (x - v)\frac{\partial u}{\partial v} + (y - s)\frac{\partial u}{\partial s}$$

that is

$$z - u = -(x - v)p + (y - s)T$$

or

$$z = -px + Ty + \mathfrak{f}_p.$$

The $(p, T, \mathfrak{f}_p)$ surface.

The equation of the tangent plane at any point of the surface is

$$z - \mathfrak{f}_p = (x - p)\frac{\partial \mathfrak{f}_p}{\partial p} + (y - T)\frac{\partial \mathfrak{f}_p}{\partial T}$$

that is

$$z - \mathfrak{f}_p = (x - p)v - (y - T)s$$

or

$$z = vx - sy + u.$$

Hence $-p$, T, $\mathfrak{f}_p$ are the tangential coordinates of the point u, s, v when the equation of the tangent plane is put in the form

$$z = lx + my + n.$$

The condition of stability in the state (v, s, u) requires that for any neighbouring state (v', s', u')

$$u' > u - p(v' - v) + T(s' - s).$$

If now the line through (v', s', u') parallel to the axis of z meets the tangent plane at (v, s, u) in the point (v', s', z) this gives

$$u' > z.$$

Hence the z coordinate of the surface is greater than that of the corresponding point on the tangent plane, that is the surface is *concave* towards the positive direction of the axis of z or u.

Hence v, $-s$, u are the tangential coordinates of the point p, T, $\mathfrak{f}_p$ when the equation of the tangent plane is put in the form

$$z = lx + my + n.$$

The condition of stability in the state $(p, T, \mathfrak{f}_p)$ in the opposite column, leads to the result that for any neighbouring state $(p', T', \mathfrak{f}_p')$

$$\mathfrak{f}_p < \mathfrak{f}_p' + v'(p - p') - s'(T - T').$$

If now the line through $(p, T, \mathfrak{f}_p)$ meets the tangent plane at the neighbouring point $(p', T', \mathfrak{f}_p')$ in the point (p, T, z') this gives

$$\mathfrak{f}_p < z'.$$

Hence the z coordinate of the surface is less than that of the corresponding point on the tangent plane, that is the surface is *convex* towards the positive direction of the axis of z or $\mathfrak{f}_p$.

[The reciprocal properties of the two surfaces are easily seen to be consequences of the theory of polar reciprocation in geometry. For supposing two surfaces

$$z_1 = f_1(x_1, y_1) \quad \text{and} \quad z_2 = f_2(x_2, y_2)$$

to be polar reciprocals with respect to the paraboloid

$$x^2 + y^2 = 2z,$$

then since the tangent plane at (x_1, y_1, z_1) is the polar plane of (x_2, y_2, z_2) the equations

$$z = x\frac{dz_1}{dx_1} + y\frac{dz_1}{dy_1} - \left(x_1\frac{dz_1}{dx_1} + y_1\frac{dz_1}{dy_1} - z_1\right)$$

and

$$z + z_2 = xx_2 + yy_2$$

are identical giving

$$x_2 = \frac{dz_1}{dx_1}, \quad y_2 = \frac{dz_1}{dy_1}, \quad z_2 = x_1\frac{dz_1}{dx_1} + y_1\frac{dz_1}{dy_1} - z_1,$$

which are exactly the same as the relations connecting the coordinates on the two surfaces with certain differences of sign.]

170. Properties of a complex.

If two phases coexist then the corresponding points on the (v, s, u) surfaces have a common tangent plane determined by the tangential coordinates $(p, T, \mathfrak{f}_p)$ which are the same for both phases.

If three phases coexist, p, T, $\mathfrak{f}_p$ are the tangential coordinates of a triple tangent plane to the three corresponding parts of the thermodynamic surface.

The boundary between any two phases is determined by a tangent plane rolling in double contact with the two corresponding parts of the surface; this plane envelopes a developable surface.

If two phases coexist then the point $(p, T, \mathfrak{f}_p)$ lies on a curve of intersection of the corresponding parts of the thermodynamic surfaces.

If three phases coexist then the point p, T, $\mathfrak{f}_p$ is at the common intersection of the three corresponding parts of the thermodynamic surface.

The boundary between any two phases is determined by the curve of intersection of the two corresponding parts of the thermodynamic surfaces, and the projection of this curve on the plane of (p, T) determines the curve of saturation referred to p, T as variables.

171. Representation of an actual complex on the (v, s, u) surface. Let (v', s', u') and (v'', s'', u'') represent two phases of the substance which can exist in the presence of each other. Then if m', m'' are the masses of the two phases occurring per unit mass in any complex formed of them, the volume, entropy and energy per unit mass of the complex are given by expressions of the form

$$v = m'v' + m''v'',$$

and hence the point (v, s, u) referring to the complex lies on the straight line joining the points (v', s', u') and (v'', s'', u''), and is the centre of mean position, or centre of mass of masses m', m'' at the two points (v', s', u') and (v'', s'', u''). The locus of such points is the developable surface enveloped by the double tangent plane to the (v, s, u) surface of the two phases.

Similarly for a complex of masses m', m'', m''' of three phases at the triple point the volume, entropy and energy per unit mass of the complex are the coordinates of a point on the triple tangent plane which is the centre of masses m', m'', m''' at the respective points of contact.

Now take the plane of (v, s) as the plane of projection; let S, L, V be the projections of the points of contact of the triple tangent plane corresponding to the solid, liquid and gaseous states, and let the thick curved lines represent projections of the loci of

points of contact of the double tangent planes. Then any point on the triple tangent plane within the triangle LVS represents a complex of three phases, any point on one of the developable surfaces between the triangle and the curved lines represents a complex of two phases, and any point outside these regions represents a simple phase only.

The continuity of the liquid and gaseous states is accounted for by supposing that as the double tangent plane rolls, the two points of contact ultimately coincide at some point which represents the critical point.

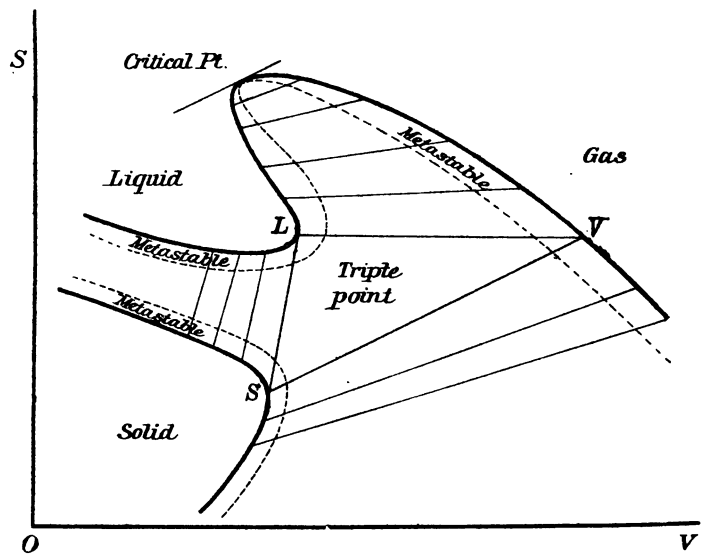

Fig. 22.

The thermodynamic surface remains concave towards the direction of v positive to some distance within the curved lines, and if the dotted lines represent the limits of concavity the substance can exist in a metastable state represented by points on the surface between the dotted and continuous lines. The curves bounding the absolutely stable and metastable regions touch at the critical point, as may be shown without difficulty.

172. The surface of dissipated energy. This name has been given to the composite surface made up of

(a) the portions of the thermodynamic (v, s, u) surface beyond the lines of contact of the double tangent planes which therefore represent essentially stable states,

(b) the developable surfaces joining the points of contact of double tangent planes representing all complexes of two phases, and

(c) the plane triangle formed by the triple tangent plane which represents all complexes of three phases.

This surface represents the locus of all points at which the energy is a minimum for given volume and entropy consistently with the thermodynamic properties of the substance. It therefore represents all absolutely stable states of the working substance.

It should be noticed that in the case of a substance, like sulphur, which is capable of existing in four different phases (not all at the same pressure and temperature) and which has three triple points, the surface of dissipated energy will include three triple tangent planes as well as the different developable surfaces (six in number) connecting them.

173. Representation of a complex in the $(p, T, \mathfrak{f}_p)$ diagram. It is easy to see that the volume, entropy and energy of an actual complex are represented in the $(p, T, \mathfrak{f}_p)$ model by the coordinates (tangential as previously specified § 229) of a plane (L say) whose equation may be written, for the respective cases of a double or triple point in the forms

$$m'L' + m''L'' = 0 \tag{325}$$

or

$$m'L' + m''L'' + m'''L''' = 0 \tag{326}$$

where m', m'', m''' represent masses of the phases occurring in unit mass of the respective complexes and

$$L' = 0, \quad L'' = 0, \quad L''' = 0$$

are the tangent planes to the sheets of the $(p, T, \mathfrak{f}_p)$ surface representing the corresponding phases.

If the $\mathfrak{f}_p$ axis is measured upwards the surface of dissipated energy consists of the portions of the thermodynamic surface which are convex upwards and extend up to but not above the double lines. The portions above these lines which are convex represent metastable states (§ 141). There is no *region* representing a complex, but when a substance passes in gradually increasing quantity from one phase to another the representative plane L turns in contact with the double line on the upper side of the surface from one tangent plane to the other.

174. Cases where the composition is variable. Except in the case of a simple system the number of variables is too great to enable the thermodynamic properties to be completely represented by a model in three dimensional space. If there are two components we have one variable too many, if there are three, we have two variables too many. It is necessary therefore to assume some further

condition or conditions before a model can be constructed. The most interesting applications of thermodynamic surfaces are those which refer to

(1) a mixture of two components when the pressure is kept constant,

(2) a mixture of three components when the pressure and temperature are both constant.

For more than three components the proportions of which are capable of independent variation a model in three-dimensional space is no longer sufficient.

The choice of coordinates depends mainly on the problem to be studied. For a detailed discussion of experimental aspects of the problem the reader is referred to the many excellent treatises on physical chemistry.

For the purposes of theoretical discussion the best variables to take are the partial potentials of the components, with the temperature as a third variable if there are only two components. For practical purposes the variables should be so chosen as to specify the percentage composition of the mixture.

175. The partial potentials of the components as coordinates. Consider first a mixture of two components a, b at constant pressure p, and take as coordinates

$$x = \mu_a, \quad y = \mu_b, \quad z = T.$$

Then since by the properties of the mixture p is a function of μ_a, μ_b and T, the equation

$$p = \text{constant} \tag{327}$$

determines a surface which is the thermodynamic model of the mixture at constant pressure p.

Moreover the points of intersection of two or three sheets of the surface determine states of phase equilibrium between two or three phases respectively.

From the equation

$$-vdp + sdT + \Sigma m d\mu = 0$$

it follows that the equation of the tangent plane can be written

$$(x - \mu_a) m_a + (y - \mu_b) m_b + (z - T) S = 0. \tag{328}$$

Hence if the tangent plane is cut by the plane $z =$ constant, its trace on that plane makes with the axis of z an angle whose tangent is $-m_a m_b$ and this determines the ratio of m_a to m_b, the actual masses in a unit mass of mixture being got by putting

$$m_a + m_b = 1.$$

Again put

$$x = y = r \cos 45^0$$

in the equation of the tangent plane; then remembering $m_a + m_b = 1$ we get

$$zS + \tfrac{1}{2} r \sqrt{2} = \text{constant}. \tag{329}$$

Hence if φ be the inclination to the axis of z of the line in which the tangent plane meets a plane making angles of 45^0 with the axes of x and y,

$$\tan \varphi = S \sqrt{2} \tag{330}$$

and hence the direction of the tangent plane determines not only the composition of the mixture but also its entropy per unit mass. This information is useful in determining whether a given change of phase is accompanied by absorption or evolution of heat.

176. In the case of three components, the equations

$$p = \text{constant}, \quad T = \text{constant}$$

determine with the fundamental equation of the mixture a single equation between μ_a, μ_b, μ_c so that taking the coordinates to be

$$x = \mu_a, \quad y = \mu_b, \quad z = \mu_c$$

the point (x, y, z) lies on a surface which is a thermodynamic model of the mixture at temperature T and pressure p.

The tangent plane to the surface is given by

$$(x - \mu_a) m_a + (y - \mu_b) m_b + (z - \mu_c) m_c = 0$$

or

$$m_a x + m_b y + m_c z - \mathfrak{f}_p = 0. \tag{331}$$

The direction of the tangent plane thus determines the percentage composition of the mixture and its position determines the potential $\mathfrak{f}_p$ (which however is known independently when m_a, m_b, m_c are known as well as the partial potentials).

If we put $m_a = 0$ we see that the tangent plane is parallel to the axis of x. This is true whether we are dealing with two or three components. The curves determined by this condition and by similar conditions representing the absence of the other component or components determine the boundary of the thermodynamic surfaces. The bounding curve $m_a = 0$ is the line of contact of an enveloping cylinder whose generating lines are parallel to the axis of x.

If through any point P of this boundary a line be drawn parallel to the axis of x and meeting another sheet of the thermodynamic surface in a point Q on the *negative* side of P, equilibrium will exist between the phase represented by Q and the phase with the absent component represented by P.

177. Case of two components when one coordinate determines the percentage composition. If x and $1-x$ are the masses of the two components in unit mass of a mixture we may take as coordinates x, T and $\mathfrak{f}_p$, x lying between 0 and 1, and the thermodynamic surface will then be given by $p =$ constant.

The equation

$$d\mathfrak{f}_p = -S\,dT + V\,dp + \Sigma\mu\,dm$$
$$= -S\,dT + (\mu_a - \mu_b)\,dx$$

shows that the equation of the tangent plane may be written in the form

$$z - \mathfrak{f}_p = -S(y-T) + (\mu_a - \mu_b)(x' - x) \tag{332}$$

if we write x' for the coordinate on the tangent plane. We have moreover

$$\mathfrak{f}_p = \mu_a x + \mu_b(1-x)$$

whence the equation of the tangent plane becomes

$$z = -S(y-T) + \mu_a x' + \mu_b(1-x'). \tag{333}$$

The tangent line in the plane $y = T$ is given by

$$z = \mu_a x' + \mu_b(1-x') \tag{334}$$

and hence μ_a, μ_b are the intercepts which it cuts off from the lines $x' = 1$, $x' = 0$ respectively.

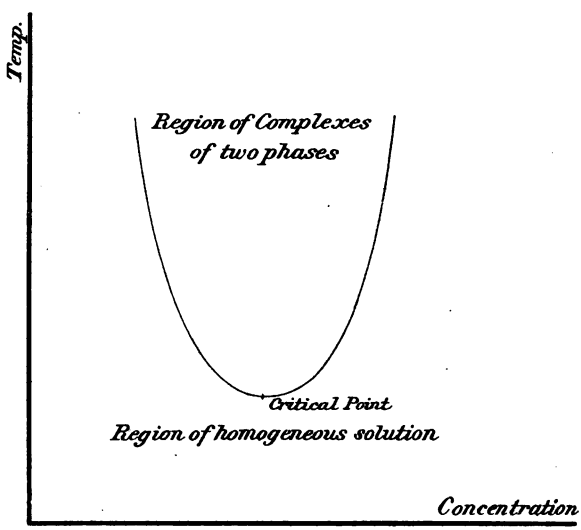

Fig. 23.

If two phases are in equilibrium, they lie in the same section $T =$ constant, and we now see that they have a common tangent line in that plane. It readily follows that in any section, a double tangent line will represent a complex of two phases, and the essentially stable states at temperature T will be represented by points on the convex line found by the sections of the thermodynamic surface and its double tangents.

Now making T variable let the double tangent move along the surface always remaining parallel to the plane $y = 0$, and let the curves which it traces on the surface be projected on the plane of (x, T). We shall thus have the plane divided into regions, showing the limits of percentage composition and temperature corresponding to single phases or a complex of two phases. These are the concentration and temperature diagrams commonly found in treatises on physical chemistry, and Fig. 23 shows an example of them, giving the relation between the concentration of a solution of dimethylamine in water and the temperature.

178. Case of three components. — Use of triangular coordinates. For three components the masses per unit mass of the mixture are connected by the relation

$$m_a + m_b + m_c = 1$$

and a convenient way of representing quantities of this kind in a plane is by the use of axial or triangular coordinates. If ABC is any fixed triangle, M any point in its plane, and if α, β, γ denote the ratios

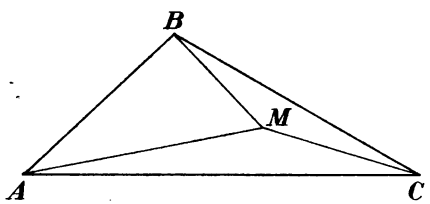

Fig. 24.

$$\frac{\Delta BMC}{\Delta ABC}, \quad \frac{\Delta CMA}{\Delta ABC}, \quad \frac{\Delta AMB}{\Delta ABC},$$

α, β, γ are the triangular coordinates of M and satisfy the relation

$$\alpha + \beta + \gamma = 1.$$

We may take α, β, γ to represent the masses of the components and a line MP perpendicular to the plane to represent the potential $\mathfrak{f}_p$, so that the coordinates of P will be

$$\alpha = m_a, \quad \beta = m_b, \quad \gamma = m_c, \quad z = \mathfrak{f}_p$$

and the thermodynamic surface is given by

$$p = \text{constant}, \quad T = \text{constant}.$$

Substituting these values in the differential equation

$$d\mathfrak{f}_p = -SdT + v\,dP + \Sigma\mu\,dm,$$

and noting that

$$\mathfrak{f}_p = \Sigma\mu m, \quad 1 = \Sigma m$$

the equation of the tangent plane reduces to

$$z = \alpha\mu_a + \beta\mu_b + \gamma\mu_c. \tag{335}$$

Putting $\beta = 0$, $\gamma = 0$, $\alpha = 1$, we get $z = \mu_a$. Hence the potentials μ_a, μ_b, μ_c are the heights of the tangent plane above the vertices

A, B, C; the condition of phase-equilibrium requires that the points representing the three phases shall have a common double tangent plane. The points of contact of these double tangent planes will divide the triangle ABC into regions representing the limits of percentage composition of single phases and of complexes of two phases.

In forming the surface of dissipated energy the double tangent plane must be rolled on the upper side of the bounding curves in the planes, $\alpha = 0$, $\beta = 0$, $\gamma = 0$, thus determining the regions representing complexes in which one constituent is absent from one of the phases, and it must also be turned about the highest points on thermodynamic surfaces above the vertices of the primitive triangle, thus determining regions in which one of the phases contains only a single constituent.

Fig. 25 (after *Wilder D. Bancroft*[1]) is an instance of the diagrams occurring in treatises on physical chemistry, the three components in this case being the nitrates of lead, potassium and sodium. It differs

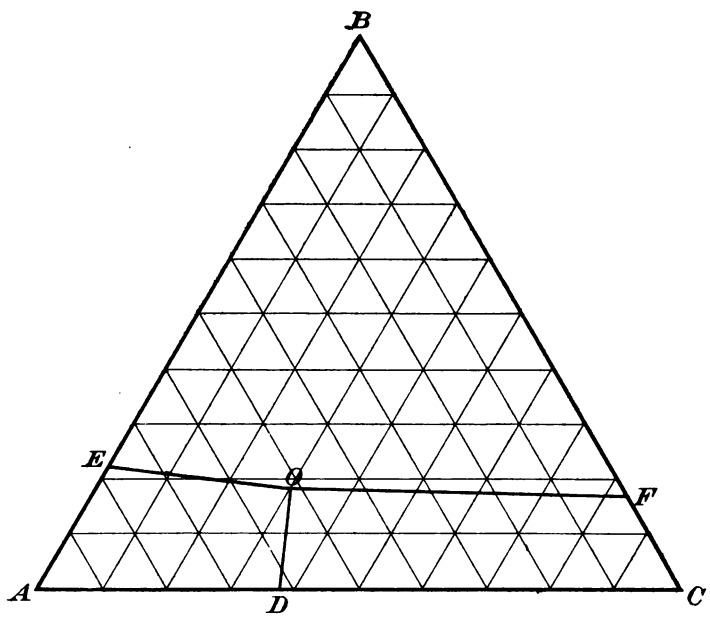

Fig. 25.

from the theoretical diagrams discussed above in the fact that the temperature is not the same at all points. To be complete, the diagram would have to be crossed by a series of isothermal lines. For a more detailed discussion the reader is referred to the treatises in question.

1) *Phase Rule.*

Description of Figure 25.

A is corner for KNO_3.

B is corner for $Pb(NO_3)_2$.

C is corner for $NaNO_3$.

At D KNO_3 and $NaNO_3$ are in proportions corresponding to eutectic alloy.

E = eutectic alloy of KNO_3 and $Pb(NO_3)_2$.

F = eutectic alloy of $NaNO_3$ and $Pb(NO_3)_2$.

Along DO, solid phases are K and Na nitrates;

Along EO, solid phases are K and Pb nitrates;

Along FO, solid phases are Na and Pb nitrates.

At O exists nonvariant system of K, Pb and Na nitrates, solution, and vapour.

Field $ADOE$ represents a divariant region of KNO_3, solution, and vapour.

Field $CDOF$ represents a divariant region of $NaNO_3$, solution, and vapour.

Field $BEOF$ represents a divariant region of $PbNO_3$, solution, and vapour.

179. Dynamical Model of Carnot's Cycle. The equations of reversible thermodynamics being analogous in form to those of rational mechanics with the addition of one extra independent variable and the corresponding dependent variable obtained by the differentiation of a potential function (the variables being temperature and entropy, and the function being the suitable thermodynamic potential), it naturally follows that a dynamical model can easily be constructed which is capable of representing the phenomena of reversible thermodynamics.

A very simple model of a simple system is shown in the Fig. 26, on p. 186. A shaft which can rotate freely about a vertical axis carries an projecting arm on which a bead of mass m can slide, and the distance r of the bead from the axis can be varied by pulling a string passing over a pulley and through the middle of the shaft. To prevent the string from twisting indefinitely with the rotation of the shaft a small swivel may be fixed in its vertical part. We suppose work done by the tension of the string to represent the mechanical work dW of thermodynamics, whereas work done by applying a couple about the axis of the shaft represents the communicated heat dQ. The source and refrigerator of Carnot's cycle may be represented by flanges rotating above and below the vertical shaft with constant angular velocities ω_1 and ω_2 respectively. Heat communication may be represented by bringing one of these flanges into

contact with flanges fixed to the shaft itself (as shown in the figure). If two flanges are only brought into contact when their angular velocities are equal the motions will be conservative and reversible as in the thermodynamical process where the working substance is only brought into contact with the source or refrigerator when their temperature are equal.

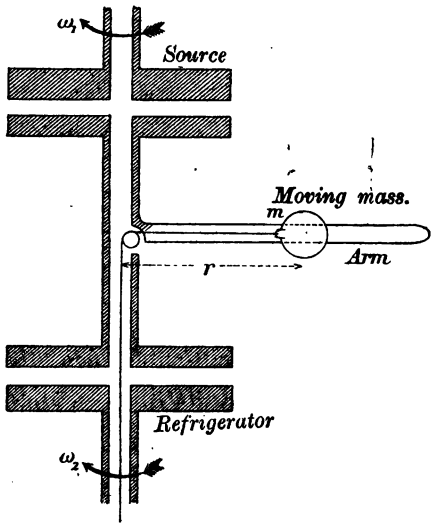

Fig. 26.

The four processes of Carnot's cycle will be represented as follows:

(1) The shaft starts with angular velocity ω_2 and is disconnected from both flanges. The string is pulled till the angular velocity of the shaft becomes equal to ω_1 the angular momentum remaining constant and the moment of inertia decreasing.

(2) The shaft is connected with the "source" ω_1 and absorbs energy Q_1 from it, this energy causing the bead to fly outwards and a certain quantity of external work being done by the tension of the string.

(3) The shaft being disconnected and free undergoes an "adiabatic" transformation in which the angular momentum remains constant and the angular velocity decreases from ω_1 to ω_2 as the bead recedes further from the axis.

(4) The shaft is now connected with the "refrigerator" ω_2 and the bead slowly drawn back to its initial position, energy Q_2 being given to the refrigerator.

A Watt's governor with a similar arrangement of rotating flanges for the source and refrigerator will lead to an essentially identical cycle.

If ϑ is the angular coordinate of the shaft, I the moment of inertia apart from the bead, the energy of the shaft is

$$L = \tfrac{1}{2}(I + mr^2) \cdot \dot{\vartheta}^2 = \tfrac{1}{2}(I + mr^2)\,\omega^2$$

and if h is the angular momentum

$$h = (I + mr^2)\,\omega, \quad L = \tfrac{1}{2}h\omega.$$

If G is the couple applied to the shaft, Lagrange's equation of motion gives

$$G = \frac{d}{dt}\left(\frac{dL}{d\omega}\right) - \frac{dL}{d\vartheta} = \frac{dh}{dt}$$

and the work done by this couple while in contact with the source is given by

$$dQ_1 = G\omega_1\, dt = \omega_1 \frac{dh}{dt}\, dt$$

whence for the whole work

$$Q_1 = \omega_1 (h_1 - h_2)$$

where h_2 and h_1 are the initial and final angular momenta. Similarly for the work energy communicated to the refrigerator

$$Q_2 = \omega_2 (h_1 - h_2)$$

leading to

$$\frac{Q_1}{\omega_1} = \frac{Q_2}{\omega_2}. \tag{336}$$

This equation is exactly analogous to the equation

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

of Thermodynamics. Angular velocity represents temperature and angular momentum represents entropy.

A further analogy is afforded by the fact that work done by the pull of the string represents available energy, whereas work cannot be obtained through the angular coordinate by reversible methods except by bringing the shaft into contact with another shaft rotating with the same angular velocity; energy communicated in this way is therefore not wholly available (compare also §§ 43, 44).

We notice that in the more general case when the shaft has a couple G applied to it in any manner

$$dQ = \omega \frac{dh}{dt}\, dt = \omega\, dh \tag{337}$$

so that

$$\frac{dQ}{\omega} = dh, \text{ analogous with } \frac{dQ}{T} = ds.$$

But ω is not the only integrating divisor of dQ. The most general form of integrating divisor is ω multiplied into a function of h, and the energy L is itself an integrating divisor, thus

$$\frac{dQ}{L} = 2\frac{dh}{h} = d \log h^2 \tag{338}$$

another analogue of the thermodynamic equation, L taking the place of temperature and $\log h^2$ + const. the place of entropy. Since

$$h^2 = 2(I + mr^2)L$$

the expression for the entropy in this case takes the form

$$s = \log L + \log(I + mr^2) + \text{const.} \tag{339}$$

resembling more closely the form for a perfect gas

$$s = \gamma_v \log T + B \log v + \text{const.}$$

and affording confirmation of the view that temperature is a quantity of the nature of the kinetic energy.

The analogy with thermodynamics does not extend to the irreversible processes arising when two shafts with unequal angular velocities are brought into contact. In the dynamical model the angular momentum or entropy remains constant and the energy decreases.

180. Monocyclic systems. The model described in the last paragraph is an example of what von Helmholtz calls a *monocyclic system* or system containing one circulating motion; a system containing more than one circulating motion is called *polycyclic*, and both are included under the general name of *cyclic system*. The coordinates defining the circulating motions are called *cyclic* or *uncontrollable* coordinates; (so that the angular coordinate of the shaft of the above model is a cyclic coordinate). The remaining coordinates (such as the distance of the sliding mass from the axis) are spoken of as *controllable* or *non-cyclic*. Exact definitions of these terms are given by the following assumed properties of the system:

(1) The kinetic and potential energies of the system do not depend on the cyclic coordinates themselves, but the kinetic energy is a function of their rate of change.

(2) In variations of the state of the system the rates of change of the non-cyclic coordinates are small and the same applies to the accelerations of both classes of coordinates.

Let q_a, q_b be types of the generalised position coordinates, the suffixes a, b referring respectively to non-cyclic and cyclic coordinates. Let p_a, p_b be the corresponding impulse-coordinates or generalised momenta, P_a, P_b the force-coordinates so that $P\,dq$ represents the work done on the system in the displacement dq. Then if U denotes the total energy expressed as a function of the position and impulse-coordinates, L, V the kinetic and potential energies, Hamilton's modification of Lagrange's equations gives for either class

$$\frac{dq}{dt} = \frac{\partial U}{\partial p} = \frac{\partial L}{\partial p} \text{ and } P = \frac{dp}{dt} + \frac{dU}{dq}.$$

In virtue however of the above assumption as to q_b, we have

$$P_b = \frac{dp_b}{dt}$$

and if dQ is the whole work communicated through the coordinates q_b in time dt

$$dQ = \Sigma P_b \, dq_b = \Sigma \frac{dp_b}{dt} \frac{dq_b}{dt} dt = \Sigma \dot{q}_b \, dp_b$$

where

$$\dot{q}_b = \frac{dq_b}{dt}.$$

If L is the kinetic energy, L is expressed in the above method as a homogeneous quadratic function of the momenta p_a, p_b, therefore

$$2L = \Sigma \left(p_a \frac{dL}{dp_a} + p_b \frac{dL}{dp_b} \right) = \Sigma \left(p_a \frac{dq_a}{dt} + p_q \frac{dq_b}{dt} \right)$$
$$= \Sigma p_b \dot{q}_b \quad \text{(neglecting } \dot{q}_a \text{ as assumed).}$$

For a monocyclic system we therefore have

$$\frac{dQ}{\dot{q}_b} = dp_b, \quad \frac{dQ}{L} = 2 d \log p_b \tag{340}$$

so that either $\dot{q}_b$ or L is an integrating divisor of dQ. These results are analogous in form to the thermodynamic equation

$$\frac{dQ}{T} = dS$$

but as Helmholtz points out, it is more difficult to obtain dynamical properties representing temperature equilibrium between two bodies, especially seeing that the condition for this in thermodynamics is that the integrating divisors of dQ for the two bodies are equal. As to the phenomena of heat flow between unequally heated bodies, a purely dynamical representation is precluded by the very character of the assumed dynamical equations, unless recourse is had to arguments of a statistical character, and even then, *some* assumption must necessarily be made.

A polycyclic system does not in general possess an integrating divisor for dQ. If however the changes which take place in it are such that all the cyclic velocity coordinates are always increased or decreased in the same ratio, then L will be an integrating divisor of dQ. It is to be observed that in this case the velocities are all expressible in terms of a single variable so that the system really remains monocyclic.

This condition is satisfied by a large assemblage of molecules whose velocities are distributed according to the usual Boltzmann-Maxwell Law of the Kinetic Theory of Gases, provided that the variations represented by dQ take place so slowly that this law of distribution continuously re-establishes itself.

181. The Clausius-Szily System. — Stationary or Quasi Periodic Motions. The results arrived at as the result of a number of papers published by Clausius and Szily between the years 1870 and 1876 may be said to lie on the borderline between non-statistical and statistical methods. In this method we consider a number of molecules whose motions individually are uncontrollable and for simplicity we shall represent them by masses m_1 at (x_1, y_1, z_1), m_2 at (x_2, y_2, z_2) and so on. We suppose in addition that there are certain controllable coordinates, $q_1, q_2, q_3, \ldots$ entering into the expressions for the energy of the system; thus for a mass of gas, the volume of the containing cylinder would be a coordinate of this character. The changes of these coordinates are so slow compared with the motion of the molecules that their velocities are neglected and the kinetic energy is therefore entirely molecular. We assume that the character of the motion is capable of variation independently of the coordinates $q_1, q_2, \ldots$ and that δQ represents energy imparted to the system by this independent variation. Taking L and V to be the kinetic and potential energies we have

$$L = \tfrac{1}{2} \Sigma m (\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$$

$$\delta V = \Sigma \left(\frac{dV}{dx} \delta x + \frac{dV}{dy} \delta y + \frac{dV}{dz} \delta z \right) + \Sigma \frac{dV}{dq} \delta q.$$

From the methods of the Principle of Least Action

$$\delta \int_{t_1}^{t_2} 2L \, dt = \Big[\Sigma m (\dot{x} \, \delta x + \dot{y} \, \delta y + \dot{z} \, \delta z) \Big]_{t_1}^{t_2}$$

$$+ \int_{t_1}^{t_2} \{ \delta L - \Sigma m (\ddot{x} \, \delta x + \ddot{y} \, \delta y + \ddot{z} \, \delta z) \} \, dt.$$

By D'Alembert's principle

$$\begin{aligned} - \Sigma m (\ddot{x} \, \delta x + \ddot{y} \, \delta y + \ddot{z} \, \delta z) &= \Sigma \left(\frac{dV}{dx} \delta x + \frac{dV}{dy} \delta y + \frac{dV}{dz} \delta z \right) \\ &= \delta V - \Sigma \frac{dV}{dq} \delta q \\ &= \delta V + \delta W \end{aligned}$$

where δW is the external work done through the q coordinates. Also by conservation of energy or the first law

$$\delta Q = \delta U + \delta W = \delta L + \delta V + \delta W.$$

It readily follows that

$$\delta \int_{t_1}^{t_2} 2L\,dt = \left[\Sigma m(\dot{x}\,\delta x + \dot{y}\,\delta y + \dot{z}\,\delta z)\right]_{t_1}^{t_2} + \int_{t_1}^{t_2} \delta Q\,dt.$$

Putting $t_2 - t_1 = ni$ where n is any numerical quantity whatever (integral or fractional), and using a bar drawn over the letters to represent mean values taken over the time interval ni, the first and last integrals become $n\delta(2i\bar{L})$ and $ni\,\bar{\delta Q}$ and we obtain

$$\frac{\bar{\delta Q}}{\bar{L}} = \delta \log (i\bar{L})^2 - \frac{\left[\Sigma m(\dot{x}\,\delta x + \dot{y}\,\delta y + \dot{z}\,\delta z)\right]_{t_1}^{t_2}}{ni\bar{L}}.$$

Now there are many definite systems performing definite motions in which we are justified in assuming that the time interval

$$t_2 - t_1 = ni$$

may be so chosen that the term

$$\left[\Sigma m(\dot{x}\,\delta x + \dot{y}\,\delta y + \dot{z}\,\delta z)\right]_{t_1}^{t_1+ni} \tag{341}$$

either vanishes or lies between finite limits however large be the value of n, so that by making n sufficiently large the quotient of this expression when divided by $ni\bar{L}$ may be made as small as we please. And the value of $\delta \log (i\bar{L}^2)$ is not affected by replacing i by a numerical multiple of i, that is by altering n, if the mean value $\bar{L}$ is taken over the same time interval ni. Such cases may be specified by introducing the term "*quasi* periodic" to characterise the particular systems performing the particular motions to which this assumption applies, and we then obtain the property that $\bar{L}$ is an integrating divisor of $\bar{\delta Q}$ the quantity taking the place of entropy then taking the form $\log (i\bar{L})^2$.

At the same time the interpretation of the quantity i raises difficulties which have to be examined in detail in applying the method to any particular case.

182. Energy accelerations. By introducing the concept of energy accelerations it is possible to obtain for a conservative dynamical system relations analogous in form and dimensions to the temperature-relations which determine the equilibrium or non-equilibrium of heat, such relations being compatible with the view that temperature is a quantity of the nature of molecular kinetic energy and is therefore a homogeneous quadratic function of the velocity-coordinates of the system.

Considering a system of masses m at points (x, y, z) moving with velocities (u, v, w) and supposing the potential energy due to their mutual actions as well as to the field in which they are placed to be V and taking the equations of motion

$$m\frac{du}{dt} = m\frac{d^2x}{dt^2} = -\frac{\partial V}{\partial x}$$

and supposing the suffixes 1, 2, ... to refer to different particles, it will be found that if we form the *first* differential coefficients with respect to t of the squares and products, such as

$$u^2, \quad uv, \quad u_1u_2, \quad v_1v_2, \ldots$$

the signs of these will be reversed by reversing all the velocities and this is not what we want, but if we form the second differential coefficients

$$\frac{d^2}{dt^2}u^2, \quad \frac{d^2}{dt^2}(uv), \ldots$$

which we call the *accelerations* of these quantities, these can be expressed in the form of quadratic functions of the velocities plus constant terms.

These forms show that the accelerations thus defined are unaltered in sign when the velocities are reversed in sign, and that the squares and products in question obey differential equations of the second order analogous in form to the equations of ordinary dynamics. For instance we should have

$$\frac{d^2}{dt^2}\left(\frac{1}{2}u_1^2\right) = \frac{1}{m_1^2}\left(\frac{dV}{dx_1}\right)^2 - \frac{u_1}{m_1}\sum\left(u\frac{d}{dx} + v\frac{d}{dy} + w\frac{d}{dz}\right)\frac{dV}{dx_1}.$$

The variables (other than position variables) occurring in these equations include those necesssary to define the components of kinetic energy corresponding to the different particles and coordinates, and the equations may be thus used to determine the conditions of energy-equilibrium as well as the variations of the energy-components relative to their equilibrium values, just as we consider in Dynamics equilibria of position and motions relative to states of equilibrium, determined by the accelerations of the position coordinates.

If two collections of particles be brought within working distance of each other the new state of energy-equilibrium must be determined with reference to the system as a whole, and energy-accelerations will be set up different to those which existed previously. These will be of such a character as to bring the systems towards a stable distribution or away from an unstable distribution just as two unequally heated bodies when placed in contact tend to a stable state of uniform temperature.

A simple illustration of redistribution of energy is afforded by two pendulums of nearly equal mass and period brought within each other's influence. If one is swinging and the other initially at rest energy passes from the former to the latter and back so as to make the *average* energy the same for both when taken over a cycle of changes. With two pendulums it is easy to separate them when the energy is all in one, but if we had a hundred pendulums and the average energy of fifty of them were initially different by a finite amount from that of the rest, the energies of the pendulums would fluctuate about an average distribution so that after a short time the average energy of the first fifty would never differ from that of the others by more than a very small fraction.

183. Duhem's Theory of false Equilibria. According to the theories of chemical equilibrium as previously discussed a substance S will pass from one phase to another as soon as its potential in the first phase becomes greater than in the second, and *vice versa.* In a thermal diagram, according to this view, the curve of transition from phase 1 to phase 2 will be identical with the curve of transition from phase 2 to phase 1, and will be the locus of points for which the potentials in the two phases are equal. Now it is found in practice that two phases may often remain in contact without any change taking place even when the conditions of equilibrium obtained by the methods of conventional — or as *Duhem* calls it "classical" Thermodynamics are not satisfied. In such cases the curve of transition from phase 1 to phase 2 will be different to the curve of transition from phase 2 to phase 1, and the curve of true equilibrium will be bordered by a region of "false equilibrium" in which the substance will remain in whichever phase it happens to be without any change taking place. If the borderline of this region is reached an explosion not unfrequently accompanies the change. These cases of false equilibrium have been explained by *Duhem* on the assumption of a resistance analogous to friction which tends to prevent a substance from passing from one phase into another. If the difference of potential in the two phases is less than the friction, the system remains in false equilibrium, if it is greater the false equilibrium breaks up. As in mechanics, the friction always acts in the opposite direction to that in which transformation tends to take place, and the amount of friction called into play is just what is necessary to prevent a change from taking place, provided that this amount is less than the limiting friction.

This frictional resistance differs from viscosity in that the latter diminishes indefinitely with the rate of change or velocity. A resistance of the latter character merely retards the tendency to

assume a state of equilibrium, but can never maintain the system indefinitely in a different state; it would not therefore account for phenomena like false equilibria. The conditions under which an explosion occurs when a state of false equilibrium is broken have also been investigated by Duhem, who has shown that they admit of a simple geometrical interpretation.

An example of false equilibrium is afforded by a mixture of oxygen and hydrogen at ordinary temperatures. If the mixture is ignited by an electric spark a violent explosion takes place.

A mechanical illustration is afforded by a cylinder containing gas, furnished with a tightly fitting piston, between which and the cylinder friction acts, and on which various loads can be placed. In the absence of friction, the load would by Boyle's law be inversely proportional to the volume, and the curve representing the relation between volume and load would be a rectangular hyperbola. Owing to friction however this "curve of true equilibrium" is bordered by a region of false equilibrium, and the boundaries of this region will be rectangular hyperbolas above and below the curve of true equilibrium at distances from it representing the limiting force of friction. One of these boundaries will represent the relation between volume and load when the piston is ascending, the other when the piston is descending.[1]) It should however be mentioned that differences of opinion exist regarding Duhem's theory.

1) J. W. Mellor, Chemical Statics and Dynamics, London, Longmans, 1904.

CONCLUSION.

GENERAL SUMMARY OF THE FOUNDATIONS OF THERMODYNAMICS.

In all the transformations of a material system considered in this book there is a certain entity which

(1) Remains constant in quantity,

(2) Is capable under certain conditions of assuming the forms of kinetic and potential energy which are dealt with under the study of Rational Dynamics.

This entity is called *energy*.

As it is only possible to study *changes* of energy the expression for the energy of a material system necessarily contains an unknown constant.

Irreversible transformations exist, and if such a transformation can take place it will do so. A reversible transformation can only be regarded as the limiting form of an irreversible one.

An irreversible transformation involving energy must from the very nature of irreversibility transform energy into forms which are less capable of further transformation than they were previously, and this fact is expressible by the statement that such a transformation involves a loss of availability.

In order that the irreversible effects of different transformations should be capable of comparison and quantitative measurement it is necessary that compensating transformations should exist. In all the problems considered in this book, it has been assumed that this is the case.

When irreversible changes have occurred in the interior of a finite system we accordingly assume that the system itself can be brought back to its initial state by a compensating transformation, but in this case changes must take place in some other part of the universe. An irreversible transformation thus leaves an indelible imprint *somewhere or other* on the progress of events in the universe considered as a whole.

The kinetic and potential energies considered in rational dynamics are under all conditions to be regarded as wholly available for transformation into other forms. We shall call these forms of energy *mechanical energy* or shortly *work*.

We may therefore measure the loss of availability of an irreversible transformation by the loss of energy capable of being transformed into work or kinetic and potential energy of visible motion, that is by loss of *available energy*. It is however necessary to specify more fully the

conditions under which energy is transformable in order to render the notion of available energy definite.

The various forms of kinetic and potential energy occurring in phenomena that can be studied by the methods of reversible dynamics, with the exclusion of statistical methods as applied to molecular dynamics are in general to be regarded as wholly available energy.

Under this heading we include those forms of energy occurring in hydrodynamics and elasticity, where the equations of reversible dynamics are applied in conjunction with the methods of the infinitesimal calculus.

Such applications involve the conception of differential elements which are large compared with the molecular structure of matter but sufficiently small to define the properties of matter treated in reversible dynamics. The conception of such elements is involved in the definitions of pressure and density *"at a point"*.

While the notion of a differential element is necessarily an artificial one and it is not possible *à priori* to draw a hard and fast line between energy which is and energy which is not available under all circumstances, experience shows that in a large number of physical phenomena the distinction is well marked. It is in such cases that thermodynamical methods become applicable.

Energy can be transferred from one body to another or from one differential element of a body to another, otherwise than by the performance of work. In such cases the energy so transferred is called heat and the quantity of energy so transferred is called the quantity of heat passing from the one body or element to the other.

Energy communicated to a body in the form of heat is in general partially but not wholly available for conversion into work, the proportion which is available depending on the physical state of the body and the external conditions to which it is subjected. Hence we cannot speak of a system as containing a definite quantity of heat or a definite quantity of work.

Passage of heat from one body to another is usually irreversible and therefore accompanied by a loss of available energy. If we define A to be hotter or colder than B according as available energy is lost or gained by the transference of heat from A to B, it follows that heat can and in general will pass from hotter to colder bodies, but the reverse change can only be effected by combining it with a compensating transformation. When no transference of heat tends in either direction the bodies are said to be in thermal equilibrium.

Carnot's cycle reversed is a compensated reversible transformation by which heat can be continuously taken from a colder and given to a hotter body or *vice versa* without loss of availability (§ 63). In this case the compensating transformation takes the form of work absorbed or produced.

The ratio of the quantities of heat passing to and from two bodies in a Carnot's cycle is called the absolute temperature-ratio of the bodies, and leads to a definition of absolute temperature which is in accordance with all the ordinary properties of temperature (§ 63).

Absolute temperature as thus defined in thermodynamics contains an indeterminate constant factor depending on the magnitude of the unit or degree which is arbitrary, and must be fixed by convention.

That thermal equilibrium between two bodies is unaffected by displacing the bodies so as to alter their relative position or orientation is not a self evident truth. On the contrary this property is deducible from a certain assumption as to the nature of the forces between the bodies, (§ 62).

The conception of *temperature at a point* of an unequally heated body rests on conventions similar to those employed in defining pressure at a point or density at a point in ordinary dynamics, and involves the consideration of differential elements. The property that the temperature at a point of a material body is the same in all directions depends on an assumption similar to that mentioned just above.

An isolated system will tend to a state of stable equilibrium in which the available energy is a minimum subject to the conditions that the total energy is constant, and it follows that the unavailable energy will be a maximum. In this state of equilibrium thermal equilibrium must exist between all parts of the system, i. e. they must be at the same temperature.

Let a finite system be in the presence of an indefinitely extended material medium all of whose parts are in thermal and mechanical equilibrium and therefore at a uniform temperature T_0. Let the system undergo any change, such, for example as an irreversible internal change, or the communication of heat from without, this heat representing energy which is not wholly available under the conditions postulated. Then the increase of *non-available* energy produced by the change is proportional to the absolute temperature T_0 of the medium. This increase when divided by T_0 is therefore a quantity depending only on the changes which take place in the system and not on the temperature of the medium. This quantity is called the *increase of entropy* produced in the system by the given transformation. From this increase the *entropy* of the system is defined, but its expression contains an unknown constant entering in the same form as an integration constant.

In some irreversible transformations the change of entropy can be expressed as a sum of differentials of the form $\frac{dQ}{T}$, in many others it is impossible to do this in any simple way.

Entropy is increased by irreversible transformations, but can never decrease. If a finite system is put through an irreversible cyclic change, there must be an increase of entropy somewhere outside the system.

When the available energy of a system is a minimum it follows from the ordinary properties of maxima and minima in analysis that its differential *in general* vanishes to the first order. For this reason the equations of reversible thermodynamics are *in general* applicable to investigate the conditions of thermodynamic *equilibrium*. The inequalities of irreversible thermodynamics are required in discussing *stability* of equilibrium.

The properties of systems in thermodynamic equilibrium are thus made to depend on potential functions similar to those occurring in statics, but with the addition of one further variable. By suitable modifications of the potential function this variable may be made to be the temperature. If such a potential function is known as a function of the corresponding variables for a given system the thermodynamic properties of the system are completely defined.

The thermodynamic properties of a simple system as represented by a homogeneous fluid are completely specified by the following data, or their equivalents:

(a) The pressure as a function of the volume and temperature for all volumes and temperatures.

(b) The specific heat at constant volume as a function of the temperature alone at one particular volume only.

The properties of a reversible thermo-electric network are determined by a single function which represents at any point the quantity of entropy gained by carrying a unit charge to that point. From the effect of electric currents on the localisation of both available and unavailable energy it appears that entropy must be regarded as capable of being located in an electric charge.

INDEX.

*** THE NUMBERS REFER TO THE PAGES. PROPER NAMES ARE PRINTED IN ITALICS.

D.

E.

F.

1) The word „heat" occurs so frequently and is used in so many different connections that it has purposely been omitted from the index. To index it separately would have involved a large amount of repetition.

ERRATA.

Pages 31 and 32, substitute L for T as the symbol for kinetic energy.
Page 39 line 18 for $A=(U-T_0 S)-(U_0-T_0 S_0)$ read
"$A=(U-T_0 S+p_0 V)-(U_0-T_0 S_0+p_0 V_0)$
or $A=(U-T_0 S)-(U_0-T_0 S_0)$".

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