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INTRODUCTION

§ 1. The concept of heat, like all other physical concepts, originates in a sense-perception, but it acquires its physical significance only on the basis of a complete separation of the events in the sense-organs from the external events which excite the sensation. So heat, regarded physically, has no more to do with the sense of hotness than colour, in the physical sense, has to do with the perception of colour.

The external events that excite our thermal sense are manifold in their variety. They may have their seat either in material bodies with which we come into contact, or they may consist of electromagnetic waves which impinge on our organs of sense. According as the case may be, then, we speak of the heat in bodies or of radiant heat. These two types are quite different and are in general independent of each other. For example, very intense radiant heat can propagate itself through very cold air without heating the air to the slightest degree. We shall treat these two kinds of heat in succession.

As a starting point we here, as in the case of electricity, again choose the only trustworthy foundation on which we can build a new structure, namely, the Principle of the Conservation of Energy. This is usually called the First Law of Thermodynamics in the theory of heat. This principle forms the link between heat theory and mechanics and so serves as a basis for what is called Thermodynamics.

§ 2. But the Principle of the Conservation of Energy does not in itself suffice for building up a complete theory of heat. This is rendered possible only by adducing another principle, the Second Law of Thermodynamics, the content of which depends on a special peculiarity of thermal processes which distinguishes them in a character-

istic way from mechanical and electromagnetic processes, and which, therefore, places the theory of heat in a special position as compared with other physical theories. That is also the reason why the treatment of the theory of heat forms the concluding volume of the present work.

For, let us imagine any (not too small) physical configuration, that is, any bodies in any electromagnetic field, which is completely cut off from its surroundings, so that the energy of the configuration remains constant (I, § 120). Within this configuration certain events will then occur the course of which is uniquely determined if we start out from a definite initial state. The following phenomenon then manifests itself. So long as only the laws of mechanics and electrodynamics are assumed to hold, the events will never come to an end and will retain their character for all time. Indeed, it may be proved that a state which has once existed can in the course of time occur any number of times again, if not in absolutely exactly the same way, at least to any desired degree of approximation (cf. § 131 below). But as soon as heat—no matter whether it be heat contained in bodies or radiant heat—enters into the question in any way the sequence of events finally, even if only asymptotically, approaches a definite end, in that the configuration tends to a state in which every mechanical or thermal change has ceased in the macroscopic sense (§ 115); this state is therefore called the state of thermal equilibrium. Hence all occurrences in which heat plays a part are in a certain sense unidirectional, in contrast with mechanical and electromagnetic events, which can equally well take place in the reverse direction, since for them the sign of the time factor is of no consequence. The essential feature of the second law of thermodynamics is that it furnishes a numerical criterion for the direction of the changes that occur in physical nature (§ 47).

In the first two parts of this book we shall deal with the heat in bodies, and afterwards, from the third part onwards, also with radiant heat.

PART ONE
THERMODYNAMICS



CHAPTER I

TEMPERATURE. MOLAR WEIGHT

§ 3. The first requirement of a theory of heat consists in defining in numerical terms the thermal state of a body concerning which our sensation when touching the body gives us only very imperfect information. To accomplish this we may make use of the experience that every body, if kept at constant pressure (say atmospheric pressure), changes its volume when heated, and so we can define the thermal state of a body by the amount of its volume at a particular instant. Instead of this, however, we may, to define its thermal state, also adduce any other property of the body which depends on the thermal state, for example, its thermo-electric e.m.f. or its galvanic resistance.

To be able to compare the thermal states of two different bodies numerically we require a further law derived from experience, which represents a special case of the general principle discussed in § 2 and which runs as follows : if two or more bodies (at rest) exert a thermal action on each other then, in contradistinction to mutual mechanical or electromagnetic actions, a state of thermal equilibrium always establishes itself, in which all change ceases. Using an expression which has been borrowed from mechanics, we then say that the bodies are in thermal equilibrium.

From this there immediately follows the important theorem : if a body *A* is in thermal equilibrium with two other bodies *B* and *C*, then *B* and *C* are themselves also in thermal equilibrium with each other. For if we make the bodies *A*, *B* and *C* form a connected ring so that each

of the three bodies makes contact with the other two, then, by our assumption, thermal equilibrium also exists at the contact of (AB) as well as at that of (AC) , and consequently also at the points of contact of (BC) . For otherwise no general thermal equilibrium would be possible at all and this would contradict the principle above laid down.

The fact that this theorem is by no means obvious can be recognized particularly clearly if we apply it to the question of electrical equilibrium, for which it does not hold. For if we bring a copper rod which is in electrical equilibrium with dilute sulphuric acid into contact with a zinc rod which is in electrical equilibrium with the same sulphuric acid, equilibrium does not exist at the point of contact, but rather electricity flows from the copper to the zinc.

§ 4. It is because the above law holds for heat that we are able to compare the thermal states of any two bodies B and C with each other without bringing them into direct contact. We need only bring each body individually into contact with the arbitrarily chosen body A , which serves as a measuring instrument (for example, a quantity of mercury ending in a narrow tube), and define its thermal state by the prevailing volume of A , or still more appositely by the difference between this volume and some arbitrarily fixed "normal volume," namely, that volume which the body A occupies when it is in thermal equilibrium with melting ice. If the unit of this volume difference is chosen so that 100 is indicated when A is in thermal equilibrium with the steam of boiling water under atmospheric pressure, then it is called the *temperature θ* (in degrees Centigrade) with respect to the body A regarded as the thermometric substance. Two bodies at the same temperature are thus always in thermal equilibrium, and conversely.

§ 5. The temperature data of two different thermometric substances in general never agree except at 0° and 100° . Hence, to complete the definition of temperature

there is no alternative but to make an expedient choice from among all substances and to use one of them to define the conventional temperature θ . It suggests itself to choose a gas for this purpose, since different gases, particularly at low densities, exhibit a very approximate agreement in their temperature data over a considerable range of temperature when used as thermometric substances. Even the absolute value of their expansion is almost the same for all gases, in so far as equal volumes when equally heated expand by the same amount, the pressure being assumed constant. The amount of this

expansion is $\frac{1}{273.2}$ of the volume for the temperature rise from 0°C. to 1°C. In the sequel we shall therefore refer the temperature θ to the gas thermometer, in particular to the hydrogen thermometer.

In spite of the advantages mentioned the temperature θ here introduced has in principle only a conventional and provisional significance. On the basis of the second law of thermodynamics we shall later, however, find it possible to define the so-called absolute temperature (§ 45) to which a real objective significance may be attached in so far as it is quite independent of the mechanical or electrical properties of individual bodies.

§ 6. In the following pages we shall occupy ourselves principally with homogeneous isotropic bodies of arbitrary shape, which have a uniform temperature and density in their interior and are subject to a uniform pressure acting everywhere normally to their surfaces and consequently themselves exert the same pressure outwards [cf. II (211)]. We shall take no account of surface phenomena. The state of such a body is determined by its chemical nature, its mass M , its volume V and its temperature θ . Thus all other properties of the state are dependent in a definite way on those just given; above all, the pressure p and the energy E depend on them. We shall discuss the former property in the present chapter and the latter in the next.

Since the pressure of a body clearly depends only on its internal constitution but not on its external shape and its mass, it follows that, besides depending on the temperature θ , the quantity p depends only on the ratio of the mass M to the volume V , that is, on the density or, respectively, on the inverse ratio, the volume of unit mass :

$$\frac{V}{M} = v \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which, following accepted usage, we call the specific volume of the body. So there exists a definite relationship, characteristic of every substance :

$$p = f(v, \theta) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which is called the *equation of state* of the substance. The function f is always positive for gases ; for liquid and solid substances it may also have negative values in some circumstances.

§ 7. The equation of state assumes its simplest form in the case of gases when their density is not too great. For by II (285) we have :

$$p = \frac{\Theta}{v} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where Θ depends only on the chemical nature of the gas and on the temperature θ (Boyle's Law, also known on the Continent as the Law of Boyle and Mariotte). On the other hand, by the definition of § 4, the temperature θ is proportional to the difference between the volume v and the "normal volume" v_0 , that is :

$$\theta = (v - v_0) \cdot P \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where P depends only on the pressure p . Accordingly we have by (3) :

$$v_0 = \frac{\Theta_0}{p} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

if Θ_0 denotes the value which the temperature function Θ assumes for $\theta = 0$.

Finally we use the empirical fact also introduced above

in § 5, that the amount of the expansion for an increase of temperature from 0° to 1° is almost the same fraction :

$$\frac{1}{273.2} = 0.00366 = \alpha \quad . \quad . \quad . \quad (6)$$

of the volume at 0° (Law of Gay-Lussac). Thus if we set $\theta = 1$, then $v - v_0 = \alpha v_0$, and equation (4) becomes :

$$1 = \alpha v_0 \cdot P \quad . \quad . \quad . \quad (7)$$

By eliminating p , P , v_0 and v from the equations (3), (4), (5) and (7) we get the temperature function :

$$\Theta = \Theta_0 (1 + \alpha\theta) \quad . \quad . \quad . \quad (8)$$

where now the constant Θ_0 depends only on the chemical nature of the gas. If we designate it by C , the equation of state (3) of a gas assumes the form :

$$p = \frac{C}{v} (1 + \alpha\theta) = \frac{CM}{V} (1 + \alpha\theta) \quad . \quad . \quad . \quad (9)$$

The numerical value of C is determined, as soon as the specific volume v of the gas is known, for any pair of values of θ and p , for example, 0° and atmospheric pressure ; the values of C for different gases at the same temperature and under the same pressure are then obviously in the same ratio as the specific volumes v , or inversely as the densities,

$\frac{1}{v}$. We may therefore say : at the same temperature and under the same pressure the densities of all gases bear perfectly definite ratios to one another. A gas is therefore often also characterized by the constant ratio of its density to the density of a normal gas at the same temperature and pressure (specific density with respect to air or hydrogen). Thus if we denote the quantities referred to hydrogen, for example, by means of a suffix H , the specific density of a gas with respect to hydrogen is :

$$\frac{1}{v} : \frac{1}{v_H} = \frac{C_H}{C} \quad . \quad . \quad . \quad (10)$$

The following are the actual specific densities of various

gases with respect to hydrogen : oxygen 16, nitrogen 14, air 14.4, water-vapour 9, ammonia 8.5, hydrogen peroxide 17.

§ 8. The equation of state (2) of a substance allows all questions concerning the behaviour of the substance with regard to arbitrary changes of temperature, volume and pressure to be answered completely. Attention must be paid to the way in which the quantities are chosen as independent and dependent variables. If, *first*, the pressure p is kept constant the changes are called isobaric or isopiestic. The term "volume coefficient of expansion" is then given to the ratio of the increase of volume for an increase of 1° to the volume at 0° , that is, to the quantity $\frac{V_{\theta+1} - V_\theta}{V_0}$. For a gas we have by the equation of state (9) that:

$$V_{\theta+1} - V_\theta = \frac{CM\alpha}{p} \quad \text{and} \quad V_0 = \frac{CM}{p},$$

so that the "volume coefficient of expansion" for all gases is equal to α . If, in the *second* place, the volume is kept constant we speak of isochoric or isosteric changes. The pressure coefficient of expansion is then the ratio of the increase of pressure for a temperature increase of 1° to the pressure at 0° , that is, the quantity $\frac{p_{\theta+1} - p_\theta}{p_0}$.

For a gas we have by the equation of state (9) that $p_{\theta+1} - p_\theta = \frac{C\alpha}{v}$ and $p_0 = \frac{C}{v}$; thus the pressure coefficient of expansion for all gases likewise becomes equal to α . If, *thirdly*, the temperature is kept constant, the changes are called isothermal and the name "isothermal coefficient of elasticity" is given to the ratio of an infinitely small increase of the pressure to the resulting contraction per unit volume; thus it is the quantity:

$$-\frac{dp}{dv} = -\left(\frac{\partial p}{\partial v}\right)_\theta \cdot v.$$

For a gas we have, by the equation of state (9) :

$$\left(\frac{\partial p}{\partial v}\right)_\theta = -\frac{C}{v^2}(1 + \alpha\theta)$$

and hence the coefficient of elasticity of the gas is $\frac{C}{v}(1 + \alpha\theta)$, that is, it is equal to the pressure p . The value of the reciprocal of the coefficient of elasticity is called the "coefficient of compressibility."

The three coefficients which characterize the behaviour of a substance in isobaric, isochoric and isothermal changes are not independent of one another, but are connected in the case of any arbitrary substance by a fixed relationship. For by differentiating the equation of state we get generally :

$$dp = \left(\frac{\partial p}{\partial \theta}\right)_v \cdot d\theta + \left(\frac{\partial p}{\partial v}\right)_\theta \cdot dv$$

If we now set $dp = 0$, we obtain the relation which holds for an isobaric change between the differentials $d\theta$ and dv ; expressed in corresponding notation this relation is :

$$\left(\frac{\partial v}{\partial \theta}\right)_p = -\frac{\left(\frac{\partial p}{\partial \theta}\right)_v}{\left(\frac{\partial p}{\partial v}\right)_\theta} \quad \dots \quad (11)$$

Accordingly, for every state of a body it is possible to calculate one of the three quantities, volume coefficient of expansion, pressure coefficient of expansion and coefficient of compressibility from the other two.

§ 9. Gas Mixtures. If different but arbitrarily great quantities of one and the same gas at the same temperature and pressure which are initially separated by partitions are suddenly brought into contact with one another by the removal of the partitions, the volume of the total system obviously remain equal to the sum of the separate volumes. Further, if the gases brought into contact are different in character, experiment shows that in this case too, provided

the temperature is kept constant and uniform and the pressure is kept uniform, the total volume remains permanently equal to the sum of the originally separate volumes, although at the same time a slow process of mixing, diffusion, takes place which is ended only when the composition of the mixture in every part of the space occupied by the gases is the same, that is, when the mixture has become physically homogeneous.

We may regard the resulting mixture as constituted in one or other of two ways. *Either* we may assume that in the process of mixing each individual gas divides up into an enormously large number of small parts, each of which, however, retains its volume and its pressure, and that these small parts of the different gases mix together during diffusion without penetrating into one another. Then each individual gas would, after the completion of the diffusion process, still retain its old volume (partial volume) and all the individual gases would have the same common pressure. *Or else*—and this is the view which, as we shall later find (§ 12), can alone be justified—we may assume that the individual gases also change in the smallest parts of their volumes and inter-penetrate one another, so that when diffusion is completed each individual gas, so far as one may still speak of such, occupies the whole volume of the mixture and fills it uniformly densely. Then, corresponding to the resulting dilution, the pressure of the individual gas has sunk to a smaller value, that of its partial pressure.

If we denote the individual gases by numerical suffixes, while the volume V , the temperature θ and the pressure p of the mixture are written without a suffix, the partial volumes of the individual gases in the mixture are (if we adopt the first view), by (9) :

$$V_1 = \frac{C_1 M_1}{p} (1 + \alpha\theta), \quad V_2 = \frac{C_2 M_2}{p} (1 + \alpha\theta) . \quad (12)$$

where :

$$V_1 + V_2 + \dots = V \quad (13)$$

and the partial pressures (if we take the second view) are :

$$p_1 = \frac{C_1 M_1}{V} (1 + \alpha\theta), p_2 = \frac{C_2 M_2}{V} (1 + \alpha\theta) \dots (14)$$

By addition we have :

$$p_1 + p_2 + \dots = \frac{V_1}{V} \cdot p + \frac{V_2}{V} \cdot p + \dots = p \dots (15)$$

which is Dalton's Law. It states that in a mixture of gases the pressure is equal to the sum of the partial pressures of all the individual component gases. We further see that :

$$p_1 : p_2 : \dots = C_1 M_1 : C_2 M_2 : \dots = V_1 : V_2 : \dots (16)$$

That is, the partial pressures, on the second view, are in the ratio of the partial volumes on the first view.

The composition of a gas-mixture is defined either by the ratios of the masses M_1, M_2, \dots or by the ratios [which, by (16), are constant] of the partial pressures or, respectively, by the partial volumes of the individual components. Accordingly we speak of either percentages by weight or percentages by volume. For example, atmospheric air contains about 23.1% of oxygen and 76.9% of nitrogen by weight but 20.9% of oxygen and 79.1% of nitrogen by volume.

The equation of state of a gas mixture is, by (12) and (13) :

$$p = \frac{C_1 M_1 + C_2 M_2 + \dots}{V} (1 + \alpha\theta) \dots (17)$$

or :

$$p = \frac{C_1 M_1 + C_2 M_2 + \dots}{M} \cdot \frac{M}{V} (1 + \alpha\theta)$$

Thus it corresponds perfectly with the equation of state (9) of a simple gas whose characteristic constant is :

$$C = \frac{C_1 M_1 + C_2 M_2 + \dots}{M_1 + M_2 + \dots} \dots (18)$$

Hence an investigation of the equation of state can never decide whether a gas is chemically simple or whether it is formed of a mixture of different simple gases.

§ 10. The equation of state (9) holds for all gases and vapours if their densities are sufficiently low. But if their densities exceed a certain order of magnitude certain deviations always occur and the equation of state must then be given a more general form. In the course of time a whole series of different equations of state has been given which fulfil their purpose more or less well. The first and simplest of them is due to van der Waals; it is of particular interest because it also applies to the liquid state. Van der Waals' equation runs :

$$p = \frac{C(1 + \alpha\theta)}{v - b} - \frac{a}{v^2} \quad . \quad . \quad . \quad (19)$$

where a and b are other constants which depend on the nature of the substance. For great values of v the equation reduces to (9), as it should do.

The functional dependence of the pressure p on the volume v and the temperature θ may be conveniently depicted by drawing "isothermal" curves; for any arbitrary constant temperature θ two associated values of v and p are plotted as abscissa and ordinate of a point in a plane. The complete family of all isothermals then gives a complete picture of the equation of state. By the equation of state (9) all isothermals are clearly rectangular hyperbolas which have the co-ordinate axes for their asymptotes. For $pv = \text{const.}$ holds for them. By van der Waals' equation (19), on the other hand, the isothermals assume quite different forms, whose character is indicated in Fig. 1. In general, as can be seen from (19), there are actually three values of v for each value of p . Hence an isothermal will in general be intersected at three points by a straight line parallel to the v -axis. But two of them may be imaginary, as actually occurs for high values of θ . At high temperatures (for example, θ' in the figure) there is thus for a given pressure only a single real volume,

represented in the figure, for example, by α , β , γ , only the smallest (α) and the greatest (γ) can signify a stable state of the substance, such as can be produced in physical nature. For in the case of the intermediate volume (β) the pressure along the isothermal clearly increases as the volume increases; that is, the compressibility is negative. Such a state is only of theoretical importance.

The point α corresponds to the liquid state; the point γ corresponds to the gaseous state at the temperature θ and at the pressure p represented by the common ordinate

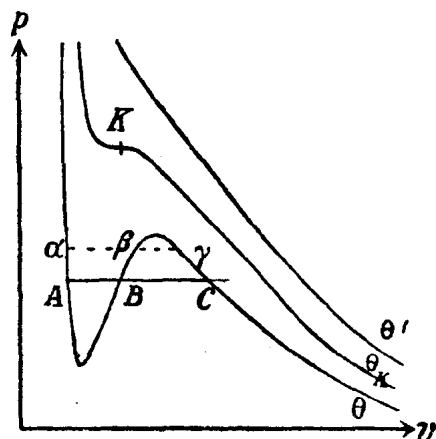


FIG. 1.

of α , β and γ . But, again, in general only one of these two states α and γ is stable (in the figure it is the state α). For if the gaseous substance, which, say, is enclosed in a cylinder with a movable piston, is compressed, the temperature θ being kept constant during the process, the successive states will be denoted in the first place by the points to the right on the isothermal θ . As the volume decreases the graph point moves continually further to the left along the isothermal until it reaches a perfectly definite point C . On further isothermal compression, however, the point does not go beyond C ; rather the substance partially condenses, that is, it resolves into a