

**THE PRINCIPLES  
OF  
THERMODYNAMICS**

by  
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## PREFACE

THIS book contains the substance of lectures given in the University of Cambridge in the summer terms of the past two years to men whose future interest may have been any of mathematics, physics, chemistry, astronomy or mechanical science. The object was to set out with care the foundation principles of the subject and to illustrate them by applications to these various branches of science, where no more than a general knowledge of the science was required for their appreciation. For this reason the relation of statistical mechanics to thermodynamics, and questions, such as the connection between magnetism and temperature, requiring a special knowledge of dynamical or physical theory, were not included.

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## PREFACE TO THE SECOND EDITION

This edition has been revised and a chapter on Nernst's heat theorem added.

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# THE PRINCIPLES OF THERMODYNAMICS

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## CHAPTER I

### PRELIMINARIES

1. *The dynamical theory of heat.* Down to the end of the eighteenth century, heat was generally regarded as substance of no appreciable mass which could pass into or out of the space between the ultimate particles of a body. This substance, 'caloric' as it was called, could neither be created nor destroyed. At that time, too, there were many who regarded heat as an effect due to the motion of the particles themselves.

The experiments of Davy (1799) on the melting of two pieces of ice by friction between them, and the observations of Rumford<sup>1</sup> on the great heat of the shavings produced in the boring of cannon were in themselves sufficient to show that heat could be generated by mechanical effort, but they were not then fully appreciated.

In the decade 1840-50 the work of three or four experimenters, of whom Joule was pre-eminent, showed that the heat developed from mechanical work was in proportion to the work spent. In 1843<sup>2</sup> Joule showed that in order to produce a unit of heat (the heat required to raise the tem-

<sup>1</sup> *Phil. Trans.* 1798.

<sup>2</sup> *Phil. Mag.* 1843.

perature of a pound of water  $1^{\circ}\text{F.}$ ) the mechanical work expended was 770 foot-pounds.

The number of units of work expended in producing a unit of heat is called the 'mechanical equivalent of heat.'

More recent determinations give the following results:

1400 ft.-lb. of work are equivalent to 1 lb.-calorie (the heat required to raise the temperature of a pound of water from  $0^{\circ}\text{C.}$  to  $1^{\circ}\text{C.}$ ),

or  $41.8 \times 10^6$  ergs of work are equivalent to 1 gram-calorie (the heat required to raise the temperature of a gram of water from  $0^{\circ}\text{C.}$  to  $1^{\circ}\text{C.}$ ).

In 1847 Helmholtz's tract *Über die Erhaltung der Kraft* appeared, in which he asserted the principle of the conservation of energy and developed the ramifications of that principle throughout natural phenomena. Of the forms of energy, Joule's experiments enabled him to count heat as one; the reception of heat by a body meant an increase in the energy of its ultimate particles.

Though Helmholtz accepted Joule's principle, Thomson (who in 1847 was the first to see the importance of Joule's work) was at this time unable to accept or reject it, because of its apparent conflict with Carnot's principle.

In 1824 Sadi Carnot published an essay on *La puissance motrice du feu*, but it was forgotten until 1845 when Thomson, who had learnt of its existence through an account of it in a memoir by Clapeyron<sup>1</sup> in 1834, realised its profound importance—'an epoch-making gift to science,' he afterwards declared. In this essay Carnot endeavours to find how it is that heat produces mechanical effect in an engine. He considers a 'cycle' of operations, at the end of which the working substance of the engine is left in the same physical condition as it was at the beginning, this being essential if the mechanical effect is to be assigned solely to the heat given to the substance. He assumes that

<sup>1</sup> *Jour. Ecole Polyt.* XIV.



since the state of the substance is unaltered by the cycle, the heat received by it from the boiler is equal to the heat given out by it to the condenser, and concludes that the heat produces mechanical work by falling from one level of temperature to another, just as water in falling from one level to another over a water-wheel can do work in proportion to the quantity which descends and the height through which it falls.

He proceeds to describe an ideal cycle of operations (now known as Carnot's cycle) which has the property of being 'reversible,' and to prove that no engine receiving heat at one temperature and emitting heat at a lower temperature can produce more mechanical work from a given quantity of heat than an engine describing a reversible cycle between the same two temperatures. The proof depends upon the equality of the heat received and rejected by the engine.

In 1849, James Thomson<sup>1</sup>, using Carnot's ideas, proved theoretically that the freezing point of water must be lowered by pressure, and calculated that the lowering of the freezing point in degrees Centigrade due to a pressure of  $n$  atmospheres in excess of atmospheric pressure should be  $(.0075) n$ .

This result was confirmed by W. Thomson's experiments in 1850<sup>2</sup> and strengthened his belief in Carnot's principle.

It was now (1850) that Clausius<sup>3</sup> resolved the difficulty of reconciling Carnot's principle (which assumed production of mechanical work without loss of heat) with the views of Joule and Helmholtz (which required equivalence between mechanical work and heat). His view was that in an engine less heat is given out at the lower level of temperature than is taken in at the upper level of temperature, and that the difference is converted into mechanical work. This con-

<sup>1</sup> *Trans. R.S.E.* Jan. 1849.

<sup>2</sup> *Proc. R.S.E.* Jan. 1850.

<sup>3</sup> *Pogg. Ann.* 1850.



clusion had been reached independently by Thomson<sup>1</sup> and was published by him in 1851.

There was still the difficulty that Carnot's proof of reversibility as the test of the most effective engine depended on the equality of the heat received at the higher temperature and the heat rejected at the lower. Clausius showed that if Carnot's principle that a reversible engine is the most efficient was to be retained with the theory he proposed, a new axiom was required, which is now known as the second law of thermodynamics. This axiom, and the principle of conservation of energy, form the foundation of modern thermodynamics.

2. *Measurement of temperature.* In a perfect thermometer equal elevations of temperature, as indicated by the divisions of the scale, correspond to equal increases in volume of the substance. As the coefficients of expansion of the substance and the material enclosing it vary with the temperature, equal elevations of temperature do not correspond to equal increases in volume of the substance.

Thus the readings of an actual thermometer depend upon the physical properties of the materials, such as mercury, air, glass, used in its construction.

It is found that if one of the 'permanent' gases is used the expansion is so uniform over a large range of temperature that the indications of such a thermometer, for example an air thermometer, are for most practical work perfect enough, though they would not be so for very low temperatures, in the neighbourhood of the point of liquefaction of the gas where the variation of expansion becomes apparent.

Lord Kelvin (Sir W. Thomson) in 1848<sup>2</sup> perceived the need of a scale of temperature independent of the properties of any particular substance and that in Carnot's principle he had the means to establish such a scale, the

<sup>1</sup> *Trans. R.S.E.* March 1851.

<sup>2</sup> *Proc. Camb. Phil. Soc.* June 1848.

absolute thermodynamical scale of temperature, which in its final form was given in his memoir on the 'Dynamical Theory of Heat<sup>1</sup>.'

3. *The laws of Boyle and Charles.* These are experimental laws which hold approximately for gases and vapours and become more and more exact the further the gas or vapour is from its point of liquefaction.

Boyle's law is 'The pressure of a given mass of a gas at constant temperature varies inversely as the volume.'

Gases expand at constant pressure according to the law  $v = v_0 \left(1 + \frac{\theta}{273}\right)$  where  $v$  is the volume at  $\theta^\circ$  C. and  $v_0$  is the volume at  $0^\circ$  C., so that if  $v_1, v_2$  are the volumes at temperatures  $\theta_1^\circ$  C.,  $\theta_2^\circ$  C.,  $\frac{v_2}{v_1} = \frac{273 + \theta_2}{273 + \theta_1} = \frac{t_2}{t_1}$ , where  $t = 273 + \theta$ . Temperatures  $t$ , obtained by adding 273 to the Centigrade temperature  $\theta$ , are called 'absolute temperatures on the gas thermometer scale.' We thus have Charles' law, which is 'The temperature of a given mass of gas at constant pressure varies directly as the volume.'

These laws are included in the formula  $pv = at$ , where  $v$  is volume of 1 gram of the gas (its specific volume) and  $a$  is a constant for a given gas.

4. *Avogadro's law* is 'All gases at the same temperature and pressure contain the same number of molecules per unit volume.' Modern work on the electrical properties of gases shows that this number (*Avogadro's number*) is  $2.70 \times 10^{19}$  per cubic centimetre<sup>2</sup> at  $0^\circ$  C. and atmospheric pressure (760 mm. of mercury).

5. *The gas constant.* Now let  $n$  be the number of molecules per c.c. and  $m$  be the mass of a molecule of a given

<sup>1</sup> *Trans. Roy. Soc. Edin.* xxi. i. 1854, or *Math. and Phys. Papers*, i. p. 235.

<sup>2</sup> A. Sommerfeld, *Atomic Structure and Spectral Lines*, p. 535.

gas in grams. Then  $mn$  is the mass in grams of 1 c.c. and  $\frac{1}{mn}$  is the volume in c.c. of 1 gram.

Hence  $pv = at$  becomes  $p \cdot \frac{1}{mn} = at$ ,

or  $p = n(ma)t = nRt$ , where  $R = ma$ .

Since, by Avogadro's law,  $n$  is the same for all gases at the same temperature and pressure,  $R$  is the same constant for all gases.

Using Avogadro's number given above,  $R$  can be calculated. For, a pressure of 760 mm. of mercury

$$= 981 \times 13.6 \times 76 \text{ dynes per sq. cm.}$$

$$= 1013600 \text{ dynes per sq. cm.}$$

$$\therefore R = \frac{1013600}{2.7 \times 10^{19} \times 273} = 13.8 \times 10^{-17}.$$

This is the 'universal gas constant' used in the kinetic theory of gases.

In physical chemistry, a unit of mass called a 'gram-molecule' or a 'mol' is very generally used. 1 mol of a substance is  $M$  grams, where  $M$  is the 'molecular weight' of the substance in the chemical sense. Thus the molecular weight of hydrogen being 2 (1.008) or 2.016, 1 mol. of hydrogen is 2.016 grams; the molecular weight of oxygen being 2 (16) or 32, 1 mol. of oxygen is 32 grams.

Now let  $n'$  be the number of mols per c.c.

Then  $n'M$  is the number of grams per c.c. and this is equal to  $nm$ ,

$$\therefore \frac{n}{n'} = \frac{M}{m}.$$

Now the molecular weight is proportional to the mass of a molecule, so that  $\frac{M}{m}$  is the same for all gases, and therefore  $\frac{n}{n'}$  is the same for all gases, and equal to  $N$ , say.

This ratio  $N$  is the number of molecules per mol and its value can be found by using the constants for oxygen:

1 c.c. of oxygen at  $0^\circ$  and 760 mm. weighs .001429 gram and 1 mol of oxygen is 32 grams,

$$\therefore n' = \frac{.001429}{32} = 44.65 \times 10^{-6}.$$

Now  $n = 2.7 \times 10^{19}$ ,

$$\therefore N = \frac{n}{n'} = \frac{2.7 \times 10^{19}}{44.65 \times 10^{-6}} = 6.06 \times 10^{23} \quad (\text{Avogadro's number per mol}^1).$$

Now  $p = nRt = n'NRt = n'R't$ ,

$$\begin{aligned} \text{where } R' &= NR, \\ &= (6.06 \times 10^{23}) (13.8 \times 10^{-17}), \\ &= 83.6 \times 10^6. \end{aligned}$$

$R'$  is also the same for all gases, and is the 'universal gas constant' used in physical chemistry.

Further, if  $v'$  is the volume of 1 mol of the gas, the number of mols per c.c. is  $\frac{1}{v'}$ ,

$$\therefore \frac{1}{v'} = n', \text{ and } p = n'R't \text{ becomes } pv' = R't.$$

Again  $pv = at$ , where  $v$  = volume of 1 gram of the gas,

$$\therefore v' = Mv,$$

$$\therefore pv' = Mat.$$

$$\text{Hence } R' = Ma \text{ or } a = \frac{R'}{M} = \frac{83.6 \times 10^6}{M};$$

$$\therefore pv = at, \text{ where } a = \frac{83.6 \times 10^6}{M}.$$

These results may be summarised as follows:

$$\text{I. } p = nRt,$$

where (i) if  $n$  is the number of molecules per c.c.,  $R = 13.8 \times 10^{-17}$ , and (ii) if  $n$  is the number of mols per c.c.,  $R = 83.6 \times 10^6$ , for all gases.

<sup>1</sup> Cf. du Noüy, *Phil. Mag.* Oct. 1924.

$$\text{II. } pv = Rt,$$

where (i) if  $v$  is the volume of 1 mol of gas,  $R = 83.6 \times 10^6$ ,  
and (ii) if  $v$  is the volume of 1 gram of gas,  $R = \frac{83.6 \times 10^6}{M}$ ,  
where  $M$  is the molecular weight of the gas.

In the above,  $pv$  has the dimensions of work, so that  $R$  is given in ergs.

Now  $41.8 \times 10^6$  ergs of work produce 1 gr.-calorie of heat, so that if  $v$  is the volume of 1 mol of gas,

$$\begin{aligned} pv &= (83.6 \times 10^6) \cdot \text{ergs}, \\ &= \frac{83.6 \times 10^6}{41.8 \times 10^6} \cdot t \text{ gr.-calories}, \\ &= 2t \text{ gr.-calories}. \end{aligned}$$

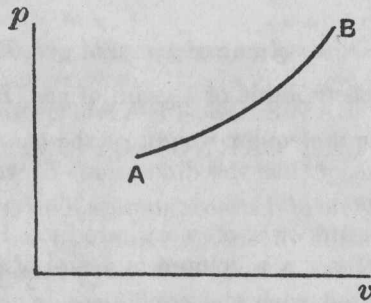
Thus using heat units,  $pv = 2t$ , where  $v$  is the volume of 1 mol.

6. *Perfect gas.* This is an ideal gas, infinitely far from the point of liquefaction, of which one of the properties is that of satisfying Boyle's and Charles' laws exactly, so that  $pv = Rt$ .

7. *Characteristic equation.* The equation  $pv = Rt$  for a perfect gas is an example of the equation  $f(p, v, t) = 0$  which holds for any 'simple' substance, such as a homogeneous fluid. Such an equation is called the 'characteristic' equation of the substance. If any two of the three variables  $p, v, t$  which determine the physical state of the substance are known, the third can be found from the characteristic equation.

Hence the 'state' of the substance is determined by any two of  $p, v, t$ .

8. *Indicator diagram.* If  $p, v$  are taken as ordinate and abscissa of a point  $A$ , this point indicates the state of the substance. If the substance passes to another state  $B$ , the changes it undergoes during the passage are shown by a

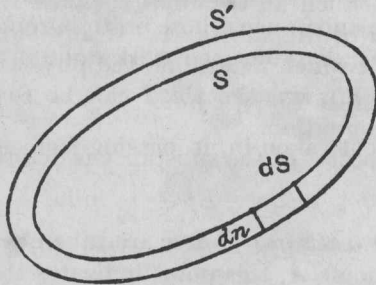


curve joining *A* to *B*. The figure is an 'indicator diagram' of the kind first used by Watt to indicate the state of the steam in the cylinder of an engine.

9. *Work done by a fluid in expansion.* Let *S* and *S'* represent the surface of a fluid before and after a small expansion against an external pressure *p* which is constant over the surface, the pressure of the substance being supposed infinitesimally greater than the external pressure, which makes the expansion possible and a slow one so that no energy of motion is developed.

Consider the element *dS* of the surface and let its displacement along the normal be *dn*. The work done by the substance is then  $\Sigma (pdS) dn$

$$= p \Sigma dS \cdot dn = p (\text{increase of volume}) = p dv.$$





## CHAPTER II

### THE TWO LAWS OF THERMODYNAMICS; THE CARNOT CYCLE

10. *The first law of thermodynamics.* This is the principle of the conservation of energy expressed so as to include the energy of heat. A body in a given state has 'internal energy' associated with the configuration and motion of its molecules. The change of its internal energy when it passes from one state to another is independent of the path between the two states and depends only on the configuration and motion in the respective states. The difference between the internal energy in any state and that in some standard state will be denoted by  $E$ .

If the substance takes in a quantity of heat  $Q$  (measured in units of work) and performs  $W$  units of external work, let the internal energy change from  $E_1$  to  $E_2$ . Then by the conservation of energy,

$$E_2 - E_1 = Q - W.$$

This is the first law of thermodynamics—in words, it is 'The heat taken in by a substance

= the increase of its internal energy

+ the work done *by* the substance.'

For a simple substance whose state is represented by a point on the  $p$ - $v$  diagram, the work done in passing from a state  $A$  to a state  $B = \int_{v_A}^{v_B} p dv$ .

Hence the heat taken in, in passing from  $A$  to  $B$ ,

$$= E_B - E_A + \int_{v_A}^{v_B} p dv,$$

$$= E_B - E_A + (\text{area } ABML).$$

Since this area depends on the form of the curve  $AB$ , both the work done by the substance and the heat taken in depend on the path from  $A$  to  $B$ .



Thus the quantity of heat which is taken in by a body in passing to any state from some standard state cannot be expressed as a function of the state; it may have any value depending on how that state was reached from the standard one.

If  $dE$  is the small increase of internal energy which accompanies the absorption of a small amount of heat  $dQ$  and the performance by the substance of a small amount of work  $dW$ , then

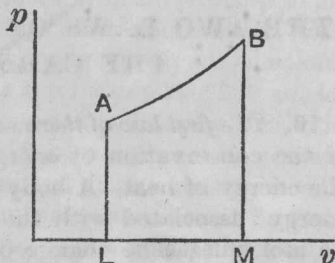
$$dE = dQ - dW.$$

But it is understood that whilst  $dE$  is the differential of a function  $E$  of the variables which determine the state,  $dQ$  and  $dW$  are not differentials of functions  $Q$ ,  $W$  of the state, as such functions do not exist.

11. *Joule's experiment on the expansion of a gas into a vacuum*<sup>1</sup>. Joule compressed air to about 20 atmospheres in a strong vessel which was connected by a pipe, containing a stop-cock, to another vessel previously exhausted. The whole was placed in a vessel of water.

On opening the stop-cock, the air rushed from the first vessel to the second so that in a short time the pressure was the same in both. On measuring the temperature of the water again, no change was perceptible.

In this experiment no external work was done by the air and no heat entered or left. Hence by the first law, the internal energy of the air was unchanged by the sudden expansion. Now the internal energy  $E$  is a function of the state and is in general a function of two of  $p$ ,  $v$ ,  $t$ , so that  $E$  is a function of  $v$  and  $t$ . But  $E$  is unaffected by change of volume and is therefore a function of  $t$  only.



<sup>1</sup> *Phil. Mag.* 1845.

This experiment was not a very delicate one, on account of the large volume of water used, which might absorb a small quantity of heat without a sensible rise of temperature. By a much more sensitive variant of this method, known as the porous plug experiment, Joule and Thomson during 1852-62 carried out a long series of determinations in which a small change of temperature was shown to occur in all the gases used (air, carbonic acid and hydrogen). The change was much less in the case of hydrogen than of air, and the former being much further from its point of liquefaction than air at ordinary temperatures is more nearly a 'perfect' gas.

It will be assumed, then, that a 'perfect' gas has also the property that in the Joule experiment, its change of temperature would be zero exactly. Hence the internal energy of a perfect gas is a function of its temperature only.

12. *Specific heat.* Let the temperature of 1 gram of a substance rise from  $t$  to  $t + dt$  owing to the absorption of a small quantity of heat  $dQ$  and let  $\frac{dQ}{dt} = c$ . Then when  $dt$  is infinitesimal,  $c$  is called the 'specific heat' of the substance at temperature  $t$ .

Any number of specific heats may be defined at a given temperature, according to the conditions under which the heating takes place. For it has been seen that the quantity of heat taken in by a substance in a given change of state depends on the path by which that change is effected.

Thus if the pressure is constant during the change  $\frac{dQ}{dt}$  has the value  $c_p$ , which is 'the specific heat at constant pressure,' and if the volume is constant during the change  $\frac{dQ}{dt}$  has the value  $c_v$ , 'the specific heat at constant volume.'

Now

$$dQ = dE + p dv,$$

$$\therefore c = \frac{dE}{dt} + p \frac{dv}{dt}.$$