A TEXTBOOK OF THERMODYNAMICS

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PREFACE TO THE FIRST EDITION

THERE are already in existence a number of books on thermodynamics dealing either with the theoretical side of the subject or with the detailed development and applications thereof in some particular direction. There appear to be, however, few books showing the variety of subjects to which thermodynamics can be applied, and it was in the hope of remedying this deficiency that this book was written. As far as possible the aim of comparing theoretical deductions with experimental results has been kept in view in order that those primarily interested in experimental work may, perhaps, appreciate more fully the aid rendered by mathematical physicists.

Although this book is designed principally to cover the course in thermodynamics necessary for an honours degree in physics, it is hoped that it will be of use, not only to students of this subject, but to all who require a general introductory treatise on thermodynamics.

My thanks are due to Dr. R. A. Robinson for reading the major portion of the manuscript, and to Mr. V. H. L. Searle, who read the whole of the proofs and made many valuable suggestions and criticisms.

F. E. HOARE.

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PREFACE TO THE SECOND EDITION

THIS edition remains substantially the same as the first, the topics dealt with and the general method of presentation remaining unaltered, although advantage has been taken of the opportunity to revise certain portions of the text where there appeared to be some obscurity or a different presentation seemed advisable. The notation has been altered throughout in accordance with the recommendations made in the recent report presented by the Joint Committee of the Chemical, Faraday and Physical Societies.

Included in this edition is a collection of examples with answers. These have been carefully designed, and it is hoped that a proper balance between examples intended as exercises in the derivation and manipulation of thermodynamical equations and those of a numerical character has been maintained. In the more difficult examples, notes indicating the method of solution have been provided; a student of average ability, well acquainted with the matter in the text, should be able to tackle the majority of the examples satisfactorily.

My thanks are due to the many correspondents who have indicated errors in the previous edition and possible improvements in this. In particular I wish to thank Professors C. H. Berry, W. E. Curtis and G. D. West.

F. E. HOARE.

EXETER,
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THERMODYNAMICS

CHAPTER I

GENERAL PRINCIPLES

1. Introductory.—The subject-matter of thermodynamics is the relation of heat to mechanical energy and the laws which govern the conversion of one into the other. It is a common fact of every-day experience that heat can be converted into work, as for example in the steam engine, which takes in heat at a high temperature and rejects heat at a lower temperature. The steam engine is typical of a large class of engines known as Heat Engines, which perform work by lowering heat from one temperature level to another, somewhat analogously to the manner in which a water-wheel does work by lowering water from a high to a low level. Without mathematical investigation it is not possible to predict how much of the heat taken in at the higher temperature can theoretically be transformed into work. Naturally the greater the amount that can be so transformed the more economical will be the engine, and from the point of view of practical thermodynamics the object of a heat engine is to get work done with the minimum expenditure of fuel. Heat differs from other forms of energy in that it is not possible to convert it all into work except in one special set of circumstances which cannot be realised practically. These circumstances demand a condenser at the absolute zero of temperature, and for any higher temperature of the condenser only a fraction of the heat supplied can be converted into work, even with a theoretically perfect engine. To the engineer it is of the utmost importance that the laws governing the transformation of heat should be known in order that the most efficient engine may be designed.

Although thermodynamics had its origin in considerations of the efficiency of heat engines, its use at the present day is by no means restricted to this field alone. By theoretical considerations it is

possible to predict the variation of physical quantities in certain circumstances and to deduce relations between them of the first importance in experimental work. Also the possibility of chemical reactions and the equilibrium between different substances, as well as a number of related problems, can be investigated by thermodynamics.

The connection between chemical equilibrium and the efficiency of a heat engine might at first seem extremely remote, but as the subject is developed it will be seen that the whole structure of thermodynamics rests upon the foundations of two simple laws, both of which are generalised summaries of experience.

2. Temperature.—Temperature is usually defined as a certain fraction of the difference between two fixed temperatures which are easily and accurately reproducible. For this purpose the melting-point of pure ice and the boiling-point of pure water under standard atmospheric pressure are universally adopted. The method of construction of a liquid in glass thermometer, e.g. the ordinary mercury thermometer, is to choose a fine tube of uniform bore and blow at one end a bulb to contain the liquid whose expansion is to be used as an indication of temperature. The bulb is carefully filled with the liquid by successive heating and cooling, and the other end of the tube sealed so that the thermometer contains only the liquid and its vapour. The instrument is placed in melting ice, and the position reached by the top of the liquid column is carefully marked. Next the thermometer is placed in steam issuing from water boiling under standard atmospheric pressure and the top of the liquid column again marked. The two positions are known as the fixed points. The distance between the marks is divided into a certain number of divisions, 100 if a Centigrade thermometer is being made, and 180 for a Fahrenheit thermometer. Each of these divisions is a degree, and equal intervals of temperature will be defined in this manner by equal amounts of difference between the expansion of the liquid and that of the glass in which it is contained. This introduces arbitrariness into the temperature as measured, for the height to which the liquid rises in the tube will depend upon the liquid chosen for the thermometric substance as well as upon the peculiarities of the glass. It is possible to construct mercury in glass thermometers which, although of uniform bore and agreeing

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at the fixed points, differ by as much as half a degree for readings in the centre of the scale.

We are not limited to liquids however as thermometric substances. Gases are in general found to have a much more uniform coefficient of expansion than liquids, and are therefore better suited for use as thermometric substances. Gas thermometers can be divided into two classes, depending upon the conditions under which they are used. In constant pressure thermometers the pressure is kept constant by adjustment of a mercury column whilst the volume varies, and in the other class the volume is kept constant by altering the pressure.

Fig. 1 represents a simple form of gas thermometer which can be used either as a constant volume or constant pressure instrument. The gas is contained in the glass bulb A which communicates by a narrow tube with the tube B. The latter is graduated in ccs., and is connected by flexible rubber tubing to a reservoir C which can be raised or lowered at will.

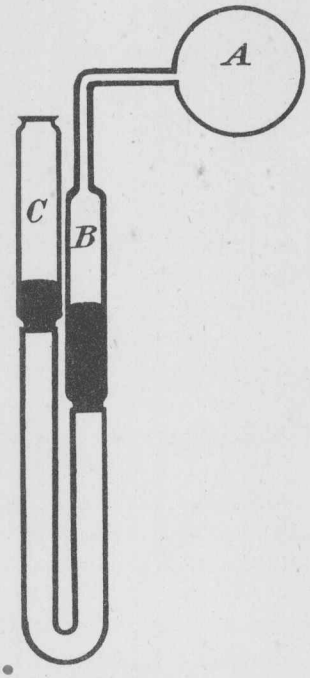

FIG. 1.
Simple Gas Thermometer.

When using the apparatus as a constant volume thermometer the mercury meniscus is adjusted to correspond with a fixed mark on B by raising the reservoir C. The pressure to which the gas is subjected is atmospheric—in cms. of mercury—plus the difference in level of the mercury in B and C.

Let the pressure be p_0 when the bulb is in melting ice and p_1 when surrounded with steam; also let the pressure be p when the bulb is in contact with the body whose temperature we desire to measure.

The Centigrade temperature t_v of the body measured on the constant volume scale with this particular thermometer is then defined as:

$$t_v = \frac{p - p_0}{p_1 - p_0} \times 100.$$

Using the instrument as a constant pressure thermometer the mercury levels in B and C are adjusted to be the same by altering the height of the reservoir C. The change in volume of the gas can be measured by the movement of the mercury in B. A small correction is necessary for the fact that the gas in B is usually not at the same temperature as that in A. As this would complicate our equations we will suppose that A and B are always at the same temperature.

Let v_0 be the volume of the gas at the ice point, v_1 the volume at the steam point, and v the volume at the temperature it is desired to measure.

The Centigrade temperature t_p of the body measured on the constant pressure scale with this particular thermometer is defined as:

$$t_p = \frac{v - v_0}{v_1 - v_0} \times 100.$$

The quantities $\frac{v_1 - v_0}{100\, v_0}$ and $\frac{p_1 - p_0}{100\, p_0}$ are the volume and pressure coefficients respectively of the particular gas and are denoted by α and β. The mean values of α and β for different gases at various initial pressures are given in the following table:

TABLE I.

Gas.	Values of $\alpha \times 10^6$.			Values of $\beta \times 10^6$.		
	p = 1,000 mm.	760 mm.	500 mm.	p_0 = 1,000 mm.	760 mm.	500 mm.
Hydrogen.	3660·0	—	—	3662·6	3662·6	3662·3
Nitrogen ·	3673·2	3669·8	3666·8	3673·9	3670·7	3667·9
Air ..	3672·8	3670·8	—	3674·4	—	—
Carbon-dioxide.	3741·0	3723·7	3706·1	3725·6	3712·3	3697·1

It will be seen that a gas at constant pressure expands by an approximately constant fraction of its volume at 0° C. for one

degree rise in temperature. Similarly the pressure of a gas at constant volume increases by a certain fraction of its pressure at 0° C. for one degree rise in temperature. If this law were obeyed to the lowest temperatures a point would be reached when the volume of the gas at constant pressure would become equal to zero. This would be at a temperature of $-\frac{1}{\alpha}$ °C., and the pressure of a gas at constant volume would become zero at $-\frac{1}{\beta}$ °C. Denoting $\frac{1}{\alpha}$ by θ_0 and $\frac{1}{\beta}$ by θ_0', we can define new scales of temperatures by the relations:

$$\theta = \frac{v}{v_0}\theta_0, \text{ and } \theta' = \frac{p}{p_0}\theta_0',$$

where the temperatures θ and θ' are measured from new zeros corresponding to $-\frac{1}{\alpha}$ °C. and $-\frac{1}{\beta}$ °C. respectively.

The zero of temperature on the new scales will not only vary from gas to gas, but will not be the same if the thermometer is used as a constant pressure or constant volume instrument. It will be noticed from Table 1, however, that the values of α and β become more nearly equal as the pressure is decreased, and it is found by experiment that as the pressure approaches zero the values become equal and the same for all gases. Consequently by extrapolating the readings of a gas thermometer to zero pressure the readings will be the same for all gases whether used in constant volume or constant-pressure thermometers.* The scale given in this case is the same as the absolute thermodynamic scale.†

3. Unit of Heat.—The unit of heat is defined as the amount of heat required to raise the temperature of unit mass of water by one degree at some particular temperature. The unit of heat depends therefore upon the units of mass and temperature and will vary according to the system of units adopted. In all modern work of a non-technical character the c.g.s. (centimetre, gram, second) system of units is used in conjunction with the Centigrade

* See Eumorfopoulos, *Proc. Roy. Soc.*, A. **90**, 187 (1914).

† Chapter III.

scale of temperature. The quantity of heat required to raise the temperature of unit mass of water one degree is not the same at all temperatures, and for this reason the initial temperature must be specified. The range 14·5° C. to 15·5° C. is most often adopted, the unit then being the amount of heat required to raise the temperature of one gram of water from 14·5° C. to 15·5° C. This is the 15° C. gram calorie.

The mean calorie, which is one-hundredth part of the heat required to raise unit mass of water from the ice point to the steam point, is sometimes employed. This is greater than the 15° C. calorie in the ratio 1·0002 to 1.

Callendar* has suggested that the calorie be defined as one-tenth of the amount of heat necessary to rise the temperature of unit mass of water from 15° C. to 25° C. The reason for this choice is that a range of 10° C. corresponds more closely to the actual experimental procedure in modern calorimetry than a temperature rise of one degree. The mean thermal unit over this range may conveniently be called the calorie at 20° C., although of course it cannot be realised practically except as a mean over a range.

It is sometimes convenient to use the large calorie. This is one-thousand times the calorie as defined above.

The specific heat of a substance is the amount of heat required to raise the temperature of one gram by one degree. The specific heat depends upon the conditions under which it is measured, and these as well as the temperature at which the measurement is made must be specified when dealing with this quantity.

4. Work and Energy.—When a body moves in any direction against an opposing force work is said to be done. The measure of the work done is the product of the opposing force and the displacement. In the c.g.s. system unit work is performed when a force of one dyne is overcome through a distance of one centimetre; this unit is the erg. If a body moves in the direction in which the applied force acts, work is said to be done by the force, whilst if the motion is in the opposite direction work is said to be done against the force. By raising a body from the surface of the earth, for instance, work is done against the force of gravitation, and in falling work is being done by the force of gravitation.

* Callendar, *Phil. Trans. Roy. Soc.*, A. **199**, 132 (1902).

A body which is capable of performing work is said to possess energy. The value of the energy is measured in terms of the work a body can do and is therefore expressed in the same units as work. The forms in which energy may be manifested are numerous, but two important forms are of constant occurrence and may briefly be described as the energy of motion, kinetic energy, and the energy of position, potential energy. Consider the simple example of a stone being thrown vertically upwards. As the stone leaves the hand it possesses a certain amount of kinetic energy which is equal to the amount of work it can do against gravity in rising to the highest point of its course. When it reaches this point it possesses no velocity but has potential energy equal in magnitude to the kinetic energy it possessed on leaving the hand, provided the effects of air resistance are negligible. Suppose the time of flight of the stone is t seconds and the initial velocity was v cms. per second; then the height to which it ascends is given by:

$$s = vt - \tfrac{1}{2}gt^2,$$

where g is the acceleration due to gravity.

But the work done is mgs, if m is the mass of the stone, and hence:

$$mgs = mg(vt - \tfrac{1}{2}gt^2) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and this is the kinetic energy originally possessed by the body.

The time of flight to maximum height is the time occupied in losing velocity v when there is a retardation of g cms. per second^2. Hence:

$$t = \frac{v}{g} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

By substitution from (2) in (1) we obtain:

$$\text{Kinetic energy} = mgs = \tfrac{1}{2}mv^2.$$

Whilst the body has been moving upwards work of amount mgs has been done against gravity, so that at its maximum height it possesses potential energy of this amount.

Besides kinetic and potential energy there are strain energy, electrical energy, chemical energy, etc., all of which can be expressed in the same units as we have employed.

5. Theories of Heat.—Since early in the seventeenth century there appear to have been two rival theories as to the nature of heat. Lord Bacon declared that heat was a form of motion and, as has been pointed out by Professor Tait,* Newton's third law of motion in its wider interpretation necessitates the equivalence of heat and mechanical energy. The suggestion of Bacon received but little attention until the beginning of the nineteenth century, and up to that time the caloric theory dominated the field of natural philosophy. According to the caloric theory heat is an imponderable fluid, incapable of being created or destroyed, which permeates the interstices of all matter. An increase in the amount of caloric in a body is shown by it getting warmer, and as it cools so it loses caloric. It must be admitted that this theory provided a plausible explanation of the experimental facts so far as they were then known. The expansion of bodies on being heated was attributed to the greater amount of caloric present. The heating of gases or other substances by rapid compression was supposed to be due to some of the caloric originally present being squeezed out and rendered sensible to a thermometer or the touch. An important part of the caloric theory was the doctrine of Latent Heat propounded by Dr. Black in 1760. When ice is contained in a vessel and heat is communicated to it, no change in temperature occurs until the whole of the ice is melted. From this it was inferred that caloric was able to enter into combination with matter and remain latent as it could not be detected by a thermometer. In the same way heat has to be communicated to water which is on the point of boiling to change it into steam; but steam has the same temperature as the boiling water from which it issues, and therefore steam and water only differ in the respect that the former contains a much greater quantity of caloric.

A direct deduction from this theory is that by rubbing two bodies together the capacity for caloric of one or both of them must be decreased, in consequence of which the caloric contained within them, without undergoing any increase, is able to raise them to a higher temperature. This deduction was tested by Rumford† in 1798 by his cannon-boring experiments. He found that a metal had the same capacity for caloric when in a finely divided state as in the form of a solid block. Also he found that

* Tait, *Recent Advances in Physical Science*, p. 32 (1876).

† Rumford, *Phil. Trans. Roy. Soc.* (1798).

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