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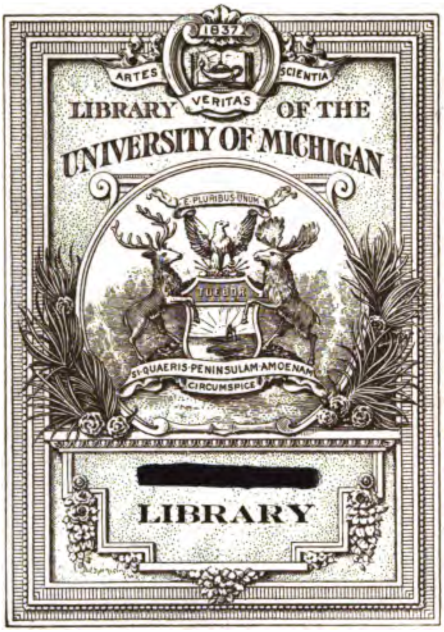

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AN OUTLINE OF THE THEORY OF THERMODYNAMICS

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OF
THERMODYNAMICS

BY

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PREFACE

In the course of studying thermodynamics I have found a considerable gap between the text-books available and the modern memoirs. This volume has been written to spare other students some of the time which I have had to spend in bridging over the gap for myself.

As the title indicates, it is not a book of applications, but a brief outline of the theory, the applications having been selected solely with a view to their illustrative value. Physical applications may be found in any large work on Physics, while in the field of Physical Chemistry M. Duhem's recent work on Chemical Mechanics * makes a new volume of applications superfluous for the present.

I am, of course, indebted to many authors. In cases where the methods used were not so well known as to be common property, I have intended to mention my sources; but I must particularly acknowledge my great indebtedness to Professor Gibbs * and M. Duhem,* whose influence will be very evident to readers familiar with their writings.

In concluding, it is a pleasure to express my thanks to Professor James Harkness of Bryn Mawr College, for aid and advice during the preparation of the manuscript, and to Professor W. S. Franklin of Lehigh University, T. W. Richard of Harvard University, and J. E. Trevor of Cornell University, for assistance in revising the proof, as well as for many valuable suggestions regarding the subject matter.

EDGAR BUCKINGHAM.

CAMBRIDGE, MASSACHUSETTS,
April 30th, 1900.

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* See list of reference books in the Appendix.

CONTENTS

CHAPTER I

THERMOMETRY

CHAPTER II

CALORIMETRY

CHAPTER III

MATERIAL SYSTEMS IN THERMODYNAMICS

CHAPTER IV

THE FIRST LAW OF THERMODYNAMICS

CHAPTER V

THE PRINCIPLES OF THERMOCHEMISTRY

CHAPTER VI

CALORIMETRIC PROPERTIES OF FLUIDS

CHAPTER VII

RECAPITULATION

CHAPTER VIII

THE SECOND LAW OF THERMODYNAMICS

CHAPTER IX

GENERAL EQUATIONS

CHAPTER X

APPLICATIONS

CHAPTER XI

THE CONDITIONS OF THERMODYNAMIC EQUILIBRIUM

CHAPTER XII

THERMODYNAMIC POTENTIALS AND FREE ENERGY

CHAPTER XIII

APPLICATIONS

APPENDIX

CHAPTER I

THERMOMETRY

Thermal Equilibrium. Equal Temperatures

1. Two solid bodies which have been at a distance from each other, exert, in general, when brought into contact, a mutual influence: one body becomes warmer to the touch while the other becomes cooler. After a time, no further change due to the contact can be perceived, and the bodies are then said to be sensibly in *thermal equilibrium* with each other. Our primitive means of detecting such change, or lack of change, is the sense of heat or cold at the surface of the human body, but the statements made as to the mutual action of the two bodies remain true, whatever artificially sensitive instrument we use for observing the changes. When the bodies have reached a state of thermal equilibrium they are said to have the *same temperature*, or *their temperatures are equal.*

It is found by experiment that if a body A is in thermal equilibrium with each of two others, B and C, taken separately, then B and C are always in thermal equilibrium with each other. This fact, which is of fundamental importance in thermometry, since we usually test equality of temperature by means of a third body,—the thermometer,—may be expressed by saying: *Two temperatures which are equal to a third are equal to each other.*[*]

2. We have spoken only of the effects of the interaction of the two bodies under consideration. In practice, these are always complicated by the presence of the surrounding bodies, which

A

[*] easily seen by forming a ring of the three  .

produce effects which are superposed on that of the mutual presence of the bodies specially under consideration. These outside influences may, however, be reduced indefinitely, at least as regards their rapidity, by surrounding the bodies to be studied with a space as nearly nonconducting and impermeable to radiation as possible. Or; we may determine the action of the outside bodies by separate experiments, and thus, by elimination of the outside action, find that of the two bodies on each other. These methods give consistent results, and by either of them we may find, as approximately as is necessary in the present state of science, what would happen in the unattainable ideal case, when all outside influence was excluded. Our statements about the two bodies are entirely legitimate, when thus understood—as they are always to be in what follows.

3. Nonmiscible liquids, or, in general, any combinations of substances where the contact is not followed by any appreciable mixing and the dividing surface remains definite, are subject to the same remarks as solids. If the substances mix upon being brought into contact, we can no longer speak of their temperatures separately, since we have no means of experimenting on the components in the mixture. Nevertheless, by the time the act of mixing is complete, the mixture reaches a state in which, considered as a single whole, it is, and remains, in thermal equilibrium with a third indifferent body—the thermometer—of the appropriate temperature. It is usual to speak of this temperature of the mixture as being also the temperature of the separate components, and this mode of expression does not lead us into any practical difficulties, although it has evidently no justification *a priori*.

Uniform Temperature

4. A single body, left to itself, attains, finally, a state of internal thermal equilibrium between its various parts; at least, so far as we can detect by experiments on various portions of it. It is then said to have the same temperature throughout, or to have a *uniform temperature.* Whether this language would be allowable if we could study infinitesimal portions of the body, is an unanswerable, but also, for our purposes, a useless question. Whenever, in future, we speak of *the temperature of a body,* we shall understand that temperature to be uniform, unless the contrary is stated.

Comparison of Different Temperatures

5. Having defined equality of temperature, we have next to consider how unequal temperatures are to be compared. Of two bodies which are not at the same temperature, the one, which, if they were placed in contact, would cool off, is said to be the hotter or to have the *higher temperature.* We have thus a convention regarding the signs of differences of temperature. As regards the mode of determining such differences, the size of the unit, and the absolute value assigned to any given temperature, our choice is purely arbitrary and dictated by convenience. The only conditions to which it is subject are, that a given temperature shall be unequivocally denoted by a given number, and that the values of temperatures, when measured, shall satisfy the algebraic law of addition and subtraction; in other words, that if T_1, T_2, and T_3 are three different temperatures,

$$(T_3 - T_2) + (T_2 - T_1) = (T_3 - T_1) \qquad \text{.................. (1)}$$

Thermometers

6. Since our sense of heat and cold is not to be relied upon quantitatively, we select some accurately measurable property or characteristic of matter, which is altered by changes of temperature. The property must be of such a nature, that for a given temperature we always get the same numerical value from our measurement, and that the same numerical value can not be obtained from two different temperatures. In other words, the property or characteristic must be unequivocally connected with the temperature we wish to measure.

The volume of a body, under a uniform and constant external pressure, is a property which for many substances—especially liquids and gases—satisfies the condition nearly enough for practical purposes. We may, then, construct a *thermometer*, by arranging a mass of such a substance so that changes in its volume may be easily and accurately measured. We then define the sizes of differences of temperature most simply, by making them proportional to the changes of volume of the *thermometric substance*. The *scale of temperature* is, finally, completely fixed by assigning arbitrary values to any two definite and easily reproducible temperatures.

For the construction, marking, calibration, etc. of the thermometers actually in use, the reader, if not already familiar with the subject, may turn to any work on experimental physics, as we are here concerned with the principles and not with the details of thermometry.

7. Thermometers of different substances give, in general, inconsistent readings, and the choice of a substance is arbitrary. The more nearly permanent gases, however, such as oxygen, hydrogen, and nitrogen have, if not too dense, almost identical fractional changes of volume at constant pressure, or of pressure at constant volume, when subjected to identical changes of temperature. We have here a considerable class of substances of similar behaviour, and the choice of one of them as a thermometric substance seems, in a certain sense, less arbitrary than in the case of other substances. For this and other practical reasons, although the mercury-in-glass thermometer is the one most used in ordinary work, the constant volume thermometer, containing hydrogen, is used as the scientific standard of comparison.* Changes of temperature are then proportional to the corresponding changes of pressure of a mass of hydrogen confined in an envelope of invariable volume.

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* This remark is subject to the modifications of article 110.

Thermometric Scales

8. By assigning to the freezing point of pure water at normal barometric pressure, the value 0°, and to the boiling point under the same circumstances, the value 100°, we get the so-called Celsius, or centigrade, scale. The temperature measured on this scale, by the changes of pressure in a constant-volume hydrogen thermometer, agrees very closely, between 0° and 100°, with that indicated by the ordinary centigrade mercury thermometer. We shall, hereafter, denote the temperature measured in this way by t.

The temperature being measured on this scale, we have, as a result of experiments on the changes of pressure of the more permanent gases

$$p_{100} - p_0 = \frac{100}{273} p_0, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

nearly; whence, if a gas be used as the thermometric substance in a constant-volume thermometer, we have

$$p_t - p_0 = \frac{t}{273} p_0,$$

or

$$p_t = \frac{p_0}{273}(t + 273), \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

all the changes being supposed to occur at constant volume, and the pressure being measured by an appropriate manometer.

If we write

$$t + 273 = T, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

we have, for a fixed mass of gas at a fixed volume,

$$p_T = \frac{p_0}{273} T; \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

and if we call T the ***absolute temperature** by the gas thermometer*, we may say: *The absolute temperature by the gas thermometer is proportional to the pressure of a given mass of gas kept at constant* *volume.* In future, we shall use T to designate this temperature read on the hydrogen thermometer.

9. We may evidently consider T to be merely the temperature measured in Celsius degrees from a point at $(-273°)$ of the ordinary scale. This point is known as the *absolute zero of the gas scale.* But since, at very low temperatures, gases cease to behave alike, and finally cease to exist as gases at all, it is best to avoid such questions as "What would happen to a gas if it were cooled to the absolute zero?" and to consider the absolute zero as a mere mathematical abstraction, introduced for convenience in our reasoning. Its greatest service is in simplifying the expression of Boyle's Law for varying temperature. For a gas which obeys Boyle's Law, we have, for a given temperature, $pv=$ constant, which gives us at once, from equation (5), the statement that

$$p_T v_T = \frac{p_0 v_0}{273} T = RT, \qquad (6)$$

R being a constant which depends only on p_0 and v_0, *i.e.*, on the quantity of gas considered. Equation (6) may be deduced as follows:—Put equation (5) in the general form,

$$\frac{dp}{dT} = f(v),$$

which it assumes when the volume is not constant. Multiplying by vT, we get

$$pv = vf(v) \,.\, T.$$

But, in its general form, Boyle's Law states that

$$pv = \phi(T).$$

Hence

$$vf(v) = \text{constant} = R,$$

and we have

$$pv = RT.^{*}$$

This equation, sometimes called the Law of Boyle and Gay-Lussac, is, in reality, merely a definition of the temperature T, by a substance which follows Boyle's Law. The "Law" of Gay-Lussac consists in the statement that for all the more permanent

*see Preston, Theory of Heat, p. 140. '27 gases—which are also the ones that follow Boyle's Law most approximately—the absolute temperatures, as defined by equation (6), are approximately the same.[*]

Of all the actual gases no one follows Boyle's Law exactly,[†] and for no two is Gay-Lussac's Law rigorously true; but we may say, in general, that these two laws are true to about the same degree of approximation, and that this approximation increases with rise of temperature and with decrease of density.

In Chapter VIII we shall give a new definition of absolute temperature; but, for present purposes, temperature as a measurable quantity has been sufficiently defined.[**]

Temperature at a Point

10. We sometimes need to speak of the *temperature at a point* in a body. If the body has not a uniform temperature, this temperature at a point is not directly measurable, and what we observe is merely a certain mean value of the temperatures of the parts immediately[‡] surrounding the thermometer. What we shall mean, then, by this expression, is the temperature which would be shown by a very small thermometer filling a hole cut in the body about the point in question. We may, if we choose, imagine the dimensions of this hole to become infinitesimal, but though this may be convenient, mathematically, and does not lead us to conclusions in conflict with experience, it is well to note that in fact our measurements are made in holes of finite size.

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[*] Strictly speaking, Gay-Lussac's statement referred only to expansion at constant pressure, but the consideration that these gases are subject to Boyle's Law leads to the statement as given above.

[†] Except for an infinitesimal interval.

[‡] The thermometer is supposed to receive no radiation, and to be influenced only by direct contact.

[**] practicable only as far as the gas thermometer can be relied upon.

CHAPTER II

CALORIMETRY

Quantity of Heat

11. WHEN an equalization of temperature follows the contact of two bodies, the fact may be very simply expressed by saying that something has passed from the hot body to the cold one. We say that a certain *quantity of heat* has passed from the hot to the cold body, and that heat continues to *flow* as long as any difference of temperature remains. We imply by this, that *heat* is something which warms a body by passing into it and leaves the body colder when it passes out.

Energy p[illegible] on[illegible] bo[illegible] to a[illegible]

The most natural and immediate conception is, perhaps, that this 'something' is a quantity of a substance, and that increase or decrease of temperature means increase or decrease of the quantity of this substance contained in the body in question. This view was the basis of the *Caloric Theory of Heat.* The idea that heat is a *substance*, in any ordinary sense of the word, had, however, to be abandoned, when it was shown, by the experiments of Davy, Rumford, and others, that heat had no weight, and that it could be produced in unlimited quantities, merely by doing mechanical work.

12. Without, however, binding ourselves to any particular mental picture of the intimate nature of the difference between a body when hot and the same body when cold, we may, without anywhere coming into conflict with experimental results, speak of a *quantity of heat* in the sense in which the term is used in article 11.

This notion of a quantity of heat as something which, during the simple contact of bodies of unequal temperature, *changes its distribution but remains constant in total amount*, is, in the present state of the theory of thermodynamics, of fundamental importance. It is well, therefore, to examine carefully the precise meaning of the expression 'quantity of heat.'

Ideas contained in the term 'Quantity of Heat'

13. It is known by experiment that bodies may be heated by doing mechanical work upon them; by friction, for example. We also know, that while a cold body is being heated at the expense of a hot one, a certain amount of mechanical work may be done by the use of mechanism actuated only by the difference of temperature of the two bodies in question, and that the degree to which the cold body is heated, depends on the amount of mechanical work obtained—the heating of the cold body being greater as the work is less, and *vice versa.* The steam engine, working between the hot boiler and the cold condenser, is an example of such a piece of mechanism.

We must, then, say that in the first case heat is produced by the work done, and that in the second, work is done by the expenditure of a quantity of heat. Hence, if we are to treat heat as constant in total amount, we must make sure that only purely thermal phenomena are under consideration, and that no mechanical work comes into play. Similar attention must be paid to possible chemical, electrical, and other actions.

14. Under these conditions, we may consider heat as unchanged in total amount during redistribution. Our first idea of heat is that of something which increases the temperature of a body when added to it and decreases the temperature when taken away.* The first addition which we make to this conception is

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* It is to be noticed that we are, in this discussion, considering only bodies which do not, within the limits of temperature in question, have any singular points as regards their behaviour. In other words, the sub-

the **assumption**, that *when a given body cools through a definite interval, the quantity of heat it gives out is always the same*, regardless of what becomes of the heat after it leaves the body in question. This addition may be considered as a matter of definition. It is an assumption, in so far as we do not know, without the test of experimental practice, whether the definition, so formed, will represent any physical quantity at all, or whether it will lead us into reasoning which contradicts our experience. Practically, we find that we are not led into any difficulty by making this a fundamental element of our notion of quantity of heat. Hence the assumption is justified by its convenience.

15. We have next to consider more closely the *equality of quantities of heat.* The questions to be answered are: When are two quantities of heat equal? and, Are two quantities of heat, which are equal to a third, equal to each other?

If a body A, in cooling from T_1 to T_2, heats a second body B from θ_2 to θ_1, no communication of heat taking place with outside bodies, the heat Q_A given out by A is, by article 12, equal to the heat Q_B received by B. If the same body A, in cooling through a different interval, T'_1 to T'_2, heats B through the same interval as before, θ_2 to θ_1, the quantity of heat Q'_A, given out by A in the second experiment, is also equal to Q_B. The same is true of the quantity Q_C given out by any third body C in cooling from T'''_1 to T'''_2, if, by this cooling, B is heated through the original interval. In general, any quantity of heat, no matter by what body or between what temperatures it is given out, is, by definition, equal to Q_B if, when it all passes into B, it raises the temperature of B from θ_2 to θ_1.

Since these quantities of heat are equal to the same quantity, it is a natural conclusion that they are all equal to one another: they must be so, if heat is to be treated as a quantity in the

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stances are not to be subject to melting, boiling, allotropic changes, chemical dissociation, etc. They are also supposed not to exhibit any such effects of thermal lag as occur in the heating and cooling of glass, or the heating and cooling of sulphur about its point of transformation at 95·4°.

ordinary sense. Yet the proposition is, in itself, neither clear nor obvious; for we have, so far, only defined equality of heat given out by one body with that received by another, whereas the quantities now under consideration are all quantities given out. To fill up this gap, we shall make it a matter of **definition** that *quantities of heat which are equal to the same quantity are equal to one another.* This addition to our notion has the same justification as the one mentioned in article 14; it is convenient, and does not lead us into reasoning which is contradicted by experience.

16. As in article 15, let A, in cooling from T_1 to T_2, and C, in cooling from T''_1 to T''_2, give off quantities of heat Q_A and Q_C which are equal to Q_B and to each other. Let T''_1 be lower than T_2. If we now take A at the temperature T_1 and C at the temperature T''_2, we find experimentally, that when they are placed in contact, C is warmed from T''_2 to T''_1 by the heat which A gives off in cooling from T_1 to T_2. Hence the quantity of heat Q'_C received by C is equal to Q_A given off by A. But by article 15, Q_C, the heat given out by C in cooling through this same interval, T''_1 to T''_2, is equal to Q_A. Hence Q_C and Q'_C are equal. We have, therefore, the result, that *a body gives out just as much heat in cooling through a given interval as it receives in being warmed through the same interval.*

17. Having thus discussed what we are to mean by equality of quantities of heat, we must find a method of comparing unequal quantities. The simplest way is to say that the magnitudes of two quantities of heat are to each other as the masses of some standard substance which they can raise through a given interval of temperature. If the substance chosen as the standard of comparison is homogeneous and isotropic, and if we do not attempt to work with very small masses of it,* this

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* We must not base any argument on the consideration of *separate* masses which are so small that their surface energy is appreciable in comparison with the energy which we are putting in or taking out in the form of heat.

method of comparing quantities of heat gives us results which are entirely satisfactory. It is, then, justified by experience.

Recapitulation

18. To recapitulate the important elements which, taken together, make up our notion of quantity of heat, we may say:

I. *Bodies lose heat while cooling, and receive it while being warmed.*

II. *The total quantity of heat does not change during redistribution; or the heat lost by one body is equal to that gained by the other, or others, which are warmed by the cooling of the first.*

III. *In cooling through a given interval, a given body always gives out the same quantity of heat.*

IV. *Quantities of heat which are equal to the same quantity are equal to each other.*

V. *A body, in cooling through a given interval, gives out the same quantity of heat as it receives in being warmed through that interval.*

VI. *Quantities of heat are proportional to the masses of a standard substance which they can warm through any fixed interval of temperature.*

These statements are all subject to the limitations of article 13, and of the notes to articles 14 and 17.

Measurement of Quantities of Heat

19. We now proceed to the practical question of measurement. The standard substance, which we use in practice, is water, and the *unit of heat* is usually defined as *the heat necessary to raise a unit mass of water one degree in temperature.* As we shall always use the C.G.S. system of units and the Celsius degree, the unit of heat is the heat needed to raise the temperature of one gram of water one Celsius degree. The quantity thus approximately defined is called the *small* or *gram calorie,* in distinction from the *large* or *kilogram calorie,* which is one thousand times as large.

This definition is still only approximate, for we have stated only the size and not the position of the interval of temperature.

It is very common to use, for the definition, the interval 0° to 1°; but for purposes of actual experiment, this interval is badly chosen. In practice, some other interval between 0° and 20° is far more often used, though the position of the interval has, within these limits, an influence of less than 1 per cent. on the value of the calorie. In the rest of the present work, we shall, if it is necessary to be exact, understand the calorie to be the heat needed to heat one gram of water from 10° to 11° Celsius.

20. To measure any quantity of heat we have, then, to find by experiment, directly or indirectly, how many grams of water it could warm from 10° to 11° Celsius.

The experimental methods in actual use for measuring quantities of heat are based on the ideas collected in article 18. For a description of apparatus and methods, the reader may consult Preston's THEORY OF HEAT or any of the larger works on experimental physics. We shall assume that he is familiar with these methods as well as with the ordinary facts concerning specific and latent heats.

21. The unit of heat defined above has been in use for a long time but has never been thoroughly satisfactory because of the difficulties in using it exactly. Several other units have been used, and some are now (1899) under discussion; but, for the present, we need not consider any except the mechanical unit, to which we shall now turn our attention.

Mechanical Production of Heat. The Mechanical Equivalent

22. As stated in article 13, heat may be produced by doing mechanical work, or *expending mechanical energy.* We may, for instance, heat two bodies by rubbing them together, all the work being done against friction and leaving the bodies, finally, with no more kinetic energy than they had at the start, but with a higher temperature. We may also produce other effects commonly caused by a supply of heat. A case in point is Davy's 'ice-rubbing experiment,' in which two pieces of ice were melted by being rubbed together, while isolated, as far as possible, from the transmission of heat from outside bodies.

23. Since we have means of measuring both work and heat, we may investigate the amount of heat produced by a known quantity of work. Such experiments were first accurately performed by Joule, in his celebrated researches on the *Mechanical Equivalent of Heat,* the publication of which was begun in 1843. The conclusion to be drawn from his experiments was, that a unit of heat required for its production the expenditure of a definite number of units of mechanical energy, no matter in what particular way the work was done, *i.e.*, the energy expended. The more accurate the experiments, the more nearly equal were the quantities of heat produced by equal quantities of work. The hypothetical generalization of this result is, that however the work may be done, *to produce a unit of heat always requires exactly the same amount of work,* or that *heat and mechanical energy are equivalent.* The number of units of work needed to produce one unit of heat is known as *the mechanical equivalent of heat,* or *Joule's Equivalent.* It is commonly denoted by the letter J.

Later experiments have confirmed the conclusions from Joule's work, and have left his value of J sensibly unchanged. If our units are the gram calorie (10° to 11°) and the erg, the value of the mechanical equivalent is $J = 42 \times 10^6$, very approximately.

24. Work may also be obtained by using up heat, and though it is here not so easy to make a quantitative test of the ratio of transformation, it is universally accepted as an exact law of nature, which has no exceptions, that heat and mechanical energy, that is, power of doing mechanical work, are equivalent in the sense that if either is produced at the expense of the other, the ratio of the quantities in question is always the same.

Heat a Form of Energy

25. We thus reach the conclusion that a quantity of heat, as we have defined it, is not a substance, but a quantity of energy;

for 'energy' is only another name for 'power of doing work.' This leads us, furthermore, to a new unit of heat. If, instead of the calorie, we take a unit $\frac{1}{42 \times 10^6}$ times as great; if, in other words, instead of the gram, we take $\frac{1}{42 \times 10^6}$ gram of water in defining our unit, the result will be that one unit of heat is equivalent to one erg, and *we may consider a quantity of heat as a quantity of energy measurable in ergs*, the erg being the common unit of energy.

In future we shall, in all our theoretical work, consider heat to be measured in ergs, as by doing so we simplify the writing of our equations. The calorie need be mentioned, only when it is necessary to refer to the results of experiments in which the calorie has been used as the unit.

volume. In future, we shall use T to designate this temperature read on the hydrogen thermometer.

9. We may evidently consider T to be merely the temperature measured in Celsius degrees from a point at ($-273°$) of the ordinary scale. This point is known as the *absolute zero of the gas scale.* But since, at very low temperatures, gases cease to behave alike, and finally cease to exist as gases at all, it is best to avoid such questions as "What would happen to a gas if it were cooled to the absolute zero?" and to consider the absolute zero as a mere mathematical abstraction, introduced for convenience in our reasoning. Its greatest service is in simplifying the expression of Boyle's Law for varying temperature. For a gas which obeys Boyle's Law, we have, for a given temperature, $pv=$ constant, which gives us at once, from equation (5), the statement that

$$p_T v_T = \frac{p_0 v_0}{273} T = RT, \qquad \text{(6)}$$

R being a constant which depends only on p_0 and v_0, *i.e.*, on the quantity of gas considered. Equation (6) may be deduced as follows:—Put equation (5) in the general form,

$$\frac{dp}{dT} = f(v),$$

which it assumes when the volume is not constant. Multiplying by vT, we get

$$pv = vf(v) \,.\, T.$$

But, in its general form, Boyle's Law states that

$$pv = \phi(T).$$

Hence $\qquad vf(v) = \text{constant} = R,$

and we have $\qquad pv = RT.$ *

This equation, sometimes called the Law of Boyle and Gay-Lussac, is, in reality, merely a definition of the temperature T, by a substance which follows Boyle's Law. The "Law" of Gay-Lussac consists in the statement that for all the more permanent

* see Preston, Theory of Heat, p. 140. '27

gases—which are also the ones that follow Boyle's Law most approximately—the absolute temperatures, as defined by equation (6), are approximately the same.[*]

Of all the actual gases no one follows Boyle's Law exactly,[†] and for no two is Gay-Lussac's Law rigorously true; but we may say, in general, that these two laws are true to about the same degree of approximation, and that this approximation increases with rise of temperature and with decrease of density.

In Chapter VIII we shall give a new definition of absolute temperature; but, for present purposes, temperature as a measurable quantity has been sufficiently defined.[**]

Temperature at a Point

10. We sometimes need to speak of the *temperature at a point* in a body. If the body has not a uniform temperature, this temperature at a point is not directly measurable, and what we observe is merely a certain mean value of the temperatures of the parts immediately [‡] surrounding the thermometer. What we shall mean, then, by this expression, is the temperature which would be shown by a very small thermometer filling a hole cut in the body about the point in question. We may, if we choose, imagine the dimensions of this hole to become infinitesimal, but though this may be convenient, mathematically, and does not lead us to conclusions in conflict with experience, it is well to note that in fact our measurements are made in holes of finite size.

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[*] Strictly speaking, Gay-Lussac's statement referred only to expansion at constant pressure, but the consideration that these gases are subject to Boyle's Law leads to the statement as given above.

[†] Except for an infinitesimal interval.

[‡] The thermometer is supposed to receive no radiation, and to be influenced only by direct contact.

[**] practicable only as far as the gas thermometer can be relied upon.

CHAPTER II

CALORIMETRY

Quantity of Heat

11. WHEN an equalization of temperature follows the contact of two bodies, the fact may be very simply expressed by saying that something has passed from the hot body to the cold one. We say that a certain *quantity of heat* has passed from the hot to the cold body, and that heat continues to *flow* as long as any difference of temperature remains. We imply by this, that *heat* is something which warms a body by passing into it and leaves the body colder when it passes out.

[illegible]

The most natural and immediate conception is, perhaps, that this 'something' is a quantity of a substance, and that increase or decrease of temperature means increase or decrease of the quantity of this substance contained in the body in question. This view was the basis of the *Caloric Theory of Heat.* The idea that heat is a *substance*, in any ordinary sense of the word, had, however, to be abandoned, when it was shown, by the experiments of Davy, Rumford, and others, that heat had no weight, and that it could be produced in unlimited quantities, merely by doing mechanical work.

12. Without, however, binding ourselves to any particular mental picture of the intimate nature of the difference between a body when hot and the same body when cold, we may, without anywhere coming into conflict with experimental results, speak of a *quantity of heat* in the sense in which the term is used in article 11.

This notion of a quantity of heat as something which, during the simple contact of bodies of unequal temperature, *changes its distribution but remains constant in total amount*, is, in the present state of the theory of thermodynamics, of fundamental importance. It is well, therefore, to examine carefully the precise meaning of the expression 'quantity of heat.'

Ideas contained in the term 'Quantity of Heat'

13. It is known by experiment that bodies may be heated by doing mechanical work upon them; by friction, for example. We also know, that while a cold body is being heated at the expense of a hot one, a certain amount of mechanical work may be done by the use of mechanism actuated only by the difference of temperature of the two bodies in question, and that the degree to which the cold body is heated, depends on the amount of mechanical work obtained—the heating of the cold body being greater as the work is less, and *vice versa.* The steam engine, working between the hot boiler and the cold condenser, is an example of such a piece of mechanism.

We must, then, say that in the first case heat is produced by the work done, and that in the second, work is done by the expenditure of a quantity of heat. Hence, if we are to treat heat as constant in total amount, we must make sure that only purely thermal phenomena are under consideration, and that no mechanical work comes into play. Similar attention must be paid to possible chemical, electrical, and other actions.

14. Under these conditions, we may consider heat as unchanged in total amount during redistribution. Our first idea of heat is that of something which increases the temperature of a body when added to it and decreases the temperature when taken away.* The first addition which we make to this conception is

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* It is to be noticed that we are, in this discussion, considering only bodies which do not, within the limits of temperature in question, have any singular points as regards their behaviour. In other words, the sub-

the **assumption**, that *when a given body cools through a definite interval, the quantity of heat it gives out is always the same*, regardless of what becomes of the heat after it leaves the body in question. This addition may be considered as a matter of definition. It is an assumption, in so far as we do not know, without the test of experimental practice, whether the definition, so formed, will represent any physical quantity at all, or whether it will lead us into reasoning which contradicts our experience. Practically, we find that we are not led into any difficulty by making this a fundamental element of our notion of quantity of heat. Hence the assumption is justified by its convenience.

15. We have next to consider more closely the *equality of quantities of heat.* The questions to be answered are: When are two quantities of heat equal? and, Are two quantities of heat, which are equal to a third, equal to each other?

If a body A, in cooling from T_1 to T_2, heats a second body B from θ_2 to θ_1, no communication of heat taking place with outside bodies, the heat Q_A given out by A is, by article 12, equal to the heat Q_B received by B. If the same body A, in cooling through a different interval, T'_1 to T'_2, heats B through the same interval as before, θ_2 to θ_1, the quantity of heat Q'_A, given out by A in the second experiment, is also equal to Q_B. The same is true of the quantity Q_C given out by any third body C in cooling from T''_1 to T''_2, if, by this cooling, B is heated through the original interval. In general, any quantity of heat, no matter by what body or between what temperatures it is given out, is, by definition, equal to Q_B if, when it all passes into B, it raises the temperature of B from θ_2 to θ_1.

Since these quantities of heat are equal to the same quantity, it is a natural conclusion that they are all equal to one another: they must be so, if heat is to be treated as a quantity in the

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stances are not to be subject to melting, boiling, allotropic changes, chemical dissociation, etc. They are also supposed not to exhibit any such effects of thermal lag as occur in the heating and cooling of glass, or the heating and cooling of sulphur about its point of transformation at 95·4°.

ordinary sense. Yet the proposition is, in itself, neither clear nor obvious; for we have, so far, only defined equality of heat given out by one body with that received by another, whereas the quantities now under consideration are all quantities given out. To fill up this gap, we shall make it a matter of **definition** that *quantities of heat which are equal to the same quantity are equal to one another.* This addition to our notion has the same justification as the one mentioned in article 14; it is convenient, and does not lead us into reasoning which is contradicted by experience.

16. As in article 15, let A, in cooling from T_1 to T_2, and C, in cooling from T'''_1 to T'''_2, give off quantities of heat Q_A and Q_C which are equal to Q_B and to each other. Let T'''_1 be lower than T_2. If we now take A at the temperature T_1 and C at the temperature T'''_2, we find experimentally, that when they are placed in contact, C is warmed from T'''_2 to T'''_1 by the heat which A gives off in cooling from T_1 to T_2. Hence the quantity of heat Q'_C received by C is equal to Q_A given off by A. But by article 15, Q_C, the heat given out by C in cooling through this same interval, T'''_1 to T'''_2, is equal to Q_A. Hence Q_C and Q'_C are equal. We have, therefore, the result, that *a body gives out just as much heat in cooling through a given interval as it receives in being warmed through the same interval.*

17. Having thus discussed what we are to mean by equality of quantities of heat, we must find a method of comparing unequal quantities. The simplest way is to say that the magnitudes of two quantities of heat are to each other as the masses of some standard substance which they can raise through a given interval of temperature. If the substance chosen as the standard of comparison is homogeneous and isotropic, and if we do not attempt to work with very small masses of it,* this

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* We must not base any argument on the consideration of *separate* masses which are so small that their surface energy is appreciable in comparison with the energy which we are putting in or taking out in the form of heat.

method of comparing quantities of heat gives us results which are entirely satisfactory. It is, then, justified by experience.

Recapitulation

18. To recapitulate the important elements which, taken together, make up our notion of quantity of heat, we may say:

I. *Bodies lose heat while cooling, and receive it while being warmed.*

II. *The total quantity of heat does not change during redistribution; or the heat lost by one body is equal to that gained by the other, or others, which are warmed by the cooling of the first.*

III. *In cooling through a given interval, a given body always gives out the same quantity of heat.*

IV. *Quantities of heat which are equal to the same quantity are equal to each other.*

V. *A body, in cooling through a given interval, gives out the same quantity of heat as it receives in being warmed through that interval.*

VI. *Quantities of heat are proportional to the masses of a standard substance which they can warm through any fixed interval of temperature.*

These statements are all subject to the limitations of article 13, and of the notes to articles 14 and 17.

Measurement of Quantities of Heat

19. We now proceed to the practical question of measurement. The standard substance, which we use in practice, is water, and the *unit of heat* is usually defined as *the heat necessary to raise a unit mass of water one degree in temperature.* As we shall always use the C.G.S. system of units and the Celsius degree, the unit of heat is the heat needed to raise the temperature of one gram of water one Celsius degree. The quantity thus approximately defined is called the *small* or *gram calorie,* in distinction from the *large* or *kilogram calorie,* which is one thousand times as large.

This definition is still only approximate, for we have stated only the size and not the position of the interval of temperature.

It is very common to use, for the definition, the interval 0° to 1°; but for purposes of actual experiment, this interval is badly chosen. In practice, some other interval between 0° and 20° is far more often used, though the position of the interval has, within these limits, an influence of less than 1 per cent. on the value of the calorie. In the rest of the present work, we shall, if it is necessary to be exact, understand the calorie to be the heat needed to heat one gram of water from 10° to 11° Celsius.

20. To measure any quantity of heat we have, then, to find by experiment, directly or indirectly, how many grams of water it could warm from 10° to 11° Celsius.

The experimental methods in actual use for measuring quantities of heat are based on the ideas collected in article 18. For a description of apparatus and methods, the reader may consult Preston's THEORY OF HEAT or any of the larger works on experimental physics. We shall assume that he is familiar with these methods as well as with the ordinary facts concerning specific and latent heats.

21. The unit of heat defined above has been in use for a long time but has never been thoroughly satisfactory because of the difficulties in using it exactly. Several other units have been used, and some are now (1899) under discussion; but, for the present, we need not consider any except the mechanical unit, to which we shall now turn our attention.

Mechanical Production of Heat. The Mechanical Equivalent

22. As stated in article 13, heat may be produced by doing mechanical work, or *expending mechanical energy.* We may, for instance, heat two bodies by rubbing them together, all the work being done against friction and leaving the bodies, finally, with no more kinetic energy than they had at the start, but with a higher temperature. We may also produce other effects commonly caused by a supply of heat. A case in point is Davy's 'ice-rubbing experiment,' in which two pieces of ice were melted by being rubbed together, while isolated, as far as possible, from the transmission of heat from outside bodies.

23. Since we have means of measuring both work and heat, we may investigate the amount of heat produced by a known quantity of work. Such experiments were first accurately performed by Joule, in his celebrated researches on the *Mechanical Equivalent of Heat*, the publication of which was begun in 1843. The conclusion to be drawn from his experiments was, that a unit of heat required for its production the expenditure of a definite number of units of mechanical energy, no matter in what particular way the work was done, *i.e.*, the energy expended. The more accurate the experiments, the more nearly equal were the quantities of heat produced by equal quantities of work. The hypothetical generalization of this result is, that however the work may be done, *to produce a unit of heat always requires exactly the same amount of work*, or that *heat and mechanical energy are equivalent.* The number of units of work needed to produce one unit of heat is known as *the mechanical equivalent of heat*, or *Joule's Equivalent.* It is commonly denoted by the letter J.

Later experiments have confirmed the conclusions from Joule's work, and have left his value of J sensibly unchanged. If our units are the gram calorie (10° to 11°) and the erg, the value of the mechanical equivalent is $J = 42 \times 10^6$, very approximately.

24. Work may also be obtained by using up heat, and though it is here not so easy to make a quantitative test of the ratio of transformation, it is universally accepted as an exact law of nature, which has no exceptions, that heat and mechanical energy, that is, power of doing mechanical work, are equivalent in the sense that if either is produced at the expense of the other, the ratio of the quantities in question is always the same.

Heat a Form of Energy

25. We thus reach the conclusion that a quantity of heat, as we have defined it, is not a substance, but a quantity of energy;

for 'energy' is only another name for 'power of doing work.' This leads us, furthermore, to a new unit of heat. If, instead of the calorie, we take a unit $\frac{1}{42 \times 10^6}$ times as great; if, in other words, instead of the gram, we take $\frac{1}{42 \times 10^6}$ gram of water in defining our unit, the result will be that one unit of heat is equivalent to one erg, and *we may consider a quantity of heat as a quantity of energy measurable in ergs*, the erg being the common unit of energy.

In future we shall, in all our theoretical work, consider heat to be measured in ergs, as by doing so we simplify the writing of our equations. The calorie need be mentioned, only when it is necessary to refer to the results of experiments in which the calorie has been used as the unit.

the billiard balls or the thermodynamic system, we have as the conditions of equilibrium not equations but inequalities. Another simple example of the same thing is that of a mass of gas, confined in a cylinder and kept in equilibrium by a force acting on the piston : we shall have an equation or an inequality according as the piston is movable without or with friction.

40. The systems which can not be treated by assuming them to have equations of equilibrium are numerous and important; but the theory which applies to them (which has only recently begun to be developed) is more complicated than in the opposite case, just as dynamics is more complicated for frictional than for frictionless systems. We shall make it a fundamental condition of the validity of our work THAT ALL THE SYSTEMS HEREAFTER CONSIDERED SHALL BE SUCH AS HAVE EQUATIONS OF EQUILIBRIUM, and we shall develop the theory only for such systems.

CHAPTER IV

THE FIRST LAW OF THERMODYNAMICS

Work done on a System during a Change of State. Specification of the Outside Actions. Generalized Coordinates and Forces.

41. Let us consider a system with $n+1$ degrees of freedom, the independent variables which determine its state being

$$x', x'', x''', \dots x^n, T.$$

Let the system be subject to outside actions of a mechanical nature only; that is, such actions, that when a change of state occurs, no energy enters or leaves the system except in the form of heat or mechanical work.*

Let the symbols

$$\delta x', \delta x'', \delta x''', \dots \delta x^n, \delta T,$$

represent any infinitesimal changes in the variables, consistent with the nature of the system; these variations are all independent, since there are $n+1$ degrees of freedom. During this change of state, the outside actions will do on the system a quantity of work δW, which depends on the nature of the change, and which may be written

$$\delta W = X'\delta x' + X''\delta x'' + \dots X^n\delta x^n + \mathcal{J}\delta T. \quad\dots\dots\dots\dots\dots(7)$$

The strength of the outside actions—their effectiveness in doing work—is completely characterized by the work they do on the system during a given change in the variables, for instance,

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* [illegible]

a unit change in each one. Hence the actions are defined, as regards intensity, by the coefficients X', X'', ... X^n, $\mathcal{J}$. If the forces acting on the system have a potential, the work they do on the system, as it passes from a state A to a state B, may be written

$$W_A^B = [f(x', x'', \dots x^n, T)]_A^B. \qquad \text{(8)}$$

In this case we have

$$X^\kappa = \frac{\partial W}{\partial x^\kappa}, \qquad \text{(9)}$$

and the coefficient X^κ is the rate at which work is done on the system as x^κ changes, while all the other variables, including the temperature, are constant. But in general, the work will not be independent of the path, and we must write

$$W_A^B = \phi[(x', x'', \dots x^n, T)_A, \ (x', x'', \dots x^n, T)_B, \ y', y'', \dots y^k],$$

where y', y'', ... y^k are quantities which are not determined by the instantaneous values of x', x'', ... x^n, T. In general, therefore, the complete expression for any one of the coefficients X^κ is

$$X^\kappa = \left(\frac{\partial W}{\partial x^\kappa}\right)_{x, T, y},$$

where the subscripts indicate, that during the change in x^κ, the other variables x', x'', ... x^n, the temperature T, and the quantities y', y'', ... y^k are all kept constant.

42. Each of the terms in equation (7) has the dimensions of a quantity of work, namely, $[W]$ or $[ml^2t^{-2}]$.* If the variable x be a length, the corresponding coefficient X will have the dimensions of a force $[Wl^{-1}]$ or $[mlt^{-2}]$: but if it have other dimensions, if it be, for example, an angle, a surface, or a volume, the term $X\delta x$ (or $\mathcal{J}\delta T$) will still have the dimensions of a quantity of work.

43. We may, if we choose, imagine the system to be connected,

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* In the statement of dimensions, *t* has the usual meaning of *time*, and is not meant to indicate the temperature on the Celsius scale.

by some sort of mechanism, the nature of which need not concern us, to $n+1$ sliding pieces, which can move independently along fixed straight bars, the mechanism being so devised, that the distances of the sliding pieces from fixed zero points on their respective bars, are proportional to the values of x', x'', ... x^n, T, and that any changes of x', etc., which are compatible with the nature of the system, are also possible for the mechanism.

Now let the actual outside actions be replaced by a number of forces on the sliding pieces, each proportional to the appropriate one of the quantities X', X'', ... X^n, $\mathcal{T}$. If the scales of x', etc., and of X', etc., have been properly chosen, the system will now, by virtue of the connecting mechanism, be influenced in the same way by these forces as it was by the outside actions which they have replaced: for if any or all of the variables change in value, the work done on the system will be the same for this new set of forces as for the original set of actions, whatever their nature may have been.

We may call the variables x', x'', ... x^n, T, the *generalized coordinates* of the system, the name being drawn from the representation of their values as lengths. We may also call the coefficients X', X'', ... X^n, $\mathcal{T}$, the *generalized forces* acting on the system, although, in reality, they do not necessarily have dimensions of mechanical forces.

The state of the system is now defined by the generalized coordinates, x', x'', ... x^n, T; and the outside actions are completely characterized by the generalized forces, X', X'', ... X^n, $\mathcal{T}$.

44. As an illustration, let the system consist of a soap bubble, which we will suppose so light that it is not influenced appreciably by gravity. The only outside action on the film is the pressure of the air inside it. We may consider the state of the film as defined by its area a (including both surfaces), and its temperature T. Let a little more air be forced in slowly, so that the area increases by δa; and suppose that the temperature is kept constant. The work done by the outside action is

$$\delta W = A\,\delta a.$$

Here A is the generalized force tending to increase the variable a, and we may easily find a simple interpretation of it. Since we have disregarded the form of the film, and considered its area to be the only thing of importance for our purposes, we may just as well imagine the film stretched between two rails $\frac{1}{2}$ cm.** apart, with a fixed perpendicular cross-piece at one end, and a frictionless sliding cross-piece at a distance of a cm. from it; so that the area of the film is, as before, a cm^2. An increase of area δa involves a motion outward, of the sliding cross-piece, through δa cm. The generalized force A is now simply the force which must act on the slide to balance* the pull of the film, or the tension of one surface of the film per centimetre length of the edge on which it is pulling. In other words, A is numerically equal to the surface tension of the film. In this example, the generalized force has the dimensions of force ÷ length, $[Wl^{-2}]$ or $[mt^{-2}]$; and its product by an area δa has the dimensions of a quantity of work, namely, W or $[ml^2t^{-2}]$.†

Choice of Independent Variables. Internal and External Variables

45. The fundamental condition, that the system shall have equations of equilibrium, may be written

$$\left.\begin{aligned} X' &= f'(x', x'', \dots x^n, T), \\ X'' &= f''(x', x'', \dots x^n, T), \\ &\dots\dots\dots\dots\dots\dots \\ X^n &= f^n(x', x'', \dots x^n, T), \\ \mathcal{T} &= f^t(x', x'', \dots x^n, T). \end{aligned}\right\} \quad \dots\dots\dots\dots(10)$$

These equations, in which the forms of the functions f must be determined by experiments on the system, fix the values of the

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* Within an infinitesimal amount.

† The work done in compressing the air has been left out of account, because the air does not form a part of the system.

** $\frac{1}{2}$, because both sides of the film come into account.

generalized forces needed to preserve equilibrium for any given values of $x', x'', \ldots x^n, T$.

We shall **assume** *that there is only a single set of outside actions, or a single set of generalized forces, which will preserve any given state of equilibrium.* So far as we know, it is always possible to select the variables in such a manner that this assumption is correct. This, in mathematical terms, is equivalent to saying that the functions f are single-valued. It is obvious, too, that they are never infinite for any attainable values of the variables, since we have no means of producing or maintaining infinite forces. They are, moreover, continuous; for any discontinuity of f', f'', etc., could arise only from a physical discontinuity in some of the outside actions. Such discontinuities do not exist in nature—a proposition which is approximately equivalent to the statement that finite effects imply finite causes, and *vice versa.*

46. It is conceivable that after we have selected a set of variables which satisfy the condition of determining a unique set of forces, $X', X'', \ldots X^n, \mathscr{J}$, for any state of equilibrium, some of these variables may not, in varying, involve any outside work at all.[*] If this is the case, certain of the coefficients in the expression for the work,

$$\delta W = X'\delta x' + X''\delta x'' + \ldots X^n\delta x^n + \mathscr{J}\delta T, \qquad \text{(11)}$$

will be constantly zero. We shall call the variables for which the work-coefficients, or generalized forces, are constantly zero, *internal variables,* while the others will be called *external variables.* When it is necessary to distinguish between the two classes, we shall denote them by the symbols x_i and x_e respectively. The generalized forces corresponding to them will be denoted by X_i and X_e. The expression for the work will then take the form

$$\delta W = \sum X_e\delta x_e + \mathscr{J}\delta T + \sum X_i\delta x_i, \qquad \text{(12)}$$

where

$$\sum X_i\delta x_i = 0, \qquad \text{(13)}$$

so that this term may be omitted from the expression, unless we choose to write it in for the sake of indicating *all* the independent variables.

[*] Evaporation into a vacuum gives an example where the sum of 2 products are equal to zero

The equations of equilibrium may now be written

$$\left.\begin{array}{l} X'_e = f'_e(x'_i,\ x''_i,\ \ldots,\ x'_a,\ x''_a,\ \ldots,\ T), \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ \mathcal{T} = f'(x'_i,\ x''_i,\ \ldots,\ x'_a,\ x''_a,\ \ldots,\ T). \end{array}\right\}\ldots\ldots\ldots\ldots(14)$$

It is often convenient to select the quantities to be used as independent variables, in such a way that a variation of the temperature alone involves no outside work, or so that

$$\mathcal{T} = 0,$$

T being now an internal variable. Variables so chosen are called ***normal variables***: such a choice seems always to be possible. With normal variables, the expression for the work done on the system by the outside actions, during any infinitesimal variation of state, becomes

$$\delta W = \sum X \delta x\,; \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(15)$$

or, if there are other internal variables than T,

$$\delta W = \sum X_e \delta x_e. \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(16)$$

Unless the contrary is stated, we shall always assume that normal variables are used for defining the state of any system that we may have under consideration.

Further Remarks on the Generalized Forces. Work Diagrams

47. The values of X and $\mathcal{T}$ occurring in equations (7), (11), (12), (15), (16) are not, during any *real* modification, $\delta x'$, $\delta x''$, ... δx^n, δT, such as would satisfy equations (10) and (14). The values of the generalized forces which appear in equations (14) are those needed to preserve equilibrium; and if, at any instant, X', X'', ... X^n, $\mathcal{T}$ had the values given by equations (14) for the instantaneous values of x'_i, ..., x'_a, ..., T, the system would be in equilibrium and no change would go on.

If the values of X', X'', ... X^n, $\mathcal{T}$ differ only very little from those needed for equilibrium, a very slow process will go on; and, conversely, if a very slow process is taking place, the values of X', X'', ... X^n, $\mathcal{J}$, at any instant of it, must be very nearly equal to those needed to bring the process to a standstill at that point.* This would not be true if kinetic energy were entering into the problem; for in the case of a moving dynamic system, the forces needed to preserve any state of equilibrium do not necessarily bring the system to rest if it reaches that state; the accelerations vanish, but the velocities do not.

All the changes of state which we shall consider, have, however, the property that the velocities (in the general sense of *rapidity of change*) vanish with the driving forces, and that there is nothing analogous to the inertia of masses, which, in dynamics, brings acceleration into such prominence.

48. If the system has only two degrees of freedom and the variables are normal, the expression for the work done by the forces during a finite change of state may be written

$$W_A^B = \int_{A\ x_1}^{B\ x_2} X\,dx, \quad \text{.........................} (17)$$

and we can represent this quantity of work graphically. Let us lay off x and X (Fig. 3) as rectangular coordinates in a plane.

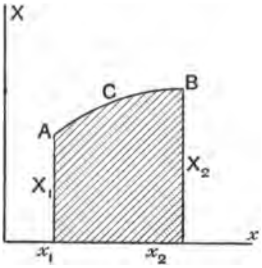

FIG. 3.

Let the original state A have the coordinates x_1, X_1, and the final state B, the coordinates x_2, X_2. Let the curve ACB represent the values which the force X assumes, as the variable x is passing

* Good example: Isothermal compression of gases.

through the values between x_1 and x_2. The work done on the system, during the process, is evidently equal to the shaded area under the curve *ACB*.

If the system change its state in such a manner, that while x passes back through the values between x_2 and x_1, the generalized force X assumes, successively, its former series of values in the inverse order, the same curve will be traced out, but in the inverse direction, *BCA*. The work done on the system will be the negative of its former value, that is, the negative of the numerical value of the shaded area.

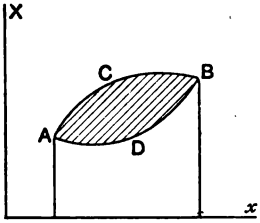

FIG. 4.

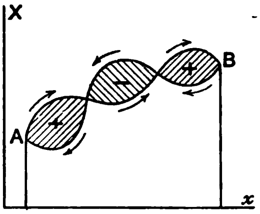

FIG. 5.

If the point which represents the simultaneous values of x and X move from A to B along the path *ACB* and then return by the path *BDA* (Fig. 4), the total work done on the system is equal to the shaded area enclosed by the curve. It is positive if the point goes round the area clockwise, and negative in the opposite case, as is seen upon comparing the two values of the force (and of the elementary work), for a given value of x, and for the two directions of rotation,—remembering that work is being done *on* the system, while x is increasing.

If the diagram has several loops (Fig. 5), the total work is the sum of the areas of the loops which are traced clockwise, minus the sum of the areas of those traced in the opposite direction.

Any process by which a system, however many be its degrees of freedom and whether the variables used be normal or not, after leaving a certain state, returns finally to the same state, is called *a cyclic process* or *a cycle.* In order to avoid circumlocution, the closed curve, representing the process on the diagram, is also spoken of as 'the cycle.' For such a system as the one we have just been discussing, namely, one with two degrees of freedom and one mechanical action, we may announce the proposition: *During any cycle the work done on the system is equal to the area of the cycle*, the signs of the areas being interpreted as above.

49. It is to be noted, that the diagram drawn with x and X as its coordinates is not a complete representation of the process, though it is of the work done; for it tells us nothing about the values assumed by the other independent variable, T. If all the states through which the system passes were states of equilibrium, we should have an equation of equilibrium

$$X=f(x, T), \qquad (18)$$

connecting x, T, and X, and we could deduce from this an equation

$$T=\phi(x, X), \qquad (19)$$

giving T in terms of x and X. Hence x and X would define the state of the system completely, and a diagram in x and X would be a complete representation of the process. But no real process does consist of states of equilibrium; for a state of equilibrium is, by definition, one in which the outside actions are such that nothing occurs to disturb the existing condition of affairs. To make the system traverse a given continuous series of states, *i.e.*, of sets of simultaneous values of the variables x', x'', ... x^n, T, outside actions, X', X'', ... X^n, $\mathcal{T}$, must be applied, which differ, at any instant, from those needed to preserve equilibrium. If the forces differ only infinitesimally from their equilibrium values, the process will go on with an infinitesimal velocity: infinitesimal alterations in the forces will be sufficient to arrest the process or to reverse its direction.

Any process, of which the direction may be reversed by infinitely small modifications of the outside actions, is called a REVERSIBLE

PROCESS. The successive states of which it is composed are infinitely near to a series of states of equilibrium; hence, during a reversible process, the generalized forces have values which approximate, within any desired amount, to the values deducible from the equations of equilibrium

$$\left.\begin{aligned} X' &= f'(x', x'', \ldots x^n, T), \\ X'' &= f''(x', x'', \ldots x^n, T), \\ &\ldots\ldots\ldots\ldots\ldots\ldots \\ X^n &= f^n(x', x'', \ldots x^n, T), \\ \mathcal{T} &= f^t(x', x'', \ldots x^n, T). \end{aligned}\right\} \ldots\ldots\ldots\ldots(20)$$

In the case of a process of this nature, performed by a system with two degrees of freedom and one mechanical outside action, the diagram in x and X comes infinitely near to being an exact representation of the whole process. For any process which is slow enough to consist *nearly* of states of equilibrium, *i.e.*, to be *nearly* reversible, the diagram is *nearly* a complete representation.

50. To illustrate what we have been saying, let us suppose that the system is a mass of gas confined in a cylinder by a frictionless piston, of area S. For such a system, the volume and temperature are normal variables, since if the volume is constant, a change in the temperature does not involve any work. Suppose the motion of the piston, during a change of volume, to be so slow that the force acting on it, at any time, is sensibly the same as would be needed to keep the piston at rest if stopped at that instant. This force is evidently equal to pS; what must we take as the generalized force, X?

During an increase of volume δv, the piston moves out through a distance $\delta v/S$, and the work done on the system is

$$\delta W = -\frac{\delta v}{S} \cdot pS = -p\,\delta v.$$

But this, by definition, is equal to $X\delta x$, or in the present case, to

$X\delta v$. Hence the generalized force is $(-p)$, and during a finite change of volume, the work done on the system is

$$W_A^B = -\int_A^B p\,dv. \qquad (21)$$

In drawing the work diagram (Fig. 6) we find it convenient to use, as coordinates, v and p instead of v and $(-p)$. The signs of

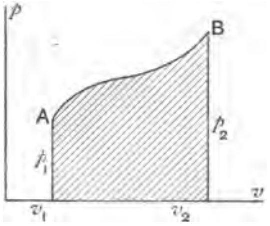

FIG. 6.

areas on the diagram must now be inverted, *i.e.*, an area that is continually on the right of the tracing point, as the point moves forward during the process, is to be interpreted as work done by the system against the outside actions, instead of as work done on the system by them. The actual value of the area cannot be found unless we have a complete knowledge of the path, or, in other words, of the simultaneous values of p and v, or of T and v, throughout the process.

Let us assume that the gas is subject to Boyle's Law, and that the temperature is measured by a thermometer filled with this same gas. We then have the equation

$$pv = RT, \qquad (22)$$

where R is a constant depending on the mass of the gas. From this equation of state, we obtain at once

$$p = \frac{RT}{v},$$

whence the expression for the work done on the system during any finite change of volume becomes

$$W_{v_1}^{v_2} = -R\int_{v_1}^{v_2}\frac{T}{v}dv. \quad\text{.........................}(23)$$

This equation shows us the value of the work done by the outside pressure on any gas which obeys Boyle's Law, during a change of volume from v_1 to v_2, the change taking place so slowly that the kinetic energy of the gas may be neglected.

Isothermal changes are of especial importance. In this case, T is constant, so that it may be taken outside the integral sign, and equation (23) reduces to

$$W_{v_1}^{v_2} = -RT\int_{v_1}^{v_2}\frac{dv}{v} = RT\log\frac{v_1}{v_2}, \quad\text{..................}(24)$$

a result which we often have occasion to use.

The gas has been imagined as contained in a cylinder, but this restriction is unnecessary. During any deformation of the confining envelope, we may imagine the change of volume to take place by a gradual, simultaneous motion along their normals, of the infinitesimal surface elements ΔS, which are so small that they may, at any instant, be treated as plane and as describing cylinders. For each element taken separately, we have

$$\Delta W = -p\Delta v,$$

and for them all taken together,

$$\delta W = \int_S \Delta W = -\int_S p\Delta v,$$

the integration being a summation for all the elements, *i.e.*, over the whole surface. But p is the same for all the elements, since we are disregarding gravity. Furthermore,

$$\int_S \Delta v = \delta v:$$

hence we have, as before,

$$\delta W = -p\delta v. \quad\text{..........................}(25)$$

It follows that equations (21), (23), and (24) are entirely general, and hold for any sort of change of volume, when the other conditions in each case are satisfied.

51. As yet, nothing has been said about the scales of the diagrams. The gaseous system which we have been discussing will serve to elucidate this point. Let the diagram be so drawn that one centimetre represents a pressure of one kilogram per square metre, or a volume of one cubic metre. The area of the diagram, in square centimetres, represents the work done, measured in units, each of which is of the magnitude

$$\frac{1\text{ kg.}}{1\text{ m.}^2}\times 1\text{ m.}^3 \quad\text{or}\quad 1\text{ kg.}\times 1\text{ m.};$$

the work is, then, given in kilogram-metres.

If the scale, in centimetres, had been one megadyne per square centimetre and one litre, an area of one square centimetre would have represented a work of

$$\frac{10^6\text{ dynes}}{1\text{ cm.}^2}\times 10^3\text{ cm.}^3, \quad\text{or}\quad 10^9\text{ dynes}\times 1\text{ cm.},$$

i.e., one thousand megergs. This illustration will serve to show the reader how, in any other case, the diagram as drawn is to be interpreted.

52. We have been discussing the changes of state of systems which have only two degrees of freedom, and we have already seen (Art. 37), that if a system has more than three degrees of freedom, changes in its state can not, in general, be represented on a single diagram. But if we construct as many plane diagrams as the system has independent variables,* taking as coordinates the pairs of values (x', X'), ... etc., ($\mathcal{T}$, T), we have, during any change of state, curves traced out which are susceptible of the same interpretation as those on the single diagram.

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*For an internal variable the curve will be merely a piece of the x axis; hence the internal variables may be left out of account.

Hence the proposition stated at the end of article 48, regarding a system with two degrees of freedom, may be extended to any system which is subject only to mechanical actions, and we may say: *During any cyclic modification of the state of a system which is subject only to mechanical actions, the work done on the system by the outside actions is equal to the sum of the areas of the curves described on the* $n+1$ *plane diagrams, by the points having for their coordinates the simultaneous values of*

$$(x', X'),\ \ldots\ \text{etc.},\ (\mathcal{T}, T).$$

Use of the Generalized Forces as Independent Variables

53. The use of the generalized forces, as coordinates in diagrams representing work done, suggests that they may be used as independent variables in determining the state of the system, in place of some of the original variables, $x', x'', \ldots x^n, T$. Let us see whether they may be so used, and if so, under what conditions.

The values of the forces $X', X'', \ldots X^n, \mathcal{T}$, which are needed to preserve equilibrium, are, by hypothesis, given *unequivocally* by the equations

$$\left.\begin{aligned} X' &= f'(x', x'', \ldots x^n, T), \\ X'' &= f''(x', x'', \ldots x^n, T), \\ &\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ X^n &= f^n(x', x'', \ldots x^n, T), \\ \mathcal{T} &= f^t(x', x'', \ldots x^n, T); \end{aligned}\right\} \ldots\ldots\ldots\ldots\ldots\ldots(26)$$

where the forms of the functions $f', f'', \ldots f^n, f^t$ are to be determined by experiment.

If none of the functions f', f'', etc., are identically zero, that is, if all the variables, including T, contribute, when varied, to the expression for the work, we may deduce from these $n+1$ equations another set, of the form,

$$\left.\begin{aligned} x' &= \phi'(X', X'', \dots X^n, \mathcal{T}),\\ x'' &= \phi''(X', X'', \dots X^n, \mathcal{T}),\\ &\dots\dots\dots\dots\dots\dots\dots\dots\\ x^n &= \phi^n(X', X'', \dots X^n, \mathcal{T}),\\ T &= \phi^t(X', X'', \dots X^n, \mathcal{T}); \end{aligned}\right\} \dots\dots\dots\dots\dots(27)$$

and a question arises, at once, as to the significance of these equations.

The functions $f', f'', \dots f^n, f^t$, which occur in the equations of equilibrium, are continuous and finite, throughout the whole possible range of our experiments. They are also, by assumption, single-valued: our theory is applicable only to systems for which a given state, as a state of equilibrium, requires a single, unique set of outside actions or generalized forces.

This, however, does not imply that the functions $\phi', \phi'', \dots \phi^n, \phi^t$ are single-valued: there may be more than one state of equilibrium which is compatible with a single set of outside actions, and we shall illustrate this in article 55. But though the functions ϕ may be multiple-valued, we shall assume that, *in general*, the values, even if infinite in number, are discrete—that they do not form a continuous series. In physical terms, this is equivalent to saying, that though there may be more than one state in which the system can be kept in equilibrium by a given set of outside actions, any state which differs only infinitesimally from one of these, will not, in general, be a state of equilibrium, under the same outside actions. We may put it in still another way: any infinitesimal displacement of a system from a given state of equilibrium, requires, in general, an infinitesimal change in the outside actions, if the new state is to be one of equilibrium; or, each separate state of equilibrium, no matter how nearly alike the states may be, requires its own separate set of outside actions.

We may illustrate our meaning in a very simple case. Let us consider a function of a single variable, $X=f(x)$; and let this equation be also put in the form $x = \phi(X)$. Let $X = f(x)$ be plotted as a curve (Fig. 7). The condition that $f(x)$ is single-valued, means that a line parallel to the axis of X can cut the curve in only one point at most. A line parallel to the axis of x may, however, cut the curve in any number of points; but these points will, *in general*, be discrete. It may happen, that for particular values of X, the curve $X = f(x)$ has horizontal straight pieces af finite length; hence, for these particular values of X, x may have an infinite and continuous series of values; but this can not happen *in general*, *i.e.*, for all values of X, but only for certain particular and discrete values.* Hence we may say, that not only does each value of x give a definite value of X, but each value of X, except certain particular discrete values, gives one or more definite values of x, which do not form a continuous series.

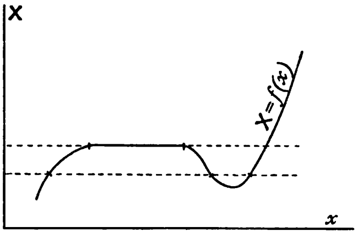

FIG. 7.

We shall assume, though we cannot demonstrate the proposition, that similar statements may be made with regard to functions of any number of variables. If this is true, any set of values of the generalized forces will, in general, determine one or more discrete states of equilibrium, although for certain particular values of X', X'', ... X^n, $\mathcal{T}$, these states may form a continuous series. Hence, *so long as we are considering states of equilibrium*, the

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* This is true, at all events, if $f(x)$ is an analytic function; and the results of physical experiments may always be represented by analytic functions to any required degree of approximation, or, for physical purposes, with practical exactness.

generalized forces $X', X'', \dots X^n, \mathcal{T}$ may, except for particular values, be used as independent variables in determining the state of the system. When so used, they are called the *inverse variables* of the former set.

When a system is in a state of neutral* equilibrium, it may have a continuous series of states of equilibrium extending through a finite range, and the forces may be the same for all these states, though they need not be. If the forces are the same, their values are a set of the particular values mentioned above. The same is true in pure dynamics: if a system has equations of equilibrium, any set of forces may determine one or more discrete states of equilibrium which are compatible with this set of forces; and so long as this is the case, the forces may be used to define the state or states of equilibrium. But in the particular case of neutral equilibrium, there may be a continuous infinity of states which satisfy the conditions.*

54. If, among the $n+1$ variables $x', x'', \dots x^n, T$, there are $m+1$ internal variables, the set of equations (26) is reduced in number to $n-m$, because $m+1$ of the functions f are incapable of experimental determination. Hence the equations (27) are also reduced in number to $n-m$. We have, in other words, $n-m$ known relations, connecting the $2n-m+1$ quantities

$$x'_i, x''_i, \dots x^{m+1}_i, x'_e, x''_e, \dots x^{n-m-1}_e, T, X'_e, X''_e, \dots X^{n-m-1}_e, \mathcal{T}.$$

Let us take, as $m+1$ of the $n+1$ quantities needed to determine the state of the system, the internal variables $x'_i, x''_i, \dots x^{m+1}_i$, the original variables being, for the present, supposed not to be normal. It remains to select $n-m$ more quantities, which, with those already selected, will suffice to fix the state of the system. For this purpose, let us take the generalized forces corresponding to the $n-m$ external variables, namely,

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* It may, of course, happen, either in dynamics or in thermodynamics, that under the action of a given set of forces no state of equilibrium at all is possible.

*There seems to be only states of stable (metastable) & unstable equilibrium.

$X'_e, X''_e \dots X^{n-m-1}_e, J$, so that the complete list of independent variables is

$$x'_i, x''_i \dots x^{m-1}_i, X'_e, X''_e \dots X^{n-m-1}_e, J.$$

The $n-m$ experimentally known relations in the set of equations (26) now enable us to express the $n-m$ variables $x'_e, x''_e \dots x^{n-m-1}_e, T$, in terms of this new set of quantities. For of the $2n-m+1$ quantities there are $n+1$ which we have taken as arbitrary, so that $n-m$ relations are enough to determine the others.

So long, then, as we are treating only states of equilibrium, we may, under the restrictions of article 53, use, as independent variables, the $n+1$ quantities

$$x'_i, x''_i \dots x^{m-1}_i, X'_e, X''_e \dots X^{n-m-1}_e, J.$$

If the original variables were normal, that is, if T was among the internal variables, the new set will be

$$x'_i, x''_i \dots x^{m}_i, X'_e, X''_e \dots X^{n-m}_e, T.$$

In either case, the new set of quantities may be called the inverse variables of the original set.

The $n-m$ known relations of the set (26) give us, for the determination of $x'_e \dots x^{n-m-1}_e, T$, the equations

$$\left.\begin{aligned} x'_e &= \phi'(x'_i, x''_i \dots x^{m-1}_i, X'_e, X''_e \dots X^{n-m-1}_e, J), \\ &\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \\ &\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \\ x^{n-m-1}_e &= \phi^{n-m-1}(x'_i, x''_i \dots x^{m-1}_i, X'_e, X''_e \dots X^{n-m-1}_e, J), \\ T &= \phi^t(x'_i, x''_i \dots x^{m+1}_i, X'_e, X''_e \dots X^{n-m-1}_e, J); \end{aligned}\right\} \text{(28)}$$

or, in the case of normal variables,

$$\left.\begin{aligned} x'_e &= \phi'(x'_i, x''_i \dots x^{m}_i, X'_e, X''_e \dots X^{n-m}_e, T), \\ &\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \\ &\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \\ x^{n-m}_e &= \phi^{n-m}(x'_i, x''_i \dots x^{m}_i, X'_e, X''_e \dots X^{n-m}_e, T). \end{aligned}\right\} \dots\text{(29)}$$

The definition of an internal variable was, that it was one for which the work done on the system, during a unit change in x_i, when x_i alone was varied, was zero. It by no means follows, that when we have selected our new set of independent variables, the work done on the system under the same circumstances will be zero; for the quantities which are kept constant are not the same in the two cases. It may, for instance, very well happen, that though the original variables were normal, the inverse variables are not. In the familiar case of a mass of gas, of which the state is defined by the normal variables v and T, the inverse variables, $(-p)$, and T, are not normal; for a variation of the temperature at constant pressure is accompanied by a certain quantity of outside work.

55. We will now illustrate, by a simple example, some of the statements made in articles 53 and 54.

Let the system consist of a mass of fluid, kept at the constant temperature T, below its critical temperature. If the fluid remains homogeneous, the normal variables v and T are enough to determine its state, and they give a unique determination of the generalized force $(-p)$, needed to preserve the system in equilibrium at any temperature T and volume v. This means

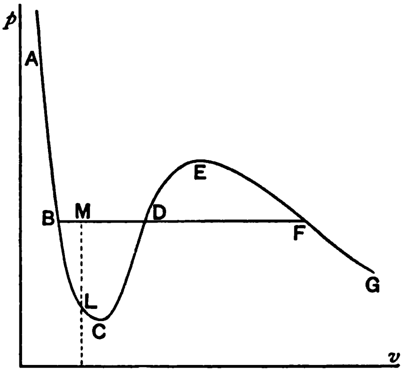

FIG. 8.

that on the diagram drawn in terms of v and p (Fig. 8), no line drawn parallel to the axis of pressures can cut the isothermal line more than once, so long as the isothermal refers to a homogeneous mass of fluid: it is immaterial whether the fluid is all liquid, as at points to the left of B, or all gaseous, as at points to the right of F.

If we accept the idea of James Thompson, that a fluid can pass continuously, and without ceasing to be homogeneous, from the liquid to the gaseous state, and *vice versa*; the condition that v and T shall give a unique determination of p, is satisfied if the isothermal has the familiar form shown in the figure; for each value of v there is one and only one value of p, under which the fluid can be in equilibrium.

The inverse variables are $(-p)$ and T; and it is obvious, that if the isothermal line has the form shown, a given value of p *may* keep the fluid in equilibrium at any one of three different volumes. This is possible for all values of the pressure greater than that indicated by the point C and less than that indicated by the point E; for any horizontal line, drawn between these limits, cuts the isothermal line in three distinct points. Outside these limits a given pressure determines a single volume, at which the system may be in equilibrium at the given temperature. In the present case, therefore, we have a system, such that the variables v and T satisfy the condition of giving a unique determination of the outside actions needed for equilibrium, but where—as we have said will be the case *in general*—the generalized forces may determine one or more states of equilibrium, but not a continuous infinity of states.

Now, suppose that the restriction to homogeneity be removed, and that superheating of the liquid and supersaturation of the vapour be prevented. The form of the isothermal line—the *empirical*, as distinguished from the so-called *theoretical isothermal*, of which we have been speaking—is shown by the broken curve, $ABMDFG$. The condition that a given set of values of the normal variables shall suffice for the unique determination of the single outside action ($-p$), is evidently fulfilled, since the curve cannot be cut by a line parallel to the axis of pressures in more than one point. It is also true, that *in general* a given set of values of the inverse variables ($-p$, T) determines a single possible volume at which the system can be in equilibrium. But suppose the pressure applied to the surface to be exactly equal to the saturated vapour pressure at the given temperature: this particular set of values of p and T does not determine a single value, nor even a number of discrete values, of the volume at which the system can be in equilibrium. The fluid may, on the contrary, be in equilibrium, at any volume whatever between that indicated by the point B and that indicated by the point F. This continuous infinity of volumes is not, however, possible *in general*, but only for this one particular value of the pressure: at the given temperature, no other value of the pressure, so far as we know, and certainly no other in the immediate vicinity of this one, will permit a continuous infinity of states of equilibrium. The remarks made in article 53, as to the nature of the functions f and ϕ, are illustrated by these two cases of a homogeneous and a heterogeneous fluid.[x]

It is necessary to state, as we have done, that the fluid is or is not homogeneous at volumes between B and F; if the question be left open, the variables v and T will not suffice for our purposes. We know by experiment the form of the empirical isothermal line, and we also know of the existence of parts, at least, of the theoretical isothermal, between B and C and between F and E; for superheated liquid and supersaturated vapour give points on these parts of the curve. The liquid may remain in equilibrium in its superheated state, under a smaller pressure than its natural vapour pressure at the given temperature, *i.e.*, under a smaller pressure than would be necessary at the same temperature, if the liquid had partially evaporated and passed over into a heterogeneous mixture of liquid and vapour. The variables v and T, therefore, do not suffice for a unique determination of the pressure needed for equilibrium, unless we include in the definition

[x] We may in addition select the relative mass of the liquid or the gas as variable.

of the 'given system' a statement that the fluid is or is not to remain homogeneous throughout its whole possible range of volumes.

Let x be the fraction of the whole mass that has changed discontinuously, from the condition or *phase* denoted by points to the left of B, into a different fluid phase. If we start with the liquid, so long as the mass remains homogeneous we have $x = 0$. We might also start with the vapour, and the fact that the mass remained homogeneous might then be represented by the equation $x = 1$. We may thus look upon x as the quantitative representation of a property of the system, a property that remains constant if no portion of the mass changes from one phase into another.

If the system is split up into two phases, liquid and vapour, x varies as the relative masses of the two phases vary. But if the fluid is to be in equilibrium, x cannot be treated as a variable independent of v and T: for, at a given temperature, the total volume is determined by the masses of the two phases present, and *vice versa.*[*] If the fluid is not in equilibrium, x may, at a given temperature and volume, have any value between zero and one, just as during the evaporation of the superheated liquid inside a rigid envelope, the pressure increases continuously till a new state of equilibrium is reached. During this change of state, x might be considered as an independent internal variable: the consideration of such explosive processes is, however, beyond the scope of our present work. Enough has already been said to show that cases may be found, in which the remarks made in articles 53 and 54 have simple physical interpretations.

Heat absorbed by a System during a Change of State

56. During a change of state, a system will, in general, beside the work done on it by the outside actions, receive a certain amount of heat from the surrounding bodies: this heat may, of course, be either positive or negative. We shall count heat taken

[*] x is determined by the amount of energy absorbed or given out by the fluid, since it passed a certain point. (Evaporation).

in as positive, just as we counted work done on the system as positive. *We shall* **assume**, *as the result of experiment, that the heat absorbed during any small change of state is equal to the heat given out when the same change takes place in the opposite direction, the outside actions being the same in the two cases.*

The quantity of heat absorbed during an infinitesimal variation of state, may be written in the form

$$\delta Q = K'\delta x' + K''\delta x'' + \dots K^n\delta x^n + C_x\delta T. \qquad (30)$$

The quantities K', K'', ... K^n are called the *thermal coefficients of the system for the variables* x', x'', ... x^n. Any one of them is equal to the heat absorbed by the system during a unit increase of the corresponding variable x, while all the other variables, including the temperature, are kept constant. The coefficients K may also be called the *latent heats of the system* for the variables in question, the name being suggested by the fact that the heat is absorbed without changing the temperature of the system. The coefficient C_x is called the *thermal capacity of the system for constant variables.*

This absorption of heat may also be expressed in terms of the inverse variables, and we may write

$$\delta Q = \sum M\delta x_i + \sum L\delta X_e + C_{X_e x_i}\delta T; \qquad (31)$$

or, in the case where T is the only internal variable in the original set,

$$\delta Q = L'\delta X' + L''\delta X'' + \dots L^n\delta X^n + C_X\delta T. \qquad (32)$$

The interpretation of the *thermal coefficients* M', M'', etc., and L', L'', etc., is the same as before: M represents the heat absorbed by the system during a unit increase of x_i when all the other independent variables are constant; L represents the heat absorbed during unit increase of X_e, and $C_{X_e x_i}$, that during unit increase of T, all the other independent variables in each case being kept constant. The quantities M and L may be called the *latent heats*, and $C_{X_e x_i}$ the *thermal capacity*, *of the system, for constant inverse variables.*

These latent heats and thermal capacities, K, L, M, C_x and $C_{X_0 x_i}$ are not, in general, constants, but functions of the independent variables used. It would be easy to deduce formulae for the transformation of one set of coefficients into the other, but we shall not stop to do so, as the results are not of immediate importance.

57. To return to our old illustration; let the system consist of a unit mass of fluid. During any infinitesimal change of state, the heat absorbed will be

$$\delta Q = K\delta v + C_v \delta T, \quad\text{.........................(33)}$$

where K is known as the latent heat of expansion, and C_v as the specific heat of the fluid at constant volume. If the change is a displacement from a state of equilibrium, we may, by using the inverse variables $(-p)$ and T, express the same quantity of heat in the form

$$\delta Q = -L\delta p + C_p \delta T, \quad\text{.........................(34)}$$

where L is the latent heat of decrease of pressure, and C_p is the specific heat at constant pressure.

If the change considered be isothermal, so that $\delta T = 0$, we have the relation

$$K\delta v = -L\delta p, \quad\text{.............................(35)}$$

or

$$K = -L\left(\frac{\partial p}{\partial v}\right)_T. \quad\text{.........................(36)}$$

The First Law of Thermodynamics

58. Let a system which is subject to purely mechanical outside actions undergo any sort of cyclic modification of state: let the total area of its $n+1$ work diagrams be different from zero. A certain amount of work, positive or negative, will be done on the system. We may represent this work by $(\int)dW$, the parenthesis around the integral sign indicating summation along a closed path. During the same time, a certain positive or negative quantity of heat, $(\int)dQ$, will have been absorbed. The total energy absorbed by the system is

$$(\int)(dW + dQ) = \Delta\epsilon.$$

Since the process is a cyclic one, the system is finally left in exactly its original state. Let us assume that $\Delta\epsilon$ is less than zero, or that we have received from the system more energy than we put into it, without leaving it in a state in the slightest degree different from its original state. The cycle may be repeated indefinitely, so that we may get from the system an infinite quantity of energy. If, on the other hand, $\Delta\epsilon$ be greater than zero, we may, by indefinite repetition of the cycle, pour into the system an unlimited quantity of energy and yet leave it, finally, in its original state.

If $\Delta\epsilon$ could be less than zero, we should have the means of producing perpetual motion: hence the conviction that perpetual motion is impossible, which has been forced upon us by the failure of innumerable devices for producing it, carries with it the conviction that $\Delta\epsilon$ can never be less than zero. We have no such striking evidence to show that it is impossible to sink an indefinite quantity of energy in any given system of bodies. We assume, nevertheless, that this, too, is impossible: the conclusion from the two assumptions taken together is, that $\Delta\epsilon$ is always equal to zero for any cyclic process.

The principle known as the FIRST LAW OF THERMODYNAMICS is contained in the foregoing assumptions; it states that no such result is possible as those we have deduced from the supposition that $\Delta\epsilon$ is different from zero. The correctness of the principle is verified, indirectly, by all the experiments which have been made to test the conclusions which can be drawn from it. It may, therefore, be considered as sufficiently established as an **experimental law**, and we now go on to put the statement of the principle in more convenient shape.

59. From the assumption that $\Delta\epsilon$ is always zero we deduce at once the statement; that for any cyclic change of state,

$$(\int)(dW+dQ)=0, \qquad\qquad (37)$$

which is a mathematical expression of the law.

Let A and B (Fig. 9) represent any two states of the system. Let I and II represent any two paths by which the system may pass from A to B. Let III represent some path by which the system may return from B to A: *we* **assume** *that it is always possible to find paths leading in both directions between any two states whatever,* and we see no reason to doubt the theoretical correctness of this assumption. To make the matter more concrete and clearer, a diagram has been drawn, but the reasoning is not limited to systems which have only two degrees of freedom.

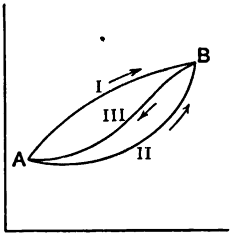

FIG. 9.

If we now turn our attention to the cycle made up of the transformations I and III, we see that we have the equation

$$\int_A^B (dW+dQ)_I + \int_B^A (dW+dQ)_{III} = (\int)(dW+dQ)=0. \quad \ldots(38)$$

For the cycle made up of the transformations II and III, we have, in the same way,

$$\int_A^B (dW+dQ)_{II} + \int_B^A (dW+dQ)_{III} = (\int)(dW+dQ)=0. \quad \ldots(39)$$

Restriction as to cyclic change removed.

A comparison of these two equations shows that

$$\int_A^B (dW+dQ)_I = \int_A^B (dW+dQ)_{II}. \quad \dots\dots\dots\dots\dots (40)$$

The paths I and II are any two paths whatever, by which the system can pass from the state A to the state B: hence the value of the integral

$$\int_A^B (dW+dQ),$$

or the amount of energy in the form of heat and work, received by the system in passing from one state to another, is quite independent of the path, that is, of the nature of the intermediate states through which the system passes. It can, therefore, depend only upon the variables which determine the original and final states, and it may evidently be expressed as the change in the value of a certain function of the independent variables, as the system passes from one state to the other.

If we let ϵ be this function, the above statement may be expressed by the equation

$$\int_A^B (dW+dQ) = \epsilon_B - \epsilon_A. \quad \dots\dots\dots\dots\dots\dots\dots (41)$$

The generality of the assumptions from which the existence of the function ϵ was inferred shows that it must be single-valued: it must also be continuous, for a discontinuity would imply a finite absorption of energy during an infinitesimal change of state. This function is known as the INTERNAL ENERGY of the system and equation (41) may be read: *During any change in the state of a system, the sum of the work and heat put into the system is equal to the increase of its internal energy.* This may be considered as another form of statement of the first law of thermodynamics.

The addition of an arbitrary constant to ϵ leaves equation (41) unaltered; hence ϵ **is not defined in absolute value but only as regards its changes.** It is allowable, therefore, to choose any state we please as a normal state, and to call the internal energy zero, when the system is in that state.

Equation (41) may be written,

$$\delta\epsilon = \delta Q + \delta W, \qquad\qquad (42)$$

in which form we shall make constant use of it.

The Conservation of Energy

60. Up to this point, we have not admitted to consideration any but mechanical actions, so that only mechanical (potential) energy and heat have been treated. We have now to remove this restriction from the generality of our reasoning.

A body or system is said to contain energy, when, by virtue of the condition it is in, it is capable, under appropriate circumstances, of doing mechanical work while undergoing some modification of state.* This work may go to producing kinetic energy, which we have excluded, or to producing potential energy; for instance, by bending a spring, raising a weight, or compressing a mass of gas. It has already been shown that a quantity of heat is to be looked upon as a quantity of energy, because we can convert heat into mechanical energy, and *vice versa.* But that these two forms of energy are not the only ones, is already implied by the restriction of our reasoning to them alone.

When the powder in a gun is ignited, the bullet receives kinetic energy equivalent to a certain quantity of the potential energy which has so often been mentioned. This kinetic energy is far greater in amount than the thermal energy of the igniting spark; it must have been stored up in the form of *chemical energy* in the powder, which, upon ignition, was subject to a chemical change, and so developed the hot gases that propelled the bullet.

A small body, charged with electricity and placed in a field of electrostatic force, tends to move in the direction of the lines of force; by utilizing this motion we may get useful mechanical work from the body. If, on the other hand, we connect the charged

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* That a modification of state is an essential part of the phenomenon, results from the conclusions of the preceding three articles.

body with the ground by means of a fine wire, the electricity 'flows into the earth,' as we say, and the wire is warmed. After this heat has been developed in the wire, the body is in a neutral state and no longer tends to move if placed in a uniform field: it has lost its *electrostatic energy*, which has been converted into heat.

Somewhat similar remarks may be made in reference to the motions of magnets in a magnetic field. Electric, thermal, and luminous radiation may also be made to produce work and heat. Evidently, then, there are various other kinds of energy beside the two to which we have hitherto confined our attention.

61. The greatest advance made by physics in the present century has consisted in the recognition of the fact, that *all forms of energy are equivalent* in the same sense in which heat and work are equivalent, and that *only transformation and not creation or destruction of energy is possible.* This general proposition was first clearly announced by J. R. Mayer in his paper entitled "Bemerkungen über die Kräfte der unbelebten Natur," published in Liebig's *Annalen der Chemie* for the year 1842. Joule had, at that time, already begun his experiments on the mechanical equivalent of heat—experiments which he afterwards extended to several other forms of energy. The proposition is known as the principle of the CONSERVATION OF ENERGY. Like all general principles in physics, it is an hypothetical generalization from a number of facts, small at first but always increasing: no case is known in which it is contradicted by experiment; it is universally accepted as an *exact law of nature*, and may be considered as sufficiently established.

Re-statement of the First Law of Thermodynamics

62. We must now turn our attention to systems that are capable of absorbing or giving out other forms of energy than heat and mechanical energy; and here we come upon a fundamental difference, between the energy represented by a quantity of heat, and some or all of the other kinds of energy that we meet with. A given quantity of kinetic or potential energy may always, by friction or otherwise, be converted into heat. Of a given quantity of heat, however, not all can be used up in producing mechanical work, but at most, only a definite fraction, which, as will be shown in Chapter VIII, depends on the temperature of the body from which the heat is taken and on that of the coldest bodies at our disposal. The remainder of the heat merely passes from a high to a low temperature, and continues to exist as heat; so that, at the end of the process, the sum of the heat remaining and the work done is equal to the original quantity of heat. All the other known forms of energy may, like mechanical energy, be converted into heat, completely. Some of them may also be converted completely* into mechanical energy, while mechanical energy may be completely* converted into any one of them. This fact may be expressed by the statement, that these latter kinds of energy have the *same value* as mechanical energy; heat has a lower value, because complete conversion is possible only in one direction. Electrostatic energy, for example, has the same value as mechanical. We may bring together two similarly charged bodies, doing work against the electric repulsion and thus increasing their electrostatic energy: by letting them return to their former positions, we may get back the work that we had to do in order to bring them together. When the charged bodies are in their nearest positions, we may, if we choose, change the electrostatic energy of the system into heat; for if we connect them to the ground by a wire, the bodies lose their electric properties while heat appears in the wire; but it is impossible to change all of this heat back into electrostatic or into mechanical energy. The energy of magnets in a magnetic field has also the mechanical value, and the same is, apparently, true of the electro-

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* Absolutely completely, only if our apparatus is ideally perfect; for in actual practice, all these conversions are attended by the appearance of a small quantity of heat, which may, however, be reduced indefinitely by perfecting the apparatus and methods for the conversion.

kinetic energy of the electromagnetic field about a constant current.

There are, on the other hand, several other kinds of energy beside heat, which, as far as our present experimental means of conversion go, seem to have lower values than potential and kinetic energy. Thermal, luminous, and electrodynamic radiation come under this head. Whether these have the same value as heat or not, is a question that has not yet been investigated completely. We shall exclude from consideration all forms of energy which we do not know to have the same value, either as heat or as mechanical energy.*

Henceforth we shall assume, that, whatever be the outside actions to which the system under consideration may be subject, these actions are of such a nature as to add to or take away from the system only those forms of energy that are of the mechanical value.

63. Let us suppose that for each separate outside action which can add or subtract non-mechanical energy, we imagine such a machine constructed as shall be capable of performing the complete transformation, in both directions, of this form and mechanical energy. After what has been said on the values of the various forms of energy to be considered, it is legitimate to assume that such machines are possible, theoretically. Let these machines supply to or abstract from the system, during any change in its state, the various quantities of energy, while themselves actuated by the application of mechanical forces from outside, or doing work against such forces. The system may now be treated as composed of the original system plus these ideal machines, and the machines may be imagined to be incapable of

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* This seemingly fundamental difference between heat and energy of the mechanical value, appears to be connected with the fact that, whereas the other forms of energy may be more or less permanently isolated in space, heat cannot be so isolated, but continually and inevitably leaks from bodies of high to bodies of low temperature, without our being able to find an effective means of preventing the leakage.

in themselves absorbing or giving out any energy, *i.e.*, to act simply as couplings between the system and outside world. The only effect of the machines is, that through them we may, by the application of mechanical forces, produce all the results that are actually produced on the system by the actual outside actions.

It follows, that all the conclusions reached by the consideration of mechanical actions remain true in the case of a system subject to any actions whatever, provided that no energy of a different value from mechanical energy or heat enters into the problem. We may, as before, select a set of variables or generalized coordinates, x', x'',...x^n, T: the strengths of the outside actions may be characterized by the generalized forces X', X'',...X^n; $\mathcal{T}$, which are connected with x', x'',... x^n, T by equations of equilibrium. The forces X', etc., may, with T and the internal variables, be used *in treating of states of equilibrium*, as a set of inverse variables (article 53). The graphical representation of work done on the system is now extended to include all the energy concerned in the process, with the exception of heat (articles 48-51).

The first law may still be stated in the three equations.

$$\left(\int\right)(dW+dQ)=0, \quad \ldots\ldots\ldots\ldots \tag{43}$$

$$\int_A^B (dW+dQ)=\epsilon_B-\epsilon_A, \quad \ldots\ldots\ldots\ldots \tag{44}$$

$$\delta\epsilon=\delta Q+\delta W, \quad \ldots\ldots\ldots\ldots \tag{45}$$

where W now refers to all energy except heat, and ϵ is still a function of the variables which determine the state of the system, and has the same properties as before.

CHAPTER V

THE PRINCIPLES OF THERMOCHEMISTRY

The Problem of Thermochemistry

64. The first law of thermodynamics has an important application in Chemistry, and in order to give the reader an idea of the practical meaning of the theory which has been set forth in Chapter IV, we shall now discuss, briefly, the fundamental principle of thermochemistry.

The experimental problem is, to find the heat developed or absorbed by a body, or system of bodies, which is the seat of a chemical reaction such as to change the original set of substances composing the system into a different set. The thermal investigation of such physical reactions as solution, evaporation, and fusion, may be included under the same heading; for the principles that regulate the thermal phenomena are the same, whether the reactions take place according to the law of definite proportions or not.

A given final state of the system may often be reached from a given initial state by more than one path; that is, through more than one series of intermediate states. Let the system in its original state consist, for example, of one gram molecule,* or 98 grams,

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* A 'gram molecule' of any chemically defined substance is a number of grams equal to the sum of the combining or atomic weights of the elements of which the substance is made up. For example: one gram molecule of carbonic acid gas is 44 grams; for the chemical formula is CO_2, while the combining weights of carbon and oxygen are 12 and 16, respectively, giving $CO_2 = 12 + 2 \times 16 = 44$.

of sulphuric acid ($H_2SO_4 = 2 \times 1 + 32 + 4 \times 16 = 98$), and ten gram molecules, or 180 grams, of water ($10H_2O = 10 \times [2 \times 1 + 16] = 180$): let the two be separate and at the temperature of 20° C. In its final state let the system consist of a homogeneous mixture of the sulphuric acid and the water at the same temperature of 20°. We may mix the two components directly and measure, calorimetrically, the heat absorbed: but we may also reach the final state by two or more steps, and measure the heat for each step. One way of doing this is to mix one gram molecule of sulphuric acid with five gram molecules of water, and, after finding the heat absorbed in this process, to mix the resulting solution with the remaining five gram molecules of water.

Such processes of mixing may be represented by equations in which the chemical symbol of a substance stands for one gram molecule of it. The equations in the present case are as follows:

$$H_2SO_4 + 10H_2O = H_2SO_410H_2O,$$

if the mixing be done all at once; and

$$\left.\begin{aligned} H_2SO_4 + 5H_2O &= H_2SO_45H_2O, \\ H_2SO_45H_2O + 5H_2O &= H_2SO_410H_2O, \end{aligned}\right\}$$

if it consist of two separate steps. A compound symbol ($H_2SO_45H_2O$) is here used to denote a mixture of the two substances represented by the two parts of the symbol.

There are many cases where a given final state, which, as far as is shown by the chemical equations, might be reached directly from a given original state, cannot, in practice, be reached by a single reaction, and where the path *must* be composed of several independent steps. It may, nevertheless, be important for us to know what the thermal phenomena would be, if the direct reaction were possible: we need, then, to know how the quantity of heat developed or absorbed depends on the path, when the original and final states are given.

65. Let us suppose that, whatever the reaction may be, it involves no outside work; this is very nearly the case when the substances composing the system are enclosed in a rigid envelope, so that no change of volume, and therefore no work by or against the outside pressure, can intervene. If the action of gravity, and of all other outside forces that can act at a distance through the envelope, is zero or negligible, the reactions inside the rigid envelope may be regarded as involving no outside work at all. Many chemical reactions are actually carried out in this way, inside a rigid containing vessel.

The influence of the nature of the path on the absorption of heat, is shown at once by the equation

$$\int_A^B (dW + dQ) = \epsilon_B - \epsilon_A.$$

Since dW is zero, we have

$$\int_A^B dQ = \epsilon_B - \epsilon_A = Q_A^B. \qquad (46)$$

But it has already been shown that ϵ_A and ϵ_B depend only on the coordinates of the states A and B; hence Q_A^B, the total heat absorbed, does not depend on the path at all, but is the same for all paths.

To return to the water and sulphuric acid: if we let Q_1, Q_2, and Q_3 be the quantities of heat absorbed in the three separate mixings, we may express the whole course of the reactions, including the absorption of heat, by the equations

$$H_2SO_4 + 10H_2O = H_2SO_4 10H_2O + Q_1, \qquad (47)$$

$$\left.\begin{aligned} H_2SO_4 + 5H_2O &= H_2SO_4\ 5H_2O + Q_2, \\ H_2SO_4 5H_2O + 5H_2O &= H_2SO_4 10H_2O + Q_3, \end{aligned}\right\} \qquad (48)$$

Our principle tells us, that if the experiments have been accurately carried out and the process of mixture has not caused any sensible change of volume of the substances,

$$Q_1 = Q_2 + Q_3. \qquad (49)$$

If the first reaction had been impossible, and the mixing had *had* to take place in the two stages, the equations (48) and (49) would, nevertheless, have enabled us to state with certainty the amount of heat Q_1, which would have been absorbed had the direct reaction been possible.

66. If the reaction is accompanied by work of the outside forces, the relations are not so simple, and the absorption of heat is, in general, not independent of the path. We must now use the general equation

$$\int_A^B (dW + dQ) = \epsilon_B - \epsilon_A,$$

or

$$W_A^B + Q_A^B = \epsilon_B - \epsilon_A, \quad\text{.........................(50)}$$

and not the heat alone, but the sum of the heat and the work, is independent of the nature of the intermediate states through which the system passes. The term 'work' is here used in the general sense, to include every sort of energy, except heat, that may enter or leave the system in consequence of the outside actions; in practice, the work to be considered is usually solely mechanical. For all paths during which $\int dW$ is the same, the heat $\int dQ$ will also be the same, just as it was in the particular case treated in article 65, in which the work was zero.

The condition that the work shall be independent of the path is satisfied if the outside forces of all sorts—the generalized forces—**have a potential.**

67. One particular case of such forces is that of article 65, where the work was constantly zero, and therefore independent of the path along which the system was led from the state A to the state B. There is another case of great practical importance, in which the forces have a potential; that, namely, where the only sensible action of outside bodies consists in a uniform, constant, normal pressure on the surface of the bodies composing the system. The work done on the system by such a pressure has the value

$$W_A^B = -\int_A^B p dv = -p\int_A^B dv = p(v_A - v_B).$$

Since v_A and v_B are fixed by the initial and final states, the work W_A^B is independent of the nature of the intermediate states. In equation (50), the terms W_A^B, ϵ_B, and ϵ_A are all independent of the path; hence the same is true of Q_A^B, the heat absorbed by the system during the reaction. If our experiments upon the sulphuric acid and water had been performed, not as before in a closed vessel, but in an open vessel and subject to the constant pressure of the atmosphere, equation (49) would still have been valid, though the quantities Q_1, Q_2, and Q_3 would not have had precisely the same values as before.

The Law of Constant Heat-Sums

68. The vast majority of thermochemical reactions take place, either in closed vessels at approximately constant volume, or in open vessels and subject to the approximately constant pressure of the atmosphere,—gravity, and all other outside actions except the pressure, being of altogether negligible importance. Hence all ordinary reactions are subject to the rule known as the LAW OF CONSTANT HEAT-SUMS which is contained in the statement, that *the total heat absorbed, when a certain set of substances is formed from a certain other set, is independent of the particular nature of the intermediate reactions.** In the few remaining cases, where neither volume nor pressure is constant, the work done by the pressure or other outside forces is usually small, in comparison with the heat concerned in the reaction; hence the law of constant heat-sums is sometimes stated as an exact and general law. It is, however, as we have seen, only an incomplete statement of the general principle expressed by the equation

$$W_A^B + Q_A^B = \epsilon_B - \epsilon_A,$$

which must, in strictness, be used whenever the outside forces do not have a potential. In such cases we have

$$Q_A^B = \epsilon_B - \epsilon_A - \int_A^B dW, \qquad (51)$$

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* G. H. Hess 1840 .

where $(\epsilon_B - \epsilon_A)$ is a constant, but $\int dW$ must be computed for each separate path: the changes in the absorption of heat, in changing from one path to another, are the same as the changes in

$$-\int_A^B dW.$$

It is to be noticed, that here, as usual, the assumption is made, that the kinetic energy of the system is negligible,—as it nearly always is in practice. It would be easy, if it were worth while, to modify the theory, so as to make it applicable to the cases in which the kinetic energy is not negligible.

69. It often happens that the initial and final states are at the same temperature. If the outside forces have a potential, so that the nature of the path is of no importance and the law of constant heat sums is valid, the absorption of heat is the same as if the reaction had gone on isothermally at the temperature of the initial and final states, the heat developed or absorbed being taken away or supplied, as fast as was necessary to prevent any change of temperature. In this case, the quantity of heat absorbed may be called the *heat of reaction at the temperature* T*. We may also, in making calculations with regard to the experiments, treat the whole process as if, at every instant during the reaction, the outside conditions of pressure, etc., had been such as would just keep the system in equilibrium at the temperature T, in the state it had at the instant in question. It is thus allowable to make the calculations with regard to a simplified ideal process, different from the actual one, but giving, *under the condition that the outside forces have a potential*, the same total absorption of heat as the process which has really taken place.

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* It is usual, in thermochemistry, to reckon heat given out as positive. We have changed this sign, for the sake of consistency with our previous notation. In taking numerical data from accounts of thermochemical measurements, it is to be remembered that the heats of reaction there are given quantities of heat given out.

Dependence of the Heat of Reaction on the Temperature

70. We will now use the remarks of the last article as an aid in finding how the heat of reaction depends upon the temperature when the reaction goes on at constant volume. Let the initial and final states in one case be A and B, both at the temperature T. In the second case, let them be A' and B', which differ from A and B, respectively, only in having the higher temperature $T+\delta T$, the other coordinates of the first pair of states being unchanged. Let x be a variable proportional to the amounts of the reacting substances which have already entered into the reaction. The two reactions, one leading from A to B, and the other from A' to B', may be represented on a diagram

I, constant volume

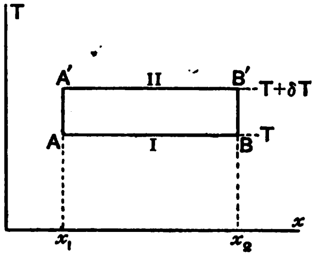

FIG. 10.

(Fig. 10) by the lines I and II. The line AA' represents a heating of the system from A to A', at constant volume and with x constant, *i.e.*, with no change in the composition of the substances forming the system: the line BB' has a similar interpretation.

Consider a process by which the system passes from the state A to the state B'. This may take place in an indefinite number of ways, of which we will consider only two,—first, that by the path ABB', and second, that by the path $AA'B'$. As the outside forces do no work, the total absorption of heat must be the same for both paths. Let the thermal capacity at constant volume of the materials composing the system be C_1, in their initial state of combination denoted by x_1. In the final state, after the reaction has gone on so as to change the composition from that indicated by x_1 to that indicated by x_2, let the thermal capacity of the system be C_2. Let the heat of reaction at the temperature T, be λ, and at the temperature $T+\delta T$, be $\lambda+\delta\lambda$. The quantity of heat absorbed in the first process is

$$\lambda + C_2\delta T,$$

and in the second,

$$C_1\delta T + (\lambda + \delta\lambda).$$

But, by the conditions of the problem, these two quantities of heat are equal, so that we have the equation

$$\lambda + C_2\delta T = \lambda + \delta\lambda + C_1\delta T,$$

or

$$\left(\frac{\partial\lambda}{\partial T}\right)_v = C_2 - C_1. \quad\text{(52)}$$

Equation (52) shows how the heat of reaction at constant volume is affected by a change in the temperature at which the reaction goes on.

If the difference of temperature is finite, we get by integration,

$$\lambda_{T_2} = \lambda_{T_1} + \int_{T_1}^{T_2}(C_2 - C_1)\,dT, \quad\text{(53)}$$

where, in order to perform the integration, the difference of the two thermal capacities, $C_2 - C_1$, must be known as a function of the temperature. In many cases, C_2 and C_1 are so nearly constant, that we have, practically,*

$$\lambda_{T_2} = \lambda_{T_1} + (C_2 - C_1)(T_2 - T_1). \quad\text{(54)}$$

II, Constant pressure.

71. The other important class of reaction, is that of the reactions at constant pressure. The same notation may be used as before, except that we will let C'_1 and C'_2 be the thermal capacities of the system, at constant pressure, and in the states of combination denoted by x_1 and x_2, respectively. A certain

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*G. Kirchhoff, Poggend. Ann. 1858

amount of outside work will, in the present case, be involved in each one of the four modifications AA', $A'B'$, AB, and BB'. Let these quantities of work be represented by W_1, W_2, W_3, and W_4. By Equation (50), (Art. 66) we have

$$W_A^{B'} + Q_A^{B'} = \epsilon_{B'} - \epsilon_A = \text{const.}$$

If we apply this equation to the two paths $AA'B'$ and ABB', we see that

$$W_1 + W_2 + C'_1\delta T + (\lambda + \delta\lambda) = W_3 + W_4 + \lambda + C'_2\delta T.$$

But since the pressure is constant and the total change of volume is the same for both paths, we have

$$W_1 + W_2 = W_3 + W_4,$$

as in any case of outside forces which have a potential.

A comparison of this equation with the last shows that

$$(\lambda + \delta\lambda) + C'_1\delta T = \lambda + C'_2\delta T,$$

whence
$$\left(\frac{\partial\lambda}{\partial T}\right)_p = C'_2 - C'_1. \qquad \text{(55)}$$

For a finite difference of temperature, this takes the form

$$\lambda_{T_2} = \lambda_{T_1} + \int_{T_1}^{T_2}(C'_2 - C'_1)dT; \qquad \text{(56)}$$

or, if C'_2 and C'_1 may be treated as constants,

$$\lambda_{T_2} = \lambda_{T_1} + (C'_2 - C'_1)(T_2 - T_1). \qquad \text{(57)}$$

CHAPTER VI

CALORIMETRIC PROPERTIES OF FLUIDS

Specific Heats of a Fluid

72. Having devoted Chapter V to an extremely simple example of the application of the first law of thermodynamics to chemistry, we will now give a few more illustrations, by discussing some of the calorimetric properties of fluids.

Let the system to be treated consist of a unit mass of a fluid, its state being defined by the normal variables v and T. Let the fluid be heated at constant volume from T to $T+\delta T$, the indicator point moving along the line AB (Fig. 11). The heat absorbed by the fluid during this change of state is equal to $C_v \delta T$. Let the fluid now expand isothermally, till its pressure has fallen from $p+\delta p$ to p, the volume increasing from v to $v+\delta v$, and the indicator point moving along the isothermal line from B to C. *Let no outside work be done by or on the system during this expansion.* This may be accomplished in the following manner: the fluid, at the temperature $T+\delta T$ and the pressure $p+\delta p$, being enclosed in a vessel of the volume v, this vessel is suddenly placed in communication with a second, *empty* vessel of the volume δv. Let both vessels be impervious to heat. The fluid expands suddenly to the volume $v+\delta v$; but as it is not expanding against any outside pressure, it does no external work. The part of the fluid which remains in the original vessel does, to be sure, some work on the part forced into the second vessel; but the work done by one part of the fluid is done on another part, so that the *external work* is zero. The fluid acquires a certain amount of kinetic energy during the sudden expansion, but by the friction of the eddy currents produced, this kinetic energy is very soon converted into heat. The part of the fluid remaining behind cools off somewhat, because it has been doing work on the other part; and this second part is warmed by the work done on it. If the whole mass be now left to itself, it will soon come to a uniform temperature, which will, in general, not be precisely the same as the temperature $T+\delta T$, before the expansion. If the fluid be next heated (or cooled) till it has the temperature $T+\delta T$, it will, during this change of temperature, absorb a quantity of heat $\lambda\delta v$. For we have the equation (article 57)

$$\delta Q = \lambda\delta v + C_v\delta T,$$

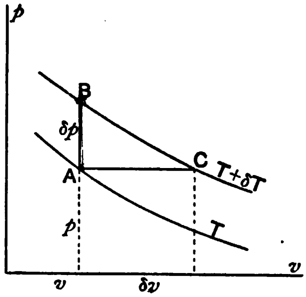

FIG. 11.

giving the absorption of heat during any infinitesimal change of state, in terms of the changes of the independent variables v and T; and since the outside work is zero for the process represented by the line BC, the final result of the passage from B, at the temperature $T+\delta T$, to C, at the same temperature, is the same, as regards absorption of heat, no matter what the path may be, and is, therefore, the same for the actual process as if the change had taken place isothermally.

The sum of the work and heat absorbed, in the passage of the system from the state A to the state C, is, therefore,

$$\int_A^C (dW+dQ)=C_v\delta T+\lambda\delta v,$$

Let the fluid be again taken in its original state, but let it now be heated at constant pressure to the temperature $T+\delta T$: the heat absorbed during this process is $C_p\delta T$, and the work done on the fluid is $-p\delta v$; so that, for this direct passage from A to C, we have the equation

$$\int_A^C (dW+dQ)=C_p\delta T-p\delta v.$$

These two expressions must, by the first law, have the same value; hence

$$C_v\delta T+\lambda\delta v=C_p\delta T-p\delta v,$$

or

$$C_p-C_v=(p+\lambda)\left(\frac{\partial v}{\partial T}\right)_p. \qquad\text{.....................(58)}$$

73. The ordinary gases obey the law $pv=RT$ approximately, when not too cold or too dense. For one of them, we have

$$\left(\frac{\partial v}{\partial T}\right)_p=\frac{R}{p}, \text{ approximately}$$

and for such a gas, equation (58) reduces to

$$C_p-C_v=R+\frac{\lambda R}{p}. \qquad\text{.........................(59)}$$

For the gases that follow Boyle's law, the value of λ is very small. This has been shown, experimentally, by allowing the gas to expand into a vacuum and observing the change in its temperature, a measurement which makes it possible to calculate what the absorption of heat would have been at constant temperature. The first experiments of this sort were performed by Gay-Lussac in 1807.* He connected a vessel filled with gas to another, empty

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* "*Memoires d'Arcueil,*" **1** (1807); Gilbert's *Annalen*, **30**, p. 249 (1808); reprinted in Mach's *Principien der Warmelehre*, Barth, Leipzig, 1896; also translated in Harper's *Scientific Memoirs*, **1**, New York, 1898.

vessel of the same volume and at the same temperature, each vessel being provided with a thermometer. He found, that after an equilibrium of pressure had been established, the temperature in the first vessel had fallen just as much as that in the other had risen; the gas had therefore, on the whole, no tendency to become warmer or cooler during the expansion; *i.e.*, no supply or abstraction of heat was needed to make the expansion isothermal. In 1844, Joule* performed somewhat similar experiments. He immersed the two vessels in the water of a calorimeter, and found that the free expansion of the gas had no appreciable effect on the temperature of the water: this result showed that the quantity λ, if not zero, was too small to be detected. Neither of these experiments was capable of great accuracy, but a different and finer method, used later by Joule and Thomson (Lord Kelvin),† showed that λ, though small, has a measurable value. The theory of these celebrated 'plug experiments' of Joule and Thomson will be discussed later: for the present, we shall merely assume that λ has been shown to be a very small quantity for the ordinary gases, at ordinary pressures and temperatures.

For such gases, then, we have very approximately

$$C_p - C_v = R. \qquad (60)$$

74. Equation (60) suggests a method of measuring the mechanical equivalent of heat. If C_p and C_v have been measured calorimetrically, and if R is known in mechanical units, from the numerical values of the quantities appearing in the gas equation $pv = RT$, we have the value in mechanical units of the quantity of heat $C_p - C_v$.

Another way of putting the same thing, is to say that the heat absorbed, during a rise of temperature at constant pressure, is greater than that absorbed at constant volume, the difference

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* *Phil. Mag.* (3), **26**, p. 369 (1845); *Scient. Papers*, **1**, p. 172.

† Kelvin's *Math. and Phys. Papers*, **1**, p. 333; reprinted from various papers in *Phil. Mag.* and *Phil. Trans.*, 1852-1862; also reprinted in Harper's *Scientific Memoirs*, **1**.

being the heat-equivalent of the work done by the gas in expanding against the outside pressure. This statement assumes the truth of the first law, and assumes, also, that λ, the latent heat of free expansion, is zero. The method has been used for finding J, the mechanical equivalent of heat; in fact, the first published value which could make any claims to accuracy, was obtained in this way by J. R. Mayer, in 1842.* It has often been said that Mayer's value, computed in this way, could make no claim to recognition, because the experiments of Joule, and of Joule and Thomson, on free expansion had not yet been performed. Mayer himself, however, states distinctly,† in a letter of September 12, 1841, that he was familiar with the results of Gay-Lussac's experiments, although, in the paper mentioned above, he does not discuss the question of the absorption of heat during free expansion. The data at Mayer's disposal were imperfect, and his value of the mechanical equivalent (365 m.kilogr.) is much too small.

75. For getting an approximate idea of the behaviour of the gases, it is often convenient to consider an IDEAL GAS, which differs only slightly in its physical properties from the gases actually existing, but which follows simpler laws. This ideal or perfect gas is usually defined by two conditions, each of which is nearly fulfilled by oxygen, hydrogen, nitrogen, and some others of the more common gases. These conditions are: I. The gas follows Boyle's Law exactly, *i.e.*, $(pv)_T = \text{const.}$; and II. The heat it absorbs during free expansion is zero, *i.e.*, $\lambda = 0$.

During a free expansion, the only change in the internal energy of a fluid is due to the absorption or emission of heat. If the free expansion is isothermal, the quantity of heat absorbed by unit mass is $\int \lambda dv$, hence we have

$$\epsilon_B - \epsilon_A = \int_A^B \lambda dv.$$

If $\lambda = 0$, it follows that $\epsilon_B = \epsilon_A$, or in other words, the internal

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* Liebig's *Annalen*, **42**, p. 233 (1842); also *Ges. Schriften*, **1**, p. 23.

† *Ges. Schriften*, **2**, p. 128.

energy does not change during the change of volume, if the temperature is constant. Hence the second condition which an ideal gas must satisfy may be stated as follows: II′. The internal energy of an ideal gas is independent of the volume, and is a function of the temperature only. $p\,dv = 0$

To these two conditions we shall add a third: III. The specific heat of an ideal gas, at constant volume, is independent of the volume and the temperature; this also is nearly true for the more common gases, at ordinary pressures and temperatures.

For such a gas we have, as already shown in article 73,

$$C_p - C_v = R.$$

The ratio of the specific heats at constant pressure and constant volume may, then, be written in the form

$C_v = \frac{R}{\gamma - 1}$

$$\gamma = \frac{C_p}{C_v} = \frac{C_v + R}{C_v} = \text{const.} \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots (61)$$

76. Instead of being heated at constant volume or constant pressure, a fluid may have its pressure or its volume changed in any arbitrary manner during a rise of temperature. Let C be the specific heat under these conditions; C is, of course, defined as the rate at which unit mass of the fluid absorbs heat, as the temperature rises in the prescribed manner.

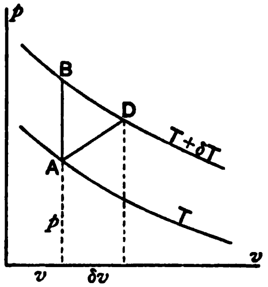

FIG. 12.

Let a unit mass of the fluid be taken in the state represented by the point A (Fig. 12). Let it be heated till its temperature has risen from T to $T+\delta T$, and let the volume change, meanwhile, at the rate $\frac{dv}{dT}$, so that the increase of volume, during the infinitesimal rise in temperature δT, is

$$\delta v = \frac{dv}{dT}\delta T.$$

The fluid is now in the state represented by the point D, and the sum of the work done on the fluid and the heat absorbed by it, as it passes along the path AD, is

$$\int_A^D (dW + dQ) = C\delta T - p\,\delta v = \left(C - p\frac{dv}{dT}\right)\delta T.$$

Now let the fluid pass from the state A to the state D, not directly but along the path ABD. During the first part of this process, the state of the fluid is modified by its having its temperature raised while the volume remains constant: the heat absorbed during this part of the process is evidently equal to $C_v\delta T$, while the outside work is zero. During the second part of the process, which is an isothermal free expansion, the work is still zero, and the heat absorbed is $\lambda\,\delta v$, or $\lambda\frac{dv}{dT}\delta T$. Hence for this second path of the system from the state A to the state D, we have the equation

$$\int_A^D (dW + dQ) = C_v\delta T + \lambda\,\delta v = \left(C_v + \lambda\frac{dv}{dT}\right)\delta T.$$

But since $\int_A^D (dW + dQ)$ is independent of the path, a comparison of the last two equations gives us

$$C - p\frac{dv}{dT} = C_v + \lambda\frac{dv}{dT}$$

whence

$$C = C_v + (p+\lambda)\frac{dv}{dT}. \quad\text{.......................(62)}$$

Since $\frac{dv}{dT}$ has any value we please, C also may have any value whatever: in other words, a fluid has an infinite number of specific heats, ranging in value from $-\infty$ to $+\infty$, and depending on the rate at which the volume is varied as the temperature rises. In the particular case where the pressure is constant, equation (62) reduces to

$$C_p = C_v + (p + \lambda)\left(\frac{\partial v}{\partial T}\right)_p, \quad \text{......................(63)}$$

an expression already obtained in article 72.

If we apply equation (62) to the case of an ideal gas, for which we have the relations

$$\lambda = 0, \quad p = \frac{RT}{v},$$

it reduces to

$$C = C_v + RT\frac{d}{dT}\log v. \quad \text{......................(64)}$$

77. Equation (62) may also be obtained in a different form, in terms of p and T as the independent variables. Let the fluid, after reaching the state D (Fig. 13), return to its initial state A by an isothermal free expansion, DB, followed by a cooling at constant pressure, BA. Let the increase of volume, needed to bring the pressure isothermally from its value at D back to its initial value at A, be denoted by $\delta' v$. During the modification DB, the work done is zero, and the heat taken in is $\lambda\delta' v$: during the modification BA, the work done on the

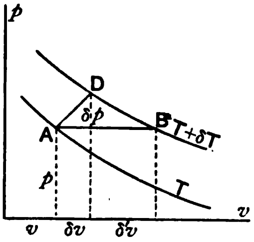

FIG. 13.

system is $p(\delta v + \delta' v)$, and the heat absorbed is $-C_p \delta T$. Hence for the whole process DBA, we have

$$\delta_1 \epsilon = \lambda \delta' v - C_p \delta T + p(\delta v + \delta' v),$$

whereas, for the change AD, the alteration in the internal energy was

$$\delta \epsilon = C \delta T - p \delta v.$$

But since the system has finally returned to its original state, we have $\delta \epsilon + \delta_1 \epsilon = 0$; whence

$$C \delta T - p \delta v + \lambda \delta' v - C_p \delta T + p(\delta v + \delta' v) = 0,$$

which gives us at once the equation

$$C = C_p - (p + \lambda) \frac{\delta' v}{\delta T}. \quad \dots\dots\dots\dots\dots\dots(65)$$

Now

$$\delta' v = -\left(\frac{\partial v}{\partial p}\right)_T \delta p = -\left(\frac{\partial v}{\partial p}\right)_T \cdot \frac{dp}{dT} \delta T,$$

since as v increases, the pressure is falling from $p + \delta p$ to p. Hence equation (65) may be written

$$C = C_p + (p + \lambda)\left(\frac{\partial v}{\partial p}\right)_T \cdot \frac{dp}{dT}. \quad \dots\dots\dots\dots\dots\dots(66)$$

In the case of an ideal gas, this reduces to the form , since $\left(\frac{\partial v}{\partial p}\right)_T = -\frac{RT}{p^2}$

$$C = C_p - RT \frac{d}{dT} \log p. \quad \dots\dots\dots\dots\dots\dots(67)$$

Adiabatic Processes

78. When a system undergoes a change of state during which it neither absorbs nor gives out heat, it is said to undergo an *adiabatic change*: such changes are the only ones possible to a system enclosed in an envelope which is impermeable to heat. A change of state may also be approximately adiabatic, if it is so rapid, that during the time it occupies, no appreciable interchange of heat can take place with outside bodies, even though there is no impermeable envelope. This is the case, for example, with the expansion and contraction of a mass of gas during the passage of sound waves, the changes being so rapid as to be nearly adiabatic.

If the system under consideration have only two degrees of freedom, the condition that no heat shall enter or leave the system reduces the number of degrees of freedom to one: hence, on any diagram representing the process, we shall have an *adiabatic line*, just as we had isothermal lines, under the condition that the temperature should be constant. It is interesting to investigate the form of these lines,—especially of those of an ideal gas.

79. To find the equation of the adiabatic lines, we make use of the condition, that during an adiabatic process

$$\delta Q = 0,$$

which reduces the main equation,

$$\delta\epsilon = \delta Q + \delta W,$$

to the form

$$\delta\epsilon = \delta W.$$

Let the unit mass of fluid have, initially, the volume v, the pressure p, and the temperature T, its indicator point being at A (Fig. 14). Let it expand adiabatically until it has reached the state $v + \delta v$, $p + \delta p$, $T + \delta T$, indicated by the point C, AC being an infinitesimal element of the adiabatic line through A. For this process we have

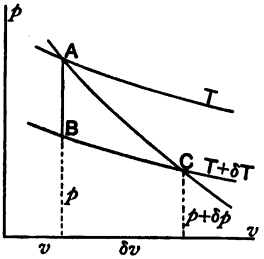

FIG. 14.

$$\delta\epsilon = \delta W = -p\,\delta v.$$

Now let the system pass from A to C by a second path: let it first change its temperature at constant volume, a change for which $\delta W=0$, and $\delta Q=C_v\delta T$; let the volume then increase, by an isothermal free expansion, during which change, $\delta W=0$ and $\delta Q=\lambda\delta v$. For the whole path we have, then,

$$\delta\epsilon=C_v\delta T+\lambda\delta v.$$

But the change in the internal energy must be the same for both paths; therefore we have

$$C_v\delta T+\lambda\delta v=-p\delta v,$$

or

$$\left(\frac{\partial v}{\partial T}\right)_Q=-\frac{C_v}{p+\lambda}. \tag{68}$$

This is the differential equation of the adiabatic lines of the fluid in the (v, T) plane.

80. Equation (68) might have been obtained from another, which has already been deduced, without going back to the beginning as we have done here. We have, namely, the general equation (see article 76),

$$C=C_v+(p+\lambda)\frac{dv}{dT}. \tag{69}$$

If we now make it a condition, that the volume shall vary with the temperature in such a way that no heat enters or leaves the system, we have

$$C=0,\quad \frac{dv}{dT}=\left(\frac{\partial v}{\partial T}\right)_Q;$$

and by putting these values into equation (69) we get

$$\left(\frac{\partial v}{\partial T}\right)_Q=-\frac{C_v}{p+\lambda},$$

as before.

By similar reasoning, we may reduce equation (66) to the form

$$\left(\frac{\partial p}{\partial T}\right)_Q=-\frac{C_p}{(p+\lambda)\left(\frac{\partial v}{\partial p}\right)_T}, \tag{70}$$

fr.... : $0=C_p+(p+\lambda)\left(\frac{\partial v}{\partial p}\right)_T\left(\frac{\partial p}{\partial T}\right)_Q$

which is the differential equation of the adiabatic lines in the (p, T) plane.

Comparison of equations (68) and (70) shows that the differential equation of the adiabatic lines in the (p, v) plane is

$$\left(\frac{\partial p}{\partial v}\right)_Q = \frac{C_p}{C_v}\left(\frac{\partial p}{\partial v}\right)_T. \qquad (71)$$

In this equation, the term $\left(\frac{\partial p}{\partial v}\right)_T$ is always negative; for in all practical circumstances, an increase of pressure is accompanied by a decrease of volume, if the temperature is constant.* For any fluid that expands upon being heated at constant pressure, $C_p > C_v$, and since both C_p and C_v are positive, it follows that $\frac{C_p}{C_v} > 1$: hence $\left(\frac{\partial p}{\partial v}\right)_Q$ has a larger negative value than $\left(\frac{\partial p}{\partial v}\right)_T$, or the adiabatic lines on the (p, v) diagram fall more sharply, as they recede from the p axis, than do the isothermal lines.

81. To find the ordinary integral equation of the adiabatic lines of a fluid, it is necessary to integrate one of the equations (68), (70), and (71). In general, this is not possible, because we have not sufficient information to enable us to express all the quantities that appear in these equations, as functions of the independent variables. In the particular case of an ideal gas, however, the problem is much simplified: for such a gas it has already been shown that γ, or $\frac{C_p}{C_v}$, is a constant (article 75). Moreover, since by definition

$$pv = RT,$$

we have

$$\left(\frac{\partial p}{\partial v}\right)_T = -\frac{RT}{v^2} = -\frac{p}{v}.$$

Substituting in equation (71), we get

$$\left(\frac{\partial p}{\partial v}\right)_Q = -\gamma\frac{p}{v};$$

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* This would not be the case if we could realise the hypothetical 'third volume' indicated by van der Waals's equation. But see page 77.

dividing by p, multiplying by dv, integrating, and removing the logarithms leads to the equation

$$pv^{\gamma} = K = \text{const.} \qquad \text{(72)}$$

The other two equations might have been integrated by a similar substitution, but the result is more simply reached by elimination between the equations

$$pv^{\gamma} = K,$$
$$pv = RT.$$

The equations of the adiabatic lines, obtained in either of these ways, are

$$\left.\begin{aligned} pv^{\gamma} &= K, \\ v^{\gamma-1}T &= \frac{K}{R}, \\ T^{\gamma}p^{1-\gamma} &= \frac{K}{R^{\gamma}}, \end{aligned}\right\} \qquad \text{(73)}$$

in the (p, v), (v, T), and (T, p) planes, respectively.*

82. It should be noticed, that to find the pressure overcome by the gas in expanding, we have used the equation of ~~condition~~ state $pv = RT$ simultaneously with an equation, $\delta\epsilon = \delta W$, which contains, as one of its terms, a quantity of work done against outside forces. This is equivalent to assuming that the pressure and the temperature have determinate values, which are the same, throughout the gas, as they would be if the gas were at rest, in equilibrium; for $pv = RT$ is an equation obtained by static experiments. Hence in order that the equations which we have deduced in articles 78 to 81 should have any meaning, the motions of the different parts of the gas, during the expansion or contraction, must not be so tumultuous as to cause any sensible non-uniformity of the pressure or the temperature throughout the mass, or any vari-

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* The reader will notice that in the treatment of ideal gases we have everywhere assumed, tacitly, that the temperatures are read on a thermometer filled with the gas in question: this is implied by the use of the equation $pv = RT$.

ation of their values from those that would be found if the gas were at rest. Similar remarks may be made upon any problem, in the treatment of which we use an equation of ~~condition~~ state obtained from *statical experiments* in connection with equations referring to processes that have a finite speed.

Reech's Theorem. Measurement of C_p/C_v

83. Equation (71) may evidently be put in the form

$$\frac{C_p}{C_v}=\frac{\left(\frac{\partial p}{\partial v}\right)_Q}{\left(\frac{\partial p}{\partial v}\right)_T}, \qquad (74)$$

and the fact expressed by this equation is known as 'Reech's Theorem.'

It gives us a simple method of measuring γ, the ratio of the specific heats of any gas at constant pressure and at constant volume: theoretically, the method is applicable to liquids as well as gases, but in practice the measurements would be difficult on account of the small compressibility of liquids. It is only necessary to measure the quantity $\left(\frac{\partial p}{\partial v}\right)$, first for an adiabatic change of volume, and second for an isothermal one; or, to measure the adiabatic and isothermal coefficients of compressibility.

This method, first used by Clément and Desormes and still known by their names, may be carried out as follows: The gas is placed in a large receptacle, provided with a delicate manometer for the measurement of the pressure, and also provided with a cylindrical tubulure, in which a piston may be moved to and fro so as to increase or decrease the internal volume of the receptacle. The whole apparatus having come to the temperature of the surroundings, the pressure is read on the manometer. The piston is then suddenly forced in a short distance, and the pressure read again as quickly as possible. If the compression is rapid enough, it is very nearly adiabatic, the heat received by the gas from its envelope decreasing in amount, as the compression decreases in duration. Let the adiabatic increase of pressure—the difference between the first and second readings of the manometer—be denoted by δp_Q. The gas, having been warmed by the adiabatic compression, now cools off until its temperature is the same as at first: meanwhile, the pressure sinks to the value it would have reached in an isothermal compression to the volume now occupied. Let the final pressure be read, and let the difference between this and the original pressure, read before the compression, be denoted by δp_T. Then, since the decrease of volume δv is the same for both the adiabatic and the isothermal compressions, we have, by Reech's theorem,

$$\frac{C_p}{C_v}=\frac{\delta p_Q}{\delta p_T}. \qquad (75)$$

Instead of a compression, an expansion, caused by pulling out the piston, might have been used just as well; for the only effect of reversing the motion of the piston would have been to change the signs of δv, δp_Q, and δp_T.

84. Measurements of γ, by the method of Clément and Desormes, are subject to several causes of error. In the first place, Reech's theorem is deduced only for infinitesimal changes in volume, whereas we have applied it to finite changes. If we make the compression or expansion very small, so as to approximate, as nearly as may be, to the conditions essential to the validity of the theory, the differences of pressure to be measured are so small that the errors of reading destroy the accuracy of the result. It has been proposed, by MM. Maneuvrier and Fournier*, to avoid this difficulty by measuring $\frac{\delta p_Q}{\delta p_T}$ for various values of δv, and finding, graphically, the limiting value of $\frac{\delta p_Q}{\delta p_T}$, as the change in volume δv approaches zero. They seem, however,

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* *C. R.* **123**, p. 228 (1896).

to have concluded, from their experimental difficulties when δv was very small, that this graphical result was less reliable than the *mean* value of γ, obtained from experiments with various small values of δv.

A second error, which has often been neglected, is due to the fact that the volume of the liquid manometer used, changes during the compression: the correction needed to eliminate this error has been computed by M. Swyngedauw.*

85. This error, as well as that due to the difficulty of making an instantaneous reading of the manometer, is ingeniously avoided in the method of M. Maneuvrier.† The receptacle *A* (fig. 15), of known volume, is connected by a fine horizontal tube with a second receptacle *B*, fitted with a manometer. The tube has a stopcock *C*, and contains an index *I* of some light liquid. When the experiment is to be performed, the piston *P* is suddenly shot in a short distance, by releasing a spring: at the instant when the piston has just finished its motion, the cock *C* is opened and then immediately closed again. If the pressure in *A*, when the cock is opened, differs from that in *B*, the index will move; otherwise it will be motionless. The experiment consists, then, in adjusting the pressure in *B*, by trial, so that when the piston is shot in and

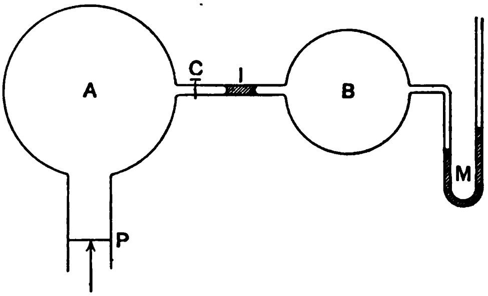

FIG. 15.

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* *Journal de Physique*, (3), **6**, p. 129 (1897).

† *C. R.* **120**, p. 1398 (1895).

the cock C opened, the index remains at rest. In this way, the change of volume due to the motion of the manometer fluid is avoided, and the readings of the pressure, after the adiabatic compression, may be made at leisure and accurately. It is thus possible to make an unusually exact measurement of δp_Q. The second part of the experiment is done away with, by computing δp_T, from the known volume of A and the area and stroke of the state piston, by means of the equation of ~~condition~~ of the gas, if that is known from other experiments.

86. Whatever be the particular form of apparatus used, the compression or rarefaction must be very sudden, or the process will not be adiabatic: but if the velocity of the piston be very great, it is questionable, whether the pressure of the gas on the piston can be regarded as sensibly the same as the pressure elsewhere. The pressure on the piston will certainly be somewhat greater, during compression, and somewhat less, during rarefaction, than in other parts of the receptacle; whereas in deducing Reech's theorem we have, by speaking of 'the pressure of the fluid,' assumed that the pressure is uniform throughout the mass. Whether this cause of error is of sensible importance, might be determined by comparing the results of experiments on compression with those of experiments on expansion.

Older and less exact varieties of the method of Clément and Desormes are described in all the larger works on experimental physics.

CHAPTER VII

RECAPITULATION

Thermometry—Chapter I

87. We began by **defining** EQUALITY OF TEMPERATURE by reference to the thermal equilibrium attained by two bodies, which when placed in contact, exercise only thermal actions on each other; and stated the important **experimental fact,** that *two bodies are at the same temperature, if each of them is at the same temperature as a third.*

The elimination of the effects of the presence of other bodies than the two in question was then considered.

Miscible bodies, when placed in contact, form mixtures. Such a mixture may attain thermal equilibrium with another body, not miscible with it; and we may thus speak of the temperature of the mixture, as equal to that of this latter body. We have no means of experimenting on the components in a mixture: hence the expression 'temperature of the components' has no definite meaning. *We agree, nevertheless, as a matter of convention, to treat the components in a mixture as having a temperature, which is that of the mixture taken as a whole.*

When a body has attained, so far as experiment can show, a state of internal thermal equilibrium, it is said to have a UNIFORM TEMPERATURE.

88. HIGHER AND LOWER TEMPERATURES are distinguished by reference to the changes that take place during the equalization of temperature, and to our sense of heat and cold. We have next to devise a set of numbers which shall denote all temperatures unequivocally, and shall satisfy the ordinary equation

$$(T_3 - T_2) + (T_2 - T_1) = (T_3 - T_1).$$

Any such set of numbers, when we have a method of determining, at any time, by experiment, the number corresponding to the temperature of any given body, constitutes a SCALE OF TEMPERATURE.

Thermal expansion provides us with such a method of experiment, and we select, arbitrarily, some convenient substance for use as a thermometer, assigning to each volume, length or pressure, of the chosen substance, a definite number,—the numbers increasing as the substance becomes warmer.

The practical choice of a thermometric substance was considered, and the CELSIUS SCALE and the ABSOLUTE GAS SCALE were defined. *The absolute gas scale is, in reality, a purely arbitrary scale;* for it makes use of the properties of some one, actually existing, gas, and no two gases are entirely alike in their properties. We retain the name because it is in common use.

THE TEMPERATURE AT A POINT in a body is not measurable, because our thermometers are all of finite size. We use the expression for the sake of brevity, to denote the temperature measured by a very small thermometer, filling a hole cut in the body about the point in question.

Calorimetry—Chapter II

89. The consideration of equalization of temperature leads to the notion of something which, by its presence, influences the temperature of the body in which it is present.

This notion of a QUANTITY OF HEAT has grown from experience: to make it precise, we must first confine ourselves to the consideration of purely thermal phenomena; then we must examine the particular characteristics of the something that we call quantity of heat.

The basis of the notion is constancy in total amount. We make, as a first addition to this, the **assumption**, that *when a body cools* *through a given interval, the quantity of heat it gives out is always the same,*—an assumption that is justified by its results. We have here to limit ourselves carefully in the choice of the bodies in question, and our statement, at best, lacks the precision which it receives later in chapters III and IV.

90. EQUALITY OF QUANTITIES OF HEAT has, so far, no meaning, except as referring to heat given out by one body and received by another. As a matter of **definition**, we agree, that *quantities of heat which are equal to the same quantity are equal to one another.*

From this it results, that *the heat given out by a body, in cooling through a definite interval, is equal to that received by it, in being warmed through the same interval.*

We **find experimentally,** that *we may treat quantities of heat as proportional to the masses of a given substance that they can warm through a certain interval;* and we select, arbitrarily, a standard substance, a standard mass of it, and a standard interval of temperature,—thus fixing the UNIT QUANTITY OF HEAT.

91. *Heat, as thus quantitatively defined, is equivalent to mechanical energy.* The two are mutually convertible—though not completely in both directions—with a fixed ratio, dependent on the units used, between the quantity of one expended and that of the other produced. *Heat is a form of energy and may be measured in terms of the unit of energy.*

Thermodynamic Systems—Chapter III

92. *We exclude from consideration, all processes that involve an appreciable amount of kinetic energy.*

A GIVEN SYSTEM has certain fixed properties. If it has any variable properties, they determine the STATE OF THE SYSTEM. Our whole knowledge of a system, at any instant, consists in a knowledge of these fixed and variable properties.

We represent the variable properties by quantities, or variables, of which the values define the state of the system. The variables may be greater but not less in number than the degrees of freedom of the system. If they are greater in number, there exist, between the variables, a number of EQUATIONS OF ~~CONDITION~~, State which reduce the whole number of variables to equality with the number of possible, arbitrary, independent variations of state of the system. *These equations of ~~condition~~ are inherent in the nature of the* state *system, and are to be considered as included in the definition of the 'given system.'*

All our work is, of necessity, only approximate: we disregard the changes of such variables as have only unimportant effects on the problem in hand.

The changes of state of a system that has only two degrees of freedom may be simply represented by the motions of a point on a plane diagram. Any condition, imposed on the mode of variation of the two variables, reduces the system to one degree of freedom, and the possible changes of state are then represented by specific lines on the diagram. If the system has more than three degrees of freedom, its changes of state can not be represented on a single diagram.

93. A system is in THERMODYNAMIC EQUILIBRIUM, when all its variables remain constant. Such equilibrium requires, for its maintenance, the application of certain ACTIONS from outside the system: these actions may be quantitatively represented by mathematical symbols. The system may, like a frictionless dynamic system, have EQUATIONS OF EQUILIBRIUM connecting the variables and the outside actions, or it may not have such equations. **We limit ourselves to the consideration of systems that have equations of equilibrium**: in other words,—for all the systems that we shall consider, *a given state of equilibrium requires a single, definite set of outside actions* in order that it may subsist.

The First Law of Thermodynamics—Chapter IV

94. The outside actions, when of a mechanical nature only, may be completely characterized by the quantities X, $\mathcal{Y}$, which appear in the expression for the work done on the system during an infinitesimal change of state; namely,

$$\delta W = \sum_1^n X\delta x + \mathcal{T}\delta T,$$

where x', x'', ... x^n, T are the independent variables. These quantities, X and $\mathcal{T}$, may, or may not, have the dimensions of force; but, at any rate, each term in the equation just given has the dimensions of a quantity of work or energy.

By the consideration of an imaginary mechanism, we may represent the variables as lengths, and the actions as forces; hence the names GENERALIZED COORDINATES and GENERALIZED FORCES.

The equations of equilibrium may be written

$$X' = f'(x', x'', \dots x^n, T),$$
$$\dots\dots\dots\dots\dots\dots\dots\dots,$$
$$\mathcal{T} = f^t(x', x'', \dots x^n, T);$$

where f', f'', etc., are finite, continuous, and single-valued, and may be determined by experiment.

For some of the variables, the coefficients X', ... $\mathcal{T}$ may be identically zero, so that the corresponding equations in the above set are wanting. The variables for which the corresponding coefficients are constantly zero, are called INTERNAL VARIABLES. If the temperature is an internal variable, the whole set of variables is known as a set of NORMAL VARIABLES. *We* **assume** *that it is always possible to select a set of normal variables,* no matter what the nature of the system may be.

In any real process, the forces do not have values that satisfy the equations of equilibrium; since in thermodynamic processes, where kinetic energy is excluded, the velocities vanish with the forces.

95. For a system with two degrees of freedom, the work done on the system is represented by an area on a diagram, of which x and X are the coordinates. In a cyclic process, the work done on the system is equal to the area of the cycle on the diagram, which is counted as positive if traced out clockwise.

This diagram is not a complete representation of the process, unless the state of the system is at all times infinitely near to a state of equilibrium; that is, unless the process is reversible.

In the case of a system consisting of a mass of fluid, we have

$$\delta W = -p\delta v.$$

For a gas that follows the equation $pv = RT$, the work done on the gas, during a finite change of state, is

$$W = -\int_{v_1}^{v_2} \frac{RT}{v} dv.$$

If the change of state is isothermal, the work done is

$$W = RT \log \frac{v_1}{v_2}.$$

In the case of a system that has $n+1$ degrees of freedom, we may represent the work done on the system by areas on $n+1$ plane diagrams, each having, as its coordinates, one of the independent variables and the corresponding force.

96. *If the system is in a state of equilibrium, the generalized forces, in so far as they are not identically zero, may be used as independent variables,* and we may change from the normal variables,

$$x'_i, x''_i, \ldots x^m_i, x'_e, x''_e, \ldots x^{n-m}_e, T,$$

to the INVERSE VARIABLES

$$x'_i, x''_i, \ldots x^m_i, X'_e, X''_e, \ldots X^{n-m}_e, T,$$

which, in general, are not normal, by means of the equations

$$x'_e = \phi'(x'_i, x''_i, \ldots x^m_i, X'_e, X''_e, \ldots X^{n-m}_e, T),$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots,$$

etc.

deduced from the equations of equilibrium,

$$X'_e = f'(x'_i, x''_i, \ldots x^m_i, x'_e, x''_e, \ldots x^{n-m}_e, T),$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots,$$

etc.

The functions f', f'', *etc., are* **assumed** *to be single-valued;* i.e., *we assume, that a given state of equilibrium can be maintained only by a unique set of outside actions.* The functions ϕ', ϕ'', etc., are not necessarily single-valued; i.e., *a single set of outside actions may maintain several different states of equilibrium, but not in general a continuous set of states.*

97. *We assume as a* **result of experiment,** *that during an infinitesimal modification of the state of a system, the absolute value of the heat absorbed by the system is the same in both directions, if the outside actions are the same.* This quantity of heat may be represented by the equations

$$\delta Q = \sum K\delta x + C_x \delta T,$$

$$\delta Q = \sum M\delta x_i + \sum L\delta X_e + C_X \delta T,$$

according as we are using normal or inverse variables. The quantities K, L, and M are the THERMAL COEFFICIENTS or LATENT HEATS of the system for the corresponding variables. The quantities C_x and C_X are the THERMAL CAPACITIES for constant normal and inverse variables, respectively.

98. *We* **assume,** *as a hypothetical generalization from experience, that in any cyclic process*

$$(\int)(dW + dQ) = 0:$$

this assumption is known as the FIRST LAW OF THERMODYNAMICS.

We **assume,** *that if a state B can be reached from a state A, the state A can also always be reached from B, by some process or other:* hence we conclude from the last equation, that

$$\int_A^B (dW + dQ) = \epsilon_B - \epsilon_A,$$

where ϵ_B and ϵ_A are the values, at B and A, of a quantity which is a function only of the variables that determine the state of the system. The function ϵ is known as the INTERNAL ENERGY OF THE SYSTEM.

The last equation, and the form

$$\delta W + \delta Q = \delta\epsilon,$$

which it assumes for an infinitesimal change, may be considered as an enlarged form of the first law. All our work since the beginning of article 94 is, however, valid only for systems upon which the outside actions are solely of a mechanical nature.

99. *Experience shows us the existence of other forms of energy than heat and mechanical energy.* **We assume, as a generalization from experience,** *that all forms of energy are equivalent in the same sense as heat and work.* This assumption is known as the PRINCIPLE OF THE CONSERVATION OF ENERGY: it is justified by the fact that no known experiment has contradicted it.

100. Two kinds of energy may or may not be completely convertible in both directions. All are completely convertible into heat, so far as we know; but there are some kinds into which heat is not completely convertible. *We make it a* **condition** *of the validity of all our future work, that the outside actions to be considered are all of such a nature, that the energy they can supply to the system is completely convertible, in both directions, with mechanical energy.*

By the use of appropriate machines, we may replace all the outside actions by mechanical forces; *i.e.*, all the processes, that actually do go on, may be produced by mechanical forces, applied to the system through the mediation of the machines. Hence all the conclusions, reached in articles 94 to 98, are valid, even when the restriction to mechanical outside actions is removed; and we have

$$(\int)(dW + dQ) = 0,$$

$$\int_A^B (dW + dQ) = \epsilon_B - \epsilon_A,$$

$$\delta W + \delta Q = \delta\epsilon;$$

as three forms of the first law, holding, with no further assumptions than those already mentioned in articles 96, 97, and 98, for the changes of state of any system acted on by outside actions of the nature specified in article 62.

Applications—Chapters V and VI

101. In chapter V, we deduced the fundamental law of thermochemistry, as an illustration of the foregoing principles. In chapter VI, we gave further illustrations, by deducing a few theorems concerning the specific and latent heats of fluids,—especially gases.

CHAPTER VIII

THE SECOND LAW OF THERMODYNAMICS

Reversible Processes

102. In our study of the mutual transformations of different forms of energy, which resulted in the enunciation of the first law of thermodynamics, we found a relation which is satisfied during any change in the state of a thermodynamic system. The applications given in Chapters V and VI are enough to show that certain useful results may be obtained by the use of this law, and the illustrations might have been greatly increased in number. But though the first law gives us a relation which holds when anything does happen, it does not tell us whether anything will happen: in other words,—it does not tell us the *Conditions of thermodynamic equilibrium.* The next subject that presents itself to us, is the study of these conditions. In this investigation our attention will be directed mainly upon reversible processes. We shall therefore add a few further remarks on the nature of these processes to what has already been said in article 49.

103. No actual process is reversible, if we construe the word 'reversible' strictly. If a process goes on in one direction, we know practically from experience, that it can not be made to go on in the opposite direction by the application of exactly the same outside actions, though by changing the actions, we may make the system traverse the same series of intermediate states in the inverse order.

If at every instant during the transformation, the forces acting differ only infinitesimally from those needed to keep the system in equilibrium in the state it then occupies, the process may be stopped by infinitesimal changes in the forces; or, the series of states may be converted into a series of states of equilibrium. By further infinitesimal changes in the forces, the equilibrium may be so disturbed that the reverse transformation takes place. The process may, then, be reversed in direction by infinitesimal changes in the values of the outside actions. We agree to call such a process—one at every instant of which the system is infinitely near to being in a state of equilibrium—a *reversible process* or a *reversible transformation.**

In strictness, we should say that the only reversible transformation is the series of states of equilibrium which forms the limit between the two inverse transformations obtained by infinitesimal changes, in one direction or the other, of the outside actions. We do not imagine any system really to undergo such a transformation; but we may, in a sense, *think* of such a process, by thinking of the system as occupying the states of equilibrium successively, without troubling ourselves as to how it gets from any one state to the next one.

For the purposes of experimental physics, where we can measure small, but not indefinitely small, quantities, it is immaterial whether we use this latter, strict definition of a reversible process, or use the former, approximate one. It is one of the fundamental assumptions of physics that only finite causes produce finite effects. Hence, if the forces acting on a system differ only infinitesimally from the forces needed to keep it in equilibrium, any transformation that is actually taking place, can have only an infinitesimal velocity. The rate of change of the state of the system is therefore inappreciable, and the system is *sensibly in equilibrium.*

104. In a reversible modification of the state of a system, the work done on the system is the negative of that done on it in the

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*Duhem: *Introduction à la Mécanique Chimique,* Chap. IX., art. 1. Paris, Carré, 1893.

inverse modification; for the generalized forces are the same, and the motions of their points of application are equal in amount, but opposite in sign, in the two cases. By 'work done on the system' we mean the total energy of the same value as mechanical energy, that enters the system. If we apply, to such a process, the first law of thermodynamics, in the form

$$\int_A^B (dW + dQ) = \epsilon_B - \epsilon_A, \quad \text{.....................(76)}$$

we see, that since reversing the direction reverses the signs of dW and of $(\epsilon_B - \epsilon_A)$, it also reverses the sign of dQ, and consequently of $\int dQ$. Hence during a reversible process, the heat taken in when the process has one direction, is the same as that given out when it has the other. This statement is, in fact, an assumption which we used in article 56, in leading up to the first law, so that it must necessarily result, when we work backward by applying the first law to a particular process.

Carnot's Cycle

105. Let us consider a system with two degrees of freedom. Let the normal variables be x and T, and let the single outside action X be of a mechanical nature. Let the system undergo reversible modifications of state, consisting of adiabatic and isothermal changes. Let the isothermal changes take place at

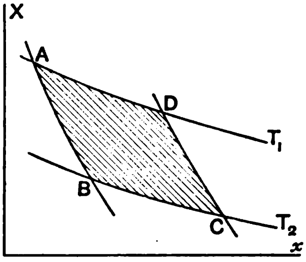

FIG. 16.

the temperatures T_1 and T_2 ($T_1 > T_2$), so that no heat enters or leaves the system except at these two temperatures. Suppose that the system performs a cycle $ABCDA$ (Fig. 16), consisting of the adiabatic change AB, the isothermal change BC at the temperature T_2, the adiabatic change CD, and the isothermal change DA at the temperature T_1. The whole process is known as a Carnot Cycle.

By the first law, we have the equation

$$\left(\int\right)(dW+dQ)=0. \qquad \text{.......................(77)}$$

If A is the total work *given out* by the system, and Q_1 and Q_2 are the quantities of heat absorbed by it at the temperatures T_1 and T_2, respectively, we have

$$A=Q_1+Q_2. \qquad \text{...........................(78)}$$

106. All experience shows, that in order to transform heat into mechanical energy, we must have at our disposal bodies of at least two different temperatures: that no thermal engine will take in heat from a given body and convert the whole of that heat into work; but that there must always be some colder body, into which the engine may reject a part of the heat that it has taken from the hot body.

no! only in a whole cycle.

The **assumption** that this conclusion from experience is a general principle, constitutes the so-called SECOND LAW OF THERMODYNAMICS. It is also known as CARNOT'S PRINCIPLE, though, strictly speaking, Carnot's principle related merely to the necessity of having bodies of at least two temperatures at our disposal. At the time when Carnot wrote his celebrated paper,* the equivalence of heat and mechanical energy was not generally recognised, and Carnot,—using the principle then accepted as true, that heat is unchangeable in total amount,—based his theory of the heat engine on the axiom, that in order to do work heat must run down from a high to a low temperature, just as water may run

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* S. Carnot, *Réflexions sur la Puissance Motrice du Feu*, Paris, 1824.

down hill and do useful work on the way, while remaining constant in amount. In 1851 the same principle was formulated by Lord Kelvin in the following terms: "*It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.*"[*] This is equivalent to the following statement: *It is impossible to obtain work by using up the heat in the coldest bodies present.*

We shall now proceed to draw some conclusions regarding the work obtainable in any cyclic process, and to put the second law of thermodynamics into mathematical form.

Carnot's Theorem

107. The ratio, $(Q_1 + Q_2)/Q_1$, of the heat converted into work and the total heat received, is known as the *efficiency* or *economic coefficient* of the system, when working as a heat engine in the manner described in article 105. It may easily be shown, that this efficiency E has a value which depends only upon the two temperatures T_1 and T_2, and not upon the nature of the system, so long as the cycle is reversible.

Suppose that a **second system**, working reversibly between the same two temperatures T_1 and T_2, and absorbing the same amount of heat Q_1 at the upper temperature, has an efficiency E', less than E, the efficiency of the first system. Let $(-Q'_2)$ be the heat which the second system gives out at the lower temperature. Then since $E' < E$, we have

$$\frac{Q_1 + Q'_2}{Q_1} < \frac{Q_1 + Q_2}{Q_1}, \quad \text{.......................(79)}$$

$$Q'_2 < Q_2,$$

and

$$-Q'_2 + Q_2 > 0. \quad \text{.........................(80)}$$

Let the second system perform its cycle in the reverse direction, the necessary work being supplied by the first system, working

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[*] *Math. and Phys. Papers*, 1, p. 179.

directly. At the end of a single cycle performed simultaneously by both systems, the source of heat at the upper temperature T_1, will have given the quantity of heat Q_1 to **the first system,** and received the quantity of heat Q_1 from the second system. On the whole, it **will have neither gained nor lost heat.** The source of heat at the lower temperature T_2, will have received $(-Q_2)$ from the first, and given $(-Q'_2)$ to **the second system**; so that, on the whole, **it will have lost the quantity of heat** $(-Q'_2+Q_2)$, which, by (80), is **greater than zero.** At the end of the process, the two systems are in all respects in the same condition as before it.

The work produced by the first system is greater than that which would have been produced by the second if working directly, and therefore greater than that expended in driving the second around its cycle in the reverse direction: **hence the total result of the cycle is an excess of useful work,** done at the expense of the heat in the colder of the two sources of heat. But this result is contrary to the assumed principle of article 106. Hence if that principle is correct, it is impossible that any system working as a heat engine between the temperatures T_1 and T_2 should have an efficiency less than that of the system we started with, *so long as its cycle is reversible.* In the same way, it may be shown that the original system can not have a smaller efficiency than any second. We are thus forced to conclude, that all systems working reversibly, in the manner indicated, between any two temperatures, T_1 and T_2, have the same efficiency, and that this efficiency is independent of everything but the two temperatures, so that

$$\frac{Q_1+Q_2}{Q_1}=f(T_1, T_2). \qquad (81)$$

If one of the two systems compared performs an irreversible cycle, we must, in order to investigate the efficiency of that cycle, take that system as the one that works directly. We can then only show that the efficiency of the reversible cycle is not less than that of the irreversible one; we are not able to prove that it can not be greater; because, though one of the cycles may be reversed in direction, the other can not.

The result of the reasoning is, therefore, that for all reversible isothermal-adiabatic cycles, performed between a given pair of temperatures by any system or systems whatever, the efficiency has the same value; and that for any irreversible cycle, the efficiency can not be greater than this. The part of this statement that refers to reversible cycles is known as CARNOT'S THEOREM.*

108. In the foregoing reasoning, we have supposed, for the sake of simplicity, that the systems under consideration had only two degrees of freedom, and only mechanical outside actions; but these restrictions are entirely unessential. If the outside actions on the two systems compared are of different kinds, we have only to couple the systems together by a machine that can perform the complete transformation, in both directions, of the forms of energy concerned. Our reasoning is then applicable directly. The restriction to two degrees of freedom and to normal variables, has not entered into the argument at all, and it was made, merely in order that the whole process might be represented on a single diagram. Carnot's theorem, and the corresponding statement referring to irreversible cycles, are therefore entirely general, and hold for any cycle, performed between any two temperatures, by any system that has equations of equilibrium and is subject to outside actions involving only energy of the same value as mechanical energy.

Efficiency of a Reversible Cycle

109. If we can find the form of the function $f(T_1, T_2)$ for any particular reversible cycle, we know its form for all. The simplest system to use for this purpose, is a mass of an ideal gas, for which

$$pv = RT,$$
$$\lambda = 0,$$
$$C_v = \text{constant}.$$

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* Carnot, *l.c.*, p. 20.

We may suppose the gas to be contained in a cylinder S (Fig. 17) fitted with a frictionless piston, which, together with the walls of the cylinder, is entirely impermeable to heat. The closed end of the cylinder is to be perfectly permeable to heat, and there is to be an impermeable cover, C, upon which the cylinder may be placed. If the cylinder be placed on the cover, the gas will be thermally isolated, and its expansions or contractions must be performed adiabatically. If, in addition, we have two bodies, A and B, of infinite thermal capacity and perfect conducting power, so that the temperatures, T_1 and T_2, of their surfaces are unchangeable; we may, by placing the cylinder on one of them, change the volume of the gas isothermally at either of the two temperatures. Such an apparatus was first devised—though of course not constructed—by Carnot,* and is known as a *Carnot engine*, whatever be the fluid enclosed in the cylinder.

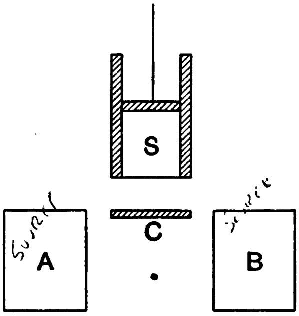

FIG. 17.

Let the gas perform the cycle a, b, c, d, a (Fig. 18), by expansions while the cylinder is in contact with A and C successively, followed by compressions while it is in contact with B and C. Since the internal energy of the gas is independent of its volume, the quantity of heat Q_1 received by it from A during the isothermal expansion ab, is equal to the work done by the

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* Carnot, *l.c.*

system during that expansion. This work we have already, in article 50, shown to be

$$\int_{v_1}^{v_2} p\,dv = RT_1 \log\frac{v_2}{v_1} = Q_1. \quad\text{.....................}(82)$$

The quantity of heat $(-Q_2)$, *given out by the system to* B, during the isothermal compression *cd* at the temperature T_2, is shown in the same manner to have the value

$$\int_{v_4}^{v_3} p\,dv = RT_2 \log\frac{v_3}{v_4} = -Q_4. \quad\text{.................}(83)$$

Hence the efficiency of this reversible cycle is

$$E = \frac{Q_1 + Q_2}{Q_1} = \frac{T_1 \log\frac{v_2}{v_1} - T_2 \log\frac{v_3}{v_4}}{T_1 \log\frac{v_2}{v_1}} \quad\text{................}(84)$$

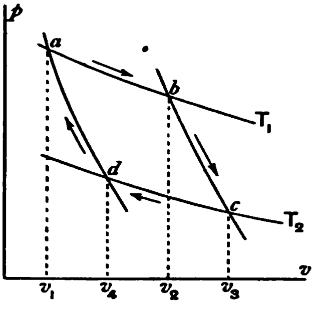

FIG. 18.

But since the curves *a*, *d* and *b*, *c* are portions of two adiabatic lines, we have the relations

$$T_1 v_1^{\gamma-1} = T_2 v_4^{\gamma-1},$$

$$T_1 v_2^{\gamma-1} = T_2 v_3^{\gamma-1},$$

whence, by division

$$\frac{v_1}{v_2} = \frac{v_4}{v_3}$$

Comparison of this result and equation (84) gives us

$$E = \frac{T_1 - T_2}{T_1} = \frac{Q_1 + Q_2}{Q_1}. \qquad (85)$$[**]

This, then, is the value of the efficiency of a system working as a heat engine round a reversible cycle between the temperatures T_1 and T_2, *these temperatures being expressed in terms of the scale of the ideal gas thermometer.*

Absolute Thermodynamic Temperature

110. In the year 1848, Lord Kelvin[*] proposed an absolute thermodynamic scale of temperature, which was independent of the properties of any particular substance whatever. The definition of this thermometric scale, as modified by its inventor a few years later, is as follows: "*The absolute values of two temperatures are to one another in the proportion of the heat taken in to the heat rejected in a perfect* (i.e., reversible) *thermodynamic engine working with a source and a refrigerator at the higher and lower of the temperatures respectively.*"[†] On this scale, therefore, any two temperatures, θ_1 and θ_2, satisfy the equation

$$\frac{\theta_1}{\theta_2} = \frac{Q_1}{-Q_2}, \qquad (86)$$

where Q_1 and Q_2 have the usual significance.

By reference to equation (85), we see that a similar relation exists between the numerical values of any two temperatures expressed in the scale of the ideal gas thermometer, namely,

$$\frac{T_1}{T_2} = \frac{Q_1}{-Q_2}. \qquad (87)$$

Hence any two temperatures, as measured on the ideal gas scale, stand in the same ratio to each other as if measured on the

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[*] *Math. and Phys. Papers,* **1**, p. 104.

[†] *Math. and Phys. Papers,* **1**, p. 235.

[**] $Q_1 : Q_2 : A :: T_1 : -T_2 : T_1 - T_2$

absolute thermodynamic scale. The efficiency of a reversible cycle may, consequently, be written in the following manner:

$$E=\frac{Q_1+Q_2}{Q_1}=\frac{\theta_1-\theta_2}{\theta_1}. \qquad (88)$$

By fixing, arbitrarily, the value of any given temperature, as the same on both scales, we may make the numerical values T and θ, which any given temperature has on the two scales, not only proportional but equal; and by assigning the right value to this temperature we may make the fundamental interval from 0° to 100° on the Celsius scale, equal to 100° on the absolute thermodynamic scale. *Hereafter, whenever we speak of temperature, we shall, unless the contrary is expressly stated, always mean the numerical value of the temperature, measured on this absolute thermodynamic scale.*

It is possible, by using the results of the plug experiments of Joule and Thomson (Kelvin), to find how nearly the absolute thermodynamic scale agrees, within our ordinary ranges of temperature, with the scale of the constant volume hydrogen thermometer, but we shall defer the theoretical discussion of this question until later. For the present, it is sufficient to state, that the difference between the two scales is so small that for most purposes they may be regarded as identical.

The Equation and the Inequality of Clausius

111. Equation (88), which is due to Clausius,* may be put in the form

$$1+\frac{Q_2}{Q_1}=1-\frac{\theta_2}{\theta_1}, \qquad \frac{Q_1}{\theta_1}+\frac{Q_2}{\theta_2}=0. \qquad (89)$$

If ΔQ be the heat converted into energy of the mechanical value, Q the heat received by the system when at the upper

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* Clausius, *Mechanische Wärmetheorie*, 3rd edition, **1**, chap. III.

temperature θ, and $\Delta\theta$ the difference between the two temperatures, equation (88) may be written

$$\frac{\Delta Q}{Q}=\frac{\Delta\theta}{\theta}, \qquad \text{.............................(90)}$$

a form in which it is often useful.

For irreversible cycles the equations (88), (89), and (90) reduce to the inequalities

$$\left.\begin{aligned} \frac{Q_1+Q_2}{Q_1} &\leqq \frac{\theta_1-\theta_2}{\theta_1}, \\ \frac{Q_1}{\theta_1}+\frac{Q_2}{\theta_2} &\leqq 0, \\ \frac{\Delta Q}{Q} &\leqq \frac{\Delta\theta}{\theta}. \end{aligned}\right\} \qquad \text{.......................(91)}$$

112. If we have at command several reservoirs of heat at the temperatures θ_1, θ_2, θ_3, etc., we may subject a system to a cyclic transformation which consists of isothermal changes at all the temperatures θ_1, θ_2, etc., and of adiabatic changes by which the system passes from one of these temperatures to another. If the system has only one outside action, the diagram will be of the form shown in figure 19. If, however, it has n outside actions,

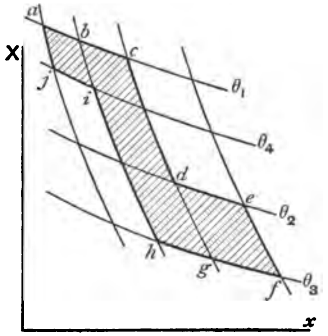

FIG. 19.

there will be n such diagrams, each with the same general characteristics as the one given.

By a suitable choice of reversible, adiabatic processes, such as those indicated by the lines *b,i* and *d,g*, we may divide the whole cycle into a number of simple cycles, each consisting of only two isothermal and two adiabatic parts. If we let the system perform all these simple cycles separately—each once, and all in the same direction—the total result is the same as if the whole original cycle were traversed once. For the total work done is, in one case, the sum of the areas of the simple cycles, and in the other, it is the area of the whole cycle, and these two areas are identical. Furthermore,—since all the isothermal changes are common to the whole cycle and to the sum of the simple cycles, the total amount of heat received by the system at any temperature is the same, whether it traverse the original cycle as a whole, or traverse the simple cycles separately.

Now since each of the simple cycles is reversible, if the whole cycle was so, we may apply to each one the equation

$$\frac{Q_1}{\theta_1}+\frac{Q_2}{\theta_2}=0.$$

By addition of all the expressions of this form, we have for the whole cycle, equivalent to a performance of the simple cycles successively, the equation

$$\sum\frac{Q}{\theta}=0 \quad\text{..............................}(92)$$

Such a cycle as the one here treated is called a *compound Carnot cycle.*

If the original cycle were irreversible, some or all of the simple cycles would also be irreversible: for these we should have

$$\frac{Q_1}{\theta_1}+\frac{Q_2}{\theta_2}\leqq 0,$$

so that the addition would give, for the whole irreversible cycle, the inequality

$$\sum\frac{Q}{\theta}\leqq 0 \quad\text{..............................}(93)$$

113. Suppose, now, that a system undergoes any sort of cyclic modification whatever, the sources of heat being as many as we please. If their number is finite the cycle may consist of a finite number of isothermal and adiabatic changes. If the system takes in and gives out heat while its own temperature varies continuously, the indicator points may describe any curves whatever on the various diagrams. If such a cycle is to be reversible, we must have an infinite number of reservoirs of heat, so that we may have one for each temperature that the system has during the cycle. Let dQ be the quantity of heat received by the system while it is at the temperature θ, and let us consider the value of the expression

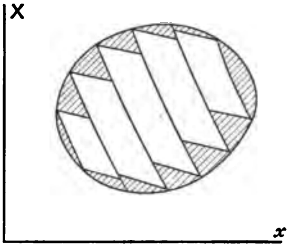

FIG. 20.

$$(\int)\frac{dQ}{\theta}.$$

Let the cycle be broken up, as before, and as shown in Fig. 20, into a number of simple Carnot cycles—each reversible—plus a number of cycles around the contour, each of which consists of an isothermal change, an adiabatic change, and a change that is a part of the original cycle, which we will, for the present, suppose to be reversible in all its parts. For the compound Carnot cycle, composed of the simple ones performed separately, we have the equation

$$\sum\frac{Q}{\theta}=0,$$

as shown in the last article. Now let the number of the simple cycles increase indefinitely, in such a manner that the lengths of the isothermal curves all approach zero. We still have for the compound Carnot cycle the equation $\sum \frac{Q}{\theta} = 0$, which here reduces to

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

As the number of the elementary cycles round the edge of the diagram increases indefinitely, the value of θ approaches a constant for each one of them, so that we have, for any one of them,

$$\left(\int\right)\frac{dQ}{\theta} = \frac{1}{\theta}\left(\int\right)dQ.$$

But $\left(\int\right)dQ$ has the same numerical value as the heat that the system converts into work in traversing this cycle; it is therefore equal to the area of the cycle. This area is an infinitesimal of the second order; for if n is the number of the cycles and n increases indefinitely, the linear dimensions of each of these cycles on the diagram or diagrams are of the order $\frac{1}{\infty}$, and the area is of the order $\frac{1}{\infty^2}$. Since θ is finite, it follows that the value of the expression

$$\frac{1}{\theta}\left(\int\right)dQ,$$

is an infinitesimal of the second order, when the integration is round one of the elementary cycles. The sum of all these expressions for all the n cycles round the contour of the original cycles, is, therefore, an infinitesimal of the first order and may be neglected.

Now the expression

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

has the same value, whether it be taken round the curve forming the contour of the original cycle, or whether it be taken once round every one of the infinite number of cycles into which we have broken up the original cycle, provided that all the cycles be traversed in the same direction of rotation. For every part of the contour will appear once and only once in the integration round the separate cycles, while every other portion of the boundaries of the small cycles will be traversed once in the positive and once in the negative direction, so that the term that it contributes to the whole integral will be zero. We have already shown, that the value of the integral is zero round the compound Carnot cycle, and infinitesimal when taken round the infinitesimal cycles bordering on the original contour. Hence if taken round the original contour directly, it is infinitesimal, and we have the result: *If a system perform any sort of reversible cycle, varying its temperature in any manner and taking in or giving out heat at any number of temperatures, the equation*

$$\left(\int\right)\frac{dQ}{\theta}=0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (94)$$

is always fulfilled.

114. Suppose, now, that the original cycle is irreversible in some or all of its parts. It is, by definition, impossible to have a reversible change of which the states are infinitely near to those of an irreversible one. Hence the compound, isothermal-adiabatic cycle will, where it comes infinitely near to the actual cycle, be itself irreversible. For some or all of its elements we shall therefore have

$$\frac{Q_1}{\theta_1}+\frac{Q_2}{\theta_2}\leqq 0,$$

and for it as a whole

$$\sum\frac{Q}{\theta}\leqq 0,$$

or

$$\left(\int\right)\frac{dQ}{\theta}\leqq 0.$$

The same reasoning as in article 113 may be applied to the infinitesimal cycles bordering on the contour of the actual cycle, so that we arrive at the proposition: *If a system performs any sort of irreversible cycle, the equation*

$$\int_{(0)}^{(0)} \frac{dQ}{t} = 0$$

may be fulfilled, but we may also have the inequality

$$\int_{(0)}^{(0)} \frac{dQ}{t} < 0.$$

In any case, we always have

$$\int_{(0)}^{(0)} \frac{dQ}{t} \leqq 0. \qquad (95)$$

Among the many important equations and theorems due to Clausius, the equation (94) and the inequality (95) are the most important, and the fact which they express is often called the THEOREM OF CLAUSIUS. These formulae are a very convenient expression of the second law of thermodynamics, as they embody, in exact form, the hypotheses of article 106 and their mathematical consequences.

Entropy

115. In the consideration of the first law of thermodynamics, we deduced, from the equation

$$\int_{(0)}^{(0)} (dW + dQ) = 0,$$

the result that if A and B are any two states of a system,

$$\int_{A}^{B} (dW + dQ) = \epsilon_B - \epsilon_A,$$

where ϵ is a function of the variables which determine the state of the system, and contains an arbitrary constant.

From the equation (94) we may draw a similar conclusion. Let A and B (Fig. 21) represent two states of a system, which can be connected by two reversible paths I and II having no states in common. The two paths taken together, one in the direction AB and the other in the direction BA, form a reversible cycle, for which we have

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

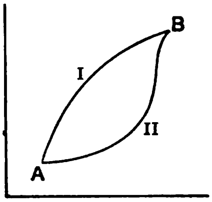

FIG. 21.

But
$$\left(\int\right)\frac{dQ}{\theta}=\int_A^B\left(\frac{dQ}{\theta}\right)_I+\int_B^A\left(\frac{dQ}{\theta}\right)_{II}$$
$$=\int_A^B\left(\frac{dQ}{\theta}\right)_I-\int_A^B\left(\frac{dQ}{\theta}\right)_{II}=0\,;$$

hence
$$\int_A^B\left(\frac{dQ}{\theta}\right)_I=\int_A^B\left(\frac{dQ}{\theta}\right)_{II}\,;\quad\text{.........}(96)$$

or the value of the integral $\int_A^B\frac{dQ}{\theta}$ is the same for any two, and therefore for all reversible transformations by which the system may pass from one of the states A and B to the other. This value may therefore be written

$$\int_A^B\frac{dQ}{\theta}=\eta_B-\eta_A,\quad\text{.........}(97)$$

where η is a function of the variables that determine the states A and B. To this function, Clausius gave the name of the ENTROPY of the system. Like the internal energy ϵ, it contains an arbitrary constant; for the addition of such a constant leaves the equation (97) unchanged. The entropy, like the energy, is, therefore, determinable only as regards its changes and not in absolute value.

If applied to an infinitesimal reversible change of state, equation (97) reduces to

$$\frac{\delta Q}{\theta}=\delta\eta, \qquad \text{.................. ....(98)}$$

or

$$\delta Q=\theta\,\delta\eta. \qquad \text{..............................(99)}$$

116. It is more difficult to form a distinct, physical idea of entropy than to form one of energy. The increase of internal energy, as a system passes from a state A to a state B by any sort of process, is the sum of all the energy put into the system, in whatever forms it is supplied—whether as heat or as energy of the mechanical value. If some state be chosen as a normal one, for which we arbitrarily set $\epsilon=0$, the internal energy of the system in any other state is the total energy it receives, while passing from the normal state to the state in question.

The value of the entropy, also, may be arbitrarily set equal to zero when the system is in the same normal state. In any second state, that can be reached from the normal state by a reversible process, the entropy of the system is the value of the integral $\int\frac{dQ}{\theta}$, taken along the reversible path, from the normal to the final state. If it is possible to connect the normal and final states by a single isothermal process at the normal temperature, followed by an adiabatic process leading to the final state, both processes being reversible, the entropy in the final state is simply

$$\eta=\frac{Q_0}{\theta_0},$$

where Q_0 is the heat that enters the system during the isothermal process; for during the adiabatic change no heat enters or leaves the system and its entropy remains constant.

We shall **assume,** *in the absence of proof to the contrary, that any two possible states of any system may always be connected by an infinite number of reversible paths.* In other words; we shall assume, that whatever be the two states considered, we may arrange between them, theoretically, at least,—an infinite number of continuous series of states, such that it is possible to apply to the system outside actions which would keep it in equilibrium in any one of these intermediate states. With this assumption, we may say, that after the normal state has been selected, the value of the entropy is fixed and definite for every other possible state of the system, whether that state has actually been reached from the normal state by a reversible process or not.

117. As examples of processes that may lead a system from one state to another, either by a reversible or by an irreversible path, we may cite the following:

The expansion of a gas from one volume to another may be a free expansion, in which case it is obviously irreversible. But the expansion may also take place against a frictionless piston; and it is possible, by proper regulation of the pressure on the piston, and by the supply or withdrawal of heat, to stop the expansion at any volume and temperature* that the gas had during its free expansion. Hence the expansion *may* be performed reversibly.

The diffusion of liquids and gases is an irreversible process. But by the use of semipermeable pistons, which allow some substances to pass through them but are impermeable to other substances, we may stop the process—that is, bring about a condition of equilibrium—at any stage that we choose. This diffusion *may*, therefore, be made reversible.

If a pair of electrified conductors, charged to different potentials, be connected by a wire, the charges redistribute themselves, so that the potential is uniform all over the conductors and the wire. During this process of redistribution, heat is developed in the wire, and the process is irreversible. But by means of a small, movable, conducting sphere, the potentials of the two conductors may be equalised by convection, *i.e.*, by motions of the electric charges with the moving sphere,—motions which may at any time be stopped by the application of appropriate mechanical forces. By the convection method, the potentials *may*, then, be equalised in an approximately reversible manner. We say 'approximately,'

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* Assuming that temperature to have been uniform.

only, because there still remains the irreversible conduction of electricity in the substance of the conductors and the sphere.

A weight falling under the influence of gravity, may be brought to rest at a lower position, either suddenly by collision, or gradually by friction. In either case, the fall is irreversible. But if the weight, while descending, raise, by a perfectly flexible and inextensible cord running over a frictionless pulley, another weight, less by an infinitesimal amount than itself; the fall of the first weight is reversible. For by an infinitesimal addition to the counterweight we may stop or reverse the motion.

It is worthy of notice, that in each of these examples, the system, in passing from a given initial to a given final state, gives out a greater quantity of energy of the mechanical value in the reversible than in the irreversible process. The bearing of this remark will be evident when we come, in Chapter XII, to the consideration of free energy.

Change of Entropy during Irreversible Processes

118. It has been shown that for any irreversible cycle

$$\left(\int\right)\frac{dQ}{\theta}\leqq 0,\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(100)$$

a cycle being irreversible if any portion of the operations com-

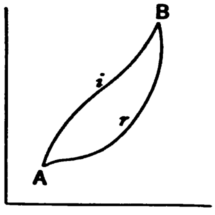

FIG. 22.

2 posing it is irreversible. Let a system pass by an irreversible path i (Fig. 22), from the state A to the state B: let it return from B to A by the reversible path r. The combination of these

The system can never return to [illegible] without some outside change remaining.

two paths forms an irreversible cycle, to which formula (100) is applicable. It gives us, when thus applied,

$$\oint\frac{dQ}{\theta}=\int_A^B\left(\frac{dQ}{\theta}\right)_i+\int_B^A\left(\frac{dQ}{\theta}\right)_r$$

$$=\int_A^B\left(\frac{dQ}{\theta}\right)_i-\int_A^B\left(\frac{dQ}{\theta}\right)_r\leqq 0.$$

But we have the equation

$$\int_A^B\left(\frac{dQ}{\theta}\right)_r=\eta_B-\eta_A.$$

Hence it follows that

$$\int_A^B\left(\frac{dQ}{\theta}\right)_i\leqq\eta_B-\eta_A;\quad\text{......................}(101)$$

or the value of the integral $\int\frac{dQ}{\theta}$, taken along an irreversible path between two states, is equal to or less than, but not greater than the increase of the entropy. If the states A and B are infinitely near together, equation (101) gives us

$$\left(\frac{\delta Q}{\theta}\right)_i\leqq\delta\eta;\quad\text{..........................}(102)$$

[illegible] or, for the heat absorbed by the system during any infinitesimal, irreversible transformation,

$$\delta Q\leqq\theta\delta\eta.\text{..........................}(103)$$

[illegible] !

Entropy of an Ideal Gas

119. In order to make the notion of entropy more concrete, it is worth while to show how its value may be found in the simple case of an ideal gas.

Let the mass of the gas be unity, its temperature θ, and its volume v. Let the normal temperature and volume be θ_0 and v_0, respectively.* Let the gas expand or contract adiabatically, till its temperature is θ_0; let it then expand or contract isothermally, till it has the volume v_0. Both of these operations are to

*and assume the entropy at this state to be zero.

be reversible. Since there is no change of entropy during the reversible, adiabatic change, the entropy is equal simply to $\frac{Q_0}{\theta_0}$.

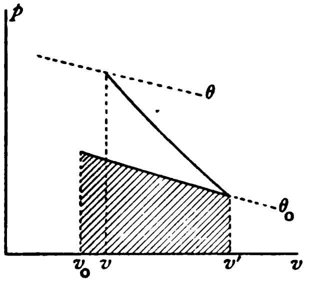

FIG. 23.

Now as the internal energy of an ideal gas is independent of the volume, the heat Q_0, which the gas would absorb in changing its volume reversibly and isothermally at the temperature θ_0 from v_0 to v', is equal to the work it would do against the outside pressure; or

$$Q_0 = \int_{v_0}^{v'} p\,dv = R\theta_0 \log \frac{v'}{v_0}.$$

But we have

$$\theta v^{\gamma-1} = \theta_0 v'^{\gamma-1},$$

or

$$v' = \left(\frac{\theta}{\theta_0}\right)^{\frac{1}{\gamma-1}} v.$$

Therefore

$$\begin{aligned} Q_0 &= R\theta_0 \log \left[\left(\frac{\theta}{\theta_0}\right)^{\frac{1}{\gamma-1}} \frac{v}{v_0}\right] \\ &= \frac{1}{\gamma-1} R\theta_0 \log \frac{\theta}{\theta_0} + R\theta_0 \log \frac{v}{v_0} \\ &= C_v\theta_0 \log \frac{\theta}{\theta_0} + R\theta_0 \log \frac{v}{v_0}, \end{aligned}$$

whence we have finally, as the value of the entropy, at temperature θ and vol. v

$$\eta = \frac{Q_0}{\theta_0} = C_v \log \frac{\theta}{\theta_0} + R \log \frac{v}{v_0}. \quad \text{.................(104)}$$

CHAPTER IX.

GENERAL EQUATIONS.

Equations resulting from the Combination of the Two Laws of Thermodynamics

120. The first law of thermodynamics may, as we have seen, be expressed by the equation

$$\delta\epsilon = \delta Q + \delta W,$$

or

$$\delta\epsilon = \delta Q + \sum X\delta x\,; \qquad \text{(105)}$$

where the sum $\sum X\delta x$ contains only terms referring to the external variables, those due to the possible existence of internal variables being all separately zero.*

The second law may, so far as it refers to reversible modifications of state, be expressed by the equation

$$\delta Q = \theta\,\delta\eta. \qquad \text{(106)}$$

By combining equations (105) and (106), we get, as a result which must be valid for all infinitesimal, reversible changes of state, the equation

$$\delta\epsilon = \theta\delta\eta + \sum X\delta x. \qquad \text{(107)}$$

If the changes of state are all reversible, the system is always infinitely near to being in a state of equilibrium, and the

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*If the variables used are not normal, the coefficient $\mathscr{T}$ is among the quantities X: we are assuming, however, that the variables are normal.

generalized forces X', X'', X''', etc., satisfy the equations of equilibrium (art. 46). The quantities X are therefore to be treated as functions of the variables x', x'', ... x^n, θ, which determine the state of the system, and we may give equation (107) the following four forms:

$$\left.\begin{aligned}&\delta\epsilon=\theta\delta\eta+\sum X\delta x,\\&\delta(\epsilon-\theta\eta)=-\eta\delta\theta+\sum X\delta x,\\&\delta(\epsilon-\theta\eta-\sum Xx)=-\eta\delta\theta-\sum x\delta X,\\&\delta(\epsilon-\sum Xx)=\theta\delta\eta-\sum x\delta X;\end{aligned}\right\}\text{..........}(108)$$

the last three being obtained from the first by subtracting $\delta(\theta\eta)$, $\delta(\theta\eta+\sum Xx)$, and $\delta\sum Xx$, respectively.

If we now let

$$\left.\begin{aligned}&\psi=\epsilon-\theta\eta,^{*}\\&\zeta=\epsilon-\theta\eta-\sum Xx,\\&\chi=\epsilon-\sum Xx,\end{aligned}\right\}\text{....................}(109)$$

we get, by comparison of equations (108) and (109), the equations

$$\left.\begin{aligned}\delta\epsilon&=\theta\delta\eta+\sum X\delta x,\\\delta\psi&=-\eta\delta\theta+\sum X\delta x,\\\delta\zeta&=-\eta\delta\theta-\sum x\delta X,\\\delta\chi&=\theta\delta\eta-\sum x\delta X.\end{aligned}\right\}\text{....................}(110)$$

It is to be noted, that since ϵ and η contain arbitrary constants A and B, the function χ contains the constant A, while ψ and ζ contain the linear function of the temperature, $A+B\theta$.

121. The first member of each of the equations (110) is the complete differential of a function of the variables x', x'', ... x^n, θ;

* Helmholtz's "Free Energy".

the same must, therefore, be true of the second member; so that we have at once the following equations:

$$\left.\begin{aligned}
\left(\frac{\partial\theta}{\partial x^\kappa}\right)_{\eta,x} &= \left(\frac{\partial X^\kappa}{\partial\eta}\right)_{x,\eta}, \\
\left(\frac{\partial\eta}{\partial x^\kappa}\right)_{\theta,x} &= -\left(\frac{\partial X^\kappa}{\partial\theta}\right)_{x,\theta}, \\
\left(\frac{\partial\eta}{\partial X^\kappa}\right)_{\theta,X} &= \left(\frac{\partial x^\kappa}{\partial\theta}\right)_{X,\theta}, \\
\left(\frac{\partial\theta}{\partial X^\kappa}\right)_{\eta,X} &= -\left(\frac{\partial x^\kappa}{\partial\eta}\right)_{X,\eta}.
\end{aligned}\right\}\quad\ldots\ldots\ldots\ldots(111)$$

The meaning of the double subscript (η, x) is, that η and all the variables x'_ι, x''_ι, ... etc., and x'_ϵ, x''_ϵ, ... etc., except x^κ, are to be kept constant during the differentiation.

The following equations are also evident upon inspection of the equations (110)

$$\left.\begin{aligned}
\theta &= \left(\frac{\partial\epsilon}{\partial\eta}\right)_x = \left(\frac{\partial\chi}{\partial\eta}\right)_X, \\
\eta &= -\left(\frac{\partial\psi}{\partial\theta}\right)_x = -\left(\frac{\partial\zeta}{\partial\theta}\right)_X, \\
X^\kappa &= \left(\frac{\partial\epsilon}{\partial x^\kappa}\right)_{\eta,x} = \left(\frac{\partial\psi}{\partial x^\kappa}\right)_{\theta,x}, \\
x^\kappa &= -\left(\frac{\partial\zeta}{\partial X^\kappa}\right)_{\theta,X} = -\left(\frac{\partial\chi}{\partial X^\kappa}\right)_{\eta,X},
\end{aligned}\right\}\quad\ldots\ldots\ldots\ldots(112)$$

Forms of the Preceding Relations for Systems subject only to a Uniform Pressure

122. When applied to the important case of a system subject to no other outside action than a uniform pressure on its surface, and having its state defined by the variables v and θ, the equations (109) to (112) assume the following forms:

Equations (109) reduce to , since $\sum X \delta x = -p\delta v$

$\varepsilon + \zeta = \psi + \chi$

$$\left.\begin{aligned} \psi &= \epsilon - \theta\eta, \\ \zeta &= \epsilon - \theta\eta + pv, \\ \chi &= \epsilon + pv. \end{aligned}\right\} \qquad (113)$$

Equations (110) reduce to

$$\left.\begin{aligned} \delta\epsilon &= \theta\,\delta\eta - p\,\delta v, \\ \delta\psi &= -\eta\,\delta\theta - p\,\delta v, \\ \delta\zeta &= -\eta\,\delta\theta + v\,\delta p, \\ \delta\chi &= \theta\,\delta\eta + v\,\delta p, \end{aligned}\right\} \qquad (114)$$

Equations (111) reduce to

$$\left.\begin{aligned} \left(\frac{\partial\theta}{\partial v}\right)_\eta &= -\left(\frac{\partial p}{\partial \eta}\right)_v, \\ \left(\frac{\partial\eta}{\partial v}\right)_\theta &= \left(\frac{\partial p}{\partial \theta}\right)_v, \\ \left(\frac{\partial\eta}{\partial p}\right)_\theta &= -\left(\frac{\partial v}{\partial \theta}\right)_p, \\ \left(\frac{\partial\theta}{\partial p}\right)_\eta &= \left(\frac{\partial v}{\partial \eta}\right)_p. \end{aligned}\right\} \qquad (115)$$

Equations (112) reduce to

$$\left.\begin{aligned} \theta &= \left(\frac{\partial\epsilon}{\partial \eta}\right)_v = \left(\frac{\partial\chi}{\partial \eta}\right)_p, \\ \eta &= -\left(\frac{\partial\psi}{\partial \theta}\right)_v = -\left(\frac{\partial\zeta}{\partial \theta}\right)_p, \\ p &= -\left(\frac{\partial\epsilon}{\partial v}\right)_\eta = -\left(\frac{\partial\psi}{\partial v}\right)_\theta, \\ v &= \left(\frac{\partial\zeta}{\partial p}\right)_\theta = \left(\frac{\partial\chi}{\partial p}\right)_\eta. \end{aligned}\right\} \qquad (116)$$

If the system requires, for the complete determination of its state, a number of internal variables, x'_i, x''_i, ... x^l_i, in addition to the normal variables, v and θ, hitherto regarded as sufficient—the system now having $l+2$ degrees of freedom—the equations (113) to (116) remain entirely unchanged, except that, in all the partial differentiations, the internal variables must be kept constant, as well as the quantities already indicated by the subscripts.

Characteristic Functions for Isothermal Processes

123. All the relations among the properties of thermodynamic systems in equilibrium, that can be deduced from the two laws of thermodynamics, are expressible in terms of the $2n+3$ quantities

$$x', x'', \dots x^n, X', X'', \dots X^n, \theta, \epsilon, \eta, \quad \text{............(117)}$$

the system having $n+1$ degrees of freedom.

If we choose, as independent, the normal variables

$$x', x'', \dots x^n, \theta,$$

a knowledge of the form of a **single** function, ψ, of these variables, enables us to express all the other quantities, and therefore all functions of them, in terms of x', x'', ... x^n, θ. For we have the equations

$$\left.\begin{aligned} X^\kappa &= \left(\frac{\partial\psi}{\partial x^\kappa}\right)_{\theta,\,x}, \\ \eta &= -\left(\frac{\partial\psi}{\partial\theta}\right)_x, \\ \epsilon &= \psi + \theta\eta = \psi - \theta\left(\frac{\partial\psi}{\partial\theta}\right)_x; \end{aligned}\right\} \quad \text{..............(118)}$$

so that all the quantities of the set (117) may be expressed in terms of ψ and the normal variables.

If we take as independent the inverse variables *

$$x'_i, x''_i, \dots x^m_i, X'_e, X''_e, \dots X^{n-m}_e, \theta, \quad \text{............(119)}$$

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* See art. 54.

we have the equations

$$\left.\begin{aligned} x^{\kappa}{}_e &= -\left(\frac{\partial\zeta}{\partial X^{\kappa}{}_e}\right)_{\theta,\, X_e,\, x_i}, \\ \eta &= -\left(\frac{\partial\zeta}{\partial\theta}\right)_{X_e,\, x_i}, \\ \epsilon &= \zeta + \theta\eta + \sum X_e,\, x_e \\ &= \zeta - \theta\left(\frac{\partial\zeta}{\partial\theta}\right)_{X_e,\, x_i} - \sum X_e\left(\frac{\partial\zeta}{\partial X_e}\right)_{\theta,\, X_e,\, x_i}; \end{aligned}\right\} \quad \ldots\ldots\ldots(120)$$

so that in this case the function ζ plays the same *rôle* as ψ in the former case.

124. In the particular case discussed in article 122, the foregoing statements may be put in the following terms:

When the volume and the temperature are used as independent variables, the equations

$$\left.\begin{aligned} p &= -\left(\frac{\partial\psi}{\partial v}\right)_{\theta,\, x_i}, \\ \eta &= -\left(\frac{\partial\psi}{\partial\theta}\right)_{v,\, x_i}, \\ \epsilon &= \psi + \theta\eta = \psi - \theta\left(\frac{\partial\psi}{\partial\theta}\right)_{v,\, x_i}, \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots(121)$$

enable us to express all the relations deducible from the two laws of thermodynamics in terms of v, θ, ψ, and the internal variables, if there are any; or, when ψ is known as a function of the normal variables x'_i, x''_i, . . etc., v, θ, all the relations may be expressed in terms of these variables.

When the pressure is substituted for the volume, as one of the independent variables, the equations

$$\left.\begin{aligned} v &= \left(\frac{\partial\zeta}{\partial p}\right)_{\theta,\, x_i}, \\ \eta &= -\left(\frac{\partial\zeta}{\partial\theta}\right)_{p,\, x_i}, \\ \epsilon &= \zeta + \theta\eta + pv = \zeta - \theta\left(\frac{\partial\zeta}{\partial\theta}\right)_{p,\, x_i} - p\left(\frac{\partial\zeta}{\partial p}\right)_{\theta,\, x_i}, \end{aligned}\right\} \quad \ldots\ldots(122)$$

enable us to express all deducible relations in terms of the inverse variables, if ζ is known as a function of those variables.

This property of the functions ψ and ζ was first pointed out by Massieu,* who employed the functions

$$H = -\psi, \qquad (v \text{ and } \theta \text{ independent})$$

and

$$H' = -\zeta, \qquad (p \text{ and } \theta \text{ independent})$$

to which he gave the name of CHARACTERISTIC FUNCTIONS, in the study of the thermal and mechanical properties of vapours.

Characteristic Functions for Isentropic Processes

125. The functions ψ and ζ, which act as characteristic functions when the temperature is one of the independent variables, are useful in the study of processes in which the temperature is constant; and these isothermal changes are very important. In reversible adiabatic processes, the entropy η is constant; hence it is convenient, in the reasoning, to take η as one of the independent variables, in place of the temperature.

If the independent variables are $x', x'', \ldots x^n, \eta$, we have, by equations (112),

$$\left.\begin{aligned} X^{\kappa} &= \left(\frac{\partial \epsilon}{\partial x^{\kappa}}\right)_{\eta, x}, \\ \theta &= \left(\frac{\partial \epsilon}{\partial \eta}\right)_{x}. \end{aligned}\right\} \qquad \text{(123)}$$

By these equations and equations (109), it is possible to express all the quantities of the set (117) in terms of the independent variables here used, if ϵ is known as a function of those variables. The internal energy ϵ acts, therefore, as a characteristic function.

* Massieu, *Mémoires de l'Académie des Sciences*, **22**, No. 2; also, *Journal de Physique*, (1), **6**, p. 216 (1877).

If the independent variables are

$$x'_a, x''_a, \dots x^m_a, X'_a, X''_a, \dots X^{n-m}_a, \eta,$$

we have, by equations (122),

$$\left.\begin{aligned} x^m_a &= -\left(\frac{\partial\chi}{\partial X^m_a}\right)_{\eta, X_a, x}, \\ \theta &= \left(\frac{\partial\chi}{\partial\eta}\right)_{X_a, x}; \end{aligned}\right\} \quad \text{.......................(124)}$$

whence, by the aid of equations (119), it is possible to express, in terms of the independent variables here used, all the quantities of the set (117), if χ is known as a function of the independent variables, $x'_a \dots x^m_a, X'_a \dots X^{n-m}_a, \eta$. Hence in this case, χ acts as a characteristic function.

Fundamental Equations

128. An inspection of the sets of dependent and independent variables appearing in equations (118) shows that a single equation, of the form

$$\psi = f(x', x'', \dots x^n, \theta), \quad \text{.......................(125)}$$

makes it possible to express all the thermodynamic properties of the system, in terms of the independent variables there used. For equations (120) an equation, of the form

$$\zeta = f(x'_a, x''_a \dots x^m_a, X'_a, X''_a \dots X^{n-m}_a, \theta), \quad \text{........(126)}$$

serves the same purpose. For equations (123) the necessary equation is

$$\epsilon = f(x', x'', \dots x^n, \eta); \quad \text{.......................(127)}$$

and for equations (124) it is

$$\chi = f(x'_a, x''_a \dots x^m_a, X'_a, X''_a \dots X^{n-m}_a, \eta). \quad \text{........(128)}$$

Now the sets of equations (118), (120), (123), and (124) are all equivalent, in substance, since they were all derived from the same original equation, namely,

$$\delta\epsilon = \theta\,\delta\eta + \sum X\delta x.$$

Therefore, any one of the equations (125), (126), (127), (128), between

$$\psi,\ x', x'', \ldots x^n, \theta;$$

or $$\zeta,\ x'_i, x''_i, \ldots x^m_i, X'_e, X''_e, \ldots X^{n-m}_e, \theta;$$

or $$\epsilon,\ x', x'', \ldots x^n, \eta;$$

or $$\chi,\ x'_i, x''_i, \ldots x^m_i, X'_e, X''_e, \ldots X^{n-m}_e, \eta;$$

is equivalent to any other, and enables us to express all the properties of the system in terms of the $n+1$ quantities, selected, in the various cases, for use as independent variables. Any such equation is called a FUNDAMENTAL EQUATION. Other characteristic functions and fundamental equations might be found, but those we have mentioned are the ones of most practical importance, on account of the manner in which it is most convenient to perform thermal experiments.

For further discussion of the subject of characteristic functions, the reader may turn to the text-books of Bertrand * and Pellat,† and the memoirs of Massieu ‡ and Gibbs §.

Nature of the Foregoing Results

127. All the equations of this chapter are mere mathematical deductions from the one original equation

$$\delta\epsilon = \theta\,\delta\eta + \sum X\delta x,$$

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* Bertrand, *Thermodynamique*, chap. VI. Paris, 1887.

† Pellat, *Thermodynamique*, note F, p. 276. Paris, 1897.

‡ Massieu, l. c.

§ Gibbs, *Trans. Connecticut Acad.*, **3** (1875-1878): translated into German by W. Ostwald, and published under the title, "Thermodynamische Studien von J. Willard Gibbs." Leipzig, Engelmann, 1892.

which is the combined expression of the two laws of thermodynamics, as given in equations (105) and (106). They add nothing, in a certain sense, to our knowledge; but they give us a set of general relations between the quantities

$$x'_i,\ x''_i,\ \ldots\ x^m{}_i,\ x'_e,\ x''_e\ \ldots\ x^{m-n}{}_e,\ X'_e,\ X''_e\ \ldots\ X^{m-n}{}_e,\ \theta,\ \eta,\ \epsilon,\ \psi,\ \zeta,\ \chi:$$

relations which are often of great use, and which it is well to have collected for reference.

It should be particularly noted, that the original equation, from which all the others were obtained, is valid during any reversible modification of the state of a system. If, therefore, all the differentials and differential coefficients, occurring in the equations, refer to displacements from a state of equilibrium, the equations of articles 120 to 126 are surely valid.

We have not, however, shown for irreversible processes, either that

$$\delta\epsilon = \theta\,\delta\eta + \sum X\,\delta x,$$

or that

$$\delta\epsilon < \theta\,\delta\eta + \sum X\,\delta x,$$

but merely that *one or the other is true.* Hence we cannot, for the present, say whether the equations of articles 120 to 126 are, or are not, valid, when referring to displacements from a state that is not one of equilibrium.

CHAPTER X

APPLICATIONS

Theory of the Plug Experiment

128. It is well, before going farther with the development of the theory, to illustrate by a few concrete examples, the use of some of the equations obtained in the last two chapters.

In those chapters we have been using the thermodynamic temperature, although we have no direct method of measuring it. As yet, all we know about it is, that it is proportional to the temperature as read from a thermometer filled with an ideal gas. We know also, that oxygen, hydrogen, and nitrogen follow Boyle's Law very closely if the pressure is not too great, and that the heat which they absorb or develop, during free expansion, is nearly zero. These gases, therefore, approximate closely to the ideal state, so that the absolute temperature, as read on a thermometer containing one of them, is, at any rate, very nearly proportional to the thermodynamic temperature. It is important that we should find, if possible, how close this agreement is, and what corrections must be applied to the readings of the gas thermometer to reduce them to the thermodynamic scale.

To answer these questions, we must first know how the gas deviates from Boyle's Law: we shall suppose, then, that the gas under consideration is one that has been investigated completely, in this regard. We must, in addition, know what are the thermal effects due to free expansion, in order that we may be able to express the internal energy of the gas as a function of its volume.

The experiments of Gay-Lussac and of Joule (art. 73) showed that the change of temperature in free expansion was, at any rate, very small; but their methods suffered from one obvious defect. The thermal effect, produced by a small mass of gas, was so distributed over vastly larger masses of solid or liquid bodies, as greatly to reduce the changes of temperature to be measured,—to the detriment of the accuracy of the results. To obviate this difficulty, it is necessary to make the free expansion as nearly as possible adiabatic; that is, to confine the heating or cooling to the gas itself. It was with this aim that the celebrated PLUG EXPERIMENT was undertaken by Joule and Thomson (Lord Kelvin), in the year 1852. We shall now give a brief discussion of the theory of this experiment: for the details of the experimental work we must refer the reader to the original memoirs.*

129. The gas to be studied was forced uniformly through a porous plug, the resistance of the plug to the passage of the gas being sufficient to reduce the pressure of the gas to that of the atmosphere, so that as the gas issued from the plug its kinetic energy was sensibly the same as before entering it. The plug consisted of a mass of silk or other fibres, compressed between two perforated brass discs: the discs and the fibres were in a boxwood tube, and this tube was carefully insulated from the influence of outside heat, so that, as the gas passed through the plug, any changes in its temperature might be due solely to the effect of its expansion. Before entering the boxwood tube, the gas passed through a long spiral pipe or worm, immersed in a vat of water. By this means, the gas was brought to a constant, known temperature before entering the plug. The measurements to be made consisted in observations of the rate of flow of the gas, together with its pressure and temperature, both before and after it had passed through the plug. Before making these observations, the

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* Thomson, *Math. and Phys. Papers*, **1**, pp. 333 to 455; Joule, *Scientific Papers*, **2**, pp. 215 to 362.

gas was kept flowing uniformly for a long time, until no further fluctuations of the temperature were perceived, and it could be assumed that a steady state had been established.

The experiments showed that hydrogen became slightly warmer in passing through the plug, while the other gases used became slightly colder. This change of temperature was found to be approximately proportional to the difference of pressure on the two sides of the plug.

Since the operation to which the gas is subjected is adiabatic, the increase of the internal energy is equal to the work done by the outside forces. Let p and p' be the values of the pressure before and after the passage through the plug: let v, ϵ and v', ϵ' be the corresponding values of the volume and internal energy of unit mass.

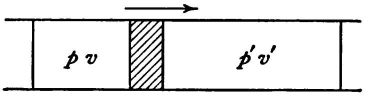

FIG. 24.

Since the gas enters the plug at the uniform pressure p, the work done on it by the driving pressure is pv. The gas issues with the uniform pressure p', it therefore does a quantity of work $p'v'$, against the outside pressure; **both these quantities refer to unit mass.** The total work done on the unit mass, during its passage through the plug, is $(pv - p'v')$, so that we have, for the increase of the internal energy, the equation

$$\epsilon' - \epsilon = pv - p'v'^{*} \quad \text{.......................(129)}$$

130. Let us now confine our attention to the case where the difference of pressure on the two sides of the plug is infinitesimal. Let T, p, v be the temperature, pressure, and specific volume of the gas as it enters the plug: let $(T + \Delta T)$, $(p + \Delta p)$, and $(v + \Delta v)$ be the values of the same quantities, as the gas issues from the plug. The difference of pressure, Δp, is always negative; the difference of specific volume, Δv, is always positive; the difference of temperature, ΔT, is negative except in the case of hydrogen. **Suppose**

* The dimensions are $\frac{pv}{M}$;

[illegible] to be measured by a [illegible] thermometer [illegible] with the gas under investigation. [illegible] the [illegible] of the gas at constant volume, and [illegible] the same scale [illegible] [illegible] experiments showed this to be nearly independent of the temperature and the volume for the [illegible] gases.

[illegible] equation [illegible] the form

$$[illegible]$$

[illegible] considering only an infinitesimal expansion,

$$[illegible] \qquad (30)$$

The expansion, which is obviously irreversible, may be represented [illegible] Fig. 25 [illegible] corresponding the normal state of the gas before it entered the plug, and [illegible] the state of the same gas after the irreversible passage through the plug.

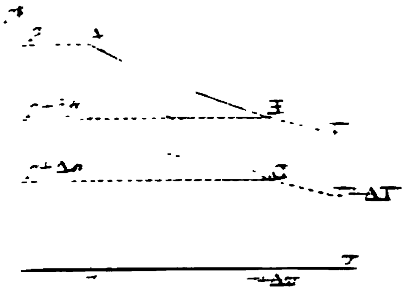

Fig. 25.

Let us imagine the gas after leaving the plug in the state $T-\Delta T$, [illegible], to be brought back at constant volume to the original temperature T. During this process it will absorb a quantity of heat [illegible] and it will now be in the state represented by the point 3 on the diagram. Since this last change of temperature goes on at constant volume, no external work is involved in it, and the internal energy of the gas [illegible]

[illegible]

increases by the amount of heat taken in, namely, $-C_v\Delta T$. If we let $(\epsilon_B - \epsilon_A) = \delta\epsilon$, we have

$$\delta\epsilon = \Delta\epsilon - C_v\Delta T,$$

or by equation (130)

$$\delta\epsilon = -p\Delta v - v\Delta p - C_v\Delta T. \quad\text{................}(131)$$

Now ϵ is a function of v and T only: therefore $\delta\epsilon$, which is the change in the internal energy of the gas as it passes from the state A to the state B, by the irreversible path ACB, is the same as the change would have been during the direct and reversible isothermal expansion from A to B. Let us now apply to this latter process the equation

$$\delta\epsilon = \delta Q + \delta W.$$

We already know the value of $\delta\epsilon$ by equation (131). We also know that

$$\delta W = -p\Delta v;$$

hence the value of the heat that the system would absorb in the reversible expansion AB is given by the equation

$$\begin{aligned}\delta Q &= \delta\epsilon - \delta W\\ &= -v\Delta p - C_v\Delta T. \quad\text{.......................}(132)\end{aligned}$$

Introduction of absolute temperature θ.

Since we are now dealing with a reversible change of state, we may also apply the equation

$$\delta Q = \theta\delta\eta,$$

which gives us, for the increase of the entropy, during the reversible, isothermal expansion AB, the value

$$\delta\eta = -\frac{1}{\theta}(v\Delta p + C_v\Delta T). \quad\text{..................}(133)$$

The results of the experiments showed, that for finite differences of temperature and pressure, these differences stood in a constant ratio to each other. Let us make the *assumption*, that this ratio still remains constant, when the difference of pressure is infinitesimal: we may then write

$$\frac{\Delta T}{\Delta p} = \mu = \text{const.} \quad \text{.......................... (134)}$$

$$\Delta T = \mu \Delta p.$$

Substituting in equation (133) gives

$$\delta\eta = -\frac{1}{\theta}(v + \mu C_v)\Delta p. \quad \text{.................... (135)}$$

We must now replace Δp by δp, the variation of the pressure that corresponds to the variation $\delta\eta$ of the entropy. The relation of Δp to δp is given by the fact, that

BC (fig 25)

$$\Delta p - \delta p = \left(\frac{\partial p}{\partial T}\right)_v \Delta T = \mu \left(\frac{\partial p}{\partial T}\right)_v \Delta p;$$

whence

$$\Delta p = \frac{\delta p}{1 - \mu\left(\frac{\partial p}{\partial T}\right)_v}. \quad \text{.......................... (136)}$$

This value of Δp, substituted in equation (135), gives the variation of the entropy in terms of the simultaneous variation of the pressure, and we have the equation

$$\delta\eta = -\frac{1}{\theta} \cdot \frac{v + \mu C_v}{1 - \mu\left(\frac{\partial p}{\partial T}\right)_v} \cdot \delta p. \quad \text{.............. (137)}$$

But, as the process to which $\delta\eta$ and δp refer is reversible, we may apply to it the general equation

$$\delta\epsilon = \theta\,\delta\eta - p\delta v.$$

If this be put in the form

$$\delta\zeta = -\eta\delta\theta + v\delta p,$$

it gives

$$-\left(\frac{\partial \eta}{\partial p}\right)_\theta = \left(\frac{\partial v}{\partial \theta}\right)_p;$$

(see 3d equation (115))

whence equation (137) gives us

$$\frac{1}{\theta}\cdot\frac{v+\mu C_v}{1-\mu\left(\frac{\partial p}{\partial T}\right)_v}=\left(\frac{\partial v}{\partial\theta}\right)_p, \quad\text{.................................(138)}$$

or

$$\theta\left(\frac{\partial v}{\partial\theta}\right)_p=\frac{v+\mu C_v}{1-\mu\left(\frac{\partial p}{\partial T}\right)_v}, \quad\text{..........................(139)}$$

a perfectly general equation for the thermodynamic temperature *on the assumption that the ratio* $\frac{\Delta T}{\Delta p}$ *is independent of the value of* Δp *even when* Δp *is infinitesimal.*

131. If the gas is one for which the thermal effect in passing the plug is zero, we have $\mu=0$, and equation (139) reduces to

$$\theta\left(\frac{\partial v}{\partial\theta}\right)_p=v\,;$$

whence, by transforming and integrating,

$$\log\theta=\log Kv \quad (p\text{ constant}),$$

or

$$\theta=Kv \quad (p\text{ constant}). \quad\text{................(140)}$$

The thermodynamic temperature is proportional to the temperature as read on a constant pressure thermometer of this gas, regardless of whether the gas obeys Boyle's Law or not.

In the general case, when μ does not equal zero, equation (139) may be put in the form

$$\frac{d\theta}{\theta}=\frac{1-\mu\left(\frac{\partial p}{\partial T}\right)_v}{v+\mu C_v}dv. \quad\text{.........................(141)}$$

If this equation be integrated between any two temperatures denoted by θ_0 and θ on the thermodynamic scale, and by T_0 and T on the constant pressure gas scale, it gives

$$\log\frac{\theta}{\theta_0}=\int_{v_0}^{v}\frac{1-\mu\left(\frac{\partial p}{\partial T}\right)_v}{v+\mu C_v}dv, \quad\text{...................(142)}$$

where v_0 and v are the volumes of unit mass of the gas, at the temperatures T_0 and T, under the constant pressure π.

The integration can not, of course, be performed, unless μ, C_v and $\left(\frac{\partial p}{\partial T}\right)_v$ are known, as functions of v; but by certain simplifying assumptions an approximate result may be obtained. Since μ is very small at most, let us treat it as constant, and give it the average value that it takes between the two temperatures in question, as found by the plug experiment. The specific heat at constant volume, since its variations are known to be small, and since it occurs only in the small correction term μC_v may also be treated as a constant. Moreover, as $\left(\frac{\partial p}{\partial T}\right)_v$, also, occurs only when multiplied by the small quantity μ, we may write

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v},$$

as if the gas obeyed Boyle's Law exactly. Under these conditions equation (142) reduces to

$$\log\frac{\theta}{\theta_0} = \int_{v_0}^{v} \frac{1 - \mu\frac{R}{v}}{v + \mu C_v} dv. \qquad \text{(143)}$$

Instead of the volume, we may now introduce, as the independent variable, the temperature T of the constant pressure gas thermometer, by using the equations

$$v = \frac{RT}{\pi}; \quad dv = \frac{R}{\pi} dT,$$

which define this temperature. Equation (143) then assumes the form

$$\log\frac{\theta}{\theta_0} = \frac{R}{\pi}\int_{T_0}^{T} \frac{1 - \mu\frac{\pi}{T}}{\frac{RT}{\pi} + \mu C_v} dT$$

$$= \left[\log\frac{(\pi\mu C_v + RT)^{\frac{C_v + R}{C_v}}}{T^{\frac{R}{C_v}}}\right]_{T_0}^{T}$$

whence we have

$$\frac{\theta}{\theta_0}=\left(\frac{\pi\mu C_v+RT}{\pi\mu C_v+RT_0}\right)^{\frac{C_v+R}{C_v}}\cdot\left(\frac{T}{T_0}\right)^{-\frac{R}{C_v}}\quad\ldots\ldots\ldots\ldots(144)$$

If $\mu=0$, equation (144) reduces to

$$\frac{\theta}{\theta_0}=\frac{T}{T_0}$$

as was shown before, equation (140).

132. Instead of treating μ as independent of the temperature, we may probably get a closer approximation to the truth by setting

$$\mu=\frac{a}{T^2};$$

for the thermal effect seemed to be nearly proportional to the inverse square of the absolute temperature.[*] If we treat $\left(\frac{\partial p}{\partial T}\right)_v$ and C_v as before, but let $\mu=a/T^2$, we have

$$\mu=\frac{R^2a}{\pi^2v^2}.$$

Substituting this value in equation (143), and rearranging,

$$\log\frac{\theta}{\theta_0}=\int_{v_0}^{v}\frac{\pi^2v^3-R^3a}{v(R^2aC_v+\pi^2v^3)}dv.$$

By separating the terms and substituting $x=v^3$, this equation may be integrated: it gives

$$\log\frac{\theta}{\theta_0}=\left[\log\left(R^2aC_v+\pi^2v^3\right)^{\frac{1}{3}}+\log\left(\frac{R^2aC_v+\pi^2v^3}{v^3}\right)^{\frac{R}{3C_v}}\right]_{v=v_0}^{v=v};$$

whence

$$\frac{\theta}{\theta_0}=\left(\frac{v}{v_0}\right)^{-\frac{R}{C_v}}\cdot\sqrt[3]{\left(\frac{R^2aC_v+\pi^2v^3}{R^2aC_v+\pi^2v^3_0}\right)^{\frac{C_v+R}{C_v}}}\quad\ldots\ldots\ldots\ldots(145)^{**}$$

Substituting from the equation $\pi v=RT$, which defines T, we get

$$\frac{\theta}{\theta_0}=\left(\frac{T}{T_0}\right)^{-\frac{R}{C_v}}\cdot\sqrt[3]{\left(\frac{\pi aC_v+RT^3}{\pi aC_v+RT^3_0}\right)^{\frac{C_v+R}{C_v}}}\quad\ldots\ldots\ldots\ldots(146)$$

[*] Result of the Joule-Thomson experiments.

[**] multiplying under the radical by $\frac{\pi}{R^2}$; $\frac{\pi^3v^3}{R^2}=RT^3$.

As before, if $\mu = 0$, *i.e.* $a = 0$, this equation reduces to the form

$$\frac{\theta}{\theta_0} = \frac{T}{T_0}.$$

133. If the necessary data are given, concerning R, C_v and μ, it is thus possible to compute the ratio, on the thermodynamic scale, of any two temperatures, such as the freezing and boiling points of water, if these temperatures have already been expressed in terms of the scale of the constant pressure gas thermometer. We may then assign to these temperatures, such numerical values, that the difference between them is the same as on the Celsius scale,—one hundred degrees, in the case just mentioned. The thermodynamic temperature of the melting point of ice, obtained in this way, is very nearly the same as it is on the absolute gas scale of a thermometer filled with oxygen, hydrogen, or nitrogen. We may then go on to compare θ and T at various other temperatures, and in this way, make out a table of corrections, by which the readings of the constant pressure gas thermometer may be reduced to the thermodynamic scale. If the corrections of the constant pressure thermometer have once been found for a particular gas, the corrections for the constant volume thermometer filled with the same gas may evidently be found, from the known deviations of the gas from Boyle's Law. The results show, that between the freezing and boiling points of water, the corrections of the normal, constant volume, hydrogen thermometer are hardly greater than the unavoidable errors of the determination of such a temperature, unless very great care be used in the determination.

These corrections have been computed, by various formulas, from the results of Joule and Lord Kelvin, regarding the value of μ, in connection with the data of other observers on the other quantities involved. As our purpose has been only to show that the computation is possible—at least to a considerable degree of approximation—we shall, for the details of such computations, merely refer the reader to the original memoirs of Joule and Lord

Kelvin,[*] and to a recent paper by Mr. R. A. Lehfeldt "On a Numerical Evaluation of the Absolute Scale of Temperature."[†]

It is to be noticed, that some writers, in elementary discussions of the plug experiment, have applied the equation

$$\delta\epsilon = \theta\delta\eta + \delta W.$$

directly, to the adiabatic change of state of the gas in passing through the plug. Such a treatment is, however, quite inadmissible, because the passage is essentially irreversible, so that it can not be assumed, that

$$\delta Q = \theta\delta\eta.$$

Having now put the idea of thermodynamic temperature on a secure basis, we proceed to consider a few other simpler applications, which illustrate the use of the principles and equations deduced in Chapters VIII and IX.

The Relation of the Elasticity of a Solid to the Temperature

134. Let $\alpha\beta\gamma$ (fig. 26) be a rectangular volume-element of a solid body: let the element be subject to a tension parallel to the edge α, and let the temperature of the element be θ. Suppose the tension f to be increased to $(f+\delta f)$, thereby increasing the length of the side α to $(\alpha+\delta\alpha)$: at the same time, such a quantity of heat is to be supplied or abstracted, as to prevent the temperature of the element from changing. Let the increase of the

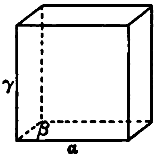

Fig. 26.

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[*] Kelvin, *Math and Phys. Papers*, **1**, p. 333.

[†] Lehfeldt, *Phil. Mag.* (5) **45**, p. 363 (1898).

tension be so slow that the element is, at all times, approximately in equilibrium, so that we may treat the increase of the length of the element as a reversible process. Let $\lambda\,\phi$ be the quantity of heat absorbed by one cubic centimeter of the solid, when it is stretched, isothermally, by an amount ϕ cms. per centimeter of its length.

During the increase of α, the work done by the tension, on the element $\alpha\beta\gamma$, is

$$\delta W = f\delta\alpha.$$

The heat absorbed during the same process is per cubic centimeter $dq = \lambda \frac{\delta\alpha}{\alpha}$

and $$\delta Q = \lambda\frac{\delta\alpha}{\alpha}\,.\,\alpha\beta\gamma = \lambda\,.\,\beta\gamma\,.\,\delta\alpha.$$

The equation

$$\delta\epsilon = \theta\delta\eta + f\delta\alpha \quad = \theta\,\delta\eta + X\,dx$$

may now be applied, and we will put it in the form

$$\delta\psi = -\eta\delta\theta + f\delta\alpha, \quad = -\eta\,\delta\theta + X\,dx$$

which shows that (111)

$$-\left(\frac{\partial\eta}{\partial\alpha}\right)_\theta = \left(\frac{\partial f}{\partial\theta}\right)_\alpha.$$

Now the increase of the entropy, due to the increase of α, is given by the equation

$$\left(\frac{\partial\eta}{\partial\alpha}\right)_\theta = \frac{1}{\theta}\left(\frac{\partial Q}{\partial\alpha}\right)_\theta = \frac{\lambda\beta\gamma}{\theta}.$$

We therefore get, by comparing the last two equations,

$$\left(\frac{\partial f}{\partial\theta}\right)_\alpha = -\frac{\lambda\beta\gamma}{\theta}. \qquad (147)$$

If F be the tension per square centimeter, or the stress, equation (147) reduces to the form

$$\left(\frac{\partial F}{\partial\theta}\right)_\alpha = -\frac{\lambda}{\theta}, \qquad (148)$$

which is a relation connecting λ, θ, and $\left(\frac{\partial F}{\partial\theta}\right)_\alpha$, the rate of increase with the temperature, of the stress, needed to produce a given state of tensile strain.

The immediate conclusion is, that for solids which expand on being heated, and for which, therefore, $\left(\frac{\partial F}{\partial \theta}\right)_a < 0$, **the latent heat of stretching, λ,** must be positive. During a slow isothermal extension, heat is absorbed: if the stretching is so sudden as to be approximately adiabatic, the solid is cooled by the strain. A stretched piece of vulcanized india-rubber contracts longitudinally, upon being heated; a sudden increase of its length should therefore be accompanied by an increase of its temperature. These conclusions have been found to be in accordance with the facts, as investigated by Joule.*

Electromotive Force of a Reversible Galvanic Cell

135. If a quantity of electricity, e, be allowed to pass through a galvanic cell, the internal composition of the cell changes, by reason of the electrolytic reactions which accompany the flow of the current. By connecting the cell with another, of greater electromotive force, acting in the opposite direction, we may force the same quantity of electricity to flow back through the cell. Let the strength of the current be infinitesimal, in both cases. If the reversal of the current reverses all the physical and chemical reactions inside the cell—so that when the quantity of electricity e has passed back, the cell has returned precisely to its initial state—the cell is said to be a *reversible cell*. The Daniell cell satisfies this condition very nearly, if we disregard the slow diffusion of the liquids, which takes place, even when the cell is inactive.

Let us consider a cell of this sort: let its electromotive force be E, when its poles are disconnected, and when its temperature

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* Joule, *Phil. Trans.*, **149**, part I, p. 91 (1859); also, *Scientific Papers*, **1**, p. 143.

is θ. The state of the cell at a given instant of time, may be changed, either by changing the temperature, or by allowing a current to pass through it, in one direction or the other. At any future instant, the state of the cell is determined by its temperature and by the quantity of electricity, e, that has passed through it since the time $t = 0$. For the chemical changes inside the cell can go on only in proportion to the quantity of electricity that traverses the liquids, and the direction of these changes is determined by the direction of the current. Let e be counted positive, when it is a quantity passing through the cell in the natural direction: this will be, through the solution from the zinc to the copper, in the case of the Daniell cell.

The cell may now be treated as a system capable of reversible modifications of state, defined by the variations of the variables e and θ. If the reactions accompanying the passage of a current do not involve the appearance or disappearance of any gaseous components, the changes in the volume of the cell are so slight as to be of no importance, and e and θ may be regarded as normal variables.

Let the following cyclic process be performed:

I. Let a quantity of electricity e pass through the cell in the positive direction, while heat is added or taken away, at such a rate as to keep the temperature constant at the value $\theta + \delta\theta$. Let the passage of the electricity be carried on reversibly: this may be done, by having the motion of the electricity outside the cell
?? consist in actual convection, taking place so slowly that the quantity of heat, i^2Rt, developed inside the cell, is negligible on account of the smallness of the current.

II. Let the supply or abstraction of heat be stopped until the temperature of the cell has fallen by an amount $\delta\theta$, an infinitesimal quantity which may be either positive or negative. This will cause an adiabatic change of state, and the electromotive force will change from its original value which was $E + \left(\frac{\partial E}{\partial \theta}\right)_e \delta\theta$, at the temperature $\theta + \delta\theta$, to the value E.

III. Let the quantity of electricity e be now passed back through the cell, by means of the convection apparatus, the temperature being kept constant at θ: this process is to be reversible like the first.

IV. Let a final, infinitesimal, adiabatic process bring the cell back to its initial temperature.

The work done *by the cell* on the convection apparatus, during the first operation, is

$$W_1 = \left[E + \left(\frac{\partial E}{\partial \theta}\right)_e \delta\theta\right] e.$$

The work done *on the cell* during the third operation is

$$W_3 = Ee.$$

As the adiabatic processes are infinitesimal in length, the work they involve is negligible: hence the total amount of work done by the cell during the cycle, *i.e.* the amount of heat it converts into work, is

$$W_1 - W_3 = e\left(\frac{\partial E}{\partial \theta}\right)_e \delta\theta = \delta Q.$$

Now, the reactions that actually go on in the cell during the passage of the current, might be made to go on, in a different apparatus, without the flow of any current. Let λ be the heat that would be developed, under these conditions, by a reaction involving the same amounts of the various substances as are actually involved during the passage of one unit of electricity through the cell, in the positive direction. Then, during the operation at the temperature $\theta + \delta\theta$, the energy λe has been developed by the reactions in the cell. But at the same time, the energy $\left[E + \left(\frac{\partial E}{\partial \theta}\right)_e \delta\theta\right] e$ has been given out in the form of electrical work, so that, on the whole, in keeping the temperature of the cell constant, we must have supplied to it the heat

$$Q = \left[E + \left(\frac{\partial E}{\partial \theta}\right)_e \delta\theta\right] e - \lambda e.$$

If we substitute these quantities in the equation

$$\frac{\delta Q}{Q}=\frac{\delta\theta}{\theta},$$

θ here represents the higher temperature (see

we get

$$\frac{e\left(\frac{\partial E}{\partial\theta}\right)_e\delta\theta}{\left[E+\left(\frac{\partial E}{\partial\theta}\right)_e\delta\theta\right]e-\lambda e}=\frac{\delta\theta}{\theta+\delta\theta},$$

or, dropping the negligible infinitesimals and simplifying,

$$\frac{\left(\frac{\partial E}{\partial\theta}\right)_e}{E-\lambda}=\frac{1}{\theta},$$

whence

$$\left(\frac{\partial E}{\partial\theta}\right)_e=\frac{E-\lambda}{\theta},\qquad\text{(149)}$$

and

$$E=\lambda+\theta\left(\frac{\partial E}{\partial\theta}\right)_e.\qquad\text{(150)}$$

We have thus obtained a relation connecting the heat of reaction, the electromotive force, and the temperature coefficient of the electromotive force. This relation, which is due to Helmholtz, has been verified by the results of numerous experiments.[*]

136. We have here, for the sake of illustration, treated the problem by means of a reversible cycle. While this method of treatment is straightforward, and uses only the simple equation

$$\frac{\delta Q}{Q}=\frac{\delta\theta}{\theta},$$

it is also long and cumbersome. We will now show how the same result may be obtained in a much more elegant manner.

Suppose the cell to be at the temperature θ, in a state of equilibrium, and with its poles disconnected. Let the infinitesimal quantity of electricity δe pass reversibly through the cell, in the positive direction. To this modification of state we may apply the equation

$$\delta\epsilon=\theta\delta\eta+\delta W.$$

[*] first derived by Gibbs , v. Helmholtz ;

The work done on the cell is

$$\delta W = -E\,\delta e,$$

so that we have

$$\delta\epsilon = \theta\,\delta\eta - E\,\delta e.$$

From this equation, we find that

$$\delta\psi = -\eta\,\delta\theta - E\,\delta e,$$

and

$$\left(\frac{\partial\eta}{\partial e}\right)_\theta = \left(\frac{\partial E}{\partial\theta}\right)_e. \quad\text{...............................}(151)$$

But

$$\delta\eta = \frac{\delta Q}{\theta} = \frac{E\,\delta e - \lambda\,\delta e}{\theta};$$

hence

$$\left(\frac{\partial\eta}{\partial e}\right)_\theta = \frac{E-\lambda}{\theta}.$$

By substitution in equation (151), we obtain the equation

$$\left(\frac{\partial E}{\partial\theta}\right)_e = \frac{E-\lambda}{\theta},$$

whence

$$E = \lambda + \theta\left(\frac{\partial E}{\partial\theta}\right)_e,$$

as before.

Equilibrium between Different Phases of a Single Substance

137. Let the system to be treated consist of a fixed mass of a single, chemically defined substance. Let it be divided into two parts, different in nature, but each homogeneous. Let the two *phases*, as they are called, be in equilibrium with each other at the temperature θ_0, and under the uniform surface pressure p_0. Such systems are of every day occurrence: a mass of ice and water at the freezing point is the commonest example. Let the two phases be denoted by I and II.

As normal variables of the system, we may use the volume and the temperature; the single outside action is then represented by the generalized force $(-p)$. This is, of course, on the assumption, that we may neglect the effects of all such outside actions as gravity and electrical forces, as well as the capillary forces that come into play at the bounding surfaces of the phases.

Let v_1 and v_2 be the specific volumes of the substance,* in the two phases: let λ be the heat absorbed by the system, when a unit mass of the substance changes, at the temperature θ_0, from the first to the second phase. Such a change may be treated as reversible, if it is slow; for the two phases are always approximately in equilibrium. The general equation may now be written

$$\delta\epsilon = \theta\,\delta\eta - p\,\delta v,$$

or

$$\delta\psi = -\eta\,\delta\theta - p\,\delta v;$$

whence

$$\left(\frac{\partial\eta}{\partial v}\right)_\theta = \left(\frac{\partial p}{\partial\theta}\right)_v. \qquad\text{.............................(152)}$$

Let an infinitesimal mass, δm, change from the first phase into the second. We then have

$$\delta Q = \lambda\,\delta m,$$

and

$$\delta\eta = \frac{\lambda\,\delta m}{\theta_0}.$$

The consequent increase of the volume of the whole system is

$$\delta v = (v_2 - v_1)\,\delta m:$$

hence we have the equation

$$\left(\frac{\partial\eta}{\partial v}\right)_\theta = \frac{\lambda}{\theta_0(v_2 - v_1)}.$$

Substituting in equation (152), we get

$$\left(\frac{\partial p}{\partial\theta}\right)_v = \frac{\lambda}{\theta_0(v_2 - v_1)}; \qquad\text{......................(153)}$$

or, since θ_0 and p_0 are the values of the temperature and pressure at which the phases are in equilibrium,

$$\left(\frac{\partial\theta_0}{\partial p_0}\right)_v = \frac{\theta_0(v_2 - v_1)}{\lambda}. \qquad\text{.........................(154)}$$

*v_1 volume of ice, v_2 of liquid, then λ heat of fusion (as example

This equation tells us, at once, how a change of pressure will change the temperature at which the two phases can coexist, if we know the values of v_1, v_2, θ_0, and λ. The correctness of this result has been tested many times, and the formula represents the results of the experiments quite accurately. The variation of freezing point with change of pressure was first deduced by James Thomson in 1849, and the conclusion was then shown to be correct, by the experiments of his brother, now Lord Kelvin,* on the influence of pressure on the freezing point of water.

In the case of a substance like water, which expands in solidifying; if $\lambda > 0$, $(v_2 - v_1) < 0$, so that $\frac{\partial \theta_0}{\partial p_0} < 0$; or, the freezing point is lowered by pressure. Most substances expand in the process of liquefaction; hence their freezing points are raised by an increase of pressure.

The equation is equally applicable to other similar changes of phase, that is, to the relation of the temperature and pressure at which two phases are capable of coexistence. As examples of such systems we may cite the following:—a liquid and its vapour; a solid and its vapour; two allotropic forms of a solid; a solid and its gaseous dissociation products.

The Change of Osmotic Pressure with the Temperature

138. Let us consider a solution, in which the osmotic pressure† is proportional to the concentration when the temperature is constant. Let p be this pressure, and let v be the dilution of the solution, that is, the volume which contains one gram molecule

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* *Math. and Phys. Papers*, **1**, pp. 156 and 165.

† We assume that the reader is familiar with the ordinary osmotic phenomena: if he is not, he will find them fully described by Ostwald, *Lehrbuch der allgemeinen Chemie*, **1**, 2nd ed., Leipzig, 1891; also *Solutions*, Longmans, 1891.

of the dissolved substance. Our supposition may be expressed by the equation

$$(pv)_\theta = \text{constant}.$$

Let a volume of the solution, containing one gram molecule of the dissolved substance, be taken; and let the dissolved substance expand, isothermally and reversibly, from the volume v to the volume $v + \delta v$. This reversible process may be carried out as follows: The solution is confined in a cylinder; in the cylinder there is fitted a semi-permeable piston, which allows the solvent to pass through it, but is impermeable to the dissolved substance. By moving the piston, it is possible to expand or contract the space in which the solution is confined, while the solvent passes freely through the piston, so that the only force exerted by the solution on the piston is that due to the osmotic pressure of the dissolved substance. If the force applied to the piston, from without, differs only infinitesimally from that needed to balance exactly the osmotic pressure of the solution, the motions of the piston will be reversible. By an appropriate supply or withdrawal of heat, the operations may be made to take place at constant temperature, or isothermally.

To this reversible expansion, we may apply the equation

$$\delta\epsilon = \delta Q + \delta W.$$

The work done by the dissolved substance during the expansion is $p\delta v$, so that we have

$$\delta W = -p\delta v.$$

If the solution had changed from its initial to its final volume by our mixing the extra quantity of solvent with it directly, a certain quantity of heat would have been developed. This is known as the heat of dilution, and we may express it by $\lambda\delta v$. The quantity λ is, obviously, the heat that would be developed if, to an amount of the solution containing one gram molecule of the dissolved substance, we added enough of the pure solvent to double the volume of the solution,—supposing that λ remains constant through so large a range of dilution. The internal energy of the system composed of the volume v, of solution, and the extra solvent needed to dilute it to the volume $v+\delta v$, would in this *irreversible* process of mixing, decrease by an amount $\lambda\delta v$: for the external work is negligible, owing to the smallness of the change caused in the total volume of the system by the mixing. During a *reversible* operation, by which the system passes from the same initial to the same final state, the decrease in the internal energy must be the same as in the irreversible process: hence we have

$$\delta\epsilon = -\lambda\delta v.$$

From the last three equations we get, as the value of the heat absorbed during the reversible expansion, the expression

$$\delta Q = -\lambda\delta v + p\delta v.$$

But since the expansion is reversible, we have

$$\delta\eta = \frac{\delta Q}{\theta} = \frac{p-\lambda}{\theta}\delta v. \qquad\qquad (155)$$

From the equation

$$\delta\epsilon = \theta\delta\eta - p\delta v,$$

we also obtain the relations

$$\delta\psi = -\eta\delta\theta - p\delta v,$$

and

$$\left(\frac{\partial\eta}{\partial v}\right)_\theta = \left(\frac{\partial p}{\partial\theta}\right)_v.$$

Substituting in this equation the value of $\delta\eta$ from equation (155), we obtain

$$\left(\frac{\partial p}{\partial\theta}\right)_v = \frac{p-\lambda}{\theta}, \qquad\qquad (156)$$

or, rearranging,

$$\frac{\delta\theta}{\theta} = \frac{\delta p}{p-\lambda}. \qquad\qquad (157)$$

If the solution is already so dilute that further dilution produces no sensible thermal effect, we may write $\lambda = 0$. Equation (157) may then be integrated, and it gives

$$\theta = p \times \text{constant}. \qquad\qquad (158)$$

The result is, that in the case of a solution in which the osmotic pressure is proportional to the concentration, that pressure, at constant concentration, is proportional to the thermodynamic temperature, if the heat of further dilution is zero.

Precisely similar reasoning might have been applied to a gas that obeys Boyle's Law. We should then have found, that if the heat of dilution, that is, the heat absorbed during an isothermal free expansion, was zero or negligible, the pressure of the gas, at constant volume, was proportional to the thermodynamic temperature. This result would, however, be nothing new; for such a gas is merely an ideal gas, and it has already been shown that the ideal gas scale and the thermodynamic scale give proportional readings.

As our object has been merely to illustrate the methods of finding the conditions of equilibrium, from the equations which apply to reversible displacements from a state of equilibrium, we shall not go on to multiply these applications. The reader will find numerous examples in the larger works on physics and physical chemistry.*

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* *E.g.*, Ostwald, *Lehrb. der allg. Chemie*; Nernst, *Theoretische Chemie*, 2nd edition, Stuttgart, 1898.

CHAPTER XI

THE CONDITIONS OF THERMODYNAMIC EQUILIBRIUM

Summary of Conditions and Hypotheses

139. The validity of the general equations given in Chapter IX rests on certain conditions and hypotheses, of which the following are the most important:

I. CONDITION: The systems considered have no appreciable kinetic energy (art. 27).

II. CONDITION: The systems considered have equations of equilibrium, which determine uniquely the outside actions needed to preserve any given state of equilibrium (arts. 40 and 45).

III. HYPOTHESIS: Kinetic energy being excluded by condition I, the speeds of all processes vanish with the driving forces (art. 47).

IV. HYPOTHESIS: No system can act as an infinite source or sink of energy (art. 58).

V. HYPOTHESIS: If a system has passed from a state A to a state B, it is always possible, by some means or other, to make it pass from B to A (art. 59).

VI. HYPOTHESIS: The principle of the conservation of energy (art. 61).

VII. CONDITION: No outside actions are to be considered, except such as involve the transference of energy which has the same value as mechanical energy (art. 62).

VIII. HYPOTHESIS: When heat is converted into mechanical energy, some heat must pass from a hot into a cold body (art. 106).

IX. HYPOTHESIS: Any two possible states of a system may be connected by a continuous series of states of equilibrium (art. 116).

140. Conditions I, II, and VII exclude a great number of problems from consideration; but, on the other hand, they are certainly fulfilled in a great many cases, to which our theory is therefore applicable.

The hypotheses IV, VI, and VIII are hypothetical, only in the sense that they are inductions from a limited, though very large, number of observations. They are not known to be distinctly contradicted by any experiment, and we may regard them as constituting, in the present state of our experimental knowledge, a set of laws found from experiment.

The remaining hypotheses, III, V, and IX, do not rest so evidently as IV, VI, and VIII, upon a large assemblage of experimental facts. They are commonly, often tacitly, made by writers on thermodynamics, and the author can think of no case in which they are not all true. If, however, such cases exist, our theory is not applicable to them, but remains valid for problems in which the conditions indicated are fulfilled. These hypotheses might have been put under the heading of conditions. The distinction has been made, for the reason that what we have called conditions are apparently not always satisfied, whereas experience seems to show that our so-called hypotheses are universally true.

The Criterion of Equilibrium

141. In Chapters VIII and IX, we have deduced certain mathematical statements relating to reversible and irreversible processes. Reversible processes consist of series of states of equilibrium, and are therefore not capable of realization. On the other hand, all actual processes are irreversible. We have now to ask, what are the necessary and sufficient conditions for thermodynamic equilibrium, and what will be the sense or direction of any real process. We wish, if possible, to find a single criterion which shall enable us to say, in any case, whether a system which is in a given state will remain in that state; or, if it tends to leave it, what will be the nature of the change.

The results of the first law, or principle of equivalence, are summarized in equations, and the sign of equality gives no indication of direction. Our criterion is, therefore, not to be sought in the first law. The second law, when applied to reversible processes, leads to equations; *i.e.*, when applied to states of equilibrium, it gives no indication of direction. But when applied to irreversible processes, a category which includes all real processes, it leads to either equations or inequalities; and an inequality may, evidently supply an indication of direction. We therefore seek our criterion in some statement of the second law; for instance one of the following:

$$\left.\begin{array}{c} (\int)\dfrac{dQ}{\theta} \leqq 0, \\ \displaystyle\int_A^B \dfrac{dQ}{\theta} \leqq \eta_B - \eta_A, \\ \delta Q \leqq \theta\,\delta\eta\,; \end{array}\right\} \text{.......................(159)}$$

or, in the combined statement of the two laws, namely,

$$\delta\epsilon \leqq \theta\,\delta\eta + \sum X\delta x. \text{ ....(160)}$$

These formulas have the common property, that when they refer to states of equilibrium, the sign of equality is to be used: for real processes we have only been able to show that one sign or the other must hold good.

If we make the **assumption** *that the sign of equality is applicable only to reversible processes*, we shall have the desired criterion. Irreversible processes will then be characterized by the sign of inequality. The equation will be the limiting form which the statement of inequality approaches, as the forces acting on the system, during the irreversible modification of its state, are so varied that the successive states of the system during the transformation approach more and more nearly to being states of equilibrium.

142. It is immaterial to which one of the formulas (159), (160), we apply our assumption, since if made for one of them it holds for the others. Let us assume, that in any cyclic change of state

$$(\int)\frac{dQ}{\theta}=0 \qquad (161)$$

only if the cycle is reversible, whereas if the cycle is irreversible

$$(\int)\frac{dQ}{\theta}<0. \qquad (162)$$

It follows from this assumption, that if, in every conceivable, infinitesimal variation of state that is compatible with the nature of the system, we have either

$$\delta\epsilon>\theta\delta\eta+\sum X\delta x, \qquad (163)$$

or

$$\delta\epsilon=\theta\delta\eta+\sum X\delta x, \qquad (164)$$

the system is surely in equilibrium. If, on the other hand, variations of the variables are possible, which make

$$\delta\epsilon<\theta\delta\eta+\sum X\delta x, \qquad (165)$$

then the system is certainly not in equilibrium. For by making it a fundamental condition that the system shall have equations of equilibrium, we have excluded the intervention of passive resistances to change*; hence, as in the dynamics of a frictionless system, if the active tendencies of the system—including in this term the outside actions—are not so balanced as to produce a state of equilibrium, some change of state will occur. The change that actually does occur, will necessarily be of such a nature that

$$\delta\epsilon<\theta\delta\eta+\sum X\delta x.$$

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* By a passive resistance is meant one analogous to friction; resistances which, like viscosity, merely retard changes of state, do not interfere with the existence of equations of equilibrium, and are not excluded by the condition that has been imposed.

143. The criterion that we have set up rests on a pure hypothesis, but an hypothesis of the same nature as those mentioned in articles 139 and 140,—one of which the truth or untruth is capable of being tested by experiment. If we ever find any fact that contradicts a logical deduction from the hypothesis, then the hypothesis is not universally true; no such fact is known to the writer. On the contrary, experiments which have tested the conclusions to be drawn from the hypothesis we have made, have given results consistent with it, and each new experiment increases the strength of the presumption that the hypothesis expresses a real law of nature. In this respect, the hypothesis, like the other statements that have been placed under the same head, differs from such special mental pictures as that of the molecular constitution of matter, or the various mechanical conceptions of the ether. For these latter, though they may in time be shown to be inconsistent with facts, and therefore false, can never, so far as we can see at present, be tested by any direct experiment. They may prove to be useful, which is the most important characteristic of hypothesis, but we can have no expectation of a direct experimental test.

Nature of the Deductions Given for the Criterion

144. Many so-called proofs have been given of the proposition that

$$(\int)\frac{dQ}{\theta}<0$$

for all real cycles, or of some equivalent proposition; but so far as the writer is aware, no one of these proofs really amounts to a demonstration. They all appear to contain, in some shape or other, an unproven assumption; and it is better to acknowledge at once, that we can not deduce the proposition from any of our previous work, but must accept it as a new experimental principle, forming a pendant to Carnot's principle.

As an illustration of the style of reasoning used in this connection the following—for which the writer alone is responsible—may be given:

Consider a number of separate bodies or systems of bodies, each at a uniform temperature, and each capable of change of state quite independently of the others and without acting on or being acted on by them, in any way whatever. Each body or system has the same entropy as if the others were not present. If we now consider all the bodies taken together, as constituting a single system, we may, by a slight extension of our idea of entropy which was reached by the consideration of systems of uniform temperature, speak of the entropy of the whole system, as equal to the sum of the entropies of all its parts taken separately, whether they are all at the same temperature or not.

If the whole system be isolated in space, so that its energy remains constant and it can neither receive nor give out heat, any inequalities of temperature will tend to decrease by conduction and radiation; and such equalization of temperature is finally inevitable, because there is no known means of completely preventing conduction and radiation. Every quantity of heat Q, conducted or radiated from a part of the system where the temperature is θ, will be received by some other part, or parts, of which the temperatures $\theta_1 > \theta_2 > \theta_3$, etc., are less than θ. The entropy of the part losing the heat will decrease by an amount $\frac{Q}{\theta}$, and the entropies of the parts receiving it will, on the whole, increase by something more than $\frac{Q}{\theta_1}$. The entropy of the whole system will therefore increase by at least $Q\left(\frac{1}{\theta_1} - \frac{1}{\theta}\right)$,—a quantity which is always positive.

Now we have reason to believe, that in any sort of process which actually occurs, there are always slight inequalities of temperature between different points of the system: hence an increase of entropy is inevitable in any real process, going on inside an isolated system of the kind we have described. The whole universe may be considered as an isolated system: hence the proposition may be made, that the entropy of the universe tends continually to increase. This proposition, known as the PRINCIPLE OF THE INCREASE OF ENTROPY, is due to Clausius, though his deduction is different from the one here given.

145. Aside from the fact that this principle contains a reference to parts of the universe which are inaccessible to us, and where we are therefore unable to test the truth of what we consider to be physical laws, there would be little to be said against it, if we could assume that it is allowable to treat the universe as made up of separate parts, each of uniform temperature, and each capable of variation of state independently of the others. But we are not justified in taking so forced an assumption as a matter of course, so that our proof is quite worthless. If, however, this principle be accepted as an hypothesis, it may be made to do the same service as the assumption, that

$$(\int)\frac{dQ}{\theta}<0$$

for all irreversible cycles. As we shall not use the principle in the general form which it received from Clausius, no further discussion of it is needed here. Our object has been merely to illustrate, by a somewhat flagrant example, the ease with which general and vague hypotheses slip into such reasoning and vitiate the result,—this result being in any case equivalent to the assumption we have adopted, namely, that contained in the statement, that for real, infinitesimal variations of state,

$$\delta\epsilon<\theta\,\delta\eta+\sum X\delta x.$$

The reader will hardly find a more useful exercise in clear thinking than the analysis of such proofs. Many of them are unsatisfactory because of an ambiguous or vacillating use of the term temperature. We have endeavoured to be consistent in using this term as meaning *the uniform temperature of the system* under consideration. To suppose that the temperature of any system is strictly uniform, would, of course, be absurd; but as we said in article 32, we make, and can make, no pretence to mathematical exactness, in the treatment of subjects about which our information is obtained by methods of limited though, perhaps, high accuracy. "Uniform" has therefore been used with the meaning "sensibly uniform." Whenever a transference of heat has taken place between the system and its surroundings, it has been supposed that the difference of temperature actuating the flow of heat was infinitesimal, in all cases in which the temperature of the outside source or sink of heat was of any importance. Thus the temperatures of the system and of the source or sink have been represented by the same symbol.

Gibbs's Form of the Criterion

146. The criterion of equilibrium may be put in various forms, at the pleasure of the person using it. Two of these new forms may be obtained as follows: If an entirely isolated system changes its state in any way, since no outside bodies are acting on it, no work is done. Hence in equations (163) and (164) the term $\sum X\delta x$ vanishes, and we have

$$\delta\epsilon \geqq \theta\,\delta\eta. \qquad (166)$$

If the energy ϵ is constant, *i.e.*, if $\delta\epsilon = 0$, we have

$$(\delta\eta)_\epsilon \leqq 0. \qquad (167)$$

If, on the contrary, the entropy is kept constant, *i.e.*, if $\delta\eta = 0$, we have

$$(\delta\epsilon)_\eta \geqq 0. \qquad (168)$$

These two results may be stated as in the following terms:

I. "For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its energy, the variation of its entropy shall either vanish or be negative."

II. "For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations in the state of the system which do not alter its entropy, the variation of its energy shall either vanish or be positive."*

These two theorems are stated and discussed by Gibbs in his memoir ON THE EQUILIBRIUM OF HETEROGENEOUS SUBSTANCES, and the second is used as a basis for his investigation of the conditions of equilibrium in such substances.

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* J. W. Gibbs, *Trans. Connecticut Acad.*, **3**, p. 109.

CHAPTER XII

THERMODYNAMIC POTENTIALS AND FREE ENERGY

Internal Thermodynamic Potential of a System at Constant Temperature

147. Under some circumstances, which are often approximately realized in practice, the condition of equilibrium

$$\delta\epsilon \geqq \theta\delta\eta + \sum X\delta x, \quad \text{........................(169)}$$

and the condition of possibility of change,

$$\delta\epsilon < \theta\delta\eta + \sum X\delta x, \quad \text{........................(170)}$$

may be put into more convenient forms.

If we confine our attention to isothermal changes of state, it is convenient to throw these two conditions into the form

$$\delta\psi \geqq -\eta\delta\theta + \sum X\delta x, \quad \text{......................(171)}$$

$$\delta\psi < -\eta\delta\theta + \sum X\delta x, \quad \text{......................(172)}$$

or, since the temperature is constant,

$$\delta\psi \geqq \sum X\delta x, \quad \text{................................(173)}$$

$$\delta\psi < \sum X\delta x. \quad \text{................................(174)}$$

In these expressions, the sum $\sum X\delta x$ contains only terms which refer to the external variables. If we wish to indicate all the variables, both external and internal, we may substitute in the above inequalities

$$\sum X\delta x = \sum X_e\delta x_e + \sum X_i\delta x_i, \quad \text{................(175)}$$

where $$\sum X_i\delta x_i = 0. \quad \text{...(176)}$$

If not only the temperature but the external variables x'_e, x''_e, ... etc., are kept constant, the conditions (173) and (174) reduce to

$$\delta\psi \geqq 0, \qquad (177)$$

$$\delta\psi < 0. \qquad (178)$$

From this we see, that if, of all the isothermal modifications of the state of the system that can be produced by changes of the internal variables, no one involves a decrease of the function ψ, the system is certainly in equilibrium; and that if any change of state actually takes place, the change must involve a decrease of ψ. In other words: when the temperature and the external variables are kept constant, ψ tends continually to decrease, and when it has reached a minimum, the system is in stable equilibrium. The condition, that $\delta\psi = 0$, might refer to a maximum value of ψ; but this would correspond to a state of unstable equilibrium. Since no such state can be realized in practice, it is unnecessary to consider the maxima of ψ.

In these modifications of state during which both the temperature and the external variables are constant, the function ψ plays a role analogous to that of the potential of the internal forces in the case of a dynamic system upon which no forces are acting from outside. For this reason, M. Duhem has given to ψ the name of the *internal thermodynamic potential* of the system. We have already seen (art. 123) that the same function, when looked at from a different point of view, acts as a characteristic function.

Remarks on the Variables

148. The external variables are the only ones over which we have any direct control. For if a change of state involves no outside work, we can not influence the change, directly and arbitrarily, by the application of outside actions of the nature of forces. We are, however, at liberty to suppose arbitrary variations imposed upon the internal variables in the course of our theoretical reasoning, even though we can not produce such variations at will.

As a familiar example of an internal variable, we may cite the quantity x, occurring in the set of variables (x, v, θ) which, as we saw at the end of article 55, might be used to define the state of a mass of fluid. We can not control directly the ratio x, between the masses of the two phases of the fluid which are, or may be, present; *i.e.* we can not, by the application of an appropriate force, give the variable x arbitrary values, independent of the volume v and the temperature θ; at least, this can be done only when the two phases are in equilibrium. Nevertheless, we saw that without x, the set of variables did not entirely satisfy the fundamental condition of sufficing for a unique determination of the outside actions which would preserve any given state of the mass, as a state of equilibrium.

The internal variables are sometimes entirely overlooked, in statements regarding the internal thermodynamic potential; and the processes performed by a system are spoken of, as if changes in its state must be due to changes of the external variables. If there were, in fact, no internal variables, a system that had both its temperature and its external variables fixed in value, would be incapable of any change of state whatever; and theorems regarding the changes of ψ would, under such circumstances, cease to have any meaning.

In the class of problems now under discussion, the internal variables are the only ones that change their values; and to investigate the changes in ψ, we have to find how it is influenced by changes in these variables. That the value of ψ may be affected by such changes is obvious: for the statement that

$$X_i \delta x_i = 0,$$

which defines an internal variable, by no means implies that

$$K_i \delta x_i = \delta Q_i = 0;$$

so that ϵ, η, and ψ are functions of the internal variables and

[illegible]

change with them, though the temperature and the external variables may not vary.

149. The most common class of problem in practice is that in which the system to be studied is subject to no outside actions except a uniform, normal pressure on its bounding surface. In such problems, the state of the system may be determined by the normal variables $x'_i, x''_i, \dots x^{n-1}_i, v, \theta$. The internal thermodynamic potential of such a system is

$$\psi = \epsilon - \theta\eta, \quad\text{.........................(179)}$$

where ϵ and η, and consequently ψ, are functions of all the variables, and not merely of v and θ.

The necessary and sufficient condition for the equilibrium of such a system, when kept at constant temperature, is, that for all possible changes of state which leave the temperature constant, we shall have

$$\delta\psi \geqq -p\,\delta v. \quad\text{.........................(180)}$$

The condition of the possibility of any change is, that it must be one for which

$$\delta\psi < -p\,\delta v, \quad\text{.........................(181)}$$

Suppose that both the temperature and the volume are kept constant, so that only the internal variables can alter their values; the condition of equilibrium then takes the form

$$\delta\psi \geqq 0\,; \quad\text{..............................(182)}$$

and the condition of the possibility of a given change is, that the change shall make

$$\delta\psi < 0, \quad\text{..............................(183)}$$

In the treatment of problems of this nature, ψ is often called the *thermodynamic potential at constant volume.*

The mass of fluid discussed in article 55 offers an illustration of the sort of system just mentioned, there being one internal variable in addition to the temperature. If a system be composed of a mixture of several substances, various changes of phase may be possible. There may be present, simultaneously, a gaseous phase, one or more liquid phases, and one or more solid phases. The number of internal variables must be sufficient to determine completely the masses and compositions of all the phases.

Total Thermodynamic Potential of a System at Constant Temperature

150. It may happen that the generalized forces acting on the system have a potential V. In other words; the outside actions may give to the system, during any variation of its state, an amount of energy which depends solely on the initial and final, and not on the intermediate states. Under these circumstances, the work of the generalized forces may be written

$$\delta W = \sum X \delta x = -\delta V, \qquad \text{(184)}$$

and the conditions (173) and (174) may be thrown into the form

$$\delta(\psi + V) \geqq 0 \qquad \text{(185)}$$

for equilibrium, and

$$\delta(\psi + V) < 0 \qquad \text{(186)}$$

for possibility of change of state.

For a system subject to such forces, the function $(\psi + V)$ acts as a potential in isothermal changes of state, just as ψ alone did when the outside work was zero: hence $(\psi + V)$ has received from M. Duhem the name of the *total thermodynamic potential* of the system. The system will be in a state of stable equilibrium when $(\psi + V)$ has decreased to a minimum, and not until then.

151. There are two important cases in which the generalized forces do have a potential. The first of these is the case where the external variables are kept at fixed values, so that the external forces do no work at all, and $\delta W = 0$. The total thermodynamic potential is then identical with the internal potential ψ, so far, at least, as its variations are concerned.

The second case is that of constant generalized forces. The potential of the outside actions is, in this case,

$$V = -\sum Xx, \qquad (187)$$

the work done on the system during a change of state being the decrease of the potential, or

$$-\delta V = \sum X\delta x.$$

Any system subject to outside actions that are represented by constant generalized forces has, therefore, a total thermodynamic potential, of which the expression is $(\psi - \sum Xx)$, or

$$\epsilon - \theta\eta - \sum Xx = \zeta. \qquad (188)$$

The familiar function ζ acts, we see, as a thermodynamic potential for constant forces and constant temperature; and the conditions of equilibrium, and of possibility of change of state, may be written;

$$\delta\zeta \geqq 0, \qquad (189)$$

for equilibrium, and

$$\delta\zeta < 0, \qquad (190)$$

for change.

If the only outside action is a uniform, normal pressure on the bounding surface of the system, ζ takes the form

$$\zeta = \epsilon - \theta\eta + pv, \qquad (191)$$

and it is then known as the ***thermodynamic potential at constant pressure.***

Further Remarks on Internal and External Variables

152. The changes to which the value of ζ is subject when the outside actions are constant, will not, in general, be due solely to changes in the internal variables: that would mean, that a system having no internal variables except the temperature would, under the action of constant forces, be incapable of any isothermal change of state at all, and we cannot assert that this is the case.

A mass of gas, if homogeneous and not subject to internal chemical change within the range of temperature and density considered, may have its state completely defined by the temperature θ, an internal variable, and the volume v, an external variable with the generalized force $(-p)$. If the temperature is kept constant, the only changes possible are those defined by changes in the volume. If the pressure acting on the gas is kept constant, the gas expands or contracts, until its volume is such that the pressure of the gas, in a state of equilibrium at that volume, is the same as the constant pressure applied from outside. When this stage has been attained, the gas is in equilibrium, but not until then. This may be expressed by the truism, that the inverse variables $(-p, \theta)$ do not fix the state of the system unless it is already in equilibrium. We can evidently not use the inverse variables to define the state of the system, when considering any changes except infinitesimal displacements from a state of equilibrium, and in other cases we must think of the state as defined by the original variables.

To this illustration, the objection may be made, that it violates the condition that the processes considered shall not involve any appreciable kinetic energy: the objection is valid, but the example has been introduced merely as an analogy and not as an actual illustration.

153. If the system has no internal variables except the temperature, which is constant, it will, if the forces are once adjusted to a state of equilibrium and kept constant, retain that state indefinitely. But if there are one or more internal variables, and the forces are merely so adjusted that they would preserve equilibrium if the internal variables could be constrained to keep the values they have at the instant in question, the state will not, in general, be one of equilibrium. For the internal variables can not be thus constrained. The freedom of the internal variables permits a change of state, even though the forces be constant. The change goes on in the direction of decreasing ζ, and comes to an end when ζ has reached a minimum.

154. The transformations thus permitted by the existence of the internal variables, are not necessarily expressible in terms of them alone, for variations of the external variables may also be involved.

To illustrate this point, let us consider another homogeneous gaseous system, but this time, one which is capable of an internal chemical change. The state of the system will depend upon one or more internal variables, beside θ and the external variable v.

At high temperatures, nitrogen dioxide, N_2O_4, decomposes or dissociates partially, according to the reaction

$$N_2O_4 \rightleftarrows 2NO_2.$$

This reaction, like many similar ones, goes on, not instantaneously, but at a measurable rate, depending on the temperature. It resembles, in some respects, a process of change of the configuration of a purely dynamic system, which has its motions strongly damped by viscous resistances, but has no frictional resistances to prevent its having equations of equilibrium.

The state of a given mass of the mixture of N_2O_4 and its dissociation product NO_2, may be defined by the normal variables (x, v, θ), x being the fraction of the whole mass which is present in the form NO_2. Let us suppose, that at the start we have the gas at ordinary atmospheric pressure and temperature. If it has been kept for some time under these conditions, most of the mixture will be in the undissociated state, corresponding to the formula N_2O_4. Let the temperature be now raised, suddenly, to a much higher point, say 400°, and then kept constant. The gas mixture, under these new conditions, is no longer in a state of equilibrium: a further decomposition into NO_2 takes place, and this change of composition is made evident* by the accompanying increase of volume, one volume of N_2O_4 giving two volumes of NO_2. The modification of state which we here choose to look

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* We are here supposing that the chemistry of the process has been thoroughly investigated, so that the quantities of N_2O_4 and NO_2 present are known, or may be found, quite independently of the volume.

upon as due to a change of the internal variable x, is accompanied by a change of the external variable v. During this change the total thermodynamic potential ζ decreases toward a minimum, and when this has been attained the reaction comes to an end.

If, after the temperature had been made stationary, the volume also had been fixed, the change of the internal variable x would have involved an increase of the pressure. The direction of the process and the condition of equilibrium would then have been seen by the consideration of the changes of the internal thermodynamic potential ψ.

155. It has just been shown, in a particular case, that the change of an internal variable, while the temperature and the forces are constant, may involve a change in the value of an external variable. The opposite is also possible: an internal variable may change without influencing the value of any external variable.

Let the system to be considered be a homogeneous gas mixture, which consists, in its initial state, of chemically equivalent masses of iodine vapour and hydrogen. These gases tend to unite and form hydrogen iodide, according to the reaction

$$H_2 + I_2 \qquad 2HI.$$

If the pressure and temperature be kept constant, the reaction goes on slowly at low temperatures, and faster, as the temperature at which the reaction occurs is raised to a higher and higher point.

The state of the mixture may be defined by the normal variables (x, v, θ), where x is the ratio of the mass of hydrogen iodide present to that which would be produced by complete combination of the two elementary components of the mixture. The process which goes on, is a change in the value of x; and in the present case the external variable, the volume, does not change with x or, at most, only very slightly. For in the production of two volumes of the hydrogen iodide, one volume of hydrogen and one volume of iodine vapour vanish. The direction of the transformation and the coordinates of the state of equilibrium are, as before, to be found by considering the changes in ζ, as the reaction goes on. If the temperature and the volume had been kept constant, instead of the temperature and the pressure, the nature of the possible changes would have been evident from the consideration of the alterations in the value of the internal thermodynamic potential ψ. If the reaction causes no change at all in the volume, the variations of ψ and of ζ are identical, so that it is of no importance which one of these functions we use.

Isentropic Potentials

156. The isothermal potentials ψ and ζ are of especial practical importance, on account of the ease with which we can keep the temperature of a system of bodies, on which we are working, nearly constant. Theoretically, however, there is nothing to prevent our keeping other quantities than the temperature constant.

The relations
$$\delta\epsilon \leqq \theta\delta\eta + \sum X\delta x, \qquad \text{(192)}$$
and
$$\delta\chi \leqq \theta\delta\eta - \sum x\delta X, \qquad \text{(193)}$$
show that ϵ and χ might be used as potentials, if the entropy and the external variables, or the entropy and the generalized forces were constant. In other words: the functions ϵ and χ might be used as internal and total *isentropic thermodynamic potentials.* Practically, however, we have no such simple means of keeping the entropy of a system constant as we have for the temperature; so that this way of looking at ϵ and χ is mainly of theoretical interest.

The Entropy Principle

157. The fundamental relation,
$$\delta\epsilon \leqq \theta\delta\eta + \sum X\delta x,$$
may be thrown into the form
$$\delta\eta \geqq \frac{1}{\theta}\delta\epsilon - \frac{1}{\theta}\sum X\delta x. \qquad \text{(194)}$$

If this statement be applied to a completely isolated system, it reduces to

$$\delta\eta \geqq 0\,; \qquad\text{......................................}(195)$$

for complete isolation implies constancy of the total energy ϵ, and absence of all outside work $\sum X\delta x$. We are thus led back to the **Principle of the Increase of Entropy.** If we consider only isolated systems, or if we include in the system all the bodies which are influenced in any way whatever by the changes of state of the bodies under our more particular scrutiny, the function $(-\eta)$ may be used as a potential. It acts as a potential for constant energy and constant external variables; for in the case of an isolated system, there are no external variables, because there are no outside actions. Any actual variation of state will involve an increase of the entropy of the system, and when the entropy has reached a maximum, the system will be in stable equilibrium.

It should be noted here, however, that we must not, without further enquiry, apply this principle to systems that do not have a uniform temperature; for our whole proof of the existence of the function η, which is called entropy, has assumed that the system under consideration had a uniform temperature. Before making such an application, we should have to extend the idea of entropy to system in which the temperature was variable from point to point.

158. If we attempt to find a function which shall act as a potential when the energy and the outside actions are constant, we are led to the expression

$$\theta\delta\eta + \sum \delta(Xx) \geqq \delta\epsilon + \sum x\delta X. \qquad\text{...............}(196)$$

In order to have, in the first member, the variation of a function of the variables which define the state of the system, we are here obliged to make the additional condition, that the temperature θ shall be constant, as well as the internal energy and the outside actions. If we let

$$\omega = -(\theta\eta + \sum Xx), \qquad\text{......................}(197)$$

we have, for constant temperature,

$$(\delta\omega)_\theta \gtreqless \delta\epsilon + \sum x\delta X ; \quad\text{.........................}(198)$$

so that ω acts as a potential, for constant energy, temperature and forces. These conditions are too complicated and artificial to deserve further consideration.

The Free Energy Principle

159. Let us return to the statements that

$$\left.\begin{array}{l}\delta\psi = \sum X\delta x, \\ \delta\psi < \sum X\delta x,\end{array}\right\} \quad\text{..........................}(199)$$

for **isothermal modifications** of state which are reversible and irreversible, respectively. The work done by the system and obtainable from it during any infinitesimal, isothermal variation of its state is expressed by $-\sum X\delta x$, which will be zero unless some of the external variables are involved in the change. Hence if we represent by F_A^B **the work obtainable from the system** while it passes isothermally from a state A to a state B, we have, by integrating (199),

$$\psi_B - \psi_A \lesseqgtr \int_A^B \sum X\delta x = -F_A^B,$$

or

$$F_A^B \gtreqless \psi_A - \psi_B. \quad\text{..............................}(200)$$

This tells us, that the work which the system can do, during any real isothermal change of state, is less than the decrease of its internal thermodynamic potential ψ. By comparison with the two statements (199), we see, that as the passage from A to B is made more and more nearly reversible, the work obtainable from the change approaches, as its limiting value, the decrease of ψ during the process. This decrease is entirely definite, whether the process be reversible or not. For the value of ψ is given by the equation

$$\psi = \epsilon - \theta\eta ; \quad\text{..........................}(201)$$

and both ϵ and η are functions only of the variables which define the two states. On account of this property of the function ψ, Helmholtz[*] gave it the name of the FREE ENERGY of the system. The free energy principle may therefore be stated as follows: *The work obtainable from a system during any isothermal change of its state is, at most, equal to the decrease of the free energy of the system.*

In all reversible processes we have

$\delta\psi = \delta\epsilon - \theta\delta\eta - \eta d\theta$

$$\delta\epsilon = \theta\,\delta\eta + \sum X\delta x,$$

or

$$\delta\psi = -\eta\,\delta\theta + \sum X\delta x;$$

whence it is evident that

$$\eta = -\left(\frac{\partial\psi}{\partial\theta}\right)_x.$$

We may therefore write equation (201) in the form

$$\psi = \epsilon + \theta\left(\frac{\partial\psi}{\partial\theta}\right)_x, \qquad\text{.................................(202)}$$

an equation which is often used as an expression of the free energy principle, and which may be interpreted as follows: *In any isothermal modification of the state of a system, the work obtainable from the process is, at most, equal to the decrease of the internal energy of the system, plus the product of the absolute temperature and the rate of increase of the work obtainable with increase of temperature.* Equation (202) may also take the form

$$\epsilon = -\theta^2\frac{\partial}{\partial\theta}\left(\frac{\psi}{\theta}\right), \qquad\text{.........................(203)}$$

in which it is sometimes useful.

160. Equation (202) might have been obtained directly from the equation

$$\frac{\delta Q}{Q} = \frac{\delta\theta}{\theta}. \qquad\text{..............................(204)}$$

Let a system pass reversibly, at the temperature $\theta + \delta\theta$, from a state A to a state B. Let it then be cooled to the temperature θ, and returned, by a reversible process at the temperature θ and

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[*] Helmholtz, *Wissensch. Abhandl.*, **2**, p. 958.

an infinitesimal rise of temperature, to its original state. The successive states in one of the isothermal processes are supposed to be identical with the corresponding states in the other, except as regards the temperature. The system has thus performed a reversible cycle between two temperatures infinitely near together.

If we let P be the work obtainable from the system during its passage from A to B at the temperature θ, and let $P+\delta P$ be the work obtainable from the same process at the temperature $\theta+\delta\theta$, the total work given out by the system during the cycle is the difference of these, or δP. During the process at the higher temperature, the energy of the system decreases by

$$\left[\epsilon+\frac{\partial\epsilon}{\partial\theta}\delta\theta\right]_A-\left[\epsilon+\frac{\partial\epsilon}{\partial\theta}\delta\theta\right]_B.$$

Therefore, since the whole work done is $P+\delta P$, the heat which the system must have taken in in order to keep its temperature constant, is

$$(P+\delta P)-\left[\epsilon+\frac{\partial\epsilon}{\partial\theta}\delta\theta\right]_A+\left[\epsilon+\frac{\partial\epsilon}{\partial\theta}\delta\theta\right]_B=Q.$$

We therefore have, by equation (204),

$$\frac{\delta P}{Q}=\frac{\delta\theta}{\theta+\delta\theta},$$

or, at the limit,

$$\frac{\delta P}{P-(\epsilon_A-\epsilon_B)}=\frac{\delta\theta}{\theta};$$

whence

$$P=(\epsilon_A-\epsilon_B)+\theta\frac{\partial P}{\partial\theta}.$$

If instead of $(\epsilon_A-\epsilon_B)$ we write simply ϵ, understanding by this the decrease of the internal energy of the system during the passage from A to B, the last equation reduces to

$$P=\epsilon+\theta\frac{\partial P}{\partial\theta}. \qquad \text{(205)}$$

Since P is the work obtainable from the system,* it has precisely the same significance as the free energy of Helmholtz, so that

* in a reversible process.

equations (202) and (205) are identical in meaning. Although this deduction is more elementary than the one first given, and comes more directly from the theorems of Carnot and Clausius, it is less easy to analyze and less clear—so, at least, it appears to the writer.

The reader will find many interesting examples of the practical application of this principle in Nernst's *Theoretical Chemistry.** One illustration will be given in the next chapter, together with an example of the use of the thermodynamic potential.

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* Nernst,, *Theoretische Chemie*, 2nd. ed., Stuttgart, 1898.

CHAPTER XIII

APPLICATIONS

Electromotive Force of a Reversible Galvanic Cell

161. We have already (arts. 135 and 136) obtained a relation between the electromotive force of a reversible galvanic cell and the heat of the reactions involved when the cell is giving out a current. We shall now give another deduction of the same result, by using the free energy equation,

$$\psi = \epsilon + \theta\frac{\partial\psi}{\partial\theta}, \quad \text{..........................(206)}$$

of which the interpretation has been given in article 159.

Let the cell, at the temperature θ, have an electromotive force E when its poles are disconnected. Let a unit quantity of electricity pass through the cell reversibly, in the positive or natural direction. The outside work, obtainable from the cell during this process, is evidently equal to the electromotive force, so that we have*

$$\text{[illegible]} = \psi = E e \qquad \frac{\partial\psi}{\partial\theta} = \frac{\partial E}{\partial\theta} e \quad \text{......................(207)}$$

The decrease of the internal energy during the process is the same as if the cell had gone from the same initial to the same

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* We are, as before, disregarding the slight changes of volume of the cell as of negligible importance: in the case of a gas battery, this would, of course, not be allowable.

final state, through any other set of intermediate states. If the cell had changed its state merely by direct chemical reaction, without producing any current, it would, at constant temperature, have developed a quantity of heat λ, where λ is the heat of reaction for quantities of the various substances equal to those actually involved in the reactions which accompany the passage of a unit of electricity through the cell. Hence its internal energy would have decreased by λ,—which is, therefore, the decrease for any path between the same two states. We have, consequently, for the value of the term ϵ, in equation (206),

$$\epsilon = \lambda,$$

and equations (206) and (207) give us

$$\mathfrak{e} E = \lambda + \theta \frac{\partial E}{\partial \theta} \mathfrak{e} \quad \text{......................(208)}$$

the same equation that we obtained in articles 135 and 136.

The mathematical formulae which we have used are the same in substance, in all three deductions: any one of the methods is equivalent to either of the others. The only difference is in the physical way of looking at the matter. To those who have grasped the notion of free energy, the present proof of equation (208) will probably seem the most satisfactory; because, admitting the truth of equation (206) as established, it is more simple than the method which uses a reversible cycle, and less mathematically abstract than the consideration of changes of entropy.

Equilibrium of Phases

162. We have already shown, in article 137, that when two phases of a single substance are in equilibrium, the temperature and pressure needed for the state of equilibrium are connected by the equation

$$\frac{\partial p}{\partial \theta} = \frac{\lambda_{12}}{\theta (v_2 - v_1)}, \quad \text{........................(209)}$$

where v_1 and v_2 are the specific volumes in the first and second states, respectively, and λ_{12} is the latent heat absorbed in the transformation of unit mass of the substance from the first to the second phase. If the phases are solid and liquid, this equation defines a curve in the (p, θ) plane (Fig. 27), such that all the points representing simultaneous values of the pressure and temperature for equilibrium of the liquid and the solid phases lie on this curve.* We may call this the solid-liquid or fusion curve (*SL*). Since the change of volume in melting is always small, the term $(v_2 - v_1)$ is always small: therefore $\frac{\partial p}{\partial \theta}$ is large, and the curve rises steeply as θ increases,—or, for substances like ice which contract in melting, as θ decreases.

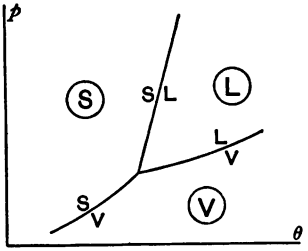

FIG. 27.

If we now let v_3 be the specific volume of the substance in the state of saturated vapour, and let λ_{23} be the latent heat of evaporation, we have in the same way, the equation

$$\frac{\partial p}{\partial \theta} = \frac{\lambda_{23}}{\theta(v_3 - v_2)}. \qquad \text{.........................(210)}$$

This is the differential equation of the liquid-vapour, or evaporation curve (*LV*), the points of which give the temperatures and pressures at which the liquid and gaseous phases can coexist. Since v_3 is, in general, for temperatures near the freezing point,

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* To plot the curve we must, of course, know by experiment the position of some one point through which it passes, in addition to knowing the values of v_1, v_2, and λ, as functions of p and θ.

enormously greater than v_2, while λ_{23} is not so much greater than λ_{12}; it follows, that at temperatures near the ordinary freezing point of the substance, the term $\frac{\partial p}{\partial \theta}$ is less than for the curve (*SL*), or the evaporation line is less steep than the fusion line.

Now consider the equilibrium between the solid and the gaseous phases. By reasoning like that used in the former cases, we obtain the equation

$$\frac{\partial p}{\partial \theta} = \frac{\lambda_{13}}{\theta(v_3 - v_1)}, \qquad (211)$$

where λ_{13} is the latent heat of sublimation. This equation defines a curve, of which the points represent the pressures and temperatures needed for equilibrium of the solid and its vapour: it is the differential equation of the solid-vapour, or sublimation curve (*SV*).

163. It may readily be shown that these three curves meet in a point. If we disregard surface energy—that is, capillary actions—we may regard the energy, entropy, and volume of a homogeneous mass of the substance, at a given temperature and pressure, as proportional to the mass: hence ψ and ζ are also proportional to the mass, **if referring to a homogeneous body.** Let ζ_1, ζ_2, and ζ_3 be the thermodynamic potentials, at constant pressure, of a unit mass of the substance, at a given temperature and in the solid, liquid, and gaseous states, respectively. These potentials are functions of the normal variables (v, θ), or also, since we are considering only states of equilibrium, of the inverse variables ($-p$, θ). Let us consider the system at a time when it contains a mass m_1 of the first phase and a mass m_2 of the second phase, the sum of these masses being constant and equal to the total mass: we have, then,

$$m_1 + m_2 = \text{constant}. \qquad (212)$$

The potential for the whole system, at constant pressure, is

$$\zeta = m_1\zeta_1 + m_2\zeta_2. \qquad (213)$$

If the system is to be in equilibrium as regards changes in the relative masses of the two phases, we must have, during any such change,

$$\delta\zeta \geqq 0.$$

But since, if both phases are actually present, any virtual change in one direction may also take place in the opposite direction, the sign of inequality is excluded, and we must have, as the condition of equilibrium,

$$\delta\zeta = 0. \qquad\qquad (214)$$

By equation (213), this condition may be expressed as

$$\zeta_1 \delta m_1 + \zeta_2 \delta m_2 = 0; \qquad\qquad (215)$$

for the change is supposed to take place at constant pressure and temperature, so that ζ_1 and ζ_2 are constant. But by equation (212) we have $\delta m_1 + \delta m_2 = 0$: hence the condition of equilibrium may be written:

$$\zeta_1 - \zeta_2 = 0. \qquad\qquad (216)$$

This equation must be satisfied for all points on the line (SL), and since ζ_1 and ζ_2 are functions of the pressure and temperature, it follows that (216) is in reality an equation between p and θ. In other words: (216) is equivalent to the integral equation of the fusion curve.

Similar reasoning may be applied to the other two pairs of phases, (LV) and (SV), so that we have, as the equations of the three curves:

$$\left.\begin{aligned} \zeta_1 - \zeta_2 &= 0, \\ \zeta_2 - \zeta_3 &= 0, \\ \zeta_3 - \zeta_1 &= 0. \end{aligned}\right\} \qquad\qquad (217)$$

It is evident at once from the form of these equations, that any point lying on two of the curves lies also on the third; or if two of the curves pass through a point, the third passes through the same point. That the curves do not coincide through any finite distance, nor even have contact, is shown by the different values of $\frac{\partial p}{\partial \theta}$ obtained, for given pairs of values of p and θ, from the equations (209), (210) and (211). Now it is always possible, by warming a solid in contact with its saturated vapour, to reach the melting point. Further addition of heat, at constant pressure, causes the liquid phase to appear and to grow, at constant temperature, at the expense of the solid phase until there are present only liquid and vapour, after which, further addition of heat, if accompanied by proper regulation of the pressure, takes the system to points on the curve (*LV*). Hence we always do have two of the curves intersecting—or at least meeting—and it follows, that there is always at least one point where the three curves meet. Such a point is called a triple point; for it is evident that at the temperature and pressure represented by this point, all three phases can coexist in equilibrium. For this particular point, we have:

$$\zeta_1 = \zeta_2 = \zeta_3, \tag{218}$$

164. If the representative point passes along one of the curves toward the triple point, there being always two phases in equilibrium, when the triple point is reached, the third phase appears, and we have the three phases coexistent. By proper regulation of the pressure and by proper supply or withdrawal of heat, any one of the phases may be made to disappear and the representative point may be made pass out along any one of the three equilibrium curves.

If, after leaving the triple point, the pressure and the temperature are not so changed as to continue to satisfy the equation of one of the curves, the representative point will pass into one of the three fields Ⓢ, Ⓛ, and Ⓥ. Suppose, for instance, that after moving out a certain distance on the evaporation curve (*LV*), we attempt, by reducing the volume, to increase the pressure at constant temperature: the result will be that the vapour will begin to disappear, and as long as both phases are present, the pressure will remain constant. After the vapour has all been condensed, the pressure may be raised as much as we like and the representative point enters the field Ⓛ. Unless we go so far as to reach a point on the fusion curve (*SL*), only the liquid phase will be present. If, on the other hand, we had attempted by increasing the volume to diminish the pressure, the liquid would have evaporated, the gaseous phase growing at the expense of the liquid, until only the vapour remained. Further increase of volume would then have been accompanied by a decrease of pressure, and the representative point would have entered the field Ⓥ, of which the points represent possible states of the unsaturated vapour.

Similar reasoning may be applied to all the curves, and we see that in the field Ⓢ only the solid phase, in the field Ⓛ only the liquid phase, and in the field Ⓥ only the gaseous phase can exist in absolutely stable equilibrium. This may be expressed analytically, by saying that in the field Ⓢ

$$\zeta_1 < \zeta_2,\ \zeta_1 < \zeta_3; \qquad (219)$$

in the field Ⓛ

$$\zeta_2 < \zeta_1,\ \zeta_2 < \zeta_3; \qquad (220)$$

and in the field Ⓥ

$$\zeta_3 < \zeta_1,\ \zeta_3 < \zeta_2. \qquad (221)$$

165. The system we have been discussing offers an example of one whose state may be defined by more than two independent variables. The normal variables which it is most natural to select are v, θ, m_1, and m_2, the mass of the third phase being connected with m_1 and m_2 by the equation

$$m_1 + m_2 + m_3 = \text{constant}.$$

It is evident that m_1 and m_2, like θ, are internal variables: the only external variable is v, and its generalized force is $(-p)$. For given values of these normal variables, the system can be in equilibrium, only under the action of a definite pressure,—they give a unique determination of the pressure needed for equilibrium.

The inverse variables are $-p$, θ, m_1, m_2, and if the system is in equilibrium—the only case in which the inverse variables can be employed—the inverse variables determine a single possible volume, if more than one phase is present. If, however, the system remains homogeneous, there may, perhaps, as stated in article 55, be more than one possible volume, but not a continuous infinity of volumes.

Though we have treated *two* of the quantities m_1, m_2, m_3 as independent variables in seeking the conditions of equilibrium, that condition, when found, leaves the system with only two instead of four degrees of freedom. If all three phases are present, both the pressure and the temperature are fixed and can not receive even infinitesimal variations; but the masses of two of the phases may be varied arbitrarily,—within limits imposed by the total mass of the substance. If two phases are present, either the pressure or the temperature may be varied arbitrarily, but only one of the masses, the other being then determined by the first. If only one phase is present, both the pressure and the temperature may be varied arbitrarily, but the mass of the single phase is constant.

166. Our general result may be stated as follows:

I. Three phases of a single substance may coexist for one or more discrete points in the (p, θ) plane. For such a set of coexistent phases, no variation of either p or θ is possible, without the disappearance of at least one of the phases. The system of phases may be called a *nonvariant system.*

II. Two phases may coexist at points lying along certain lines in the (p, θ) plane. One of the variables (p, θ) may be changed arbitrarily; but if the two phases are to continue in equilibrium, the other variable must have a value determined by that of the first. The system is capable of one arbitrary variation of state, and may be called a *univariant system.*

III. At any other point in the plane, only one phase can exist in absolutely stable equilibrium. Its temperature and pressure may be varied independently, so long as only one phase is present. The system is now capable of two independent, arbitrary variations of state, and may be called a *bivariant system.*

The triple point is sometimes called a *point of transition,* because as the representative point passes through it, following first one and then another of the curves, one phase disappears and another appears in its place. The curves (SL), (LV), and (SV) are often known as the *boundary curves* for the given set of phases.

167. In practice, it is found impossible to follow the sublimation curve above the triple point. The triple point, when the phases under discussion are solid, liquid, and vapour, is the melting point of the solid under the pressure of its saturated vapour; and when this temperature is reached, the solid invariably begins to melt, unless the pressure is changed so as to keep the representative point in the field Ⓢ (Fig. 28) or on the curve (SL). It is thus not possible to find points in the field Ⓛ, which correspond to the coexistence of the solid and its vapour.

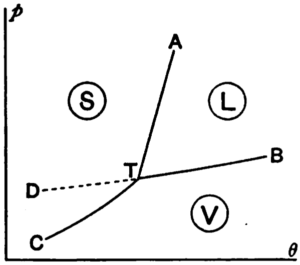

FIG. 28.

By using proper precaution, it is, however, possible to cool a liquid in contact with its vapour below the freezing point, and we may thus reach points on the curve (TD) which is the continuation of the liquid-vapour curve. The points on the curve (TD) represent states of equilibrium of the liquid and gaseous phases, but not states of absolutely stable equilibrium. The equilibrium is not unstable; for though it may easily happen that a sudden change of the liquid into the solid form is induced by some slight disturbance, yet such a finite change is not caused by an infinitesimal disturbance. The two phases are in a state of equilibrium, but the state is not the most stable possible at the given temperature and pressure. Such states of equilibrium, which are not unstable, neutral or absolutely stable—*i.e.*, the most stable possible under the given conditions—are known as *metastable states.*

For all the points on the curve (TD) we have the relation

$$\zeta_2 = \zeta_3 > \zeta_1; \qquad \text{(222)}$$

or in other words: if the two coexistent phases change into the third, the system will finally have a smaller thermodynamic potential and will be in a state of more stable equilibrium —the most stable possible at the given temperature and pressure.

All the relations of the different states of equilibrium possible to a fixed mass of a single substance, may be much more clearly represented by the use of surfaces. If at every point of the (p, θ) plane we erect a perpendicular, and mark off on it lengths proportional to the values of ζ_1, ζ_2, and ζ_3, the assemblage of points thus obtained will lie on three surfaces—or three sheets of a single surface—intersecting in curves, of which the curves (SL), (LV), and (SV) (Fig. 27) are the projections on the (p, θ) plane. The relations between ζ_1, ζ_2, and ζ_3, and the relative stability of certain states, may be seen at once from the form of the surfaces. The consideration of these thermodynamic surfaces would, however, lead us too far away from our immediate object, which is a mere illustration of the theoretical principles already deduced. For the study of such thermodynamic surfaces we may refer the reader to Gibbs.* Many examples of their use will be found in various papers which have appeared in the *Zeitschrift für physikalische Chemie*, by van der Waals and others.†

168. It has not yet been proved that the sublimation curve (TC) (Fig. 28) really does lie below the continuation (TD) of the

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* Gibbs, *Trans. Conn. Acad.*, **2**, p. 382; **3**, p. 172-189; also *Thermodynamische Studien*, Leipzig, 1892.

† van der Waals, **5**, p. 133 (1890).

evaporation curve; but we may easily do so, by referring to the differential equations of the two curves,—namely

$$\frac{\partial p}{\partial \theta} = \frac{\lambda_{23}}{\theta(v_3 - v_2)}, \quad \text{.........................} (233)$$

$$\frac{\partial p}{\partial \theta} = \frac{\lambda_{13}}{\theta(v_3 - v_1)}. \quad \text{.........................} (224)$$

Let us consider the curves at points infinitely near the triple point; that is, let us see how they are arranged upon starting out from the triple point. In the first place, p and θ may be treated as the same for both curves. In the second place, since v_3 is very much larger than v_1 and v_2, which are nearly equal, we have

$$v_3 - v_2 = v_3 - v_1,$$

very nearly. But $\lambda_{13} > \lambda_{23}$: at the triple point, in fact,

$$\lambda_{13} = \lambda_{12} + \lambda_{23},$$

—or the latent heat of sublimation is the sum of the latent heats of fusion and of evaporation. For direct sublimation leads, by a process involving the same amount of external work, to the same final state as successive fusion and evaporation. It follows, that $\frac{\partial p}{\partial \theta}$ is greater for the sublimation curve than for the prolonged evaporation curve. Hence, as it leaves the triple point, it at first sinks faster than the evaporation curve, and it always remains below, unless it returns to meet the evaporation curve in a new triple point. The vapour pressure of a solid is, therefore, always less than that of the supercooled liquid at the same temperature.

169. The conclusions reached, as to the possible states of equilibrium of a substance which can separate into a solid, a liquid, and a gaseous phase, are quite general. The phases may also be two allotropic solid forms of the substance and a liquid or a gaseous phase. Whatever the possible phases, so long as there is present only a single, chemically definite substance, three coexistent phases form a nonvariant system, two a univariant system, and one a bivariant system.

This statement is a particular case of a general theorem, due to Gibbs and known as the PHASE RULE. The theorem may be stated somewhat as follows:

Let us consider a system consisting of one or more different phases in contact with one another, each phase being homogeneous. Let the phases consist of mixtures, in various proportions, of **K different* substances**, the mass of each one of the substances contained in any one of the phases being variable independently of the masses of the other substances in that phase. Let the only outside action be a uniform pressure on the bounding surface of the system of phases:

Then the maximum number of phases that can exist simultaneously in a state of equilibrium is $(K+2)$. This number of phases can coexist only for particular discrete points in the (p, θ) plane, and the phases form a nonvariant system.

If $(K+1)$ phases are coexistent, they form a univariant system, the relation of the pressure and temperature needed for equilibrium being shown by lines in the (p, θ) plane.

Any number of phases less than $(K+1)$ may coexist in equilibrium at other points in the (p, θ) plane.

From any multiple point where $(K+2)$ phases can exist together in equilibrium, $(K+2)$ boundary curves start out, along any one of which $(K+1)$ phases may coexist, forming a univariant system.

We shall now proceed to give a partial proof of these statements. The discussion will not be either complete or rigorous: for a thorough treatment of the subject the reader may be referred to the original memoir of Professor Gibbs.*

The Phase Rule

170. Let the system be composed of a mixture of **K substances** $S_1, S_2, \dots S_K$: let the total amount of each of the substances be

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* Gibbs, *Trans. Conn. Acad.*, **3**; compare also Riecke, *Zeitschr. für phys. Chem.* **6**, p. 268 (1890); Duhem, *Journal of Physical Chemistry*, **2**, pp. 1 and 91 (1898); and Saurel, *ibid.* 3, p. 137 (1899).

* independent of each other.

fixed. The substances must be such that it would be possible to vary the quantity of any one of them present in the heterogeneous mass, without varying the quantities of the others. Let these substances be called the *components* of the heterogeneous mass. Let the whole mass be at the uniform temperature θ, and let the only outside action be a uniform pressure p on the bounding surface. Let the pressure be uniform all through the mass: in other words, let us disregard gravity, capillarity, electrostatic forces, etc., and let no portion of the whole system be solid. Let the number of separate, homogeneous phases into which the mass is divided, be ι.

Since the only influence which one homogeneous phase can have on another is at the surface dividing the two phases, the *amount* of each phase present has no effect on the conditions of pressure, temperature, and concentration needed for equilibrium: this is a well-known experimental fact.

The components of the mass must be such that in any one phase it is possible to vary their concentrations independently. If the mass of any component in a given phase is not zero, it may receive both positive and negative variations, and it is called an *actual component* of the given phase. If in any phase a given component is not present but might be, *i.e.*, if its mass in that phase can receive positive but not negative variations, it is called a *possible component* of that phase.

We shall assume that each phase is continuous and in contact with every other phase, so that infinitesimal variations of composition need never involve motions of matter through finite distances, but only across dividing surfaces. The geometrical forms of the phases are otherwise of no importance, and do not enter into consideration.

The state of any phase of fixed composition is defined by the normal variables (v, θ), or for equilibrium, by the inverse variables $(-p, \theta)$. If the phase is considered as of variable composition, its state is defined by the values of the quantities $(v, \theta, m_1, m_2 \dots m_\kappa)$, where m_1, m_2, etc.—the masses of the various components of the phase—are internal variables. The state of the phase may also, for equilibrium, be defined by the inverse variables $(-p, \theta, m_1, m_2 \ldots m_K)$.

The state of the phase *as influencing the other phases* depends on its concentrations, and not on its total mass. Hence we may consider its state as, for this purpose, defined by the quantities

$$\left(p,\ \theta,\ \frac{m_1}{v},\ \frac{m_2}{v},\ \ldots\ \frac{m_K}{v}\right),\ \text{ or }\ (p,\ \theta,\ c_1,\ c_2,\ \ldots\ c_K).$$

I State of the system determined by the variables alone. (not by concentration)

171. The state of the whole system is determined by the values of the variables which determine the states of all its various phases. These are the following $[i(K+1)+1]$ quantities:

$$\left.\begin{array}{l} \theta,\ v',\ m'_1,\ m'_2,\ \ldots\ m'_K, \\ \quad v'',\ m''_1,\ m''_2,\ \ldots\ m''_K, \\ \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ \quad v^i,\ m^i_1,\ m^i_2,\ \ldots\ m^i_K, \end{array}\right\} \ldots\ldots\ldots\ldots\ldots\ldots(225)$$

where v^x denotes the volume of the phase x, and m^x_y, the mass of the component S_y in the phase x.

These quantities are greater in number than the degrees of freedom, or possible arbitrary variations of state of the system. We have, in the first place, the K equations:

$$\left.\begin{array}{l} \sum_1^i m_1 = \text{const.} \\ \sum_1^i m_2 = \text{const.} \\ \ldots\ldots\ldots\ldots\ldots\ldots \\ \sum_1^i m_K = \text{const.} \end{array}\right\} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(226)$$

Moreover, each phase has an equation of state of the form

$$p = f(v,\ \theta,\ m_1,\ m_2\ \ldots\ m_K)\ ;\ \ldots\ldots\ldots\ldots\ldots\ldots(227)$$

and since we have made it a condition, that the pressure shall be the same throughout the system, this gives us $(i-1)$ independent equations between the quantities of the set (225). Hence the number of variables remaining quite independent is

$$[i(K+1)+1]-K-(i-1)=iK-K+2.$$

If we use the inverse variables for the determination of the states of the separate phases, we have, for the determination of the state of the whole system, the $(iK+2)$ quantities :

$$\left.\begin{array}{l} p,\ \theta,\ m'_1,\ m'_2,\ \dots\ m'_K \\ \qquad m''_1,\ m''_2,\ \dots\ m''_K \\ \qquad \dots\dots\dots\dots\dots\dots \\ \qquad m^i_1,\ m^i_2,\ \dots\ m^i_K. \end{array}\right\} \dots\dots\dots\dots\dots\dots(228)$$

Among these there still exist the K equations of the set (226), so that the number of independent variations is as before $(iK-K+2)$, **which is the number of degrees of freedom of the system.**

II. State of system determined by concentrations

172. If we consider the state of each phase as determined by the concentrations, so far as its possible influence on the other phases is concerned, we have as our variables the $(iK+2)$ quantities

$$\left.\begin{array}{l} p,\ \theta,\ c'_1,\ c'_2,\ \dots\ c'_K \\ \qquad c''_1,\ c''_2,\ \dots\ c''_K \\ \qquad \dots\dots\dots\dots\dots\dots \\ \qquad c^i_1,\ c^i_2,\ \dots\ c^i_K\,; \end{array}\right\} \dots\dots\dots\dots\dots\dots(229)$$

or in other words ; the K relations of the set (226) are now lacking, and **the system has $(iK+2)$ degrees of freedom.** We may, then, impose *at most* $(iK+2)$ conditions upon the variables of the set (229). If we do so, not only the concentrations of all the components in all the phases, but also the temperature and the pressure, will be fixed : the system can satisfy the conditions only for certain discrete points of the $(p,\ \theta)$ plane, and it is nonvariant. If we impose $(iK+1)$ conditions, the temperature and pressure may vary, but only along certain curves in the $(p,\ \theta)$ plane, and the system is univariant. If the number of conditions imposed is less than $(iK+1)$, the temperature and pressure may vary simultaneously.

Let us now ask: What are the conditions imposed by the fact that the phases are in equilibrium, and how does the number of these conditions depend upon the number of the coexistent phases? In answering this question, we shall assume that each of the K substances, of which the system is composed, is an actual component of every one of the i phases.

173. Let us first consider **a single phase** containing the masses $m_1, m_2, \dots m_K$ of the various components, at the temperature θ and the pressure p,—the pressure being that needed to preserve the phase in equilibrium at the given temperature, when isolated from the other phases. The equation of state of the phase will have the form

$$p=f(v,\ \theta,\ m_1,\ m_2,\ \dots\ m_K). \qquad (230)$$

If the composition of the phase be invariable and the phase be subject to any reversible change of state, the variation of its internal energy is given by the equation

$$\delta\epsilon = \theta\delta\eta - p\delta v\ ; \qquad (231)$$

and the internal energy is to be regarded as a function of the entropy and the volume.

If, however, the phase be of variable composition, its internal energy must be treated as a function of the masses, as well as of the entropy and volume. This means that we may alter the energy of the phase by forcing into it, reversibly, a mass δm of any one of the components, and yet have the volume and entropy of the phase the same after the change of composition as before it. The statement about the volume presents no difficulty; but that about the entropy is not so clear in meaning. The mass δm before it is forced into the phase, has its own entropy $\delta\eta$, and if it is forced into combination with the phase, we must expect the entropy of the united mass, after the combination, to be different from the entropy of the phase alone at the beginning of the process. We may, however, during the process, add to or take away from the phase, such a quantity of heat as just to offset the increase of the entropy which would be caused if the forcing in were adiabatic. We may, in other words, make this addition or withdrawal of heat such, that if the phase, with its altered composition, passes reversibly from its actual state of temperature and pressure to the normal state, keeping its composition constant, the value of the integral $\int \frac{dQ}{\theta}$ is the same as if the phase, with its original composition, had passed reversibly from the state it was then in to the same normal state. Thus the composition of the phase will have been altered, though its volume and entropy will be the same as before. The internal energy of the phase will, in general, have changed during the change of composition; for we have no reason to assume that the heat withdrawn, during the addition of the mass δm, is equal to the work done on the mass in forcing it into the phase.

If the phase be, then, considered as of variable composition, we must write

$$\epsilon = f(\eta, v, m_1, m_2, \dots m_\kappa). \qquad (232)$$

For any reversible change of state we have

$$\delta\epsilon = \left(\frac{\partial\epsilon}{\partial\eta}\right)_{v,m} \delta\eta + \left(\frac{\partial\epsilon}{\partial v}\right)_{\eta,m} \delta v + \sum_1^\kappa \left(\frac{\partial\epsilon}{\partial m}\right)_{\eta,v,m} \delta m, \qquad (233)$$

where the subscript η, v, m means, that η, v, and all the masses except that referred to in the denominator, are to be kept constant.

But we already know, that for a modification which leaves the masses unchanged, the variation of the internal energy is given by the equation

$$(\delta\epsilon)_m = \theta\,\delta\eta - p\,\delta v. \qquad (234)$$

Hence we see, that

$$\left.\begin{aligned} \left(\frac{\partial\epsilon}{\partial\eta}\right)_{v,m} &= \theta, \\ \left(\frac{\partial\epsilon}{\partial v}\right)_{\eta,m} &= -p, \end{aligned}\right\} \qquad (235)$$

Let us also write

$$\left.\begin{array}{l} \left(\dfrac{\partial \epsilon}{\partial m_1}\right)_{\eta, v, m} = \mu_1, \\ \left(\dfrac{\partial \epsilon}{\partial m_2}\right)_{\eta, v, m} = \mu_2, \\ \dots\dots\dots\dots\dots\dots\dots \\ \text{etc.} \end{array}\right\} \dots\dots\dots\dots\dots\dots\dots\dots(236)$$

We now have, as the expression for the variation of the internal energy of the phase during any reversible change of its volume, entropy, and composition, the equation

$$\delta\epsilon = \theta\,\delta\eta - p\,\delta v + \sum_1^{\kappa} \mu\,\delta m. \dots\dots\dots\dots\dots\dots(237)$$

The quantity μ^x_y is called the *potential* of the component S_y in the phase x.

174. Now consider the whole set of phases composing the system, the total masses of the various components being invariable. For any reversible, infinitesimal modification of state, we have the equation

$$\Delta\epsilon = \theta\Delta\eta - p\Delta v, \dots\dots\dots\dots\dots\dots\dots\dots(238)$$

where v is the total volume of the system, and where $\Delta\eta = \dfrac{\Delta Q}{\theta}$, ΔQ being the heat absorbed from the outside by the whole system.

If we disregard surface energy, as we have agreed to do, we have the equations:

$$\left.\begin{array}{l} \Delta\epsilon = \sum_1^{i} \delta\epsilon, \\ \Delta\eta = \sum_1^{i} \delta\eta, \\ \Delta v = \sum_1^{i} \delta v, \end{array}\right\} \dots\dots\dots\dots\dots\dots\dots\dots(239)$$

where the symbol Δ refers to the whole system, and the symbol δ

to the separate phases. By adding together the equations of the form (237) for all the phases, and remembering that for equilibrium the temperature and pressure must be uniform throughout the system, we arrive at the equation

$$\sum_1^i \delta\epsilon = \theta \sum_1^i \delta\eta - p \sum_1^i \delta v + \sum_1^i \sum_1^K \mu \delta m. \dots\dots\dots\dots (240)$$

By comparison with (239), this reduces to

$$\Delta\epsilon = \theta \Delta\eta - p\Delta v + \sum_1^i \sum_1^K \mu \delta m. \dots\dots\dots\dots (241)$$

But we know that for any reversible, infinitesimal change of state of any system taken as a whole,

$$\Delta\epsilon = \theta \Delta\eta - p\Delta v. \dots\dots\dots\dots (242)$$

Hence, if the phases are in equilibrium, so that all infinitesimal changes are reversible, we have

$$\sum_1^i \sum_1^K \mu \delta m = 0. \dots\dots\dots\dots (243)$$

Since the variations δm are all independent and arbitrary, with the exception that

$$\sum_1^i \delta m_1 = 0; \quad \sum_1^i \delta m_2 = 0; \dots \sum_1^i \delta m_K = 0; \dots\dots (244)$$

it follows, that equation (243) can be satisfied only if

$$\left.\begin{array}{l} \mu'_1 = \mu''_1 = \mu'''_1 = \dots = \mu^i_1, \\ \mu'_2 = \mu''_2 = \mu'''_2 = \dots = \mu^i_2, \\ \dots\dots\dots\dots\dots\dots \\ \mu'_K = \mu''_K = \mu'''_K = \dots = \mu^i_K, \end{array}\right\} \dots\dots\dots\dots (245)$$

These $K(i-1)$ independent equations must be fulfilled by the potentials $\mu_1, \mu_2, \dots \mu_K$, as a necessary condition of equilibrium.

As the state of the system is determined by the values of the $(iK+2)$ quantities of the set (229), these conditions of equilibrium (245) must be relations between those quantities. The potentials must, therefore, be functions of those quantities, and equations (245) are equivalent to the same number of equations between the quantities of the set (229).

175. We have for each phase an equation of state, of the form

$$p=f(v,\ \theta,\ m_1,\ m_2,\ \dots\ m_K). \quad \dots\dots\dots\dots\dots\dots(246)$$

Since the phase is homogeneous, the pressure needed for equilibrium at a given temperature depends, not on the total volume and the total masses of the components of the phase, but on their ratios, *i.e.*, on the concentrations. For to a unit volume of the phase at the same temperature and concentrations, we should have to apply the same pressure for equilibrium, as to any other volume of the phase. Hence equation (246) is, in reality, an equation connecting the pressure, the temperature, and the concentrations; and it may be written

$$\phi(p,\ \theta,\ c_1,\ c_2,\ \dots\ c_K)=0. \quad \dots\dots\dots\dots\dots\dots(247)$$

There is an equation of this sort for each one of the i phases, so that we have i additional conditions imposed upon the variables.

The result is, that upon the $(iK+2)$ degrees of freedom of the system, we have imposed $[K(i-1)+i]$ conditions as necessary, if the set of i coexistent phases is to be in equilibrium. The number of degrees of freedom remaining is therefore

$$(iK+2)-[K(i-1)+i]=K+2-i. \quad \dots\dots\dots\dots(248)$$

From this it is evident, that if

$$i=K+2,$$

all the quantities of the set (229) are determined, and the system is nonvariant. A set of $(K+2)$ phases can exist in equilibrium at certain discrete points in the $(p,\ \theta)$ plane; but the temperature and pressure can not be varied continuously. A greater number of phases than $(K+2)$ would impose more conditions on the system than it had degrees of freedom originally, and it is therefore impossible that the number of phases coexistent in a state of equilibrium should be greater than $(K+2)$.

If $i=K+1$, the system has one degree of freedom remaining: hence $(K+1)$ phases can coexist along lines in the (p, θ) plane, and form a univariant system. At other points in the (p, θ) plane, i must be less than $(K+1)$.

176. The conditions of equilibrium, which have been expressed in equations (245), might have been obtained by slightly different considerations. The difference is only formal to be sure, but the second method is interesting.

Let the thermodynamic potentials of the separate phases, at constant pressure and temperature, be $\zeta', \zeta'', \ldots \zeta^i$. The thermodynamic potential, Z, of the whole system of phases, will be the sum of these—surface energy being disregarded—and we have

$$Z=\sum_1^i \zeta. \qquad \text{(249)}$$

The condition of equilibrium, at constant pressure and temperature, is

$$\delta Z \geqq 0. \qquad \text{(250)}$$

Since each component is an actual component of every phase, any virtual variation of state which is possible in one direction is also possible in the other. The condition (250) thus reduces to

$$\delta Z=0, \qquad \text{(251)}$$

which may also be written

$$\sum_1^i \delta\zeta=0. \qquad \text{(252)}$$

Since the only changes are those of the masses, this again may be written in the form

$$\sum_1^i \sum_1^K \frac{\partial\zeta}{\partial m}\delta m=0. \qquad \text{(253)}$$

But the variations δm are subject only to the conditions

$$\sum_1^i \delta m_1 = 0\,;\ \sum_1^i \delta m_2 = 0,\ \ldots \text{ etc.} \quad\ldots\ldots\ldots\ldots(254)$$

Hence from (253) we see, that the condition of equilibrium is equivalent to the equations

$$\left.\begin{array}{l} \dfrac{\partial\zeta'}{\partial m_1} = \dfrac{\partial\zeta''}{\partial m_1} = \ldots = \dfrac{\partial\zeta^i}{\partial m_1}, \\[2ex] \dfrac{\partial\zeta'}{\partial m_2} = \dfrac{\partial\zeta''}{\partial m_2} = \ldots = \dfrac{\partial\zeta^i}{\partial m_2}, \\[2ex] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\[2ex] \dfrac{\partial\zeta'}{\partial m_K} = \dfrac{\partial\zeta''}{\partial m_K} = \ldots = \dfrac{\delta\zeta}{\partial m_K}\,; \end{array}\right\} \quad\ldots\ldots\ldots\ldots(255)$$

which, as before, are $K(i-1)$ in number.

Now for any particular phase, we have the equation

$$\delta\epsilon = \theta\delta\eta - p\delta v + \sum_1^K \mu\delta m\,; \quad\ldots\ldots\ldots\ldots(256)$$

and if, as usual, we define ζ by the equation

$$\zeta = \epsilon - \theta\eta + pv, \quad\ldots\ldots\ldots\ldots(257)$$

we have

$$\delta\zeta = -\eta\delta\theta + v\delta p + \sum_1^K \mu\delta m\,; \quad\ldots\ldots\ldots\ldots(258)$$

or in other words,

$$\mu_1 = \frac{\partial\zeta}{\partial m_1}\,;\ \mu_2 = \frac{\partial\zeta}{\partial m_2}\ \ldots \text{ etc.} \quad\ldots\ldots\ldots\ldots(259)$$

The equations (255) are therefore identical with the equations (245).

The method of proof first employed consisted virtually in using the isentropic potential ϵ. In the second method we have used the isothermal potential ζ. We might also have used the isothermal potential ψ or the isentropic potential χ, the different methods being based on the consideration of different forms of the same equation. This is equivalent to the statement that the potentials μ may be expressed in various ways, depending on what variables we select as defining the state of the system. For if, for a single phase, we write, as usual,

$$\left.\begin{array}{l}\psi=\epsilon-\theta\eta,\\ \zeta=\epsilon-\theta\eta+pv,\\ \chi=\epsilon+pv;\end{array}\right\} \qquad (260)$$

we have

$$\left.\begin{array}{rl}\delta\epsilon= & \theta\delta\eta-p\delta v+\sum_1^K\mu\delta m,\\ \delta\psi= & -\eta\delta\theta-p\delta v+\sum_1^K\mu\delta m,\\ \delta\zeta= & -\eta\delta\theta+v\delta p+\sum_1^K\mu\delta m,\\ \delta\chi= & \theta\delta\eta+v\delta p+\sum_1^K\mu\delta m;\end{array}\right\} \qquad (261)$$

whence

$$\mu_x=\left(\frac{\partial\epsilon}{\partial m_x}\right)_{\eta,v,m}=\left(\frac{\partial\psi}{\partial m_x}\right)_{\theta,v,m}=\left(\frac{\partial\zeta}{\partial m_x}\right)_{\theta,p,m}=\left(\frac{\partial\chi}{\partial m_x}\right)_{\eta,p,m}. \qquad (262)$$

177. A complete treatment of the question of the equilibrium of a system of homogeneous phases requires the removal of several restrictions, which have been imposed in order to simplify the problem. The components of a mixture are, in general, not actual components of all the phases, so that the effect of this limitation has to be considered. Furthermore, we have not discussed the effect of capillarity, solidity, possibility of chemical combination of the different components, etc. Any such complete discussion would be merely a reproduction of the memoir of Professor Gibbs "On the Equilibrium of Heterogeneous Substances."* As one of the main objects of the present book has

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* *Trans. Conn. Acad.* **3.**

been to prepare the reader for an intelligent study of that memoir, any further treatment of the subject would be superfluous here. For a complete qualitative account of the application of the phase rule to the problems of physical chemistry the reader is referred to the recent work of Professor Wilder D. Bancroft. *

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* *The Phase Rule*, Ithaca, N.Y., 1897, published by *The Journal of Physical Chemistry.*

APPENDIX

The following list contains the titles of a number of works which I have found useful, either for my own information or as reference books for my students:

Bertrand, *Thermodynamique*; Paris, 1887, Gauthier-Villars.

Clausius, *Mechanische Wärmetheorie*; 3rd ed., Braunschweig, 1887, Vieweg.

Duhem, *Le Potentiel Thermodynamique et ses Applications*; Paris, 1886, Hermann.

Duhem, *Introduction à la Mécanique Chimique*; Paris, 1893, Carré.

Duhem, *Traité Élémentaire de Mécanique Chimique*, 4 vols.; Paris, 1897-1899, Hermann.

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* The insertion of this title is an exception to the rule by which the rest of the list is composed, for I have not yet seen the French translation. The fact that M. Le Chatelier is its sponsor, vouches for its quality.

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INDEX

The numbers refer to pages

ERRATA.

Page 80, line 15—for "equation of condition" read "equation of state."
,, 81, ,, 3— ,, ,, ,, ,,
,, 84, ,, 8— ,, ,, ,, ,,
,, 88, ,, 2 and 5—for "equations of condition" read "equations of state."

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